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Stephen David Gabelnick
(Ph. D. Thesis)

January 1969

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SPECTROSCOPIC AND KINETIC STUDIES OF IODINE MONOFLUORIDE CHEMILUMINESCENCE

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ABSTRACT

Chemiluminescence from electronically excited ($^3\Pi_{0+}$) iodine monofluoride has been observed under flow conditions in the room temperature gas-phase reaction of molecular iodine and fluorine. Observations have been made throughout the visible wavelength region, from 4300 to 7300A, under varying conditions of reactant flow rates, total cell pressure, and partial pressure of inert diluent gas. Between pressures of 20 and 100 mtorr, substantial changes in the relative intensities of band progressions could be detected.

Quantitative interpretation of spectral features requires the knowledge of the transition matrix elements $\langle\psi_v'|R_e(r)|\psi_v''\rangle^2$. These have been calculated by first constructing Rydberg-Klein-Rees potential curves from known spectroscopic data and then evaluating Franck-Condon overlap integrals based on wave functions obtained from numerical solution of the Schrödinger wave equation using these RKR potentials. A variational method, based on the $\bar{r}$-centroid approach, for obtaining the transition-moment function $R_e(r)$ from low-resolution spectra is presented. Results of these calculations indicate changes in the transition moment of two orders of magnitude for changes in the $\bar{r}$-centroid of 0.4A. This large variation in the transition moment has been attributed to changes in the coupling of electronic orbital and spin angular momentum to the internuclear axis and is brought about by strengthening

(weakening) of the electric field along the internuclear axis as the internuclear distance decreases (increases). The actual transition matrix elements based on the computed transition-moment function and those obtained by use of the $\bar{r}$-centroid method are generally in good agreement.

Calculations of the relative vibrational populations of the excited electronic state of IF were made for constant flow rates of iodine and fluorine with varying amounts of added argon. Approximate average vibrational temperatures (for v' up to 5) ranged from ~2700°K with no argon present (cell pressure 30 mtorr) to ~1800°K with 50 mtorr of argon added. At the same time, apparent rotational temperatures based on integrated bandwidth measurements and best calculated fits to the observed spectra indicated changes in the rotational temperature from ~750 to ~550°K. Calculations of the translational temperature based on the heat input from the chemical reaction yield a value of only ~320°K. At a total reactant pressure of 20 mtorr, bands apparently not belonging to the $^3\Pi_{0^+} \rightarrow {}^1\Sigma^+$ system were observed. The possibility of transitions from highly excited vibrational levels of the $^3\Pi_1$ state is suggested.

The populating of low-lying vibrational levels was assumed to take place through collisional deactivation of vibrationally excited molecules formed in the three-body recombination of iodine and fluorine atoms. Based on a stepladder deactivation model and the Landau-Teller theory, an approximate value of the ratio of the electronic quenching to vibrational-deactivation rate constants of 0.15 was obtained. Similarly, a ratio of the fluorescence to vibrational-deactivation rate constants was calculated to be $\sim 5\times10^{14}$ molecules/cm^3. Assumption of a vibrational relaxation time of 10^{-7} sec at one atmosphere yields a fluorescence lifetime of $\sim 10^{-2}$ seconds for the partially forbidden $^3\Pi_{0^+} \rightarrow {}^1\Sigma^+$ transition.

I. INTRODUCTION

In recent years much attention has been paid to the processes of vibrational-translational and rotational-translational energy transfer because of their deep influence on our knowledge of reactive chemical systems. Although these processes themselves are not chemical in the sense that new bonds are formed or broken, they are always involved as precursors of unimolecular dissociation and as essential steps in the stabilization of newly formed bonds. Study of such processes can also provide much knowledge about interaction potentials between collision partners without causing chemical (and complicating) changes in the reactant species (1).

Much of the early experimental information was gained through ultrasonic studies involving only low lying vibrational levels of stable molecules (1,2). These studies involved measurement of bulk properties of non-reacting systems, specifically the velocity of sound vs. frequency. In order to study energy transfer processes of more highly excited quantum levels, investigators have turned to fluorescence methods, which provide direct information concerning the populations of specific quantum states. These have consisted of both steady state observations from levels other than the one to which the molecule was initially excited (3) and time decay studies of populations of the initially excited state and subsequently populated states (4). Direct information has also been obtained concerning the role of energy transfer processes in unimolecular reactions (5).

Of recent interest, also, have been more ambitious studies of relaxation processes in chemically reactive systems with specific reference to understanding the nature of combustion processes (6) and to the possibilities of achieving population inversions leading to development of molecular lasers (7). Knowledge of this latter subject has been gained through the

study of chemiluminescing systems, both those leading to vibrationally excited species (8) and to electronically excited species (9). It is with reference to obtaining information about vibrational and rotational distributions in systems producing electronically excited species that the present work has been undertaken.

Determination of vibrational populations for vibrationally excited species as observed by radiation in the infrared requires the knowledge of the vibrational matrix elements $\langle v_i|M(r)|v_f\rangle$ where $\langle v_i|$ is the wave function of the initial state, $|v_f\rangle$ is the wave function of the final state and $M(r)$ is the electric dipole moment function. These matrix elements have been the subject of well developed theoretical (10) and experimental (11) studies. Analogously, determination of vibrational populations for electronically excited species as observed in the visible wavelength region requires evaluation of matrix elements of the form $\langle v'|R_e(r)|v''\rangle$ where $\langle v'|$ is the vibrational wave function of the upper electronic state, $|v''\rangle$ the vibrational wavefunction of the lower electronic state, and $R_e(r)$ is the electronic transition moment. Only for the simplest molecules has a theoretical evaluation of this electronic transition moment been attempted (12). In all other cases of which studies have geen made, the transition moment function has had to be evaluated semi-empirically. Since the value of the transition moment can vary by well over a factor of 10 for a particular electronic band system, its knowledge is prerequisite to further interpretation of results of chemiluminescent studies.

In previous work, determination of transition moments has been restricted to well resolved emission spectra with little or no overlapping of bands. The scope of this study is both to provide a general method

for the evaluation of the transition matrix elements $\langle v'|R_e(r)|v''\rangle$ and to apply the results to the study of vibrational and rotational relaxation processes involving electronically excited iodine monofluoride produced in the gas phase reaction of iodine and fluorine.

II. EXPERIMENTAL

A. Introduction

Experimental apparatus for quantitatively studying emission intensities of a chemiluminescing species is described in detail in the following sections. The problems encountered in such studies are three-fold. First, since it is often desirable to perform studies at low pressures (10-100 mtorr) one has to measure low light levels which typically amount to 500-1000 photons/sec after monochromation. Methods for improving signal to noise (S/N) ratio recently discussed by Akins et al. (14) were employed. Secondly, because bands often overlap and bands of nearly equal intensity are occasionally separated by only a few Angstroms, it is necessary to accurately calibrate the spectral wavelength tracking of the monochromator. This is especially true when the slits are wide open and the resolution is not sufficient to separate component peaks. Most atomic line sources commonly used in wavelength calibrations do not have sufficient line density to characterize the response of the monochromator employed in these studies. However, use of a thorium iodide discharge provided an abundance of non self-reversed lines which could be used to obtain the desired calibration. Lastly, since one wishes to obtain accurate intensity information over a wide spectral region, one must measure the wavelength intensity response of the optical system. This was accomplished by using a tungsten ribbon lamp as a spectral irradiance standard and measuring the output from the photomultiplier tube. A block diagram for the complete experimental apparatus is shown in Fig. 1.

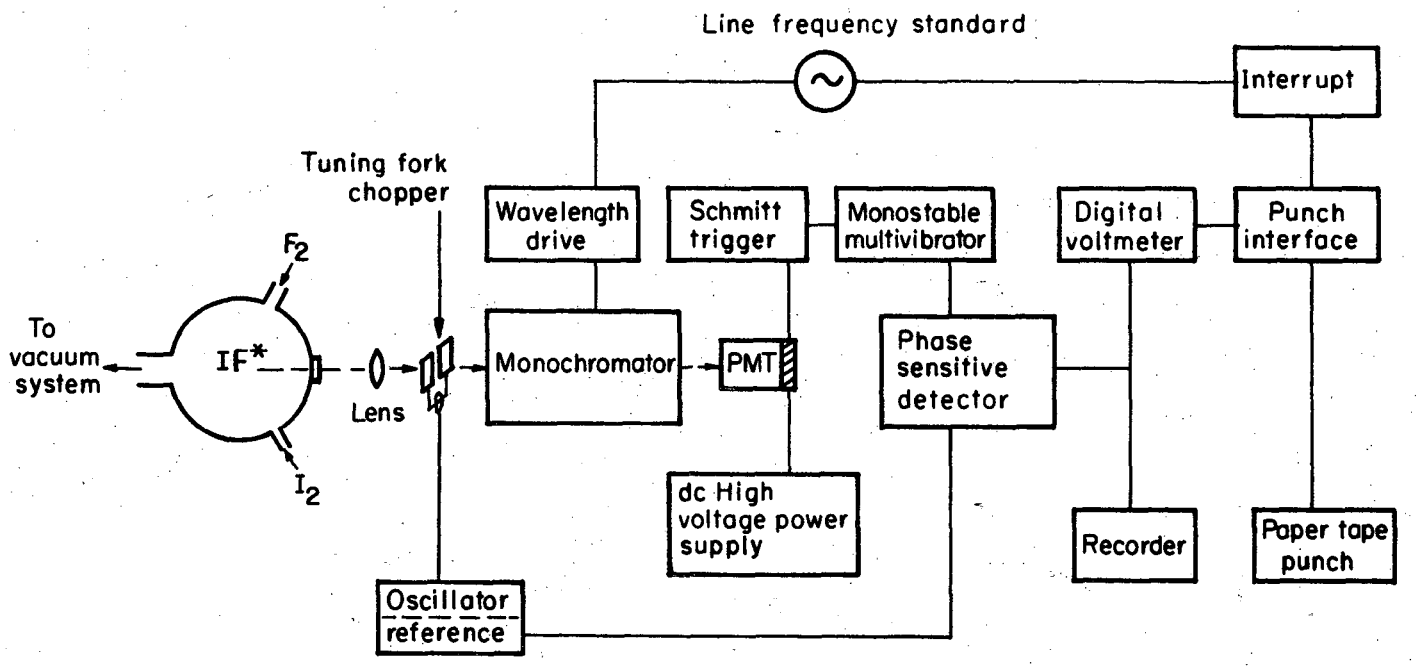

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Figure 1 Block diagram of experimental apparatus

B. The Monochromator

A Jarrell-Ash Ebert Scanning Spectrophotometer (Model 82-020) having a focal length of 500 mm and an effective aperture ratio of f/8.6 was used for the monochromation of the chemiluminescence. The instrument was equipped with a Dual Unilateral Entrance and Exit Slit assembly (Model 82-093) with curved jaws adjustable from 5 to 400μ in width. Slit height was controlled by means of an adjustable mask; heights of 0 to 20 mm were attainable. The grating employed was ruled at 590 lines/mm, resulting in a dispersion of 32A/mm, and was blazed for maximum intensity at 7500A in first order, which provided ample intensity over the range of spectral interest, viz. 4400 to 7500A.

Several attempts were made to calibrate the spectral wavelength response of the monochromator using Hg, Hg-Cd, and alkali metal arcs. Although adjustment of the sine-bar drive mechanism brought tracking to within ±2A over the region 4000 to 8000A, the error function (λ_{true}-λ_{obs}) did not appear to be monotonic or even slowly varying. The results obtained by using these lamps were inconclusive. It was decided to use a thorium discharge which had the advantage of providing an abundant number of lines showing few signs of self-reversal. Many of the thorium lines have been measured interferometrically to very high accuracy and intensities of these and many others have been measured by Zalubas (15). Approximately 600 of the more than 5000 lines enumerated by Zalubas in the region 4400 to 5600A were used in the calibration. Assignments of the true wavelengths to the wavelengths shown on the spectrometer were made on the basis of intensity and spacing. The error function vs. spectrometer wavelength is shown in Fig. 2. Superimposed on a slowly varying deviation with wavelength is a sinusoidal

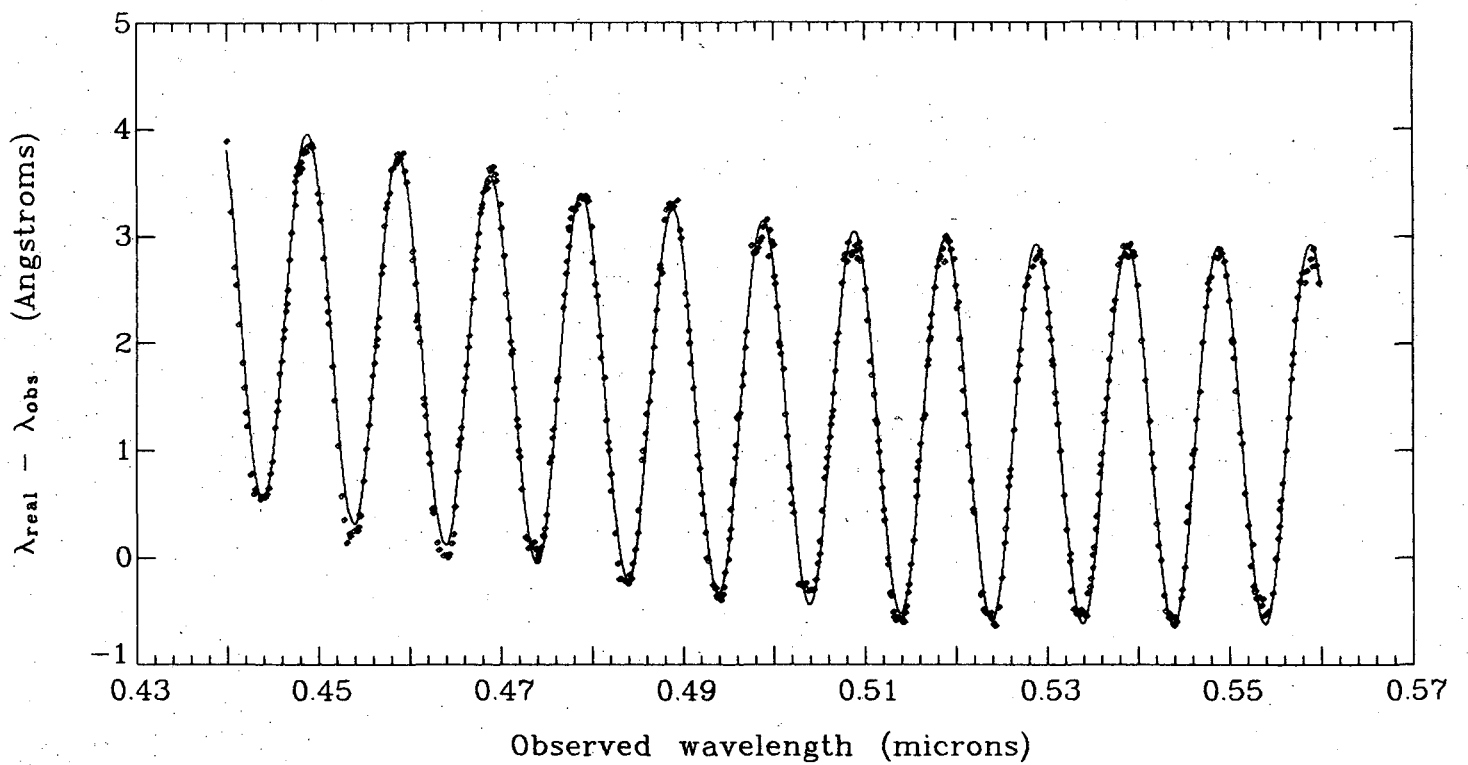

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Figure 2. Spectrometer wavelength error function.

function having a period of very nearly 100A and a peak-to-peak amplitude of about 4A. The solid line represents a least squares fit to the error function of the form

$$\lambda_{true} - \lambda_{obs} = a + b\lambda + c\lambda^2 + d \sin (e\lambda + f) \qquad (1)$$

where the constants were found to be

$a = 35.45 \quad b = -0.0126 \quad c = -1.156 \times 10^{-6} \quad d = 1.766$

$e = 0.062864$ and $f = -4.202$

when λ is expressed in Angstroms. The error function was found to be reproducible to within ± 0.1A. The most likely cause of the fluctuation is a slight wobbling of the worm gear drive with each rotation of the drive screw (occurring once each 100A). All wavelengths were corrected according to Eq. (1).

Measurement of the spectral slit function is also necessary for interpretation of the spectral data. Knowledge of this function is needed to compute the response of the monochromator and subsequent electronics to an emission line (or group of such lines) having a natural or Doppler width narrower than the spectral resolution of the monochromator. The response of the system to isolated atomic emission lines was recorded on a strip chart recorder. Care was taken to scan slowly enough so that RC broadening by the electronics was negligible. A typical response appears in Fig. 3; the slit openings were 0.35 mm corresponding to a full width at half maximum intensity (FWHM) of 11.2A. This latter number should be considered as approximate, however, since it is not known how well the fiduciary markings on the slit control correspond to the actual slit openings. After the wavelength corrections were applied, the slit function could be approximated by an isosceles triangle having a FWHM equal to 11.50 ± 0.05A. The function was found to be the same

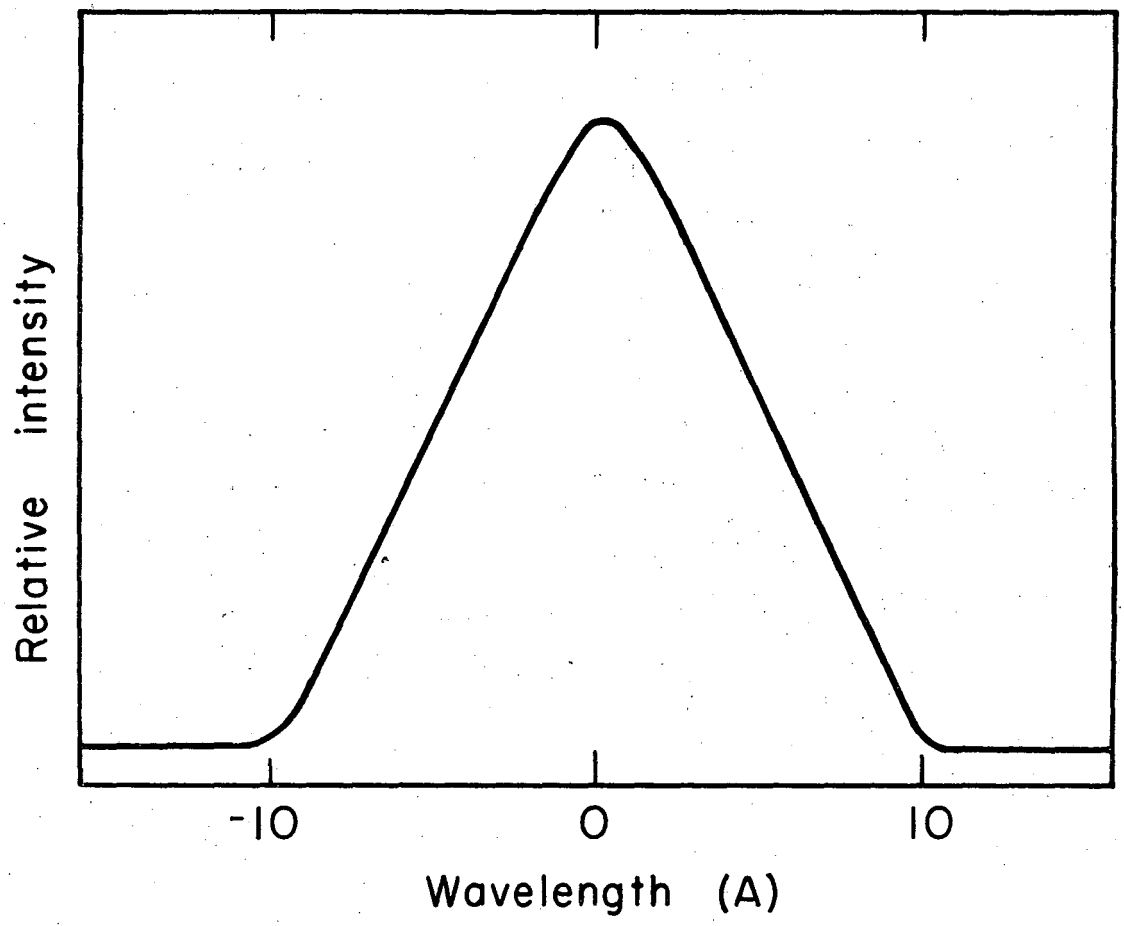

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Figure 3. Spectrometer slit function (no RC broadening).

within the stated tolerance for all atomic lines which were scanned.

C. The Photomultiplier Tube

An EMI 9558QA photomultiplier tube having an S-20 type spectral response and a quartz window was used as the optical detector. Its large photosensitive area (44 mm diameter) eliminated the necessity of focusing the exit slit of the monochromator onto the tube. Dark pulses arising from thermionic emission from the photo-cathode were reduced from over 3000/sec to about 40/sec by cooling the tube to dry ice temperatures in a cryostat similar in design to that of Lipsett and Horita (16). In order to eliminate the likelihood of erratic noise being introduced by the presence of metal close to the photocathode surface but at vastly different potential from it, (see ref. 17), the tube was operated with the cathode at ground potential and the anode at high voltage. The resolved pulses caused by photons striking the photocathode were then capacitively coupled out by keeping the load resistor small (10 KΩ) and the time response consequently fast. A discussion of the problems of S/N is given in the next section. The photomultiplier tube was powered by Fluke Model 412B high voltage d-c power supply operated at a voltage of 1500V (corresponding to a gain of 5×10^5).

D. Signal Processing - The Electronics

When a photon of energy $h\nu$ strikes the photocathode surface, there exists a probability which is a function of the type of photosensitive surface, the photon energy, and the cathode to first dynode voltage, that an electron will be emitted from the surface and make its way to the first dynode. The function of the dynodes is to multiply the number of electrons reaching the anode, thus passing a measurable current

through the load resistor R_L. The voltage across the resistor is given by

$$v = \frac{q}{c} = \frac{it}{c} \qquad (1)$$

where i is the current through the load resistor, t is the time duration of the pulse, and c is the stray capacitance across R_L and is on the order of 50 pf. The time resolution of the network is given by the RC time constant, $c \times R_L$, which is kept small ($\sim 10^{-6}$ sec) so that coincidence losses are negligible. Pulses caused by photons striking the photocathode surface (signal pulses) are not the only pulses detected, however. Even when no light falls on the photomultiplier tube, random pulses can be detected. These pulses can be subdivided into three categories, each having a different origin. It should be stated at this point that signal pulses are not of one unique voltage but rather have a spread in voltages because the gain of each dynode stage is statistical in nature (as well as depending on the voltage between the dynodes). Frequently, pulses much larger than signal pulses are detected in a sudden burst. These are throught to be the result of external radio-activity causing radiation from the tube window and from cosmic rays striking the photocathode; they occur at the rate of about 20/minute for a tube of the dimensions used (17). A second class of pulses is caused by thermionic emission from the photocathode surface. For red sensitive tubes, such as the EMI 9558, the work function of the surface is low and the number of electrons having sufficient thermal energy to escape from the photocathode is large (~3000/sec). These pulses can in no way be distinguished from normal signal pulses when light is falling on the tube. As mentioned previously, their number can be greatly reduced by cooling the tube to -40°C or lower. Thirdly, the dynodes themselves can give rise to

thermionic emission. However, the work function for the dynode material is higher than that of the photocathode and fewer stages of gain are undergone; hence, these pulses are fewer in number and have typically lower voltages than those originating at the photocathode. Nevertheless, since the dynodes are in the interior of the vacuum tube, they are not cooled as readily as is the photocathode surface. Further contribution to dark noise is reported to come from the effects of strong field emission from whiskers in the dynodes (18). These pulses, too, although possibly numberous, will be of lower voltage than signal pulses.

Conventionally, all these current sources are blended together and the signal voltage measured across a large R_L (slow time constant); consequently, no differentiation between them is possible. Recently, it has been reported (14) that improvements in S/N can often be obtained when working at low signal levels without resorting to actual pulse counting techniques. These procedures were followed in the present studies. The pulses from the load resistor, after being sent through an emitter-follower, were fed into a combination Schmitt trigger-monostable multivibrator. The level could be set such that almost no pulses of the third category would trigger an output pulse. Furthermore, since all output pulses were of the same height and width, the disproportionate contribution of the large pulses of the first category was greatly reduced.

The output of the monostable multivbrator was fed into a Princeton Applied Research Model JB-5 lock-in amplifier (phase sensitive detector). The advantages of using a-c electronics are well known: freedom from drift and cancellation of d-c signal components to name but two. The light signal was chopped at 400 hertz by an American Tim Products Type 5A

tuning fork chopper which also provided a reference signal to the phase sensitive detector. The output of the phase sensitive detector was then fed to both a strip chart recorder (Texas Instrument recti-riter 1ma) and to an A to D converter consisting of a Digitec Model 251 digital voltmeter interfaced to a Model SP-2 Friden paper tape punch. In a typical experiment, an interupt system dependent on line frequency would periodically cause the reading of the digital voltmeter to be punched out as the monochrometer scanned through the spectrum. In that way, raw intensities at known wavelength intervals were available in convenient form for computer calculation.

The function of the lock-in amplifier is to add signals arriving in the light on period and subtract from the sum those signals arriving in the light off period thus, cancelling out contributions of dark (thermal) pulses. Since the dark events are random in nature, however, they still contribute to noise in the signal. Each pulse arriving at the tuned signal channel of the amplifier produces a component at the fundamental chopping frequency. This component rings in an exponentially decaying fashion (68), thus spreading out the contribution of each pulse. It is this 400 hertz component that is added and/or subtracted by the lock-in amplifier. For a step by step tracing of the electronic signal, see Fig. 4.

By simultaneously feeding signals into the lock-in detection system and into a Hewlett-Packard digital counter, a calibration of output voltage versus counts/sec was made. In this way an equivalence between dark pulses and output voltage could also be made. The signal to noise ratio is given by

$$S/N = \frac{V_L}{\sqrt{V_L + V_D}} \qquad (2)$$

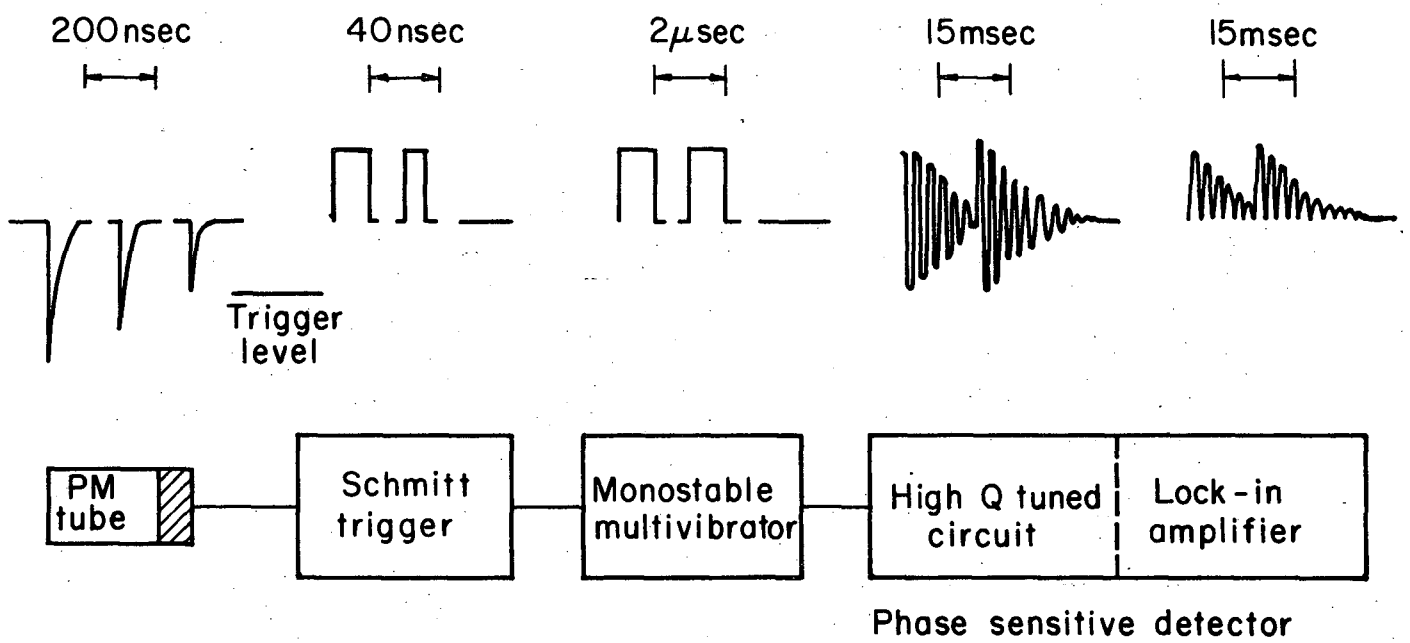

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Figure 4. Electronic signal processing

where V_L is the voltage output at a given light intensity L and V_D is the equivalent voltage of the dark pulses from the photomultiplier tube.

The discriminator level on the Schmitt-trigger is set to maximize the signal-to-noise ratio. For a fixed input signal, the number of signal counts is measured as a function of discriminator setting. The number of dark counts versus trigger level is measured with no light falling on the photomultiplier. In the limit that $V_L \gg V_D$, $S/N = \sqrt{V_L}$; hence it is desirable to set the level quite low, eliminating only those pulses originating at a stage beyond the photocathode. Contributions from cosmic ray induced electron bursts are also reduced in this way. In the other limit ($V_D \gg V_L$), $S/N = V_L/\sqrt{V_D}$. Since V_L as a function of level setting should be the same within a multiplicative factor for any light intensity L, a moderate intensity can be used for the calibration. V_D is measured, of course, with no light falling on the tube. One then plots $V_L/\sqrt{V_D}$ and examines the plot for a maximum. The best value for the trigger level will then lie somewhere between these two limiting values and will depend on the light levels encountered. In the present studies a moderately low level of the trigger level (2 mv) was found most suitable. Typical light levels were around 1000 pulses/sec. A pulse width of 1μsec assured that coincidence losses were kept to considerably less than 1%.

E. Intensity Calibration of the Optical System

For the purposes of this calibration a General Electric 30A/T24/17 tungsten ribbon lamp was used as a spectral irradiance standard. The power supply for the lamp was stabilized by an unusual photo-feed-back system. Light from the ribbon fell onto a photo diode after passing through a blue Corning No. 5030 filter. The current through the tungsten

ribbon was maintained such that the resistance of the photo diode always matched that of an adjustable helipot. The purpose of the blue filter was to make the light falling on the photodiode as sensitive as possible to temperature changes of the ribbon. Ribbon temperatures, as measured by a Leeds and Northrup Model 8622-C optical pyrometer, calibrated at the Lawrence Radiation Laboratory D.C. Standards Laboratory, were found to vary by less than ±1 to 2°K over the course of the calibration. It is more than likely that even this variance was the result of technique in measurement rather than actual fluctuations of temperature. Indeed, abrupt changes in the supply current to the lamp, which otherwise would have resulted in current decreases (or increases) by as much as 4 amps through the ribbon, were compensated for by the regulatory circuitry to the extent that no detectable change in the output of the lamp (as observed in the blue) was found.

The Planck distribution law for black body radiation can be expressed as

$$I d\lambda = \frac{a d\lambda}{\lambda^4 (e^{10^8 hc/k\lambda T} - 1)} \qquad (3)$$

where I is in units of quanta /sec/cm^2 radiating surface/unit solid angle/unit wavelength (A), λ equals wavelength in Angstroms, T equals temperature in degrees Kelvin, a equals 5.99586×10^{34}, h = Plancks constant, c = speed of light, and k = Boltzmann's constant.

The above expression holds only for a true black body. For all normal radiating materials, specifically a tungsten ribbon, deviations from the black body curve are observed. The emissivity for a substance [$E(\lambda,T)$] is defined as the ratio of emission of the substance at temperature T and wavelength λ to the radiation given off by a black

body at the same temperature and wavelength. Thus, for a non-black body we find

$$I\,d\lambda = \frac{a\,E\,(\lambda,T)\,d\lambda}{\lambda^4(e^{10^8 hc/k\lambda T}-1)} \qquad (4)$$

The emissivities used in this work are those obtained by De Vos (19). In order to use the above relationship, the true temperature of the tungsten ribbon must be measured. With an optical pyrometer one can measure the brightness temperature S of an object, i.e. that temperature at which a black body would radiate the same amount of energy as the object at temperature T at a given wavelength. The relationship between brightness temperature and true temperature is given by (20)

$$\frac{1}{S} - \frac{1}{T} = \frac{1}{c_2} \ln\,(t\,E(\lambda,T)) \qquad (5a)$$

where $c_2 = 1.498$ cm deg, λ is fixed at about 6500A by a filter in the pyrometer and the cut-off in sensitivity of the human eye. t is the transmission coefficient of any material between the emitting surface and the pyrometer, viz. the Pyrex envelope of the tungsten lamp which has a transmission factor of 0.92. Thus,

$$\frac{1}{S} - \frac{1}{T} = 1.04 \times 10^{-4} \log\,[0.92\,E(\lambda,T)] \qquad (5b)$$

Calculations of S versus T were carried out on a CDC 6600 computer by interpolating the emissivity data of De Vos. A plot of these values is given in Fig. 5. The true temperature obtained from the measured brightness temperature was then substituted in Eq. (4) and the intensity distribution calculated.

The lamp was carefully masked so that light from only the central section of the ribbon was allowed to fall on the monochromator entrance

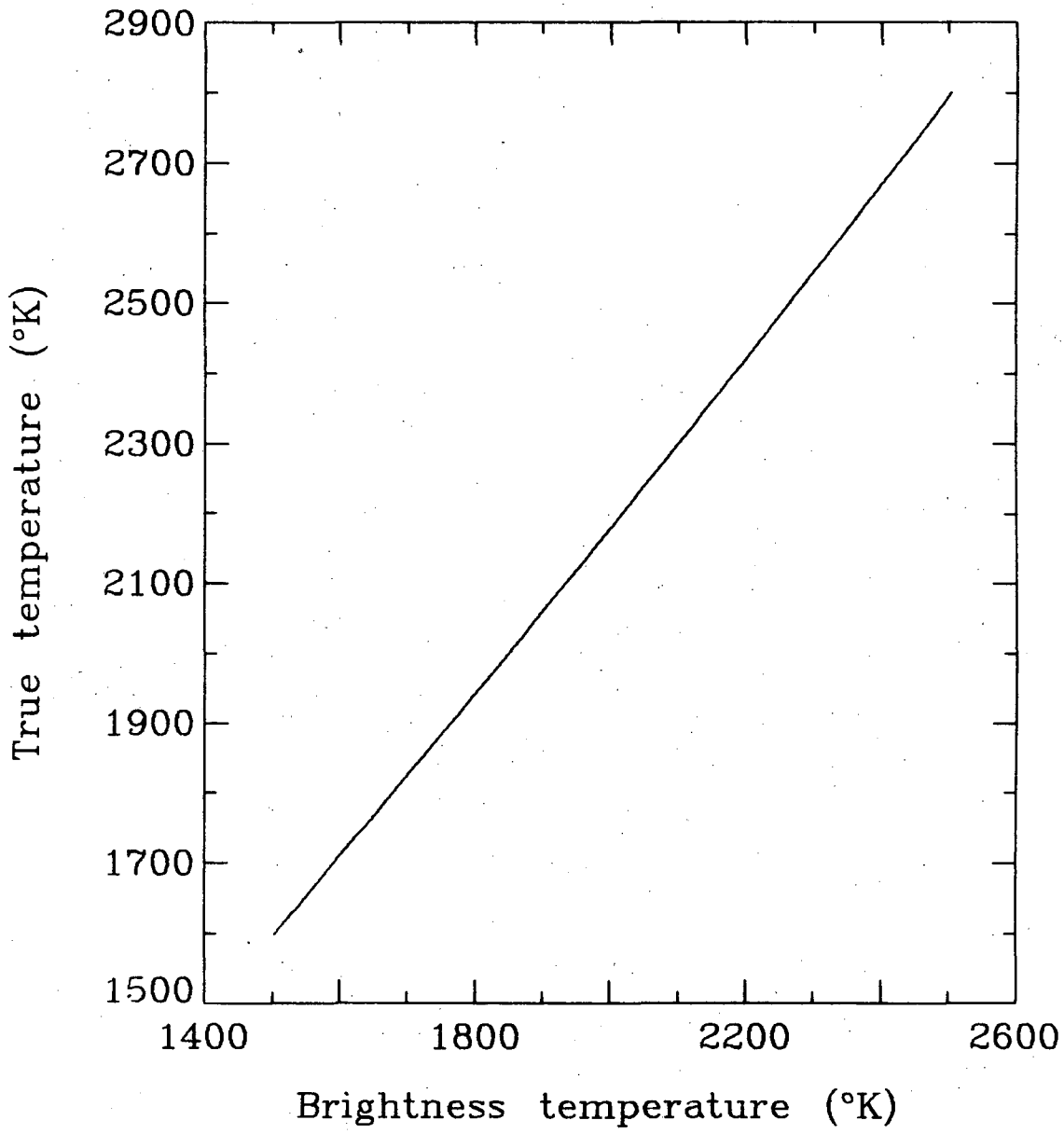

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Figure 5. True (thermodynamic) vs brightness temperature for tungsten ribbon lamp having envelope transmission coefficient equal to 0.92.

slit. No intervening lenses were used; however, in order to eliminate second order contributions, a Corning No. 3060 sharp cut filter (transmission less than 1% at wavelengths less than 3750A), calibrated on a Cary 14 spectrophotometer, was placed in front of the entrance slit.

The correction curve was obtained by dividing the computed spectral distribution by the system's response. Corrections obtained from two different lamp settings (S = 1957°K and 2064°K, T = 2127°K and 2250°K, respectively), normalized at one point, gave nearly identical results. The resultant calibration curve is shown in Fig. 6. All raw data intensities were then corrected for the response of the monochromator and photomultiplier tube before being used in subsequent calculations.

F. The Vacuum and Gas Delivery Systems

A diagram of the chemiluminescence cell is shown in Fig. 7. The cell, constructed from stainless steel, was equipped with two inlets and one larger outlet 120° apart. The calcium (lithium) fluoride observation window was sealed to the cell by means of a Viton-A "O" ring. All static "O" ring seals were found not to be attacked by the corrosive gases. Fluorine, obtained from the Matheson Company (98% purity typically) was passed through a tube containing activated NaF to remove any HF impurity and was stored in a 34 liter tank at pressures less than one atmosphere. The fluorine was metered into the reaction cell by means of a Vactronic Vari-Vac adjustable bellows-type leak valve. Flow rates were measured by use of a Hastings-Raydist Model LF-50 calorimetric mass flowmeter in which the fluorine came into contact with only monel metal surfaces. The principles of operation of the flowmeter have been discussed by Brown and Kronberger (21). Argon of 99.996 percent purity

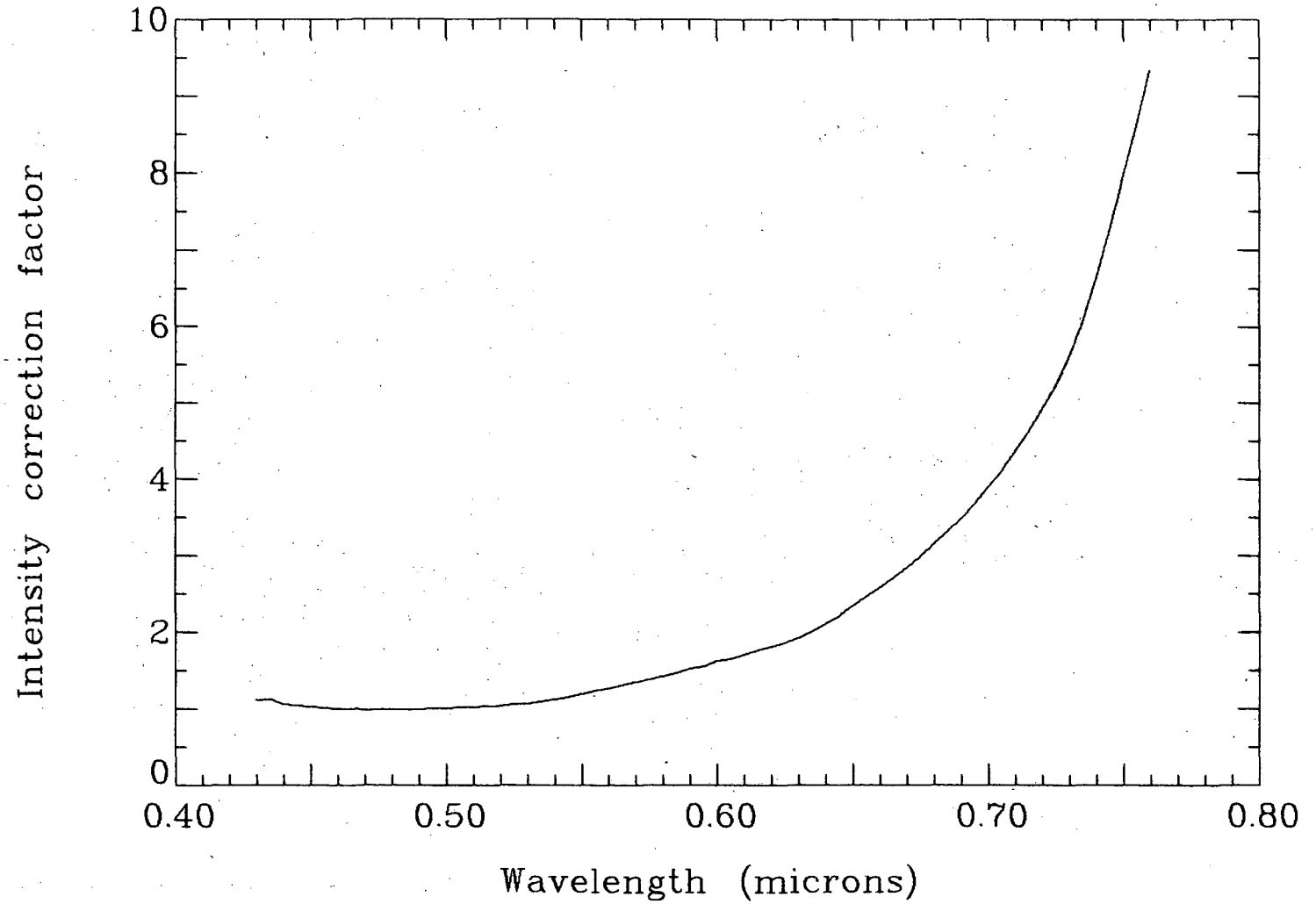

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Figure 6. Spectral sensitivity correction curve for optical system

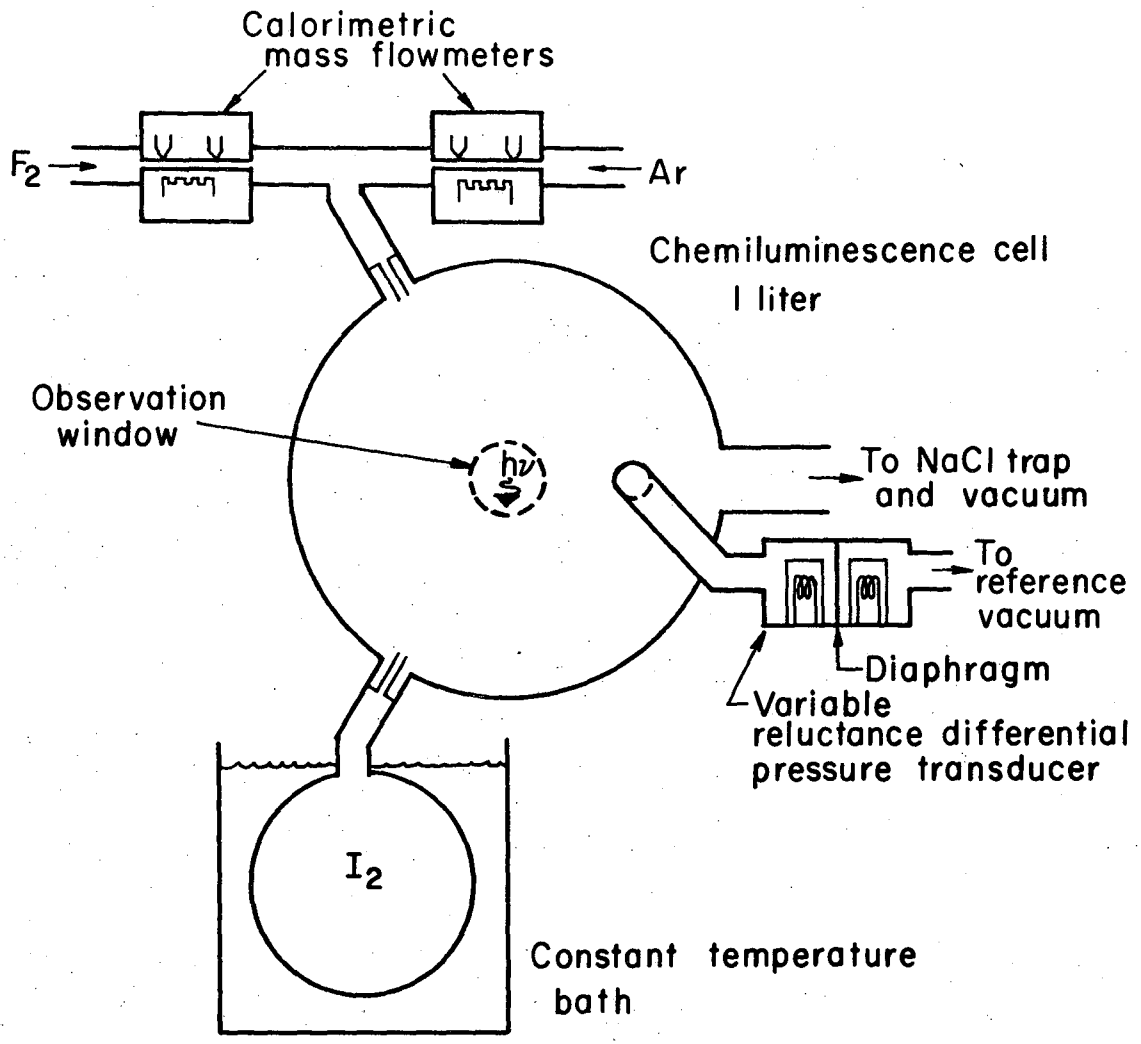

Figure 7. Block diagram of chemiluminescence cell and associated apparatus.

was obtained from Linde Inc. A metering valve and mass flowmeter identical to those used for fluorine were used to measure and control the flow of argon. These two gases were mixed prior to entering the cell.

Analytical reagent grade iodine, obtained from Mallicrockdt Chemical Works, was doubly vacuum distilled prior to use in these experiments. The glass bulb containing the I_2 was maintained just below room temperature (20.6°C) in a thermostated water bath in order to prevent crystallization of the iodine in the lines. Since the vapor pressure of I_2 is only 200 mtorr at the bath temperature, it was not feasible to measure the flow of I_2 with a flowmeter of the type described because of the flowmeter's low conductance. It was found that pressure heads in the 10's of torr were needed to obtain the desired gas flows through the pressure transducers. Consequently the I_2 was allowed to flow directly into the cell. A Westglass greaseless stopcock was used to meter the flow.

Pressures on the interior of the cell were measured by means of Pace Engineering Co. Model P7D - CD25 variable reluctance differential pressure transducer, one side of which was connected to the cell and the other to a reference vacuum. Its all stainless steel construction readily permitted use with fluorine. Calibration of the instrument was made against a more accurate, factory calibrated Datametrics Type 1014 Barocel Electronic Manometer by connecting both transducers to the cell and simultaneously measuring pressures of an inert gas. Measurements with the Pace transducer could be made to within ±2 m torr.

The volume of the cell was measured by expansion of gas from a container of known volume using the calibrated Pace transducer to

measure the pressures. The flowmeters could then be calibrated for each gas used in the experiments by closing the cell to the vacuum pump and measuring pressure differentials as a function of time. From these data the pumping speed of the vacuum system could be calculated by measuring the pressure of a gas under normal flow conditions (exit port open) at a known flow input rate. This known, the relationship between equilibrium iodine pressure under flow conditions to its flow rate was readily established.

The effluent gases passed over NaCl crystals heated to 100°C to replace any excess F_2 by Cl_2 before passing a liquid N_2 trap.

III. THEORY

A. Spectroscopic Energies

1. Electronic, Vibrational, and Rotational Constants.

The emission spectrum of iodine monofluoride, the last of the diatomic interhalogen compounds to be discovered, was first reported spectroscopically by Durie (22) in 1951. Observation of the new species was made in a flame produced by the presence of iodine crystals in a fluorine atmosphere. The simple banded structure of the spectrum led Durie to assume the emitting species to be diatomic, but confirmation of this was not established until the high resolution spectrum was published in 1966 (23). In that work the rotational and slightly revised vibrational frequencies of the molecule were made available. The equilibrium internuclear distance calculated from the rotational spacing was in good agreement with that expected from the average of the iodine and fluorine bonds lengths, thus giving strong evidence that the species was indeed diatomic. Thirty two bands from v' = 0 to v' = 11 (and J' up to 120) were reported in high resolution as well as fourteen additional bands obtained under low resolution. Values of the electronic, vibrational, and rotational constants, obtained by least squares fits to Durie's data, are given in Table I. The vibrational spacings are given by

$$G(v',v'') = T_e + \omega_e' (v' + 1/2) - \omega_e x_e' (v' + 1/2)^2 + \omega_e y_e' (v' + 1/2)^3 - [\omega_e'' (v'' + 1/2) - \omega_e x_e'' (v'' + 1/2)^2 + \omega_e y_e'' (v'' + 1/2)^3] \quad (6)$$

where primes refer to the upper (excited) electronic state and double primes to the lower (ground) electronic state. Rotational constants are given by

$$B_v = B_e - \alpha_v (v + 1/2) + \gamma_v (v + 1/2)^2 \quad (7)$$

Table I. Molecular constants of iodine monofluoride

	$^1\Sigma^+$	$^3\Pi_{0^+}$
ω_e	611.1(2)	410.0(1)
$\omega_e x_e$	3.3(0)	2.3(0)
$\omega_e y_e$	0.006	-0.12(6)
B_e	0.27984	0.22725
α_e	$1.873(6)\times10^{-3}$	$1.420(2)\times10^{-3}$
γ_e	-7.13×10^{-6}	-8.189×10^{-5}
D	2.4×10^{-6}	2.8×10^{-6}
r_e	1.909(3)A	2.118(7)A
D_e (dissociation energy)	23534±100	4884±100
T_e	19054.0	
μ	16.52457 amu I = 126.9044 F = 18.9984 (C_{12} = 12,000)	

All units in cm^{-1} unless otherwise noted

where v refers to either v' or v", and finally, the rotational spacings are given by

$$F_v(J) = B_v J(J+1) - D J^2(J+1)^2 \qquad (8)$$

where, again v and J refer either to the upper or the lower electronic states.

Because slight perturbations in both the vibrational spacings and rotational B_v values for v=10 and 11 were observed, these levels were omitted in the calculation of the least squares constants.

2. Electronic States for IF and Their Dissociation Energies.

The transition of IF in the visible region of the spectrum was attributed to the $^3\Pi_{0^+} \rightarrow {}^1\Sigma^+$ system analagous to that found for I_2. The dissociation products for the two states are two normal ($^2P_{3/2}$) atoms for the ground state and one normal ($^2P_{3/2}$) and one excited ($^2P_{1/2}$) atom for the excited electronic state (24). The transition, which is not allowed in Hund's coupling case a, does become allowed in Hund's coupling case c which is applicable for molecules containing heavy nuclei (25). Although there is no a priori reason for ruling out the upper state being the $^3\Pi_1$ component of the $^3\Pi$ system [which dissociates into 2 normal ($^2P_{3/2}$) atoms], sufficient evidence exists which eliminates that possibility. For the latter case, each virational level has two closely spaced components of opposite rotational symmetry (Λ doubling); consequently, one would expect to find a Q branch as well as P and R branches in the high resolution spectrum. In the former case, the two components ($^3\Pi_{0^+}$ and $^3\Pi_{0^-}$) are sufficiently separated so that each can be considered as an entirely different electronic state (25). In that case, no Λ doubling is found, and P and R branches, only, are to be

expected. According to Durie (23), no Q branches are observed, thus eliminating the possibility of the transition occurring from the $^3\Pi_1$ state. It is interesting to note, however, that in the cases of IBr (26) and ICl (27) strong afterglows from the $^3\Pi_1$ state have been reported and only very weak emission from the $^3\Pi_{0+}$ states has been observed upon atom recombination. Other examples of transitions from the $^3\Pi_{0+}$ state do occur in the cases of Br_2 (28), Cl_2 (27, 29), BrCl(27, 30), and BrF (23). In the case of Br_2, strong luminescence from the $^3\Pi_1$ state has also been reported (26).

The question of the dissociation energy of the ground state of IF is also illuminated by the study of the high resolution spectrum. The a priori possibilities are that the dissociation products of the $^3\Pi_{0+}$ state are either $I(^2P_{3/2})$ and $F(^2P_{1/2})$ or $I(^2P_{1/2})$ and $F(^2P_{3/2})$. The excitation energies (with respect to normal ground state atoms) are 404 and 7598 cm^{-1} respectively. The dissociation energy of the $^3\Pi_{0+}$ state has been obtained from a conventional Birge-Sponer extrapolation and is reported (23, 31) as 4884 ± 100 cm^{-1} with respect to the potential minimum. Also, from the vibrational analysis of the spectrum, the energy difference between the potential minima for the two electronic states has been found to be 19054 cm^{-1}. This yields a dissociation energy of 23534 or 16339 cm^{-1}, depending upon the set of dissociation products. Since IF is known to be chemically unstable with respect to disproportionation to I_2 and IF_5 (32), Durie and Gaydon (31) favored the lower value (44 kcal) on the grounds that such a choice would support this fact whereas choice of the higher bond energy (66 kcal) would predict IF to be a stable species. Unfortunately, this arguement rests on a mistaken value of the bond energy of IF_5. The value of 194.6 kcal/mole reported by Woolf (33) is not the bond energy of IF_5, as assumed by

Durie and Gaydon in their calculation, but rather the heat of formation from the elements. Taking the heat of sublimation of I_2 into account, one obtains a bond energy of 315 kcal/mole for IF_5. This value would make IF_5 the thermodynamically stable species even if the higher bond energy were chosen for IF. Indeed, it has been pointed out by Slutsky and Bauer (34) that it would be highly unusual for the molecule IF_5 to have an average energy per bond (63 kcal) greater than that of IF itself.

The strongest evidence in favor of the higher bond energy, however, is the fact that predissociation in the rotational fine structures has been observed for v' = 11 beginning at J' = 45. No predissociation of the v' = 10 level is observed, thus indicating that the electronic state* responsible for the predissociation crosses the $^3\Pi_{0+}$ state nearly horizontally. (See Fig. 8.) The onset of predissociation occurs almost

---

* Mulliken (35) and Mathieson and Rees (36) have indicated that two different halogen ground state atoms can correlate with the following states in Hund's coupling case c: $0^+(2)$, $0^-(2)$, 1(3), 2(2), 3(1). Strong interaction (avoidance of crossing) with the excited (0^+) electronic state from which transitions are observed could be caused by the second (and presumably repulsive) 0^+ state correlating with ground state atoms. This possibility does not exist for homonuclear diatomic molecules since the second 0^+ state would be of the wrong inversion symmetry in that case (g vs. v for the upper state). The selection rules for perturbation are (in case c) $\Delta\Omega = 0, \pm 1$, $0^+ \leftrightarrow 0^+$, $0^- \leftrightarrow 0^-$, $0^+ \not\leftrightarrow 0^-$ (and $u \not\leftrightarrow g$). Thus, weaker interaction (predissociation without avoidance of crossing) could be caused by one of the $\Omega = 1$ states.

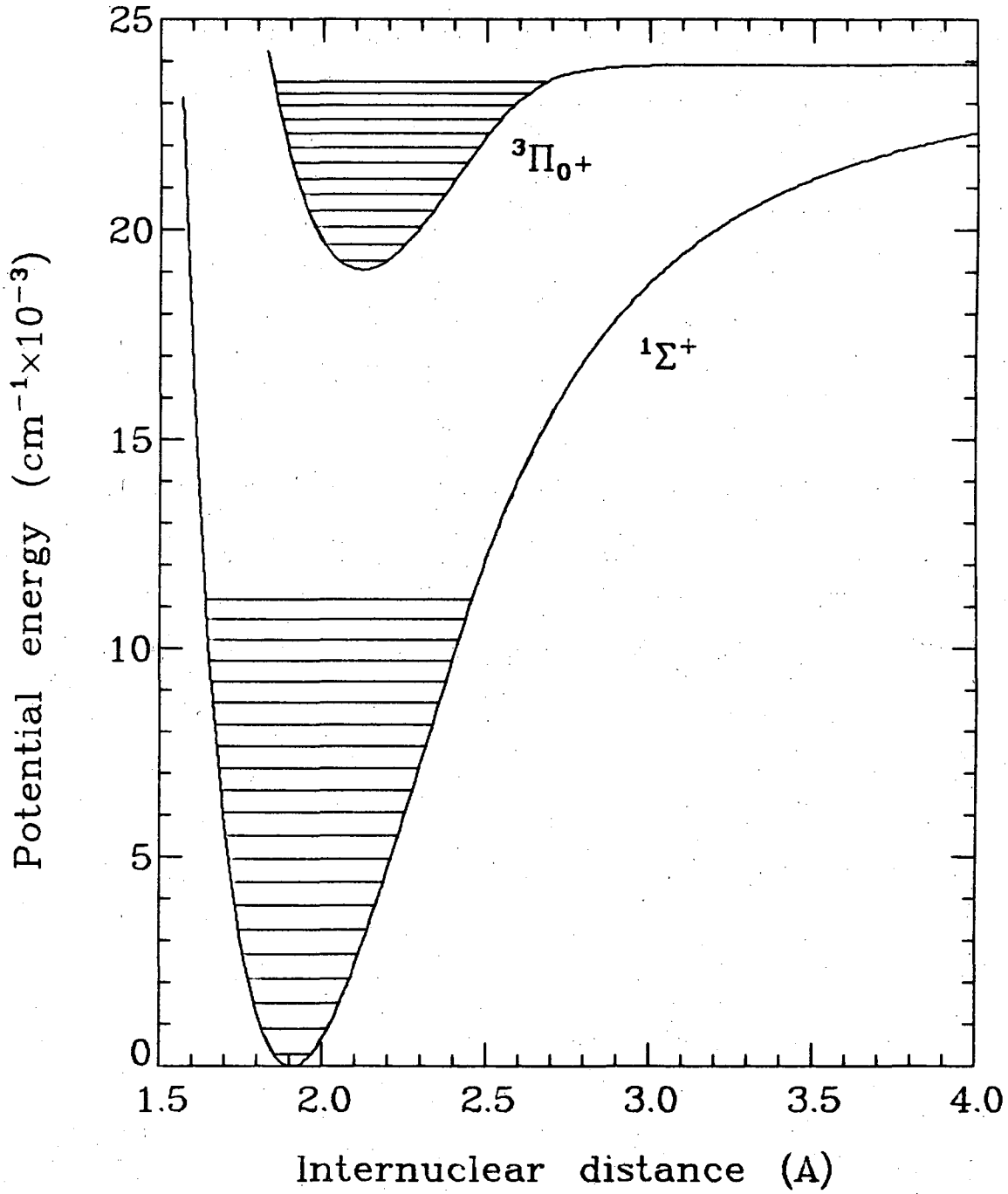

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Figure 8. RKR potential curves and energy levels for IF.

exactly at the higher possible dissociation energy of IF (once the height of the rotational barrier for $J' = 45$ is taken into account). It would be nearly impossible for the responsible state to cross the $^3\Pi_{0+}$ state without strongly perturbing several vibrational levels if the dissociation energy of the $^1\Sigma^+$ state were the lower of the two values under consideration.

In conclusion, choice of the higher bond energy is consistent with that found for ICl as reported by Clyne and Coxon (27) in which case the dissociation products of the $^3\Pi_{0+}$ state have been identified as $I(^2P_{3/2})$ and $Cl(^2P_{1/2})$. Recent observations (37) of the photodissociation products of several interhalogen compounds by ultra violet absorption spectroscopy have shown the dissociation products of I Br to be $I(^2P_{3/2})$ and $Br(^2P_{1/2})$ and those of BrCl to be $Br(^2P_{3/2})$ and $Cl(^2P_{1/2})$. Results for ICl were inconclusive. Thus, in all known cases, the lighter of the two atoms has been the electronically excited $(^2P_{1/2})$ product in the dissociation of $^3\Pi_{0+}$ states of the interhalogens.

B. Interpretation of Spectral Intensities

1. General Discussion

In this section general consideration is given to those factors governing intensity distribution in an electronic band emission spectrum of a diatomic molecule. Parts of the discussion are due to Herzberg (25) and his text is recommended for a more detailed explanation. The intensity of emission of a spectral line (in quanta/sec) is given by the product of the population of the emitting state and the Einstein transition probability for spontaneous emission as follows:

$$I_{em}^{nm} = N_n A_{nm} = \frac{64\pi^4 \nu_{nm}^3 N_n |R^{nm}|^2}{3h} \tag{9}$$

where n refers to the upper state, m to the lower state, R^{nm} is the matrix element for the transition, and ν_{nm} is its frequency. For the specific case of a single vibration rotation line from an electronic band, we have (in emission)

$$I_{v''J''}^{v'J'} = \frac{64\pi^4 \nu_{v'J'v''J''}^3 N_{v'J'}}{3h} \frac{\left| \sum_{i,k} R_{v''J''_k}^{v'J'_i} \right|^2}{d_{v'J'}} \tag{10}$$

where the transition matrix element now consists of a sum of individual transition matrix elements connecting the various degenerate sublevels of each rotational state, and $d_{v'J'}$ is the degeneracy of the emitting state (equals 2J'+1).

If the system is in rotational equilibrium, we can express the population of a particular rotational level as

$$N_{v'J'} = \frac{N_{v'} (2J'+1)}{Q_{rot}} \exp\left[- \frac{B_{v'J'}(J'+1)}{kT_r} \right] \tag{11}$$

where Q_{rot} is the rotational partition function and equals $kT_r/B_{v'}$.

The rotational line strength, $S_{J''}^{J'}$, represents that part of the transition matrix element due to overlap of the rotational wave functions and can be factored from the rest of the matrix element which contains the electronic and vibrational contributions. These rotational line strengths, commonly called Honl-London factors (38), will be discussed in more detail in a subsequent section. Thus, combining the above expressions, we have

$$I_{v''J''}^{v'J'} = \frac{64\pi^4 \nu_{v'J'v''J''}^3 S_{J''}^{J'} N_{v'} B_{v'}}{3h\ k\ T_r} \exp\left[-\frac{B_{v'J'}(J'+1)}{kT_r}\right] \tag{12}$$

$$|R_{e''v''}^{e'v'}|^2$$

The transition moment can be expressed as

$$R_{e''v''}^{e'v'} = \langle \psi_{e'} \psi_{v'} | M | \psi_{e''} \psi_{v''} \rangle \tag{13}$$

where the ψ_e's are the electronic wavefunctions, the ψ_v's the vibrational wavefunctions, and M is the transition moment, a vector with components $\Sigma e_i x_i$, $\Sigma e_i y_i$ and $\Sigma e_i z_i$. Separation of the transition moment into two parts, one depending only on the positions of the nuclei, M_n, and one depending only on the coordinates of the electrons, M_e, yields

$$R_{e''v''}^{e'v'} = \langle \psi_e' | \psi_e'' \rangle \langle \psi_v' | M_n | \psi_v'' \rangle + \langle \psi_v' | R_e | \psi_v'' \rangle \tag{14}$$

where $\quad R_e = \langle \psi_e' | M_e | \psi_e'' \rangle$

For a transition between two different electronic states, the first term goes to zero due to the orthogonality of the electronic wave functions. R_e is called the electronic transition moment. Since the electronic wavefunctions, under the Born-Oppenheimer approximation (39), are only slightly dependent on internuclear distance, the electronic

transition moment is often removed from under the second integral sign and is considered to take on an average value, $\bar{R}_e$, thus yielding

$$|R^{e'v'}_{e''v''}|^2 = |\bar{R}_e| \ \langle\psi'_v|\psi''_v\rangle^2 \tag{15}$$

where the squared integrals $\langle\psi'_v|\psi''_v\rangle^2$ are the well known Franck-Condon factors (40). Writing the expression for the intensity in final form, we have

$$I^{v'J'}_{v''J''} = \frac{C\ N_{v'}\ B_{v'}}{T_r} \exp\left[-\frac{B_{v'J'}(J'+1)}{kT_r}\right]|\bar{R}_e|^2 \langle\psi'_v|\psi''_v\rangle^2\ \nu^3_{v'J'v''J''}\ S^J_{J''} \tag{16}$$

where $C \equiv 64\pi^4/3kh$. The assumption that $\bar{R}_e$ can be separated from the vibrational overlap integral is discussed further in Section III-B-3.

2. Calculation of the Franck-Condon Factors

In Section II-A the potentials for the upper and lower electronic states were discussed in terms of their dissociation energies and electronic term values. In order to compute the Franck-Condon overlap integrals, however, the vibrational wave function themselves must be determined and this necessitates accurate knowledge of the exact shape of the potential. Correlation of the states of the separated atoms with that of the diatomic molecules provides us with certain qualitative information about the electronic states and potential curves, but the exact form of the potential has to be determined empirically from the spectral constants. Any useful potential for a bound state must meet at least the following criteria:

1) it must have a potential minimum, the minimum occurring at the equilibrium internuclear distance;

2) it must take on a value equal to the dissociation energy as the internuclear distance becomes very large;

3) it must become infinite, or nearly so, as the internuclear distance approaches zero. (This, naturally, is due to the mutual repulsion of the nuclei.)

Varshni (41) has discussed the usefulness of many potentials which meet the above criteria in an extensive review article. The potential used most widely until recently has been that due to Morse (42) mainly because substitution of this potential into the Schrodinger wave equation in many cases yields energies closely approximating those observed spectroscopically, and, further, because it yields analytical wave functions with which one can calculate overlap integrals in a straight-forward manner. The Morse function has the form

$$U(r) = D_e(1-e^{-\beta(r-r_e)})^2 \tag{17}$$

where D_e is the dissociation energy and r_e the equilibrium internuclear distance. Vibrational energies are given by (25)

$$G(v) = \beta \sqrt{\frac{D_e h}{2\pi^2 c\mu}} (v + 1/2) - \frac{h\beta^2}{8c\pi^2\mu} (v + 1/2)^2 \tag{18}$$

for the rotationless molecule.

Equating the coefficients of $(v + 1/2)$ and $(v + 1/2)^2$ to the spectroscopic constants ω_e and $\omega_e x_e$ yields

$$\beta = \sqrt{\frac{2\pi^2 c\mu}{D_e h}} \omega_e \tag{19}$$

$$D_e = \frac{\omega_e^2}{4\omega_e x_e} \tag{20}$$

Applicability of the Morse potential can be determined by comparing the D_e predicted by Eq. (20) with the true dissociation energy. Also, a Birge-Sponer diagram, according to Eq. (19), should yield a straight line all the way to the intercept of ΔG with the v axis. Although such a plot is linear as far as the energy levels have been measured for the $^1\Sigma^+$ state of IF, definite curvature can be seen in Fig. 9 in the case of the $^3\Pi_{0+}$ state. A similar method of determining the reliability of the Morse potential is to determine from a least squares fit to the energy levels the necessary number of terms in the Taylor series expansion of $(v + 1/2)$ required to give an accurate fit. If terms higher than $(v + 1/2)^2$ are significant, the Morse potential is inadequate. We find that in the case of the $^1\Sigma^+$ ground state the $\omega_e y_e$ term [see Eq. (6)] is quite small (Table I). However, for the $^3\Pi_{0+}$ state, the $\omega_e y_e$ becomes rather significant. Coolidge et al. (43) suggest that not only should a correct potential give accurate vibrational energies, but that it should also predict correct rotational constants (B_v values). A solution of the Schrodinger using the Morse potential and including rotational energy terms has been obtained by Pekeres (44) using perturbation methods [see Pauling and Wilson (45), pg. 272 ff]. The vibration rotation interaction term, α_e, is given by

$$\alpha_e = \frac{3h\omega_e x_e}{4\pi^2 \mu r_e^2 \omega_e c} \left(\frac{1}{\beta\, r_e} - \frac{1}{\beta^2 r_e^2} \right) \tag{21}$$

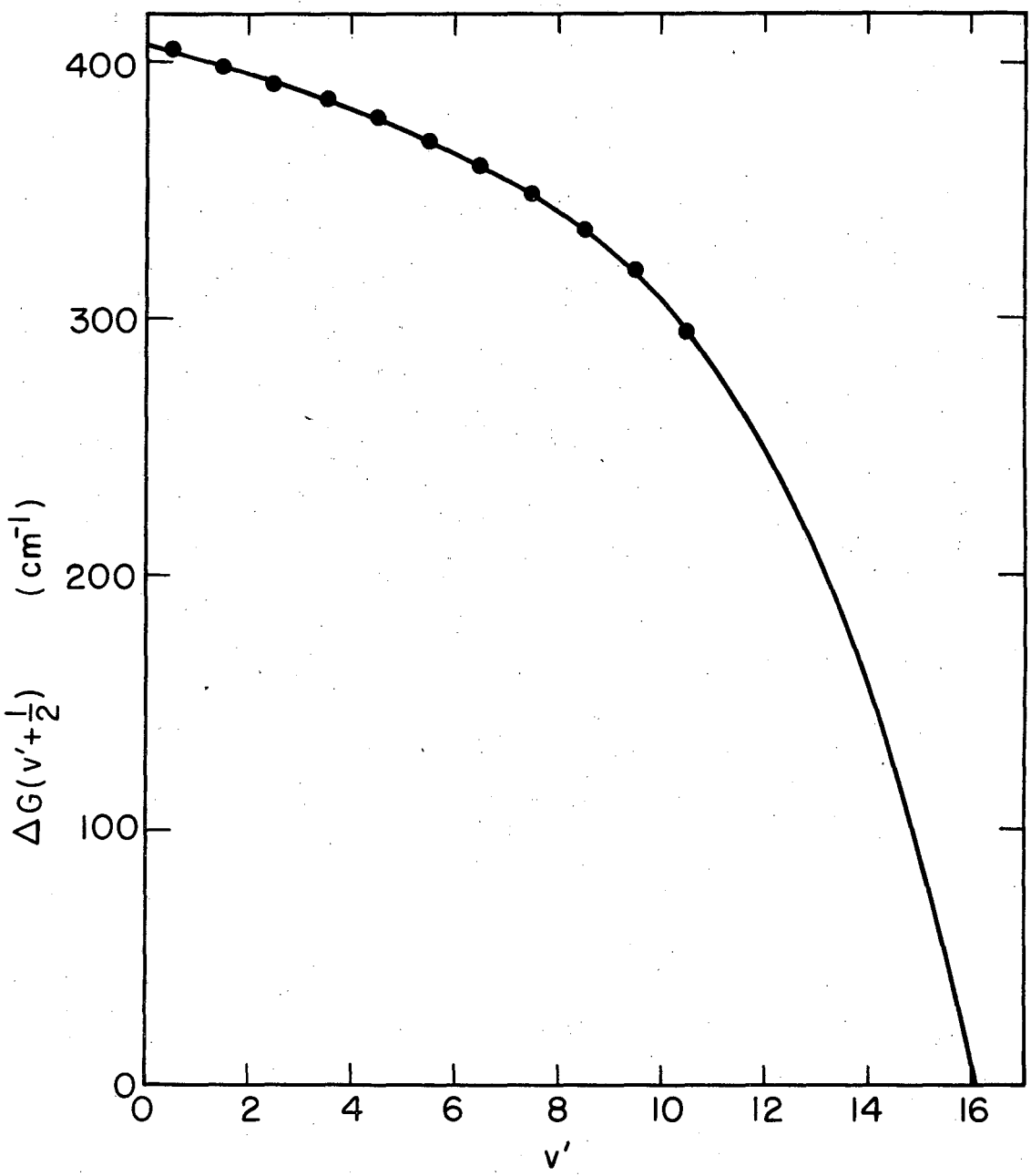

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Figure 9. Birge-Sponer extrapolation for the $^3\Pi_{0^+}$ state of IF.

Using β calculated from Eq. (19), we find that for the $^1\Sigma^+$ state α_e (Morse) = 1.821×10^{-3} cm^{-1} compared to the actual value (as determined from the rotational fine structure spectra of Durie) of 1.874×10^{-3}. However, for the $^3\Pi_{0+}$ state α_e(Morse) = 1.258×10^{-3} as compared to the true value 1.420×10^{-3}. We recall that the rotational B_v's are given approximately by $B_v = B_e - \alpha_e(v + 1/2)$ where $B_e = h/8\pi^2 c\mu r_e^2$. Thus, while the Morse potential seems adequate to describe the $^1\Sigma^+$ ground electronic state, it does not satisfactorily predict either the rotational constants or vibrational energy levels of the upper electronic state.

The advent of the high speed electronic computer has greatly facilitated the calculation of Franck-Condon factors based on potentials yielding non-analytic wave functions. Recently, Zare (46) has published programs for the calculation of potentials and Franck-Condon factors based on the semi-classical method of Rydberg-Klein-Rees (47). The essence of Rydberg's original method was to consider the case of the classical rotating vibrator having a total energy $U = p_r^2/2\mu + V_{eff}(r)$ where p_r is the radial momentum (momentum of the vibration) and $V_{eff}(r)$ is the sum of the potential energy $V(r)$, and the rotational energy, K/r^2, where K equals $p_\theta^2/2\mu$, p_θ being the angular momentum. For an oscillatory motion, the action I is defined as $\oint p_r dr$. In what is commonly considered to be a Wentzel-Kramers-Brillouin (WKB) approximation, the classical action is set equal to its quantum mechanical equivalent $h(v + 1/2)$. Thus, substituting for p_r we have

$$I = (2\mu)^{1/2} \oint [U-V_{eff}(r)]^{1/2} dr = h(v + 1/2) \qquad (22)$$

The classical expression for the energy of rotation is $E_{rot} = K\overline{(1/r^2)}$ where the average is to be taken over the period of vibration, τ_v.

Making use of the definition of p_r $(= \mu \frac{dr}{dt})$, we have

$$E_{rot} = K\left(\frac{1}{r^2}\right) = \frac{R}{\tau_v} \oint \frac{1}{r^2}\, dt = \frac{K\mu}{\tau_v} \oint \frac{dr}{r^2 p_r} \tag{23}$$

Now, since $\tau_v = \frac{dI}{dE}$, we obtain upon substitution of the quantum mechanical equivalent of K

$$E_{rot} = B_v J(J+1) = \frac{h^2}{8\pi^2}\frac{J(J+1)}{\mu} \oint \frac{1}{r^2}\,[U-V_{eff}(r)]^{1/2}\, dr$$

$$\oint [U-V_{eff}(r)]^{-1/2}\, dr \tag{24}$$

or

$$B_v = \frac{h^2}{8\pi^2\mu} \oint_{r_1}^{r_2} [U-V_{eff}(r)]/r^2\, dr \oint_{r_1}^{r_2} [U-V_{eff}(r)]^{-1/2}\, dr \tag{25}$$

where the limits of r are such that $V_{eff}(r_1) = V_{eff}(r_2) = U$. Rydberg adjusted the potential such that graphical evaluation of the integrals gave good agreement with the experimental observables. Difficulty arises in evaluation of the integrals in Eqs. (24) and (25) since the integrand becomes infinite at the limits of integration (the classical turning points). Klein, in formulating the problem, started with the above equations but was able to evaluate the turning points r_- and r_+ in terms of two functions f and g according to relation

$$r_\pm = \frac{f}{g} + f^2{}^{1/2} \pm f \tag{26}$$

where f and g are defined as follows

$$f = \frac{\delta S(U,K)}{\delta U} \quad g = \frac{\delta S(U,K)}{\delta K} \quad S(U,K) = (2\pi^2\mu)^{-1/2} \int_0^I [U-E(I,K)]^{1/2}\, dI \tag{27}$$

$E(I,K)$ is the sum of the rotational and vibrational energies in terms of the previously defined quantities I and K and I', the limit of integration, is reached when the integrand goes to zero. Rees determined analytical solutions for the case in which

$$E(I,K) = \omega_e(v + 1/2) + \omega_e x_e(v + 1/2)^2 + B_v J(J + 1) + D_v J^2(J + 1)^2 \tag{28}$$

where the quantum mechanical equivalents of I and K have been substituted. However, as determined in the discussion of the Morse potential, terms higher than quadratic in $(v + 1/2)$ are necessary to fit the observed energy levels. For the purposes of the present calculations, terms as high as $(v + 1/2)^3$ were considered. Although Rees has also indicated analytical solutions for cases in which terms cubic in $(v + 1/2)$ were present, the method is rather cumbersome and involves the calculation of elliptical integrals making use of a computer necessary. Therefore, it was decided to use Zare's programs (with some modifications and adaptions for the CDC 6600 computer) for the calculation of RKR potentials and the associated wave functions. Discussion of the principles employed in the numerical calculations is given by Zare (48) and Zare and Cashion (49).

The chief advantage of the RKR method is that it does not necessitate knowledge of a particular functional form for the potential. Instead, all the spectroscopic information available for the molecule may be utilized directly in the calculations. Although detailed knowledge of the rotational constants B_v for each level are required, even such refinements of the Morse potential as the Hulburt-Hirschfelder potential (41,50) also require knowledge of B_e and α_e in order to obtain more realistic potentials.

Gaydon (51) has commented that since the RKR method is a WKB approximation and semi-classical in nature, the potential should not be considered accurate for the lower vibrational levels. Schiff (52), in a discussion of the WKB method, also comments that reliability of WKB approximations is guaranteed only for $v \gg 1$. However, Rees (47) has shown that when $E(I,K)$ includes terms of quadratic and lower order in $(v + 1/2)$, as predicted in the solution to the Schrodinger equation for the Morse potential, and when the Morse formulations of α_e and D_e are consistantly used, the calculated RKR potential agrees with the Morse potential to the extent that expressions for r_e, in terms of B_e, and for $(r_+ - r_-)$ are in complete harmony. In this connection, Jarmain (53) and Vanderslice et al. (54) have shown that the Dunham (55) potential, which gives an accurate description of the potential for H_2 near the minimum, and the RKR potential are in complete agreement.

The reasons for this apparent success of the RKR method even at low vibrational quantum levels have been put forth in a paper by Zhirnov (56) in which the hypothesis is made that RKR method, rather than being a consequence of the usual WKB method, is the result of a more generalized WKB method proposed by Miller and Good (57). According to this method, the RKR wave functions are expanded in terms of a set of basis functions which are exact solutions to the Schrodinger equation for a potential which closely approximates the potential to be calculated. In terms of this new potential $W(r)$, the action may be written

$$I = (2\mu)^{1/2} \int_{r_2}^{r_1} [E^* - W(r)]^{1/2} \, dr \qquad (29)$$

where E^* is the total energy with respect to the minimum of $W(r\ )$. Equation (29) is then expressed as

$$I = (2\mu)^{1/2} \int_{r_1}^{r_2} [E - U(r)]^{1/2} dr = (2\mu)^{1/2} \int_{r_1^*}^{r_2^*} [E^* - W(r\ )]^{1/2} dr \tag{30}$$

Only for the case in which W(r) is a Morse potential (or harmonic oscillator potential) can the expression be shown to equal $h(v + 1/2)$. Thus, the standard RKR procedure is claimed to be a perturbation method for which the Morse wave functions form the basis set. Applicability criteria for use of the RKR procedure are based upon the product of two factors, one of which is related to closeness of approach to the classical limit and the other to the difference between the basis and true potentials. In the region of low v, for which the classical limit $[(\oint p dr = h(v + 1/2)]$ does not apply, the difference between the true potential and a suitable Morse potential is always nearly zero, hence the perturbation method is justified, and yields the same results as in the classical limit. For higher v, the deviation between the true potential and Morse potentials increases, but approach to the classical limit then renders the method valid. Only for very high v , i.e. when approaching the dissociation limit, does the descrepency between the asymptotic behavior of the Morse potential deviate so greatly from the behavior of the true potential that the effect of approach to the classical limit does not counter it sufficiently to meet the applicability criterion given by Zhirnov. Thus, in conclusion, one can expect the RKR wave functions to be highly reliable, except in the region where the dissociation limit is being approached or when perturbations from other electronic states are present.

3. <u>The Electric Transtion Moment.</u>

As stated in Section III-B-1, the separation of the electronic

transition moment from under the integral sign in the evaluation of the transition matrix element, although often applied, is not necessarily valid. The assumptions underlying the approximation are that R_e is a smooth and slowly varying function of the internuclear distance r and that the main contributions to the overlap integral come from ranges of r considerably more limited than the extent of r for which the wave function has non-zero value. However, once the transition moment has been separated from the integral, it is not necessary to consider it to take on an average value for all transitions between pairs of energy levels of two electronic states. A new approach in the determination of the dependence of the transition moment on the internuclear distance was first introduced by Fraser (58) and Turner and Nicholls (59). Associated with each band in the system (v',v") is an average value of the internuclear distance called the $\bar{r}$-centroid given by

$$\bar{r}_{v'v''} = \frac{\langle v'|r|v''\rangle}{\langle v'|v''\rangle} \tag{31}$$

where we have adopted the shorthand notation $\langle v'|$ for the vibrational wave function $\langle \phi_v'|$. The transition moment is then considered to be a function of the $\bar{r}$-centroid. Thus,

$$\langle v'|R_e(r)|v''\rangle \cong R_e\ (\bar{r}_{v'v''})\ \langle v'|v''\rangle \tag{32}$$

This expression is easily shown to be exact for the case in which the transition moment is a linear function of $\bar{r}$. The validity of the approach for transition moments containing quadratic and higher order terms rests on the degree to which

$$\overline{r^n_{v'v''}} \equiv \frac{\langle v'|r^n|v''\rangle}{\langle v'|v''\rangle} = (\bar{r}_{v'v''})^n \tag{33}$$

Only when this criterion is met, is Eq. (32) strictly true. Fraser (58),

in justification of the above assumption, has shown the relation to hold true for up to n = 12 by comparing both sides of Eq. (32) for the case in which $R_e(r)$ is assumed to be of the form $e^{-\alpha r}$ where terms for n up to 12 are significant in the Taylor series expansion. The particular wave functions used were Morse functions obtained by Jarmain and Nicholls (60) for the first positive system of N_2.

Evaluation of the actual transition moment is accomplished through semi-empirical means as follows. For a given resolved progression of bands emanating from a particular v', the intensity of the band, divided by the product of the appropriate frequency factor (ν^3 if I is in quanta/sec, ν^4 if I is in energy flux/sec) with the calculated Franck-Condon factor, is plotted against the value of the $\bar{r}$ centroid for the band. The same is done for each progression and the curves are normalized to one another (because of the differences between the populations of the emitting states) according to the area underneath the curves (59). A weighted least squares fit to all the experimental points has been suggested and the results used to evaluate more accurate transition matrix elements. The purpose of the weighting is to account for the fact that when the overlap integral is very small, abrupt changes in the values of the $\bar{r}$-centroid and higher order centroids are sometimes encountered.

Halevi (61) has suggested that Eq. (32) would be improved by expanding the transition moment in a Taylor series about the $\bar{r}$-centroid as follows:

$$R_e(r) = R_e(\bar{r}) + \left.\frac{\delta R_e(r)}{\delta r}\right|_{\bar{r}}(r-\bar{r}) + \frac{1}{2}\left.\frac{\delta^2 R_e(r)}{\delta r^2}\right|_{\bar{r}}(r-\bar{r})^2 \qquad (34)$$

Evaluation of the transition matrix element yields

$$\langle v'|Re(r)|v''\rangle = R_e(\bar{r}) + 1/2\ R_e''(\bar{r})(\langle v'|r^2|v''\rangle - \bar{r}\langle v'|r|v''\rangle) \qquad (35a)$$

$$= R_e(\bar{r})\ \langle v'|v''\rangle\left[1 + 1/2\ \frac{R_e''(\bar{r})}{R_e(r)}\ (\overline{r^2} - (\bar{r})^2)\right] \qquad (35b)$$

Thus, although Eq. (33) often holds quite well for small values of n, it is also necessary to consider the magnitude of $R_e''\ (\bar{r})/R_e(\bar{r})$. Halevi has calculated this correction term for selected bands of the first and second positive systems for N_2 and of the comet tail system of CO^+. In the first two cases, correction factors for the 0,0 bands were found to be about 1% ($|R_e''/R_e| \approx 10$). However, in the latter case, a correction of 17% was found for the 0,0 band [$(R_e''/R_e) \approx -135$]. Although one might expect larger correction factors to be obtained only for bands having very small transition moments, by using the transition moment function for the above system as obtained by Robinson and Nicholls (49), one obtains values of $R_e''(\bar{r})/R_e(\bar{r})$ varying from 133 to 195. These numbers should be considered cautiously, however, since the functional dependence of the transition moment on internuclear distance will no longer be given by the relation of Robinson and Nicholls if Eq. (35) is used rather than Eq. (32) in the interpretation of the observed intensities.

The advantages of the above approach are limited, however. The $\bar{r}$-centroid can be determined approximately without actually evaluating the overlap integrals by the method of Jarmain [see ref. (58)] once given the potential curves for the two electronic states. It is easily shown that

$$E_{v'} - E_{v''} = V_{v'}\ (\bar{r}_{v'v''}) - V_{v''}(\bar{r}_{v'v''}) \qquad (36)$$

where the E's are the total vibrational energies (relative to their respective potential minima) and the V's are the potential energies for the two states. In order to determine the $\bar{r}$-centroid for a particular band one simply finds that value of the internuclear distance for which the difference in vibrational energies for the upper and lower states is equal to the difference in potential energies. This approximation holds to the extent that the difference in potential energies of the upper and lower electronic states is a linear function of the internuclear distance, which in general is a good approximation. There is no such simple method for evaluation of the r^2-centroids needed in Eq. (35). The integrals $\frac{\langle v'|r^2|v''\rangle}{\langle v'|v''\rangle}$ must be obtained by numerical integration and are conveniently available from Zare's programs as are the numerically integrated values of the $\bar{r}$-centroids. Instead of computing the values of the centroids, however, one can easily modify the program such that values of the transition matrix elements themselves are obtained for some assumed functional form of $R_e(r)$. The $\bar{r}$-centroid approach can be used to obtain an approximate function $R_e(\bar{r})$. The validity of the approach can then be tested by comparing the integrals $\langle v'|R_e(r)|v''\rangle$ directly with $R_e(\bar{r})\ \langle v'|v''\rangle$. A re-iterative procedure could then be used to obtain the best $R_e(r)$.

The above procedure has been utilized by many investigations in an effort to determine the importance of the transition moment in band intensities. In a recent review, Ortenberg and Antropov (12) have enumerated systems of diatomic molecules for which Franck-Condon factors have been calculated and further discuss some systems for which the transition moment $R_e(r)$ has been evaluated and, in a few cases, theoretically calculated.

The dependence of the transition moment on internuclear distance is given for 20 systems, some of which have been measured by more than one investigator and by other (lifetime) techniques.

As in the above cases, accurate intensity measurements could be obtained, heretofore, only for systems in which the individual vibration rotation bands were completely or nearly non-overlapping. For partially overlapping bands the techniques of Robinson and Nicholls (13) have often been employed. In the case of low resolution spectra, in which individual rotation lines are not distinguished, the total intensity of a band (area under curve) is inferred from intensity measurements of a small non-overlapped fraction of the band; e.g., if the band heads are not overlapped, the intensity might be taken as proportional to the height of the band head (assuming that the band head encompasses a constant fraction of the total intensity of the band). For high resolution spectra, measurement of intensities of individual non-overlapped rotational lines can be plotted appropriately and the total intensity of the band inferred from an individual line intensity and the rotational temperature obtained from the plot.

In many cases, however, overlapping occurs to such an extent that neither of the above resolving methods can be reliably employed. In order to derive quantities of interest from the spectra, e.g. relative populations of excited vibrational levels of the emitting state for the kineticist or transition moment functions for the spectroscopist, the problem must be attacked in an integrated fashion. The relative populations [scaling factors used in the method of Turner and Nicholls (59)] cannot be accurately obtained without a detailed knowledge of the transition moment function $R_e(r)$, nor can $R_e(r)$ be obtained over the entire region of spectral interest without knowledge of the population factors. A new

method of approach is described in the following section.

4. Details of Calculations

According to the theory for diatomic molecules described above, it should be possible to reconstruct any emission spectrum given the following quantities: 1) the electronic configurations of the states, 2) the vibrational and rotational levels of each electronic state, 3) the vibrational and rotational temperatures (or the relative vibrational populations themselves for the upper electronic state if the system is not in a Boltzmann equilibrium with respect to the vibrational degree of freedom), 4) the transition matrix elements $\langle v'|R_e(r)|v''\rangle$ for each band, and 5) the spectral slit function of the monochromator used to make the measurements and the spectral wavelength response of the optical system. Conversely, given all but the function $R_e(r)$ and the vibrational populations of the emitting state, one can determine by the method of least squares the set of vibrational populations and values of the transition moment at specified internuclear distances which best reproduce the complete spectrum. This method has two obvious advantages. First, overlapping of bands does not cause any serious problems since the fact that each intensity measurement (at a particular wavelength) is actually a composite of contributions from several bands is taken into account in the calculations. Secondly, the entire observed spectrum, not just those progressions having many distinct bands, can be utilized in the calculation of the transition moment. Indeed, Jeunehomme and Schwenker (63) have claimed that the $R_e(r)$ obtained by using the scaling procedure of Turner and Nicholls in treating intensity data of King (64) for the A to X transition of C_2 does not yield the same $R_e(r)$ curve obtained by treatment of their lifetime data. The difficulty arises in the attempt to determine the

scaling factor (relative population of v') for a short progression by graphical means because of the experimental scatter in the data. It was found that the intensity data could be satisfactorily accounted for by the $R_e(r)$ function determined in (63) if a different set of scaling factors from that determined by Nichols (65) was employed. In the present method the weighting factors (excited state populations) and the transition moment function are determined simultaneously. Once the transition moment function has been satisfactorily determined, it can then be used in the treatment of other sets of data in which the populations are of interest. The calculations are broken down into two parts, as follows.

a. Calculation of individual band shapes. For a particular band having upper vibrational quantum number v' and lower vibrational quantum number v", the intensity for a single vibration-rotation line, apart from contributions of the transition matrix element (other than that dependent on rotational factors) and the effect of the overall population of the vibrational level, has been shown in Sec. III-1 to be

$$I_{v''J''}^{v'J'} = \frac{64\pi^4 B_{v'}}{3hkT_r} \nu_{v'J'v''J''}^3 S_{J''}^{J'} e^{-B_{v'}J'(J'+1)/kT_r} \qquad (37)$$

In Hund's coupling case c, the Honl-London factors, or line strengths, for a transition of the type $0^+ \rightarrow 0^+$ are given by (25)

$$\begin{aligned} R_{branch} \quad & S_{J''}^{J'} = J' \quad \text{where } J'' = J' - 1 \\ P_{branch} \quad & S_{J''}^{J'} = J' + 1 \text{ where } J'' = J' + 1 \end{aligned} \qquad (38)$$

The rotational contribution to the energy is given by [see Eq. (8)]

$$\nu_{rot} = B_{v'}J'(J'+1) + D_{v'}J'^2(J'+1)^2 - B_{v''}J''(J''+1) - D_{v''}J''^2(J''+1)^2 \qquad (39)$$

Adopting the indexing system in which $m=J'$ for the R branch lines and $-m=J'+1$ for P branch lines, we can write the rotational energy expression as

$$\nu_{rot}(m) = (B_{v'}+B_{v''})m + (B_{v'}-B_{v''} - D_{v'}+D_{v''})m^2 - 2(D_{v'}+D_{v''})m^3 - (D_{v'}-D_{v''})m^4 \qquad (40)$$

where m can take on all integer values, positive and negative, except 0, which corresponds to the missing line at the band origin. The vibrational contribution to the energy $\nu_{v''}^{v'}$ is given by Eq. (6). Thus, the expression for the intensity of an individual vibration-rotation line becomes

$$I_{v''}^{v'}(m) = \frac{64\pi^4 B_{v'}}{k\ T_r}\left(\nu_{v''}^{v'} + \nu_{rot}\ (m)\right)^3 |m|\, e^{-B_{v'}m(m+1)/k\ T_r} \qquad -\infty < m < \infty \qquad (41)$$

If the resolution of the monochromator were comparable to the Doppler line widths (or somewhat greater than the rotational spacing), one would observe individual lines at frequencies $\nu_{v''}^{v'} + \nu_{rot}\ (m)$ having intensities $I_{v''}^{v'}\ (m)$. However, as discussed in Section II, intensities are low enough in most chemiluminescent experiments, so that only low resolution spectra can be obtained (slits are wide open). The intensity observed at frequency ν_o then becomes the convolution of the intensity expression and the spectral slit function summing over all rotational lines, i.e.

$$I_{v''}^{v'}\ (\nu_o) = \sum_{m=-\infty}^{\infty} I_{v''}^{v'}(m)\ f\left[\nu_{v''}^{v'} + \nu_{rot}(m) - \nu_o\right] \qquad (42)$$

Because the band pass of the monochromator is a constant number of Angstroms, it is most convenient to define the spectral slit function in terms of wavelength rather than frequency. Let $\lambda_{v''}^{v'}(m)$ equal the wavelength in air corresponding to frequency $(\nu_{v''}^{v'} + \nu_{rot}(m))$ where the correction factors from vacuum to air have been taken from Ref. 66. We now write

$$I_{v''}^{v'}(\lambda_0) = \sum_{m=-\infty}^{\infty} I_{v''}^{v'}(m)\ f[\lambda_{v''}^{v'}(m) - \lambda_0] \tag{43}$$

The actual monochromator slit function, when no RC broadening takes place, has the approximate form (see Section II-B)

$$f(\lambda - \lambda_0) = \left(1 - \frac{|\lambda-\lambda_0|}{\Lambda}\right) \qquad |\lambda-\lambda_0| \leq \Lambda \tag{44a}$$

$$f(\lambda - \lambda_0) = 0 \qquad |\lambda-\lambda_0| > \Lambda \tag{44b}$$

where λ is the wavelength of the emission line, λ_0 is the wavelength of observation, and Λ is the spectral slit width (FWHM). Under actual experimental conditions, however, an RC time constant is applied to improve signal-to-noise. Depending on the scanning rate and the time constant, displacement of the observed line center from the true line center can vary from a fraction of one to several Angstroms. Let us consider the response of a simple RC series circuit having a time constant τ to an input voltage having the form described by Eqs. (44a-44b). Further let T equal the time necessary to scan one spectral slit width,

$$\text{i.e.} \qquad \text{scan speed} = \frac{-d\lambda_0}{dt} = \frac{\Lambda}{T} \tag{45a}$$

and let our zero time reference be when $\lambda_0 = \lambda + \Lambda$ (scanning takes place in direction of high wavelength to low wavelength), i.e.

$$t = \frac{(\lambda-\lambda_0+\Lambda)}{\Lambda} T \tag{46}$$

We break up the time region into the following three domains

1) $0 \leq t \leq T$ in which the input signal is equal to

$$\frac{t\partial f(\lambda-\lambda_0)}{\partial t} = \frac{t}{T} ;$$

2) $T \leq t \leq 2T$ in which the input equals

$$f(\lambda - \lambda_0)\big|_{t=T} - (t-T) \frac{\partial f(\lambda-\lambda_0)}{\partial t} = 1 - \frac{t-T}{T}$$

and 3) $t \geq 2T$ in which the input equals zero.

The response, E, to each of these input signals is obtained by solving the differential equation governing the behavior of the simple series R-C circuit and matching solutions at the boundaries. Thus we straightforwardly obtain

$$E_1 = \frac{\tau}{T}\left(\frac{t}{\tau} + e^{-t/\tau} - 1\right) \quad 0 \leq t \leq T \tag{47a}$$

$$E_2 = \frac{\tau}{T}\left(2\frac{T}{\tau} - \frac{t}{\tau} + (1-2e^{T/\tau})\, e^{-t/\tau} + 1\right) \quad T \leq t \leq 2T \tag{47b}$$

$$E_3 = \frac{\tau}{T}\left(1 - e^{T/\tau}\right)^2 e^{-t/\tau} \qquad t \geq 2T \tag{47c}$$

The corresponding set of equations in terms of wavelength become, after substituting for t according to Eq. (46),

$$f_1(\lambda-\lambda_0) = 1 + \frac{\lambda-\lambda_0}{\Lambda} + \frac{\tau}{T}\left(e^{-(\lambda-\lambda_0+\Lambda)T/\tau\Lambda} - 1\right)$$

$$\lambda_0-\Lambda \leq \lambda \leq \lambda_0 \tag{48a}$$

$$f_2(\lambda-\lambda_0) = 1 - \frac{\lambda-\lambda_0}{\Lambda} + \frac{\tau}{T}\left[\left(1-2e^{T/\tau}\right)e^{-(\lambda-\lambda_0 + \Lambda)T/\tau\Lambda} + 1\right]$$

$$\lambda_0 \leq \lambda \leq \lambda_0 + \Lambda \qquad (48b)$$

$$f_3(\lambda-\lambda_0) = \frac{\tau}{T}\,(1-e^{T/\tau})^2 \quad e^{(\lambda-\lambda_0+\Lambda)\ T/\tau\Lambda} \quad \lambda_0+\Lambda \leq \lambda \qquad (48c)$$

We still have $f(\lambda-\lambda_0) = 0$ for $\lambda \leq \lambda_0 - \Lambda$ (Eq. 44b). Also, for the conditions under which most of the spectral data were obtained, viz. $\tau = 3.14$ sec and $T = 17.25$ sec, $\Lambda = 11.5$Å, the spectral slit function had decayed to zero for $\lambda \geq \lambda_0 + 2\Lambda$. Thus, the sum over m in Eq. (43) does not have to be taken over an infinite set of rotational lines, but over only those lines for which $\lambda_0-\Lambda \leq \lambda_{v''}^{v'}(m) \leq \lambda_0 + 2\Lambda$. A diagram of the RC broadened spectral slit function appears in Fig. (10) for two different values of T.

A similar set of equations can be derived for double section filtering in which case the output of the first RC filter network, suitably buffered to prevent loading, is fed into a second RC network. Letting τ_1 equal the RC time constant of the first network and τ_2 equal that of the second, we obtain

$$f_1(\lambda-\lambda_0) = 1 + \frac{\lambda-\lambda_0}{\Lambda} - \frac{1}{T}\left(\tau_1+\tau_2+\frac{\tau_1^2}{\tau_1-\tau_2}\ e^{-(\lambda-\lambda_0+\Lambda)T/\Lambda\tau_1}\right.$$

$$\left. - \frac{\tau_2^2}{\tau_1-\tau_2}\ e^{-(\lambda-\lambda_0+\Lambda)T/\Lambda\tau_2}\right) \quad \lambda_0-\Lambda \leq \lambda \leq \lambda_0 \qquad (49a)$$

$$f_2(\lambda-\lambda_0) = 1 - \frac{\lambda-\lambda_0}{\Lambda} + \frac{1}{T}\left(\tau_1+\tau_2 + \frac{\tau_1^2}{\tau_1-\tau_2}\left(1-2e^{T/\tau_1}\right)\right.$$

$$\left. e^{-(\lambda-\lambda_0+\Lambda)/\Lambda\tau_1} - \frac{\tau_2^2}{\tau_1-\tau_2}\left(1-2e^{T/\tau_2}\right)e^{-(\lambda-\lambda_0+\Lambda/\Lambda\tau_2}\right)$$

$$\lambda_0 \leq \lambda \leq \lambda_0 + \Lambda \qquad (49b)$$

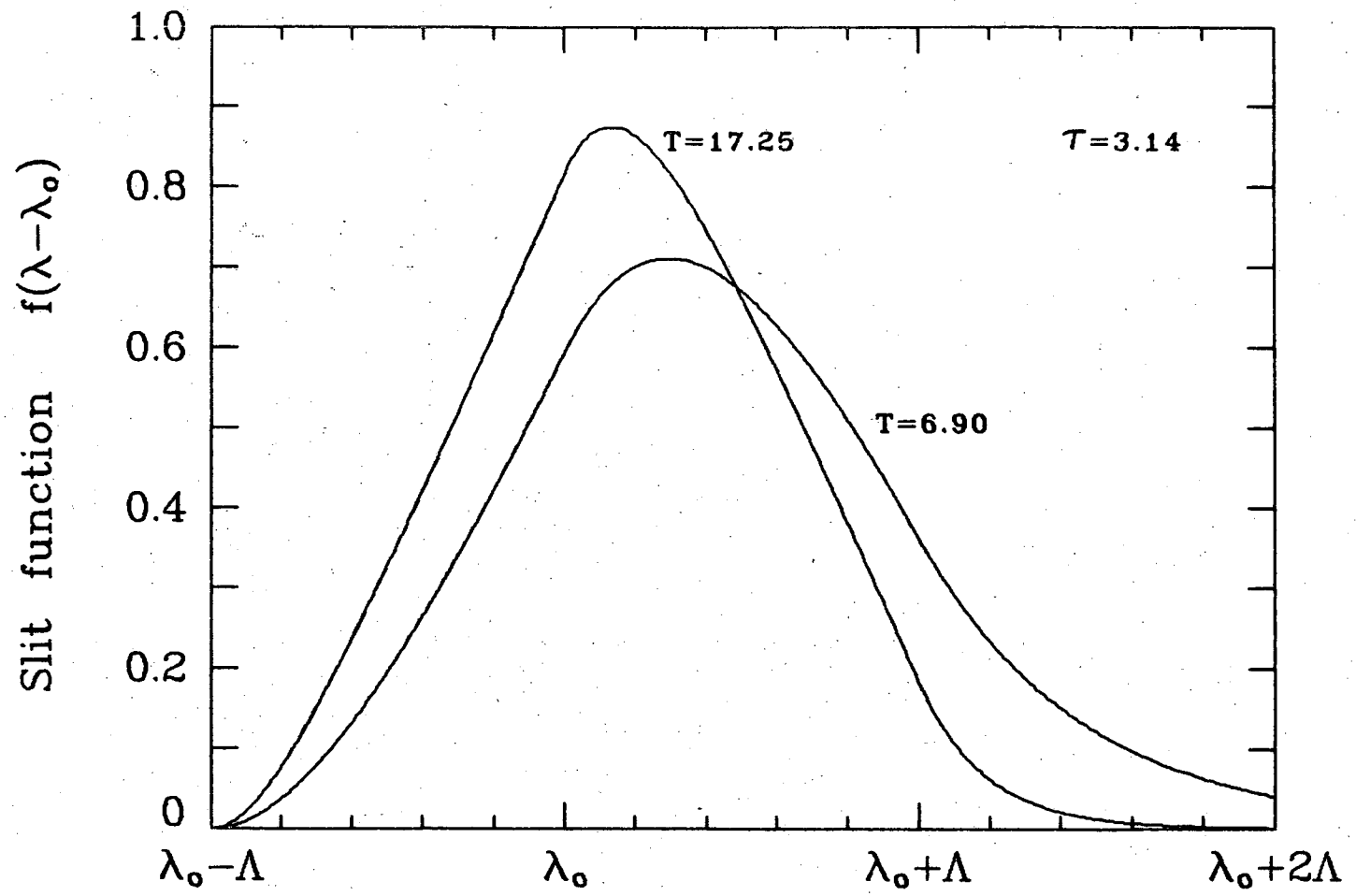

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Fig. 10. RC broadened spectral slit function vs. λ.
τ = single section RC time constant (sec),
T = time to scan spectral slit width (Λ),
λ_o = wavelength of observation, λ = wavelength of emitting line.

$$f_3\ (\lambda-\lambda_0) = \frac{1}{T}\left(\frac{\tau_1^{\ 2}}{\tau_1-\tau_2}\left(1-e^{T/\tau_1}\right)^2 e^{-(\lambda-\lambda_0+\Lambda)/\Lambda\tau_1} - \frac{\tau_2^{\ 2}}{\tau_1-\tau_2}\left(1-e^{T/\tau_2}\right)^2 e^{-(\lambda-\lambda_0+\Lambda)/\Lambda\tau_2}\right) \quad \lambda_0+\lambda \leq \lambda \qquad (49c)$$

where T, Λ, λ, and λ_0 are the same as defined previously.

The RC time constants τ_1 and τ_2 (or τ in the case of single section filtering) can be obtained by performing a least squares fit of the output of the amplifier to a step input function according to the applicable equations.

The band shapes were numerically calculated for all bands (approximately 175) in the region 4350 to 7220A according to the above method. Because of the exponential Boltzmann factor in the individual line intensity expression [Eq. (41)], the band width of the integrated vibration-rotation band will depend upon the rotational temperature. Figure 11 shows the vibration-rotation envelope for the $v' = 0 \rightarrow v'' = 4$ transition at three different rotational temperatures and normalized such that the peak height is a constant. By comparing the observed band shape to band shapes calculated at various temperatures, one is able to estimate the rotational temperature to within ±100°K.

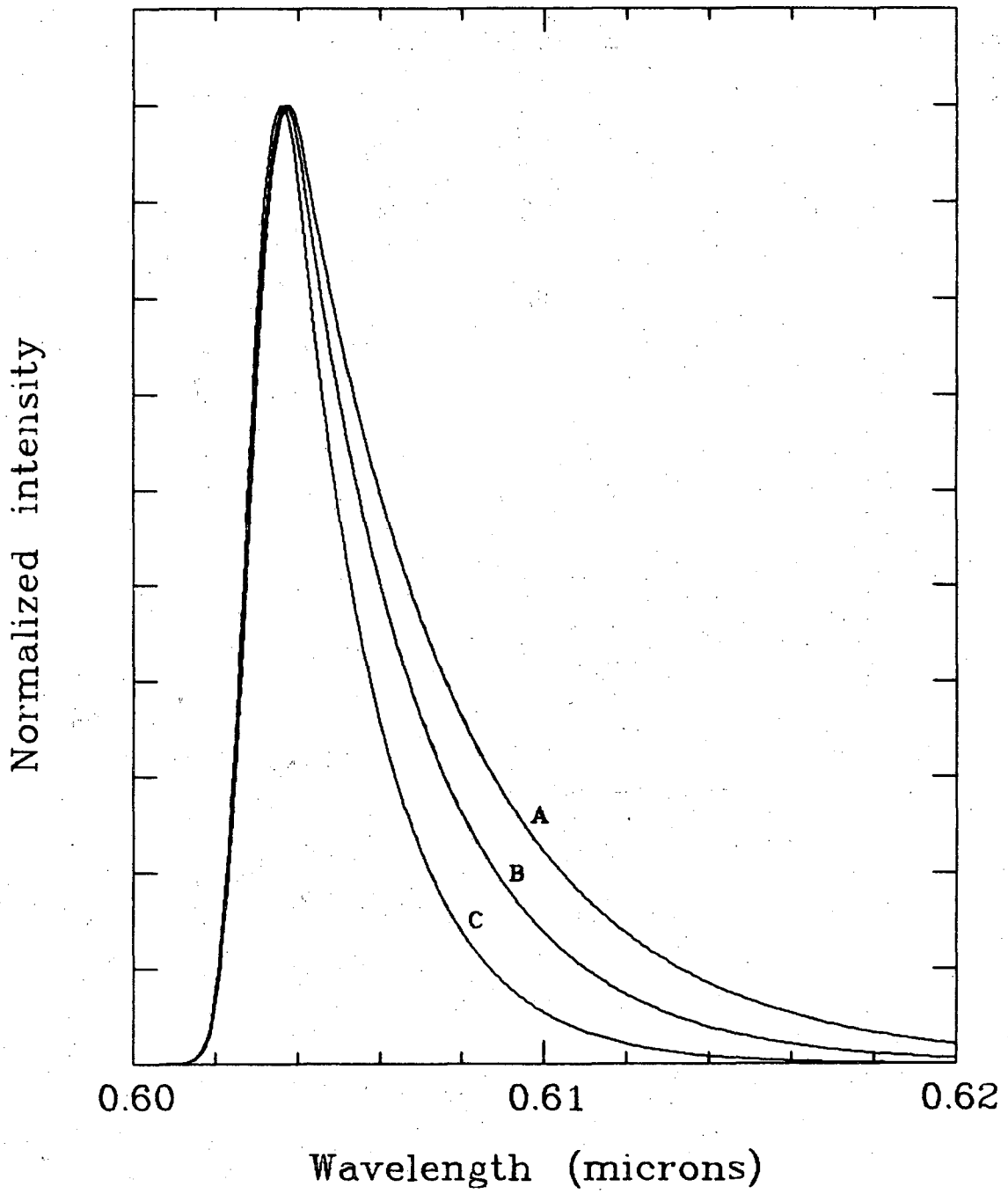

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Figure 11. Normalized integrated band intensities for the 0,4 ($^3\Pi_{0^+} \rightarrow {}^1\Sigma^+$) transition of IF at 3 values of the rotational temperature. A. 800°K B. 600°K C. 400°K.

b. Decomposition of the spectra by method of least squares. First let us concern ourselves with the solution of the problem assuming that the transition moment function, $R_e(r)$, is known. We let B_i represent the total observed intensity (corrected for the spectral sensitivity of the optical systems) at some wavelength λ_i. Further, let N_j represent the population of vibrational level $v' = j$ of the excited electronic state. We may then write

$$B_i = \sum_j A_{ij} N_j \tag{50}$$

where the A_{ij}'s represent the contributions of all peaks emanating from $v' = j$ at wavelength λ_i, excluding the population factor, i.e.

$$A_{ij} = \sum_{v''} I_{v''}^{v'=j}(\lambda_i) \langle j|R_e(r)|v''\rangle^2 \cong \sum_{v''} I_{v''}^{v'=j} R_e^2(\bar{r}_{jv''})\langle j|v''\rangle^2 \tag{51}$$

Usually there is only one term in the sum, or at most two, since the bands forming a particular $v'=j$ progression overlap only to a very small extent. The range of j is over a limited manifold since the dissociation limit for the $^3\Pi_{0+}$ state of IF occurs at $v'=16$ and the onset of predissociation at $v'=11$. Under most conditions the populations of states having v' greater than 8 or 9 is so low, because of collisional deactivation, that the range of j can be limited to $v' = 0\text{-}9$. However, at low pressures (below 40 m torr) certain features begin to appear in the spectrum which would indicate significant population of states having v' greater than 9. A difficulty in treating such spectra arises because the accuracy of the RKR potential and wavefunctions diminishes as the dissociation limit is approached (see Sec. III-B-2) and certainly is affected by the electronic state causing the observed predissociation. Consequently, results of calculations including states having $v'' = 11$, 12 and higher

must be considered with a certain degree of caution.

In general, the number of data points, m, greatly exceeds the number of unknowns to be determined, n, the vibrational populations of the $^3\Pi_{0+}$ state. In order to solve this over-determined set of simultaneous equations, the method of least squares is employed, i.e. that set of N_j's if found which satisfies the following criteria:

$$\frac{\partial}{\partial N_j}\left(\sum_{i=1}^{m}\left(B_i - \sum_{j=0}^{n-1} A_{ij} N_j\right)^2 w_i\right) = 0 \qquad j = 0,1 \ldots n \qquad (52)$$

where w_i is a weighting factor and is chosen such that each experimental point is weighted by the inverse of the square of the standard deviation of the measurement σ [see reference 67] where σ equals the noise in signal, i.e. $\sqrt{V_L+V_D}$, as discussed in Section II-D. Roughly speaking, then, the weighting factor equals one over the raw data intensity, not the actual corrected B_i value, since the noise is a characteristic of the number of electrons emitted by the photo cathode surface per unit time rather than of the number of photons entering the monochromator per unit time. A standard linear least squares computer program obtainable from the Lawrence Radiation Laboratory Computer Center Library (see App. B) was used to perform the actual calculations after evaluating the elements of the matrix A and the vector B.

From the solution vector, N, it is possible to obtain effective vibrational temperatures from the following relationship

$$\frac{N_{v'}}{N_0} = e^{-\left(E(v')-E(0)\right)/kT_{v'}^{vib}} \qquad (53)$$

where $$E(v') = \omega_e'(v' + \tfrac{1}{2}) + \omega_e x_e'(v' + \tfrac{1}{2})^2 + \omega_e y_e' (v' + \tfrac{1}{2})^3 + \dots \quad (54)$$

Thus, $$T_{v'}^{vib} = -\Big(E(v') - E(0)\Big)/k \ \ln (N_{v'}/N_0) \quad (55)$$

Further, one can easily reconstruct a computed spectrum at each point i by forming the sum $\sum_i A_{ij} N_j$. This spectrum can then be compared to the original.

Standard deviations in the individual populations, the above temperatures, and in the relative populations $N_{v'}/N_0$ were computed from the variance-covariance matrix $\underset{\sim}{V}$ in the following manner, as described in reference 68. For an arbitrary function f of a set of n adjustable parameters $X_1 \dots X_j \dots X_n$ and a vector of independent variables $\bar{a}$, where the X_j's are to be determined by a least squares fit to a set of m independent data points b_i corresponding to a set of independent variables $\bar{a}_i$, the variance-covariance matrix is defined as

$$\underset{\sim}{V} = \underset{\sim}{\Phi}^{-1} \frac{\left[\sum_{i=1}^{m} w_i \Big(b_i - f_i(X_1 \dots X_j \dots X_n, \bar{a}_i)\Big)^2\right]}{(m-n-1)} \quad (56)$$

where $$\Phi_{jk} = \sum_{i=1}^{m} w_i \, G_{ij} \, G_{ik} \quad (57)$$

and $$G_{ij} = \left.\frac{\partial f(X_1 \dots X_j \dots X_n; \bar{a}_i)}{\partial X_j}\right|_{\bar{X} = \bar{X}_{best}} \quad (58)$$

The dimensions of the matrices $\underset{\sim}{\Phi}$ and $\underset{\sim}{V}$ are both equal to the number of adjustable parameters n; the standard deviation σ_j associated with the best determined value of the parameter X_j is given by $(V_{jj})^{1/2}$.

For the particular case in point, the derivatives G_{ij} are given by the matrix elements A_{ij}. Thus the $\Phi_{jk} = \sum_{i=1}^{m} A_{ij} A_{ik} w_i$ and are not dependent upon the parameters N_j, and the expression in the numerator of Eq. (56) is just that expression which is differentiated with respect to N_j in Eq. (52). It should be emphasized that m in the denominator is Eq. (56) is the number of <u>statistically independent</u> data points. In the case of many of the spectra, points were recorded at periods less than that needed to assure statistical independence, viz. $2 \times \tau_{RC}$ (18) in the case of single section filtering (or $4 \times \tau_{RC}$ in the case of double section filtering). For these cases, m in Eq. (56) should be replaced by $\frac{T}{2\tau_{RC}}$ m(or $\frac{T}{4\tau_{RC}}$ m) where T is the elapsed time between data points.

The variance associated with some function $g(X_i, X_2)$ where X_1 and X_2 are any two parameters of the set $X_1 \ldots X_j \ldots X_n$, is given by (55)

$$V[g(X_1,X_2)] = \left(\frac{\partial g}{\partial X_1}\right)^2 V_{11} + \left(\frac{\partial g}{\partial X_2}\right)^2 V_{22} + 2\,\frac{\partial g}{\partial X_1}\,\frac{\partial g}{\partial X_2}\,V_{12} \qquad (59)$$

and again $\sigma[g(X_1,X_2)] = [V(X_1,X_2)]^{1/2}$.

For the populations relative to that of $v' = 0$, $g(N_{v'}, N_0) = N_{v'}/N_0$. Upon evaluation of Eq. (21) we obtain

$$\sigma(N_{v'}/N_0) = \frac{1}{N_0}\left[\left(\frac{N_{v'}}{N_0}\right)^2 V_{00} + V_{v'v'} - 2\,\frac{N_{v'}}{N_0}\,V_{0v'}\right]^{1/2} \qquad (60)$$

We may also evaluate the standard deviation of the effective vibrational temperature for each state. Using Eqs. (55) and (59), we obtain

$$\sigma(T_{v'}^{vib}) = (T_{v'}^{vib})^2 \frac{k}{N_0} \left[\left(\frac{N_v'}{N_0} \right)^2 V_{00} + V_{v'v'} - 2 \frac{N_{v'}}{N_0} V_{0v'} \right]^{1/2}$$

$$/ \left[N_{v'} \left(E(v') - E(0) \right) \right]^{1/2} \qquad (61)$$

c. Determination of the transition moment. We would now like to generalize the calculation so that account may be taken of the possibility of variation in the transition moment. If one proceeded in the manner described in the previous subsection assuming $R_e(r) = 1$, the results of the calculation would yield a set of quantities $N_{v'}$ which, instead of being proportional to the actual populations, would be proportional to the true populations times a weighted average of $R_e^2(\bar{r}_{v'v''})$ summed over all v" associated with a particular v' in the calculation. The computed spectrum would then overpredict the intensities of some bands of a progression while underestimating the intensities of others.

One could perform the calculation many times using only a limited portion of the data each time. If each portion of the spectral data were to contain not more than one band from a given v', one would obtain a quantity equal to $N_{v'}R_e^2(\bar{r}_{v'v''})$ for each band. The method of Fraser (58), previously discussed, could then be applied and a plot of $R_e(\bar{r})$ obtained. This is a rough starting point, for it is clear that for two very closely spaced bands it would be impossible to determine the correct decomposition without knowledge of the rest of the spectrum.

Having determined an approximation to $R_e(\bar{r})$, one would next select some functional form for $R_e(\bar{r})$ which, upon adjustment of the parameters, could reproduce the plotted data. Using Eq. (13), one would calculate a new A matrix and repeat the above calculations, obtaining corrections

to the rough plot of $R_e(\bar{r})$ vs $\bar{r}$. By repeated iterations the solution would eventually converge upon the best $R_e(\bar{r})$ curve.

We have found it more convenient and less tedious to approach this best $R_e(r)$ curve by a different means. Starting off in the same way, one obtains an initial approximation to $R_e(r)$. Again, some plausible functional form is chosen (say $R_e(r) = c_1 + c_2 r + c_3 r^2 + \ldots$) and estimates of the parameters made which approximately reproduce the $R_e(r)$ plot. Now, utilizing all the spectral data, one employs a non-linear least squares routine that is capable of adjusting the transition moment function parameters c_i as well as the populations N_j. The function to be minimized is

$$\sum_i w_i (B_i - \sum_j A_{ij} N_j)^2$$

as in the previous case, but the A_{ij} are not functions of the parameters c_i (Eq. 51) and the problem becomes non-linear. The nature of the dependence of this function on the c_i makes evaluation of the derivatives of the function with respect to the c_i quite cumbersome. For this reason a procedure involving internally approximated gradients has been chosen. The program is again available from the Lawrence Radiation Laboratory Computer Center Library (See Appendix B). Because nearly all programs written for the purpose of solving non-linear least squares problems do so by adjustment of an initial set of "approximate" values or guesses of the values of the parameters so as to minimize the above-mentioned function, it may sometimes be of important that the guesses be not too far from the final values; otherwise the possibility of convergence on a local minimum rather than the absolute minimum exists. It is for this reason that it is best to use Fraser's method to obtain an approximate $R_e(r)$ as an initial guess.

Most previous work cited in Section III-B-3 has attempted to fit plots of $R_e(\bar{r})$ vs $\bar{r}$ to short power series in $\bar{r}$ or to exponential functions of $\bar{r}$. In the present work it was found that neither of these types of functions was suitable for fitting the intensity data over the entire range of $\bar{r}$-centroid values encountered, viz. 1.85 to 2.25 A. The trend of $R_e^2(r)$ was to fall off nearly linearly with decreasing r, as if to pass through zero. Since $R_e^2(r)$ cannot cross the zero axis, it must turn sharply to approach zero asymptotically. Since no simple analytic function has these properties, it was decided to construct a "function" by letting the adjustable transition moment function parameters become actual points on an $R_e(r)$ vs $\bar{r}$ plot; i.e. the number of fitting parameters was increased and the computer program adjusted values of the transition moment at certain fixed values of $\bar{r}$. Values of the transition moment for $\bar{r}$ values between the selected points were obtained by linear interpolation. In this manner no functional constraints were applied to the transition moment "function"; indeed no a priori reason exists for imposing such a restriction. That the function be relatively smooth, as is commonly accepted, is imposed by the linear interpolation. Further smoothing could be attained by using orders of Lagrangian interpolation higher than one or by applying other standard curve smoothing techniques to the adjustable points in order to obtain the value of the transition moment at any value of $\bar{r}$ between the end points.

IV. RESULTS

A. Theoretical

Rydberg-Kelin-Rees potential curves for the $^3\Pi_{0+}$ (excited) and $^1\Sigma^+$ (ground) states of iodine monofluoride have been obtained by means of Zare's programs(46). For the ground electronic state, least squares values of ω_e, $\omega_e x_e$, $\omega_e y_e$, B_e, and α_e obtained from Durie's data were used in the calculation; for the upper electronic state, however, the vibrational $\Delta G(v+1/2)$ values and rotational B_v's themselves were employed directly since no satisfactory constants which fit all the levels could be determined. The classical turning points for the $^1\Sigma^+$ state are presented in Table II, and those for the $^3\Pi_{0+}$ state in Table III. In each case, the corresponding turning points and eigen energies for the best Morse potentials are given for comparison. The constants for the Morse potentials were obtained by adjustment of ω_e', $\omega_e x_e'$, ω_e'', $\omega_e x_e''$ and T_e to give the best fit to the observed energy levels. These constants and the corresponding values of β [Eq. (19)] and D_e [Eq. (20)] are given in Table IV. The potentials so obtained are quasi-Morse potentials rather than true Morse potentials since the dissociation energies do not correspond to the observed dissociation energies of the molecules. Forcing of the potential to the correct value of D_e, particularly in the case of the $^3\Pi_{0+}$ state, and use of the correct ω_e result in potentials which give eigen energies (and wave functions) far less accurate than those obtained by use of the quasi-Morse potentials.

In order to calculate accurate wave functions, the "complete" potential curves must be determined. Since the RKR turning points can

Table II. Classical turning points for IF ($^1\Sigma^+$)

	RKR			MORSE		
v"	Energy (cm^{-1})	r_-(A)	r_+(A)	Energy	r_-	r_+
0	304.73	1.854	1.970	304.56	1.854	1.970
1	909.26	1.818	2.019	908.94	1.817	2.019
2	1507.24	1.794	2.055	1506.97	1.794	2.055
3	2098.70	1.776	2.086	2098.67	1.775	2.086
4	2683.67	1.760	2.114	2684.02	1.760	2.113
5	3262.20	1.747	2.140	3263.03	1.746	2.139
6	3834.33	1.736	2.165	3835.71	1.734	2.163
7	4400.08	1.725	2.188	4402.04	1.724	2.187
8	4959.49	1.716	2.211	4962.04	1.714	2.209
9	5512.61	1.707	2.233	5515.69	1.705	2.231
10	6059.45	1.699	2.255	6063.00	1.697	2.253
11	6600.08	1.692	2.276	6603.98	1.689	2.274
12	7134.51	1.685	2.297	7138.61	1.682	2.294
13	7662.79	1.679	2.318	7666.90	1.675	2.315
14	8184.94	1.673	2.338	8188.86	1.669	2.335
15	8701.01	1.667	2.359	8704.47	1.663	2.355
16	9211.05	1.662	2.379	9213.74	1.657	2.375
17	9715.06	1.657	2.399	9716.68	1.652	2.394

Constants for extrapolated RKR potential

$a = 6.3599\times10^{-6}$; $b = 2.8704\times10^{-4}$; $c = -8.8283\times10^{5}$; $d = 4.746(\times10^{0})$

Table III. Classical turning points for $IF(^3\Pi_{0+})$

	RKR			MORSE		
v'	Energy	r_-	r_+	Energy	r_-	r_+
0	204.39	2.050	2.192	206.27	2.053	2.194
1	609.38	2.006	2.252	613.36	2.010	2.256
2	1008.63	1.978	2.298	1012.44	1.983	2.303
3	1401.38	1.955	2.336	1403.87	1.963	2.344
4	1786.87	1.937	2.373	1787.56	1.946	2.382
5	2164.37	1.921	2.406	2163.52	1.931	2.418
6	2533.09	1.907	2.440	2531.73	1.918	2.452
7	2892.29	1.895	2.473	2892.21	1.907	2.485
8	3241.21	1.884	2.507	3244.94	1.897	2.518
9	3576.21	1.873	2.543	3589.94	1.888	2.550
10	3895.71	1.865	2.581	3927.20	1.879	2.582
11	4190.71	1.857	2.629	4256.72	1.871	2.614
12	4457.71	1.850	2.679			

Constants for extrapolated RKR potential

$a = 8.729\times10^{6}$; $b = -5.9112\times10^{3}$; $c = -5.8015\times10^{13}$; $d = 2.6016\times10^{1}$

Table IV. Quasi-Morse parameters for iodine monofluoride

	$^1\Sigma^+$	$^3\Pi_{0^+}$
ω_e	610.4(9)	414.7(3)
$\omega_e x_e$	3.2(1)	3.8(7)
β	$1.774A^{-1}$	$1.948A^{-1}$
α_e	1.837	2.343
D_e	29211	11108
T	1905.0	

All units in cm^{-1} unless noted otherwise

be determined only up to the highest known vibrational level, the left and right ends of the potentials have been extended by a fit to the forms

$$U_{left}(r) = a/r^{12} + b + D_e \tag{63}$$

$$U_{right}(r) = c/r^{d} + D_e \tag{64}$$

These constants are given in the footnotes to Tables II and III. Both the quasi-Morse and complete RKR potentials for the $^3\Pi_{0^+}$ state are presented in Fig. 12. The correspondence is relatively good for energy levels below v'=10; above this level, however, the discrepancy becomes large very rapidly.

Franck-Condon factors based on the above potentials are given in Tables V and VI. A listing of the program used for the Morse calculations appears in Appendix B. Because the analytical Morse wave functions are given in part by associated Laguerre polynomials, and consequently are functions of differences of large numbers, it was found necessary to perform the calculations using double precision arithmetic, i.e. keeping track of up to 30 significant figures. Accuracy of the wavefunctions was tested by checking their orthogonality. Excellent results were obtained only after switching to double precision arithmetic. In this respect, it should be noted that many previous calculations of Morse Franck-Condon overlaps have been performed on IBM computers, which have no more significant figures in double precision than the CDC computers have in single precision. Thus, small overlap integrals at very high quantum numbers obtained by Nicholls (69) should not be regarded as entirely accurate. The interval for integration in computing the RKR overlaps and $\bar{r}$-centroids was taken as .001A. For the Morse calculations,

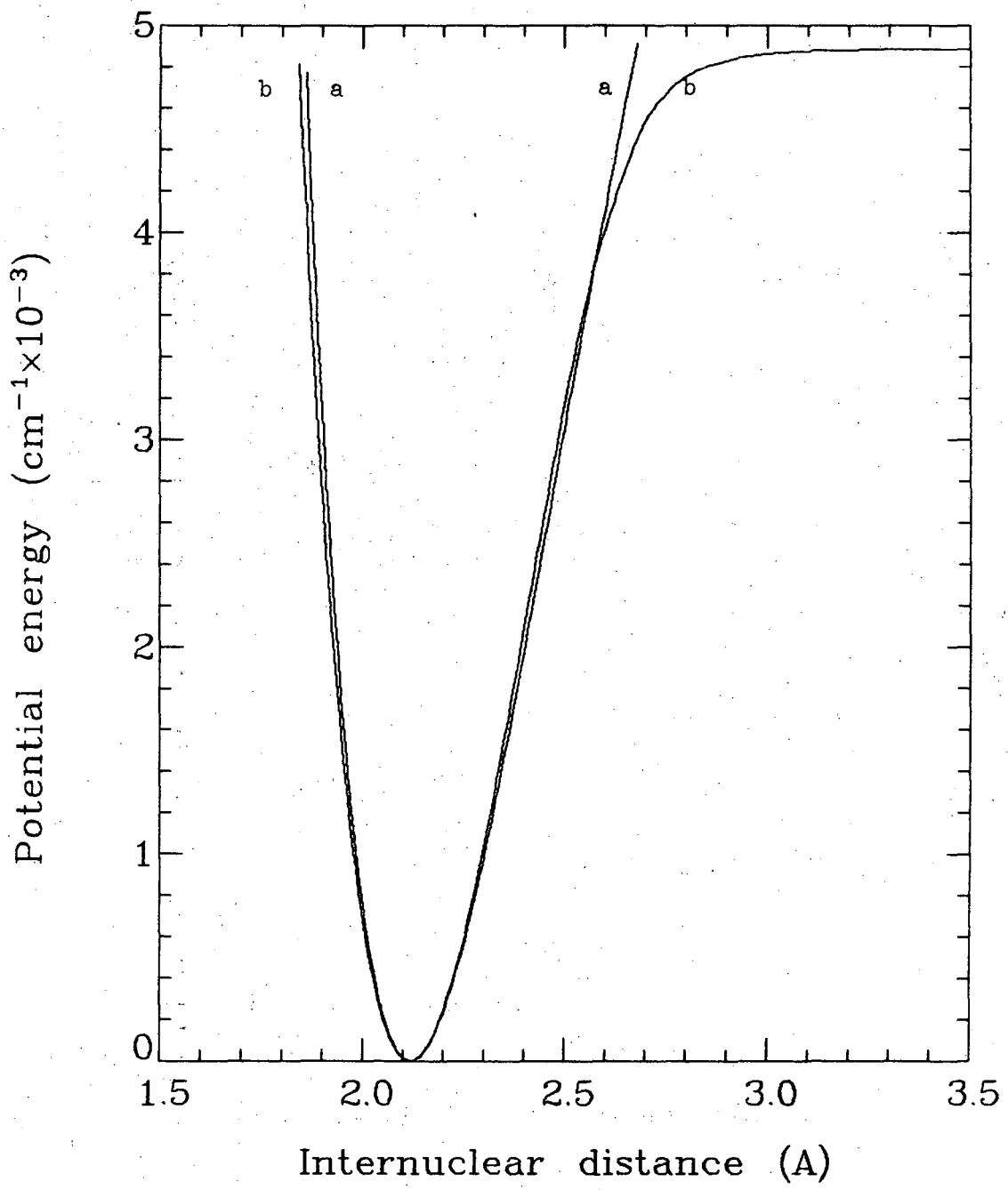

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Figure 12. Comparison of Morse (a) and RKR (b) potentials for $^3\Pi_{0^+}$ state of IF.

TABLE V. Franck-Condon factors obtained from RKR potentials

v'' \ v'	0	1	2	3	4	5	6	7	8	9	10	11	12
0	5.000-3*	2.245-2	5.302-2	8.919-2	1.195-1	1.342-1	1.316-1	1.160-1	9.456-2	7.196-2	5.139-2	3.515-2	2.307-2
1	3.039-2	9.015-2	1.307-1	1.202-1	7.176-2	2.268-2	5.947-4	7.707-3	3.008-2	5.228-2	6.446-2	6.543-2	5.770-2
2	8.784-2	1.493-1	9.737-2	1.889-2	2.891-3	3.831-2	6.704-2	6.092-2	3.343-2	8.714-3	6.528-6	5.261-3	1.528-2
3	1.602-1	1.183-1	7.914-3	2.464-2	7.322-2	5.547-2	1.153-2	1.660-3	2.405-2	4.502-2	4.496-2	2.987-2	1.338-2
4	2.065-1	3.059-2	2.965-2	8.448-2	3.050-2	1.035-3	3.567-2	5.410-2	3.098-2	4.409-3	2.037-3	1.565-2	2.645-2
5	1.998-1	3.013-3	9.732-2	2.850-2	1.032-2	5.935-2	3.822-2	1.524-3	1.303-2	3.830-2	3.694-2	1.742-2	2.842-3
6	1.507-1	6.710-2	6.683-2	7.922-3	7.015-2	2-319-2	4.745-3	4.274-2	3.920-2	7.581-3	1.938-3	1.808-2	2.739-2
7	9.057-2	1.423-1	3.554-3	7.558-2	2.783-2	1.307-2	5.573-2	1.934-2	1.904-3	2.967-2	3.607-2	1.534-2	9.571-4
8	4.400-2	1.572-1	2.915-2	6.923-2	7.234-3	6.452-2	1.037-2	1.596-2	4.550-2	1.794-2	1.733-4	1.581-2	2.676-2
9	1.742-2	1.167-1	1.103-1	6.309-3	7.149-2	1.705-2	2.450-2	4.833-2	3.729-3	1.530-2	3.665-2	1.914-2	1.267-3
10	5.667-3	6.391-2	1.478-1	2.388-2	6.012-2	1.487-2	5.769-2	8.129-4	3.269-2	3.522-2	2.059-3	9.694-3	2.546-2
11	1.529-3	2.696-2	1.191-1	1.041-1	2.668-3	7.441-2	4.734-3	4.091-2	3.166-2	9.753-4	3.113-2	2.750-2	3.996-3
12	3.439-4	9.010-3	6.702-2	1.417-1	3.271-2	4.384-2	3.106-2	4.226-2	3.382-3	4.416-2	1.583-2	1.926-3	2.143-2
13	6.396-5	2.433-3	2.814-2	1.117-1	1.120-1	3.142-5	7.398-2	1.589-4	5.307-2	1.103-2	1.334-2	3.533-2	1.213-2
14	9.869-6	5.335-4	9.162-3	6.026-2	1.364-1	5.218-2	2.335-2	5.192-2	2.058-2	1.987-2	3.977-2	2.036-3	1.184-2
15	1.305-6	9.425-5	2.360-3	2.396-2	9.821-2	1.242-1	6.409-3	6.272-2	1.011-2	5.081-2	2.358-4	2.894-2	2.669-2
16	1.345-7	1.366-5	4.838-4	7.317-3	4.871-2	1.276-1	7.818-2	5.925-3	6.755-2	3.413-3	3.876-2	2.416-2	7.522-4
17	8.433-9	1.678-6	8.039-5	1.760-3	1.788-2	8.125-2	1.318-1	2.509-2	4.139-2	3.183-2	3.446-2	4.338-3	3.517-2

*Abbreviated notation for 5.000×10^{-3}

TABLE VI. Franck-Condon factors obtained from quasi-Morse potentials

v'' \ v'	0	1	2	3	4	5	6	7	8	9	10	11	12
0	3.985-3*	1.723-2	4.031-2	6.785-2	9.226-2	1.079-1	1.127-1	1.081-1	9.688-2	8.236-2	6.710-2	5.285-2	4.951-2
1	2.588-2	7.651-2	1.162-1	1.177-1	8.554-2	4.317-2	1.186-2	1.422-4	5.276-3	1.945-2	3.507-2	4.723-2	5.398-2
2	7.893-2	1.398-1	1.065-1	3.480-2	4.010-4	1.477-2	4.463-2	5.959-2	5.249-2	3.283-2	1.339-2	2.054-3	4.413-4
3	1.505-1	1.249-1	1.810-2	9.647-3	5.618-2	6.561-2	3.390-2	4.697-3	2.308-3	1.911-2	3.629-2	4.202-2	3.563-2
4	2.017-1	4.205-2	1.571-2	7.742-2	5.013-2	3.528-3	1.102-2	4.107-2	4.727-2	2.769-2	6.380-3	1.780-4	8.597-3
5	2.022-1	2.606-4	8.741-2	4.666-2	4.926-4	4.036-2	5.392-2	2.032-2	2.117-5	1.347-2	3.370-2	3.664-2	2.309-2
6	1.577-1	5.135-2	8.089-2	4.194-4	5.728-2	4.589-2	1.555-3	1.749-2	4.372-2	3.248-2	7.092-3	8.042-4	1.407-2
7	9.827-2	1.305-1	1.309-2	5.705-2	4.977-2	3.167-4	4.090-2	4.361-2	6.833-3	5.020-3	2.905-2	3.511-2	1.830-2
8	4.986-2	1.590-1	1.289-2	8.251-2	1.840-5	5.293-2	3.591-2	8.045-5	2.931-2	4.033-2	1.323-2	2.298-4	1.504-2
9	2.088-2	1.282-1	8.727-2	2.267-2	4.846-2	4.335-2	2.415-3	4.649-2	2.916-2	2.684-5	1.994-2	3.583-2	1.924-2
10	7.295-3	7.632-2	1.424-1	5.549-3	7.769-2	1.621-4	5.554-2	2.205-2	5.346-3	4.010-2	2.608-2	5.678-4	1.203-2
11	2.142-3	3.538-2	1.321-1	7.247-2	2.139-2	5.163-2	3.166-2	9.950-3	4.911-2	1.196-2	6.356-3	3.424-2	2.503-2
12	5.316-4	1.317-2	8.474-2	1.330-1	6.138-3	7.101-2	2.994-3	5.772-2	7.696-3	1.946-2	4.055-2	7.652-3	5.633-3
13	1.120.4	4.010-3	4.085-2	1.286-1	7.341-2	1.395-2	6.032-2	1.689-2	2.443-2	4.207-2	6.712-4	2.345-2	3.373-2
14	2.011-5	1.012-3	1.544-2	8.334-2	1.306-1	1.173-2	6.038-2	1.234-2	5.293-2	8.352-5	3.654-2	2.668-2	1.023-4
15	3.078-6	2.135-4	4.697-3	3.986-2	1.221-1	8.343-2	5.103-3	6.874-2	4.022-3	4.176-2	2.476-2	4.538-3	3.731-2
16	4.024-7	3.788-5	1.169-3	1.477-2	7.629-2	1.308-1	2.372-2	4.429-2	2.932-2	3.815-2	6.059-3	4.454-2	7.518.3
17	4.490-8	5.672-6	2.409-4	4.366-3	3.502-2	1.128-1	9.810-2	8.846-5	7.053-2	3.149-4	5.253-2	6.231-3	2.249-2

*Abbreviated notation for 3.985×10^{-3}

no difference was found between results obtained by using a wider interval, .01A, and those obtained by use of a .001A interval. $\bar{r}$-centroids calculated from the RKR potentials are given in Table VII.

B. Spectra

Emission spectra of iodine monofluoride have been recorded under a variety of experimental conditions. Such quantities as the flow rates of iodine and fluorine, the resultant total pressure, and the partial pressure of the "M" gas argon were among the parameters varied. In Appendix A, the measured intensities, corrected for the spectral sensitivity of the optical system (see Fig. 6), have been tabulated as a function of wavelength [which has been corrected according to Eq. (1)]. In addition to the pertinent chemical conditions for each experiment, values of the scanning speed and RC time constant(s) are given so that the spectral slit function corrections [Eqs. (48 and 49 a,b,c)] may be applied in the analysis of the spectra.

At the end of a scan, a check of the intensity levels of the peaks occurring at the beginning of the scan was made to assure that experimental conditions had remained nearly constant during the course of the scan. In nearly all cases, the intensities were found to match to within ~2-5%.

As a further aid in the examination of the observed spectra, a list of band heads of the $^3\Pi_{0^+} \rightarrow {}^1\Sigma^+$ system of IF arranged in order of increasing wavelength is given in Table VIII.

C. Quantities Derived from Spectra

Having obtained the emission spectrum of the chemluminescing species, one is able to apply the methods developed in Section III-B-4 so as to deduce quantities of interest. In order to study the effects of

TABLE VII. r-centroids obtained from RKR potentials

v'' \ v'	0	1	2	3	4	5	6	7	8	9	10	11	12
0	2.007	1.991	1.975	1.960	1.946	1.932	1.918	1.905	1.892	1.880	1.868	1.857	1.847
1	2.031	2.014	1.998	1.983	1.986	1.953	1.935	1.928	1.915	1.902	1.890	1.879	1.869
2	2.055	2.038	2.021	2.003	1.998	1.978	1.963	1.949	1.936	1.924	1.927	1.900	1.890
3	2.080	2.061	2.039	2.032	2.014	1.998	1.982	1.980	1.960	1.946	1.934	1.923	1.914
4	2.105	2.084	2.073	2.053	2.035	2.038	2.009	1.994	1.979	1.962	1.963	1.947	1.936
5	2.131	2.125	2.095	2.074	2.068	2.046	2.029	2.003	2.006	1.990	1.977	1.965	1.952
6	2.158	2.142	2.119	2.112	2.086	2.066	2.064	2.041	2.024	2.006	2.011	1.991	1.979
7	2.186	2.168	2.134	2.130	2.107	2.101	2.078	2.059	2.063	2.036	2.021	2.007	1.983
8	2.215	2.195	2.180	2.154	2.147	2.119	2.095	2.092	2.072	2.054	2.092	2.035	2.022
9	2.246	2.224	2.205	2.171	2.165	2.139	2.133	2.111	2.082	2.086	2.068	2.052	2.027
10	2.278	2.254	2.234	2.218	2.189	2.180	2.153	2.101	2.124	2.104	2.074	2.084	2.068
11	2.311	2.286	2.264	2.244	2.199	2.201	2.166	2.166	2.142	2.162	2.117	2.100	2.080
12	2.345	2.320	2.295	2.273	2.256	2.225	2.214	2.187	2.191	2.156	2.134	2.148	2.117
13	2.382	2.354	2.329	2.304	2.283	2.482	2.238	2.314	2.200	2.172	2.174	2.151	2.132
14	2.421	2.390	2.363	2.338	2.314	2.295	2.261	2.251	2.221	2.216	2.191	2.153	2.171
15	2.455	2.430	2.399	2.373	2.347	2.324	2.316	2.276	2.269	2.237	2.141	2.208	2.187
16	2.503	2.471	2.439	2.409	2.382	2.357	2.335	2.294	2.289	2.246	2.252	2.227	2.258
17	2.633	2.507	2.480	2.447	2.418	2.391	2.367	2.349	2.316	2.304	2.275	2.280	2.247

Table VIII. Calculated band heads of IF ($^3\Pi_{0^+} \rightarrow {}^1\Sigma^+$)

v'	v"	λ(A)	v'	v"	λ(A)	v'	v"	λ(A)
12	0	4307.6	9	6	5318.0	8	10	6157.6
11	0	4357.5	1	1	5330.7	2	6	6160.4
10	0	4414.3	4	3	5334.1	11	12	6204.6
12	1	4422.8	7	5	5350.7	6	9	6219.3
11	1	4475.5	2	2	5387.8	3	7	6226.8
9	0	4477.4	12	8	5388.3	9	11	6235.4
10	1	4535.4	10	7	5388.8	0	5	6249.8
12	2	4543.0	5	4	5393.8	7	10	6292.8
8	0	4546.2	8	6	5415.4	4	8	6295.0
11	2	4598.6	3	3	5446.1	12	13	6307.3
9	1	4602.0	0	1	5448.4	1	6	6315.8
7	0	4619.5	6	5	5455.6	10	12	6320.4
10	2	4661.8	11	8	5466.7	5	9	6365.4
12	3	4668.5	9	7	5483.1	8	11	6369.7
8	1	4674.7	4	4	5505.9	2	7	6382.9
6	0	4697.4	1	2	5506.3	11	13	6415.0
11	3	4727.2	7	6	5519.7	6	10	6438.4
9	2	4732.2	12	9	5553.9	9	12	6450.4
7	1	4752.2	10	8	5556.3	3	8	6451.6
5	0	4780.3	2	3	5565.2	0	6	6481.6
10	3	4794.1	5	5	5567.6	7	11	6514.5
12	4	4799.6	8	7	5586.6	4	9	6522.1
8	2	4809.2	3	4	5625.4	12	14	6522.2
6	1	4834.8	6	6	5631.4	10	13	6538.7
11	4	4861.7	0	2	5631.9	1	7	6549.9
4	0	4868.1	11	9	5637.2	8	12	6594.2
9	3	4868.5	9	8	5656.6	5	10	6595.0
7	2	4891.3	4	5	5687.2	2	8	6619.3
5	1	4922.5	1	3	5691.7	11	14	6637.3
10	4	4932.4	7	7	5697.7	6	11	6670.6
12	5	4936.7	12	10	5727.9	9	13	6678.1
8	3	4950.0	10	9	5732.5	3	9	6690.4
3	0	4961.3	5	6	5750.8	0	7	6728.4
6	2	4978.7	2	4	5752.5	12	15	6749.4
11	5	5002.4	8	8	5766.9	7	12	6749.5
9	4	5011.3	3	5	5814.7	4	10	6763.4
4	1	5015.8	11	10	5816.5	10	14	6769.9
7	3	5037.0	6	7	5816.8	1	8	6799.1
2	0	5059.9	0	3	5826.0	8	13	6832.3
5	2	5071.9	9	9	5839.4	5	11	6838.9
10	5	5077.4	4	6	5878.5	2	9	6871.0
12	6	5080.2	7	8	5885.3	11	15	6872.8
8	4	5097.6	1	4	5887.8	6	12	6917.3
3	1	5114.7	12	11	5911.0	9	14	6919.4
6	3	5129.9	10	10	5918.1	3	10	6944.5
11	6	5149.8	5	7	5944.3	12	16	6990.1
9	5	5161.0	2	5	5950.6	0	8	6991.6
1	0	5164.2	8	9	5956.9	7	13	6999.2
4	2	5170.9	11	11	6005.4	10	15	7015.1
7	4	5190.0	6	8	6012.5	4	11	7020.2
2	1	5219.6	3	6	6014.8	1	9	7064.8
5	3	5228.8	0	4	6031.6	8	14	7085.1
10	6	5229.3	9	10	6032.0	5	12	7098.4
12	7	5230.6	4	7	6080.8	11	16	7122.6
8	5	5252.6	7	9	6083.4	2	10	7139.3
0	0	5274.6	1	5	6095.5	9	15	7175.7
3	2	5276.1	12	12	6103.9	6	13	7179.7
6	4	5288.6	10	11	6113.8	3	11	7215.5
11	7	5304.4	5	8	6148.8	12	17	7245.4

chemical conditions on the vibrational population distribution of the electronically excited state of iodine monofluoride produced in the reaction of fluorine and iodine, the transition moment function, $R_e(r)$, was first obtained by separate fits to Spectra II-112-3, II-113-1 and II-113-2, each covering the range 4300-7200A, but taken at successively lower total pressures and flow rates (See Appendix A). For each calculation, the transition moment was allowed to vary at each of 16 values of the internuclear distance from 1.84 to 2.25A, covering the range of $\bar{r}$-centroids for the 177 bands in the region covered by the spectra. The value of the transition moment between these points was obtained by linear extrapolation on a semi-logarithmic plot. Use of the logarithmic plot was found advisable because of the wide range of values of the transition moment. In addition to the 16 adjustable transition moment parameters, the populations of up to 13 vibrational levels were allowed to vary. The intensity was measured at about 850 points for the latter two spectra. The results of these calculations are shown in Fig. 13. Agreement was found to be quite satisfactory to within a constant factor which arises from the different overall intensities at the different pressures. The sets of points depicted in Fig. 13 have been normalized to the transition moment curve obtained from II-113-1.

Each of the other spectra has been fit by allowing adjustment of vibrational populations alone in a particular calculation. Several values of the rotational temperature were used to calculate the band shapes and that temperature giving the minimum deviation of the weighted sums of the squares of the difference between computed and observed intensities was assumed to be the correct rotational temperature. Such estimates of the rotational temperature are probably not more accurate than 50-100°K.

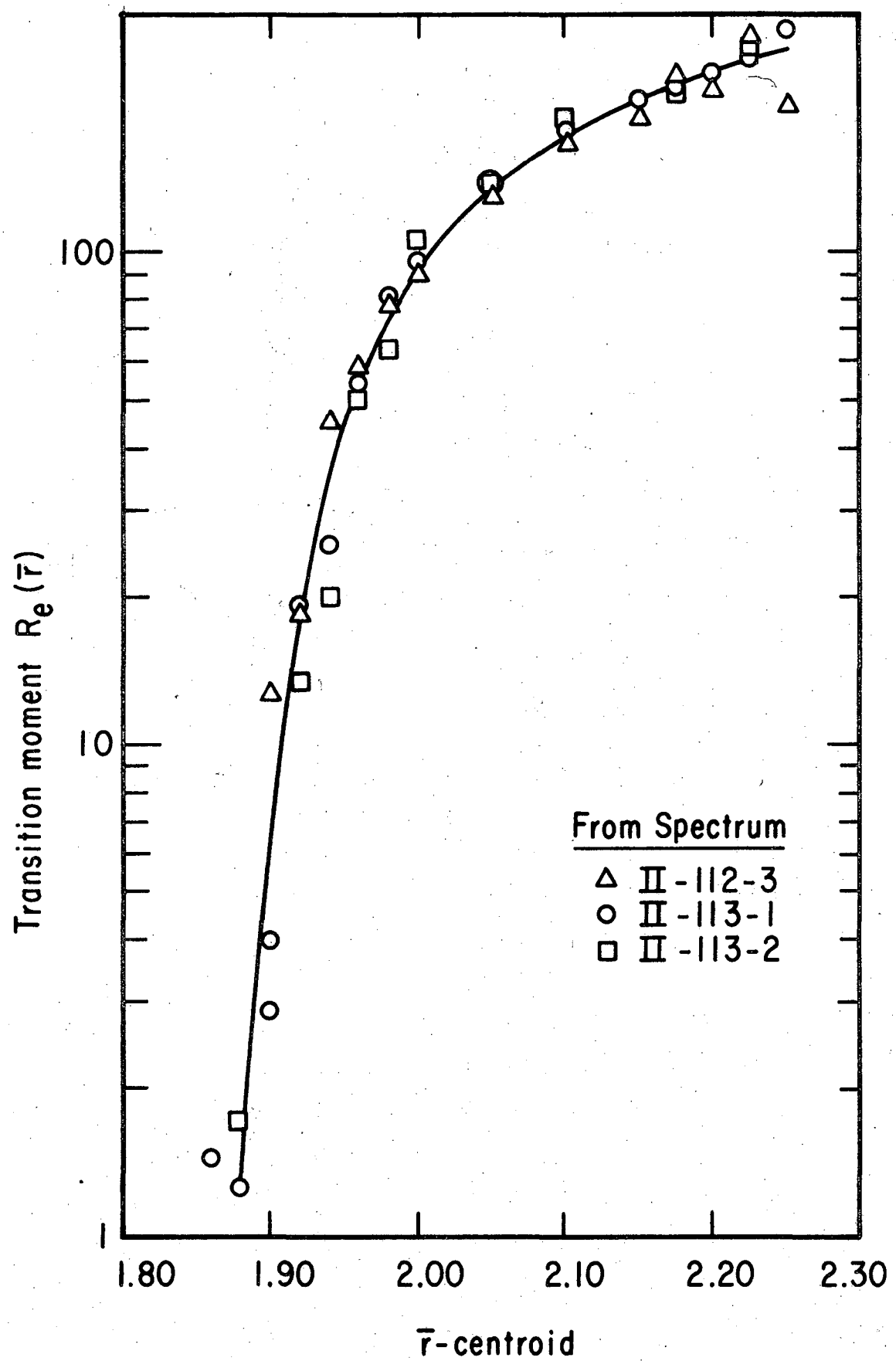

100
10
1
Transition moment $R_e(\bar{r})$
1.80
1.90
2.00
2.10
2.20
2.30
$\bar{r}$-centroid
From Spectrum
△ II-112-3
○ II-113-1
□ II-113-2

Fig. 13

In Table IX the results of the calculations for selected spectra are presented. In addition to the relative vibrational populations, temperatures, and their respective statistical standard deviations, as arbitrarily scaled index giving a comparison of the intensities of the ground vibrational level under each set of experimental conditions is also given. For certain sets or groups of spectra the intensity was checked periodically under specific "standard" conditions so that systematic errors which might affect the comparison of one spectrum with another in the series could be eliminated or significantly reduced.

Calculated spectra were constructed from the experimentally obtained transition moment function and the least squares values of the vibrational populations according to Eqs. (50) and (51). In Figs. 14a-u both the experimental points and calculated spectra are given for each set of experimental conditions.

A plot of calculated vibrational populations for the series of spectra II-111-4, II-111-5, II-112-1, and II-112-2 is presented in Fig. 15. Although a population inversion is indicated, the large standard deviations in populations of levels with v' higher than 5-6 cast considerable doubt over that observation.

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 111-4 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 650 °K Computed v'=0 population factor = 8.787E-01

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$ (°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0	-	-
1	7.340E-01	3.179E-02	1884	264
2	6.852E-01	3.413E-02	3061	403
3	4.941E-01	4.198E-02	2443	294
4	5.151E-01	4.258E-02	3432	428
5	3.967E-01	5.459E-02	3050	454
6	1.659E-01	6.704E-02	1865	420
7	3.589E-01	7.439E-02	3774	763
8	5.101E-01	8.498E-02	6491	1606
9	2.402E-18	1.393E-01	120	>10000
10	8.956E-18	3.993E-01	136	>10000
11	9.926E-01	2.184E-01	>10000	>10000
12	3.755E-01	5.848E-01	6338	10076

χ^2 = 1.149

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum II-111-4 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 550°K Computed v'=0 population factor = 9.441E-01

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	—	—
1	7.364E-01	2.902E-02	1904	245
2	6.847E-02	3.085E-02	3055	363
3	4.904E-01	3.826E-02	2417	265
4	4.800E-01	3.830E-02	3102	337
5	3.449E-01	4.965E-02	2649	358
6	1.156E-01	6.131E-02	1553	382
7	2.878E-01	7.071E-02	3105	612
8	4.473E-01	7.991E-02	5430	1206
9	9.489E-15	1.319E-01	150	>10000
10	1.490E-01	3.844E-01	2797	3790
11	8.777E-01	2.047E-01	>10000	>10000
12	3.893E-14	5.652E-01	201	>10000

χ^2 = .935

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum II-111-4 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 700°K Computed v'=0 population factor = 9.858E-01

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	—	—
1	7.245E-01	2.747E-02	1808	213
2	6.753E-01	2.919E-02	2948	325
3	4.847E-01	3.668E-02	2378	248
4	4.550E-01	3.618E-02	2892	292
5	3.322E-01	4.726E-02	2559	330
6	1.193E-01	5.861E-02	1576	364
7	2.558E-01	6.799E-02	2837	553
8	4.158E-01	7.739E-02	4979	1056
9	6.678E-15	1.265E-01	149	>10000
10	9.891E-02	3.739E-01	2302	3761
11	7.967E-01	1.964E-01	>10000	>10000
12	2.217E-16	5.529E-01	172	>10000

x^2 = .854

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 111-5 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 550°K Computed v'=0 population factor = 9.821E-01

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	—	—
1	7.019E-01	2.825E-02	1646	187
2	6.701E-01	3.053E-02	2891	329
3	4.151E-01	3.672E-02	1959	197
4	4.380E-01	3.785E-02	2758	289
5	3.871E-01	4.930E-02	2972	399
6	1.474E-01	6.026E-02	1750	374
7	2.685E-01	7.055E-02	2941	588
8	4.553E-01	7.651E-02	5553	1186
9	2.533E-15	1.165E-01	144	>10000
10	6.978E-17	3.604E-01	143	>10000
11	7.840E-01	1.961E-01	>10000	>10000
12	1.441E-01	5.278E-01	3205	6059

χ^2 = 1.168

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum II-111-5 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 650°K Computed v'=0 population factor = 1.054E+00

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	—	—
1	7.030E-01	2.632E-02	1653	176
2	6.689E-01	2.817E-02	2878	301
3	4.090E-01	3.417E-02	1926	180
4	4.050E-01	3.483E-02	2519	240
5	3.460E-01	4.587E-02	2657	332
6	9.955E-02	5.630E-02	1452	356
7	1.974E-01	6.793E-02	2384	505
8	3.925E-01	7.347E-02	4672	935
9	2.087E-15	1.127E-01	144	>10000
10	7.822E-03	3.539E-01	1098	>10000
11	6.888E-01	1.879E-01	>10000	>10000
12	1.439E-14	5.206E-01	195	>10000

χ^2 = .989

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum II-111-5 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 700°K Computed v'=0 population factor = 1.100E+00

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	—	—
1	6.905E-01	2.514E-02	1574	155
2	6.584E-01	2.689E-02	2769	271
3	4.051E-01	3.308E-02	1906	172
4	3.818E-01	3.324E-02	2365	214
5	3.316E-01	4.408E-02	2554	308
6	1.070E-01	5.435E-02	1499	341
7	1.736E-01	6.576E-02	2209	478
8	3.490E-01	7.180E-02	4151	811
9	5.768E-16	1.094E-01	138	> 10000
10	2.824E-16	3.475E-01	149	> 10000
11	6.150E-01	1.821E-01	> 10000	7235
12	1.113E-15	5.138E-01	180	> 10000

χ^2 = .917

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 112-1 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 550°K Computed v'=0 population factor = 1.182E+00

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	—	—
1	6.709E-01	2.117E-02	1460	115
2	5.940E-01	2.267E-02	2222	163
3	3.996E-01	2.805E-02	1878	144
4	3.954E-01	2.874E-02	2454	192
5	2.930E-01	3.764E-02	2297	240
6	1.186E-01	4.591E-02	1571	285
7	1.907E-01	5.053E-02	2334	373
8	3.550E-01	5.863E-02	4219	673
9	3.656E-02	8.930E-02	1467	1083
10	8.899E-02	2.799E-01	2201	2861
11	3.662E-01	1.486E-01	5750	23233
12	1.361E-02	4.145E-01	1445	> 10000

χ^2 = .993

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 112-1 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 650°K Computed v'=0 population factor = 1.267E+00

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	—	—
1	6.709E-01	2.024E-02	1460	110
2	5.917E-01	2.146E-02	2205	152
3	3.936E-01	2.680E-02	1847	135
4	3.633E-01	2.716E-02	2249	166
5	2.591E-01	3.597E-02	2088	215
6	7.513E-02	4.405E-02	1294	293
7	1.409E-01	5.023E-02	1973	359
8	2.978E-01	5.780E-02	3607	578
9	7.934E-15	8.856E-02	150	> 10000
10	1.831E-02	2.816E-01	1331	5117
11	3.167E-01	1.466E-01	5024	2023
12	1.027E-14	4.183E-01	193	> 10000

χ^2 = .882

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 112-1 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 700°K Computed v'=0 population factor = 1.319E+00

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	—	—
1	6.597E-01	1.983E-02	1401	101
2	5.833E-01	2.103E-02	2147	144
3	3.919E-01	2.663E-02	1838	133
4	3.415E-01	2.658E-02	2119	154
5	2.483E-01	3.543E-02	2024	207
6	8.463E-02	4.363E-02	1357	283
7	1.204E-01	4.997E-02	1827	358
8	2.645E-01	5.791E-02	3285	541
9	2.405E-19	8.819E-02	113	>10000
10	3.834E-20	2.833E-01	119	>10000
11	2.531E-01	1.458E-01	4203	1763
12	6.347E-19	4.227E-01	148	>10000

χ^2 = .858

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 112-2 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 550°K Computed v'=0 population factor = 1.355E+00

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	——	——
1	6.272E-01	1.533E-02	1249	65
2	5.191E-01	1.624E-02	1765	84
3	3.570E-01	2.049E-02	1672	93
4	3.005E-01	2.112E-02	1894	111
5	2.375E-01	2.767E-02	1961	159
6	9.656E-02	3.405E-02	1434	216
7	1.243E-01	3.756E-02	1855	269
8	2.519E-01	4.348E-02	3169	397
9	4.307E-15	6.714E-02	147	>10000
10	1.006E-04	2.050E-01	578	>10000
11	2.825E-01	1.117E-01	4569	1429
12	6.687E-14	3.004E-01	205	>10000

χ^2 = .714

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 112-2 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 650°K Computed v'=0 population factor = 1.444E+00

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	—	—
1	6.244E-01	1.699E-02	1237	72
2	5.138E-01	1.786E-02	1737	91
3	3.536E-01	2.274E-02	1657	103
4	2.702E-01	2.321E-02	1740	114
5	2.052E-01	3.069E-02	1781	168
6	6.502E-02	3.800E-02	1226	262
7	8.068E-02	4.341E-02	1536	328
8	1.789E-01	4.980E-02	2539	411
9	1.176E-17	7.737E-02	125	> 10000
10	1.730E-15	2.397E-01	157	> 10000
11	2.270E-01	1.275E-01	3895	1476
12	1.087E-16	3.526E-01	169	> 10000

χ^2 = .843

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 112-2 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 700°K Computed v'=0 population factor = 1.500E+00

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	—	—
1	6.131E-01	1.778E-02	1191	71
2	5.051E-01	1.870E-02	1694	92
3	3.516E-01	2.414E-02	1647	108
4	2.497E-01	2.428E-02	1641	115
5	1.959E-01	3.230E-02	1730	175
6	7.705E-02	4.023E-02	1307	266
7	6.415E-02	4.618E-02	1408	369
8	1.455E-01	5.335E-02	2266	431
9	4.771E-17	8.263E-02	129	> 10000
10	5.352E-17	2.577E-01	142	> 10000
11	1.900E-01	1.353E-01	3478	1491
12	3.554E-16	3.811E-01	175	> 10000

χ^2 = .931

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 112-3 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 550°K Computed v'=0 population factor = 6.478E+00

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	—	—
1	7.113E-01	1.496E-02	1711	106
2	5.519E-01	1.794E-02	1947	106
3	3.400E-01	2.522E-02	1596	110
4	2.626E-01	2.967E-02	1703	144
5	2.332E-01	3.500E-02	1937	200
6	1.291E-01	3.918E-02	1637	243
7	1.087E-01	4.837E-02	1743	349
8	1.765E-01	5.363E-02	2519	441
9	1.750E-02	6.188E-02	1200	1049
10	1.856E-02	1.307E-01	1336	2359
11	2.280E-01	8.064E-02	3907	935
12	2.463E-01	1.990E-01	4430	2544

χ^2 = 21.41

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 112-3 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 650°K Computed v'=0 population factor = 7.000E+00

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	——	——
1	6.955E-01	1.579E-02	1605	100
2	5.491E-01	1.899E-02	1930	111
3	3.426E-01	2.676E-02	1608	117
4	2.310E-01	3.128E-02	1554	144
5	1.999E-01	3.739E-02	1752	204
6	9.355E-02	4.181E-02	1414	267
7	4.158E-02	5.216E-02	1216	480
8	1.282E-01	5.822E-02	2127	470
9	1.553E-13	6.700E-02	165	>10000
10	6.193E-02	1.463E-01	1914	1626
11	1.217E-01	8.784E-02	2742	940
12	4.889E-03	2.236E-01	1167	>10000

χ^2 = 23.55

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 112-3 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 700°K Computed v'=0 population factor = 7.182E+00

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	—	—
1	6.897E-01	1.787E-02	1568	109
2	5.503E-01	2.166E-02	1937	128
3	3.369E-01	3.048E-02	1583	132
4	2.159E-01	3.563E-02	1485	160
5	1.862E-01	4.252E-02	1678	228
6	9.865E-02	4.779E-02	1447	303
7	1.877E-02	5.966E-02	973	778
8	1.116E-01	6.723E-02	1993	547
9	2.024E-20	7.719E-02	107	>10000
10	2.756E-02	1.710E-01	1483	2561
11	9.789E-02	1.015E-01	2485	1109
12	3.300E-20	2.621E-01	138	>10000

χ^2 = 29.64

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 113-1 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 550°K Computed v'=0 population factor = 9.399E-01

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	——	——
1	7.695E-01	1.969E-02	2224	217
2	6.515E-01	2.353E-02	2700	228
3	4.613E-01	3.316E-02	2226	207
4	4.406E-01	3.833E-02	2778	295
5	3.128E-01	4.543E-02	2426	303
6	1.441E-01	5.046E-02	1730	313
7	2.934E-01	6.094E-02	3154	534
8	3.697E-01	6.902E-02	4390	824
9	9.080E-14	7.950E-02	162	>10000
10	1.129E-02	1.702E-01	1188	3993
11	5.920E-01	1.048E-01	11017	3721
12	5.277E-01	2.603E-01	9712	7496

χ^2 = 29.33

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 113-1 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 650°K Computed v'=0 population factor = 1.012E+00

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$ (°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	——	——
1	7.589E-01	1.866E-02	2112	188
2	6.507E-01	2.235E-02	2693	215
3	4.663E-01	3.151E-02	2257	200
4	4.103E-01	3.629E-02	2556	254
5	2.677E-01	4.332E-02	2140	263
6	9.183E-02	4.834E-02	1403	309
7	2.155E-01	5.912E-02	2520	450
8	2.976E-01	6.679E-02	3605	668
9	1.604E-17	7.768E-02	126	>10000
10	2.327E-02	1.692E-01	1416	2738
11	4.730E-01	1.021E-01	7716	2224
12	3.193E-01	2.593E-01	5438	3868

χ^2 = 25.72

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 113-1 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 700°K Computed v'=0 population factor = 1.043E+00

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	——	——
1	7.468E-01	1.912E-02	1996	175
2	6.471E-01	2.303E-02	2658	217
3	4.658E-01	3.259E-02	2254	206
4	3.966E-01	3.742E-02	2462	251
5	2.524E-01	4.485E-02	2048	264
6	8.914E-02	5.015E-02	1386	323
7	1.942E-01	6.123E-02	2360	454
8	2.820E-01	6.980E-02	3452	675
9	9.582E-22	8.111E-02	100	>10000
10	2.087E-02	1.787E-01	1376	3046
11	4.324E-01	1.069E-01	6889	2031
12	2.349E-01	2.743E-01	4286	3454

χ^2 = 26.85

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 113-2 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 550°K Computed v'=0 population factor = 2.787E-01

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	——	——
1	7.894E-01	3.574E-02	2464	472
2	7.573E-01	4.331E-02	4162	856
3	6.920E-01	6.236E-02	4679	1145
4	6.176E-01	7.000E-02	4724	1111
5	4.431E-01	8.168E-02	3465	785
6	1.541E-01	9.123E-02	1792	567
7	5.558E-01	1.106E-01	6584	2229
8	5.124E-01	1.245E-01	6534	2373
9	4.267E-15	1.435E-01	147	>10000
10	4.888E-02	3.066E-01	1764	3665
11	9.162E-01	1.908E-01	>10000	>10000
12	7.632E-01	4.683E-01	>10000	>10000

χ^2 = .840

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 113-2 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 650°K Computed v'=0 population factor = 3.008E-01

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	—	—
1	7.757E-01	3.391E-02	2294	395
2	7.555E-01	4.123E-02	4128	804
3	6.957E-01	5.939E-02	4746	1117
4	5.805E-01	6.639E-02	4186	880
5	3.881E-01	7.807E-02	2980	633
6	9.024E-02	8.764E-02	1393	562
7	4.671E-01	1.073E-01	5081	1534
8	4.316E-01	1.207E-01	5200	1731
9	2.668E-14	1.407E-01	155	>10000
10	2.007E-02	3.055E-01	1362	5307
11	7.595E-01	1.859E-01	>10000	>10000
12	5.966E-01	4.677E-01	>10000	>10000

χ^2 = .7447

(continued)

Table IX. Calculated vibrational populations and temperatures relative to v' = 0

Spectrum 113-2 τ_{RC} = 3.14 sec (single section) Λ = 11.5A Scan speed 40A/min

Trial rotational temperature = 700°K Computed v'=0 population factor = 3.107E-01

v'	$N_{v'}/N_0$	$\sigma(N_{v'}/N_0)$	$T_{v'}$(°K)	$\sigma(T_{v'})$ (°K)
0	1.000E+00	0.	——	——
1	7.636E-01	3.344E-02	2160	351
2	7.546E-01	4.092E-02	4109	791
3	6.970E-01	5.915E-02	4772	1122
4	5.635E-01	6.588E-02	3969	809
5	3.673E-01	7.779E-02	2816	595
6	8.089E-02	8.747E-02	1332	573
7	4.416E-01	1.069E-01	4731	1401
8	4.144E-01	1.214E-01	4960	1650
9	4.612E-14	1.414E-01	158	>10000
10	7.729E-12	3.106E-01	208	>10000
11	7.014E-01	1.873E-01	>10000	>10000
12	5.281E-01	4.763E-01	9724	>10000

χ^2 = .7221

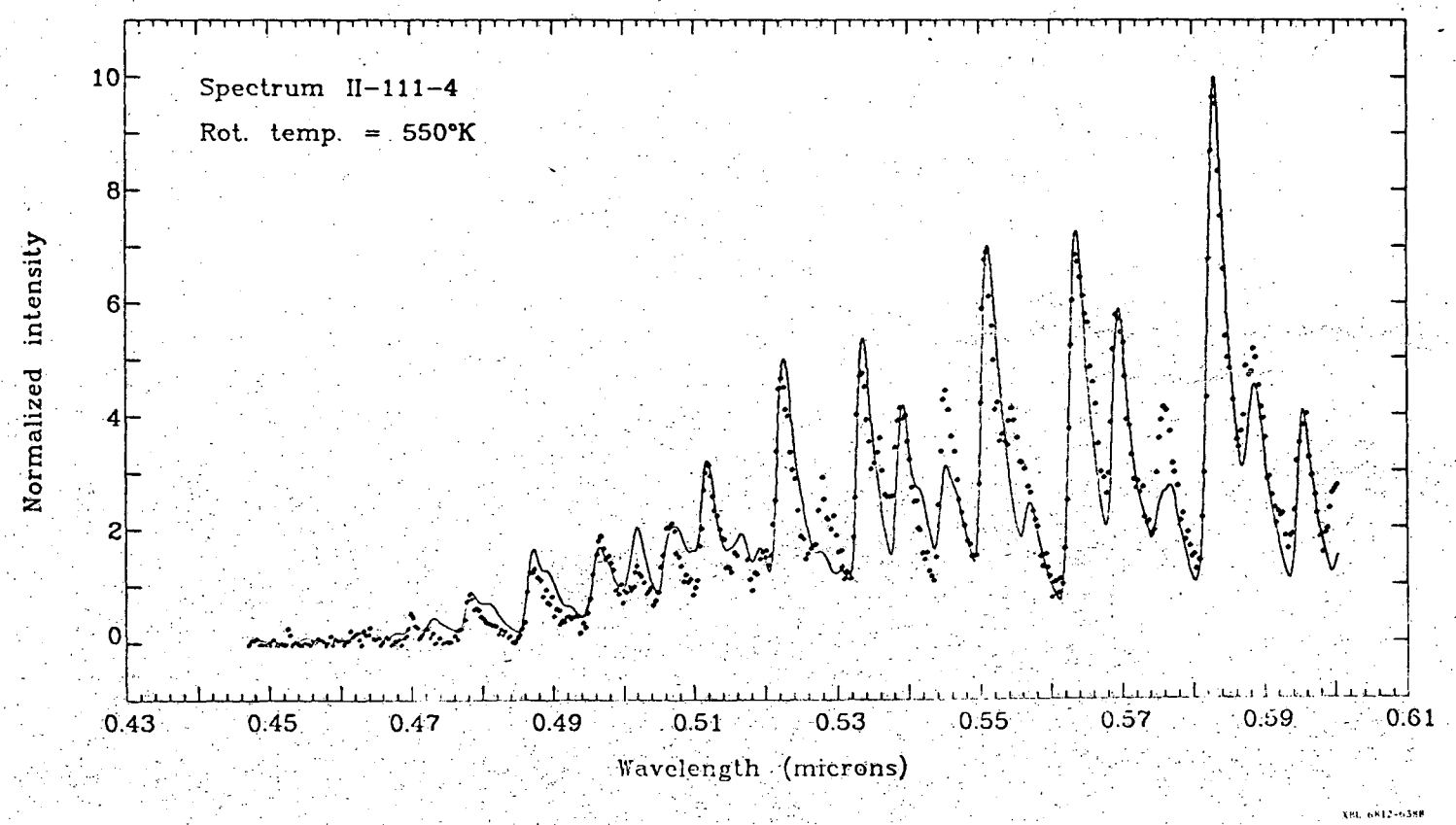

Spectrum II-111-4
Rot. temp. = 550°K
Normalized intensity
10
8
6
4
2
0
0.43
0.45
0.47
0.49
0.51
0.53
0.55
0.57
0.59
0.61
Wavelength (microns)

Fig. 14 a

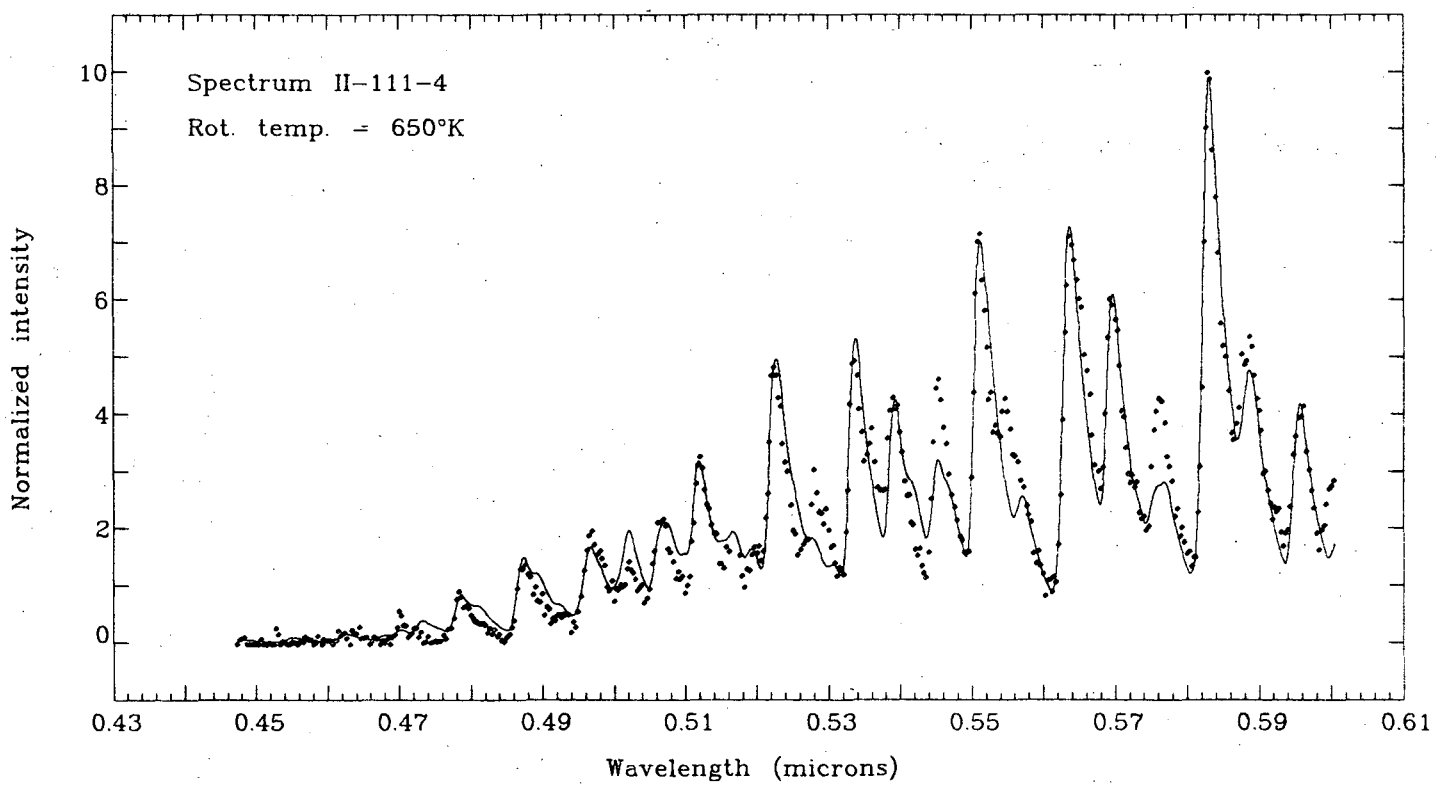
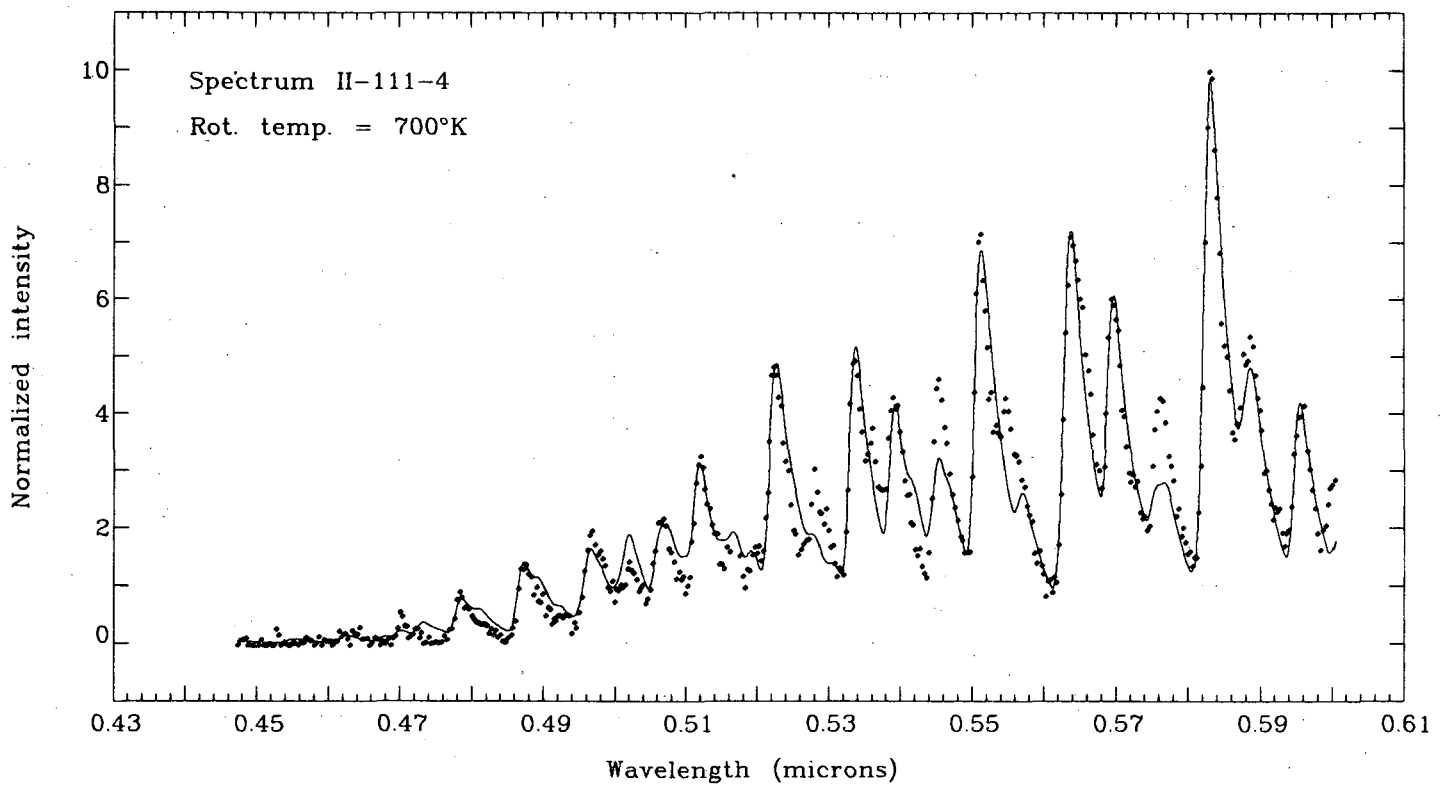
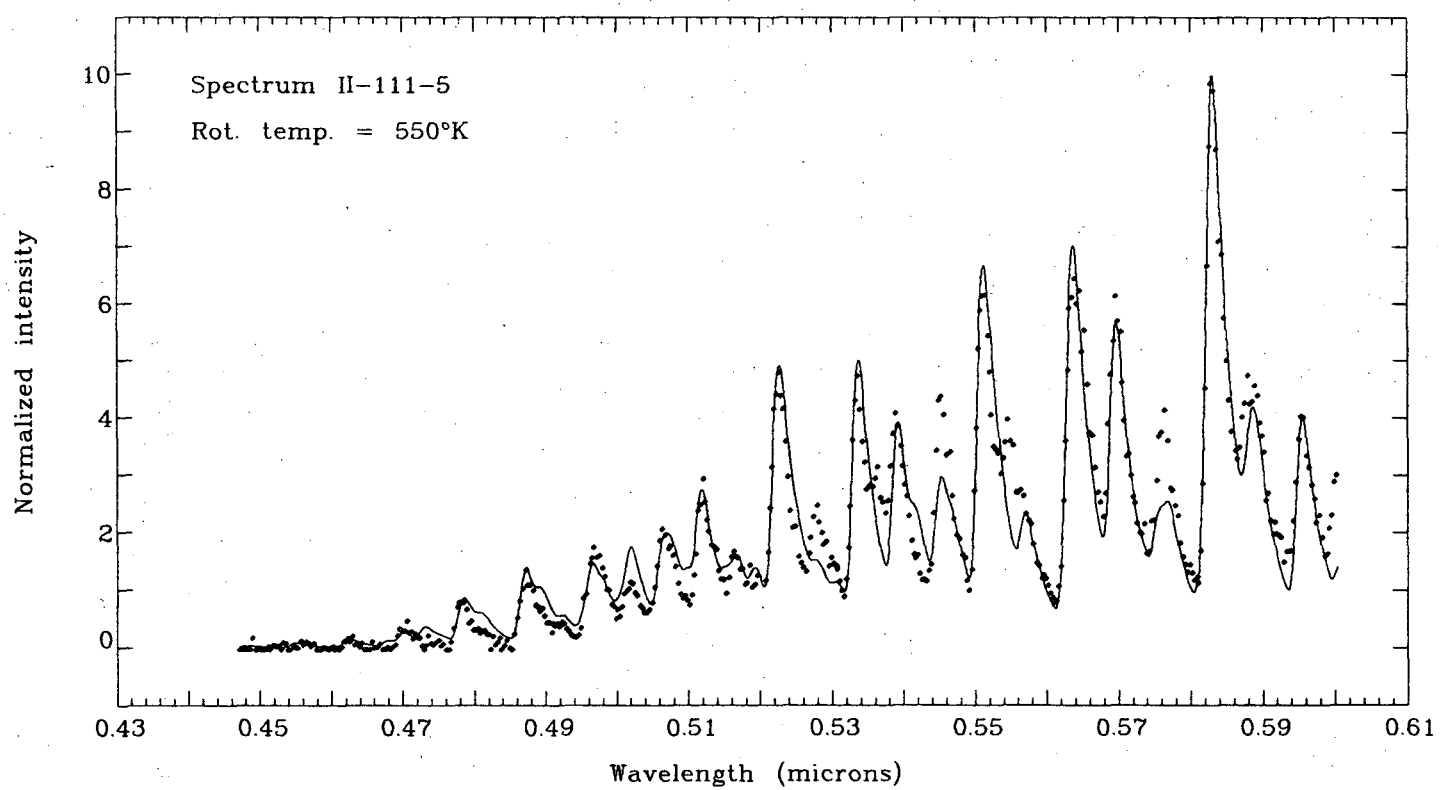

Spectrum II-111-4
Rot. temp. = 650°K
Normalized intensity
0
2
4
6
8
10
0.43
0.45
0.47
0.49
0.51
0.53
0.55
0.57
0.59
0.61
Wavelength (microns)

Fig. 14b



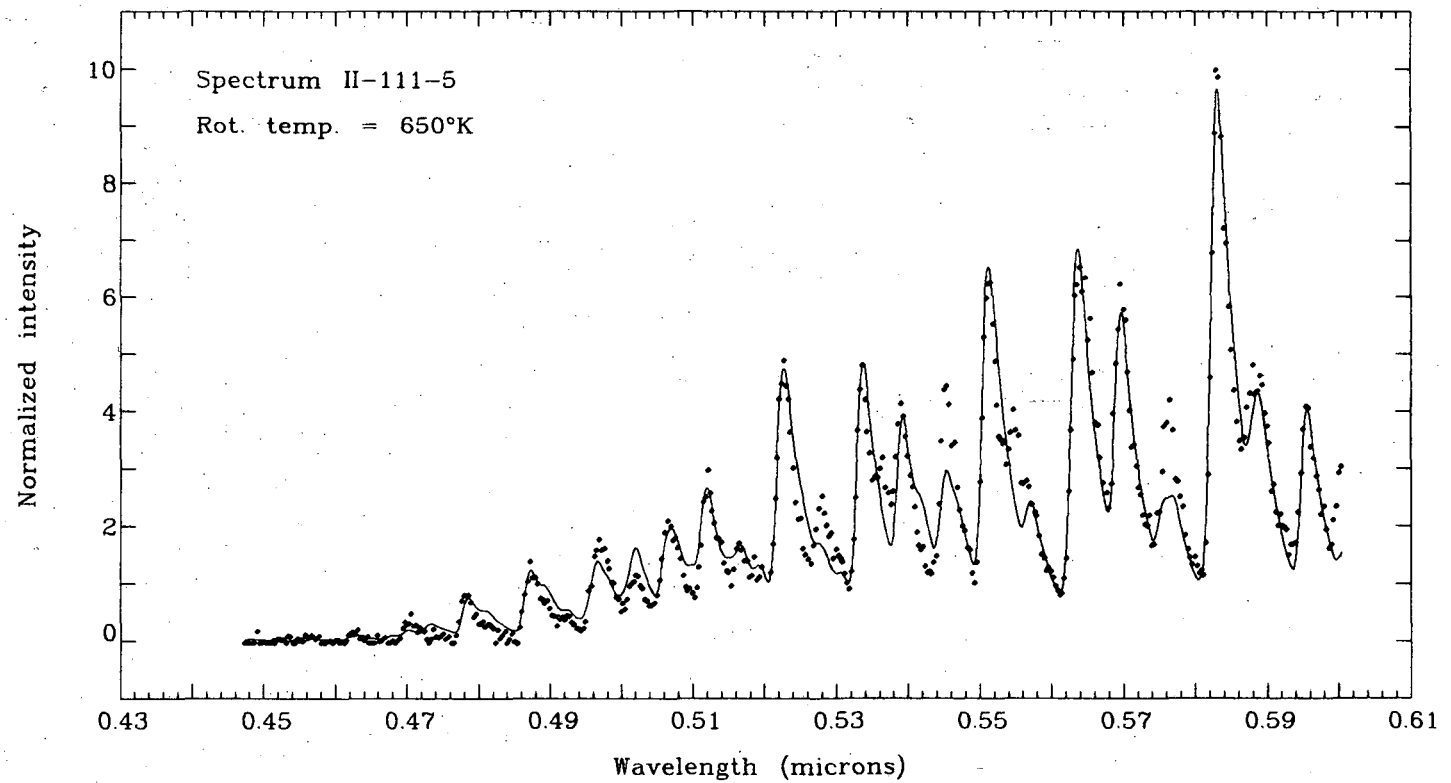
XBL 6812-6383

Fig. 14c



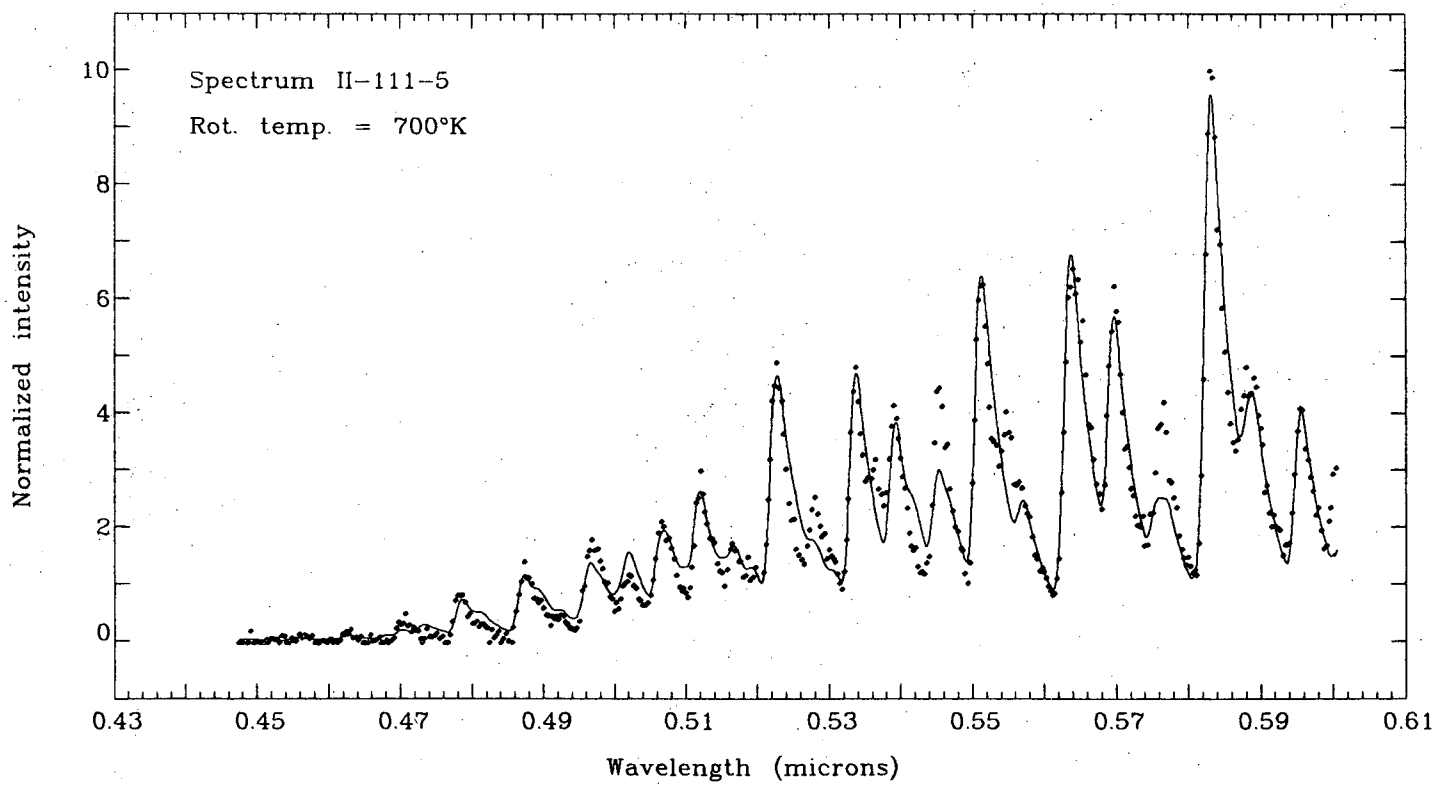
XBL 6812-6384

Fig. 14d



XBL 6812-6385

Fig. 14e



XBL 6812-6386

Fig. 14f

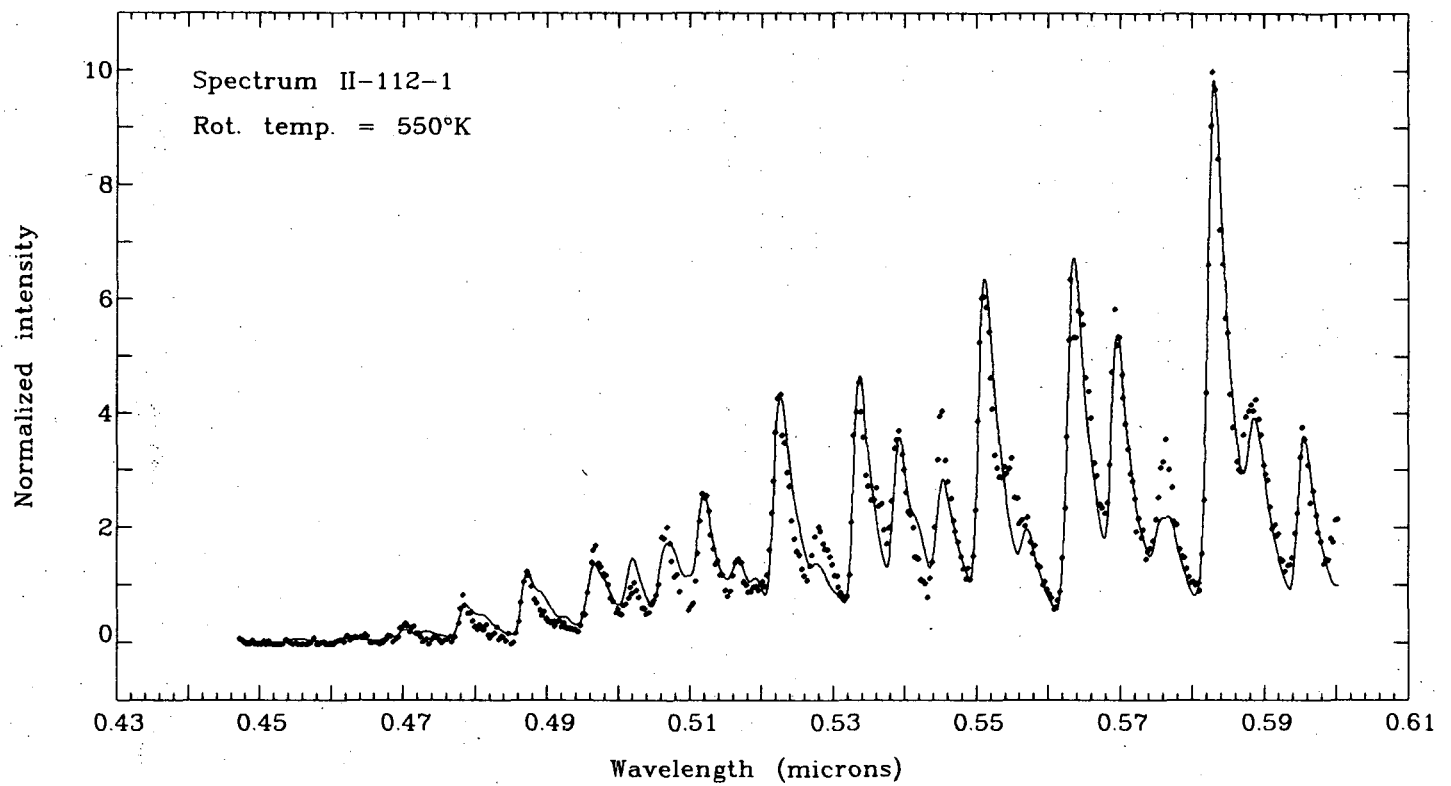

Spectrum II-112-1
Rot. temp. = 550°K
Normalized intensity
0
2
4
6
8
10
0.43
0.45
0.47
0.49
0.51
0.53
0.55
0.57
0.59
0.61
Wavelength (microns)

Fig. 14g

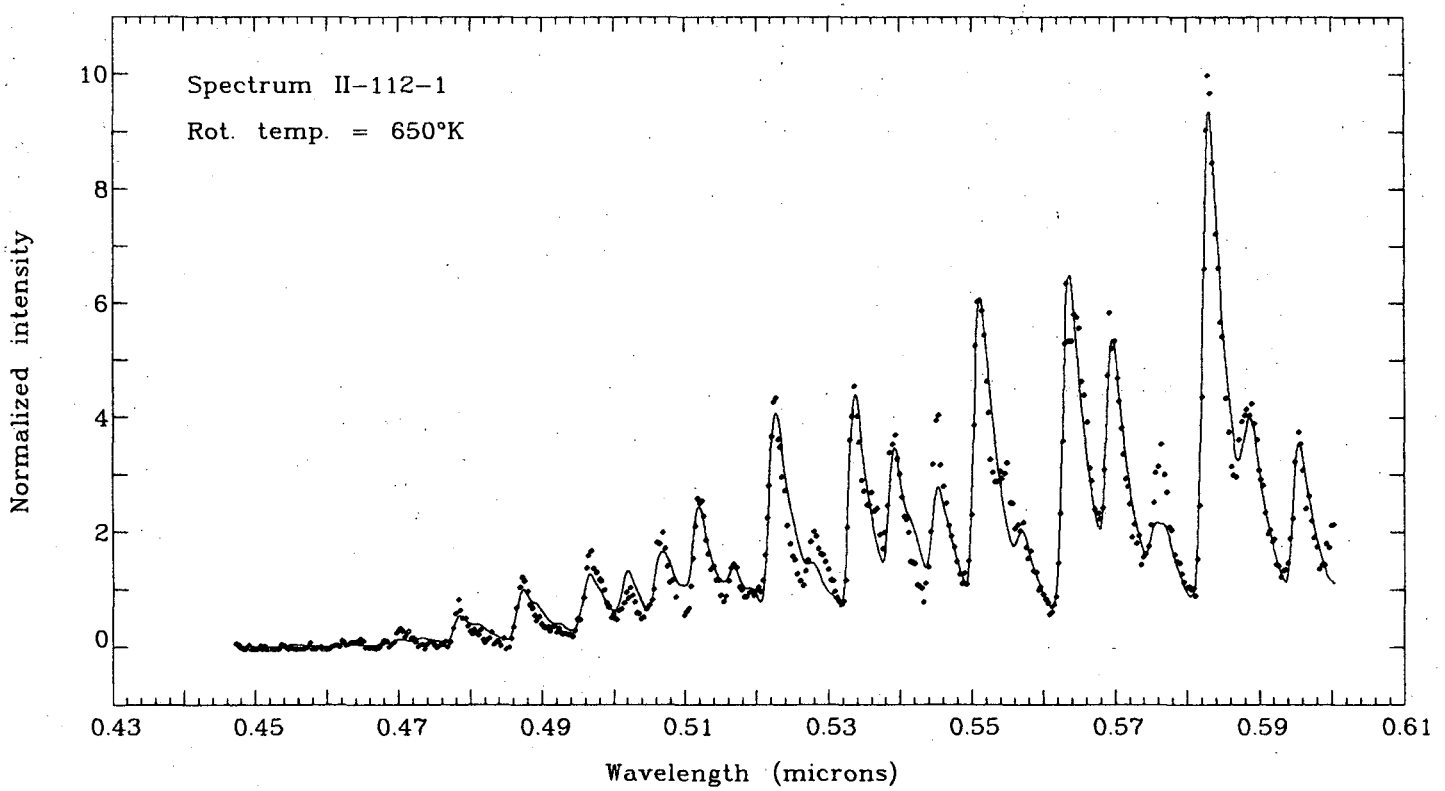
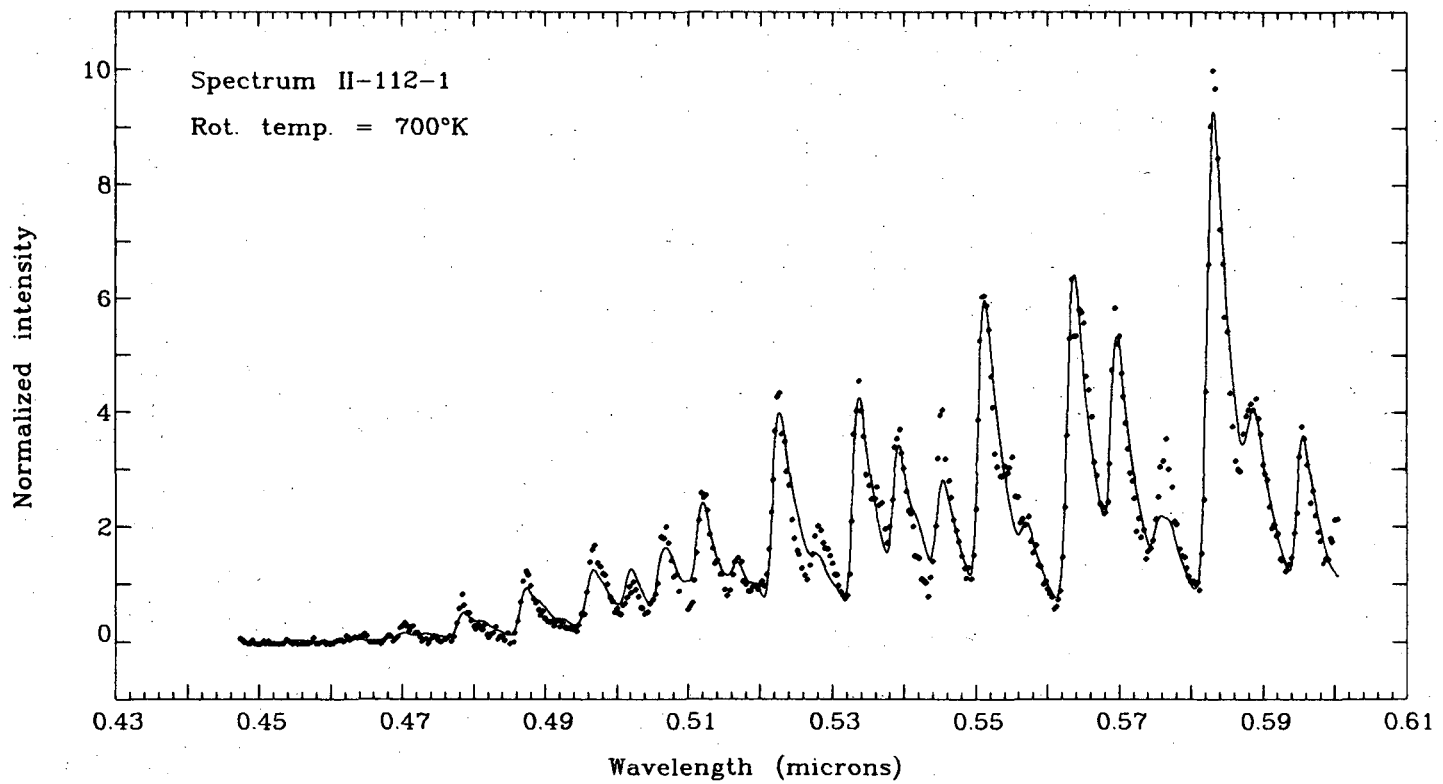


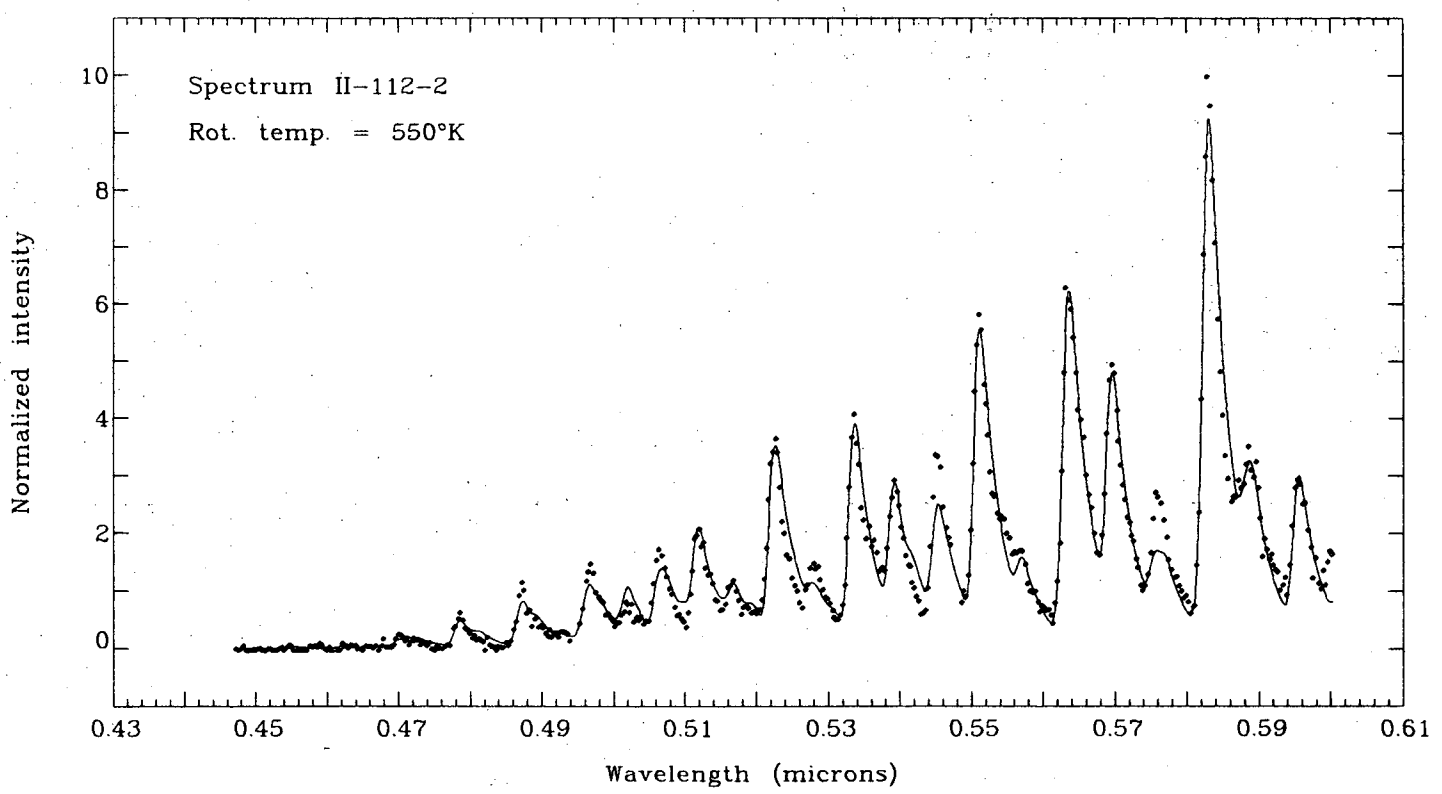
Fig. 14h

XBL 6812-6387



XBL 6812-6402

Fig. 14i



XBL 6812-6401

Fig. 14j

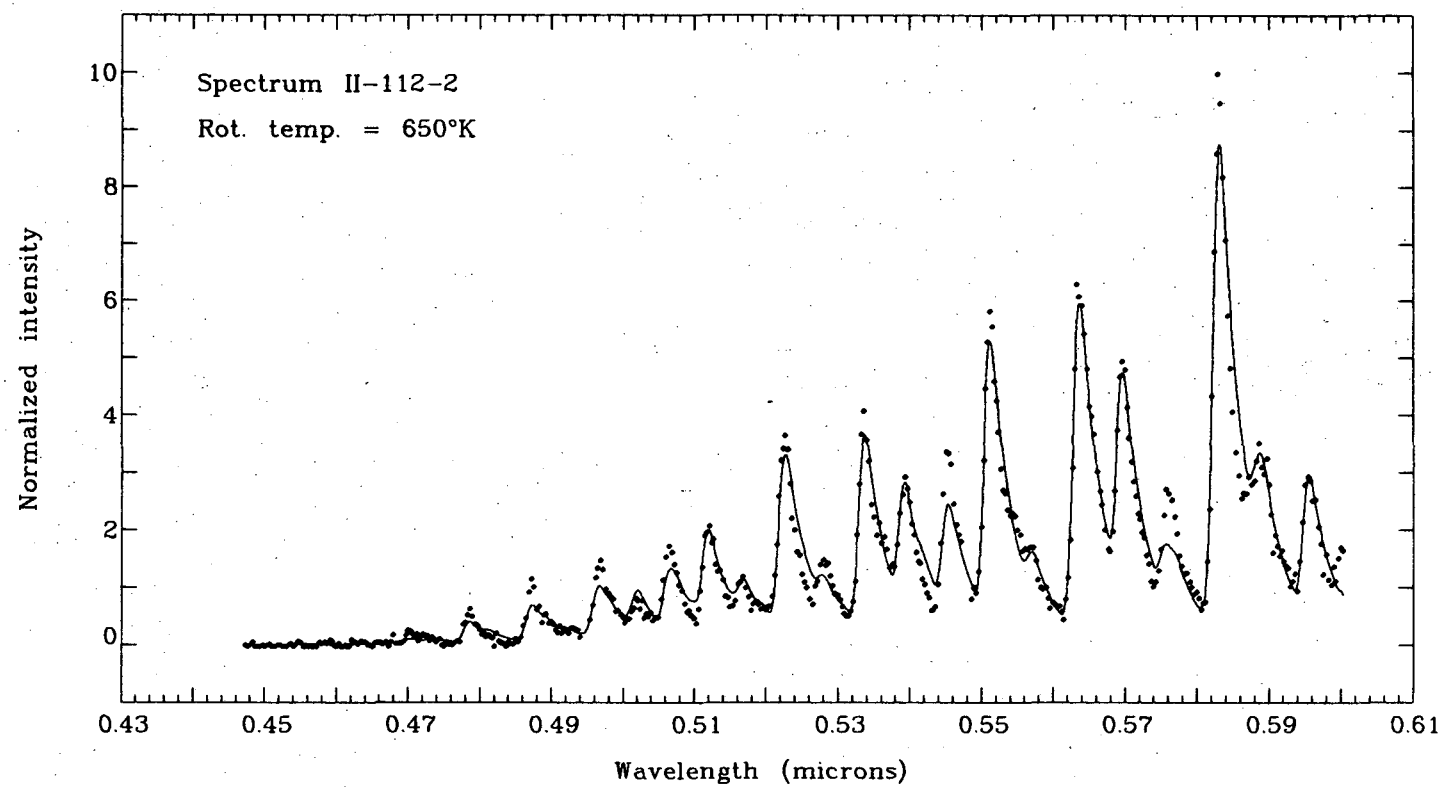


Fig. 14k

XBL 6812-6399

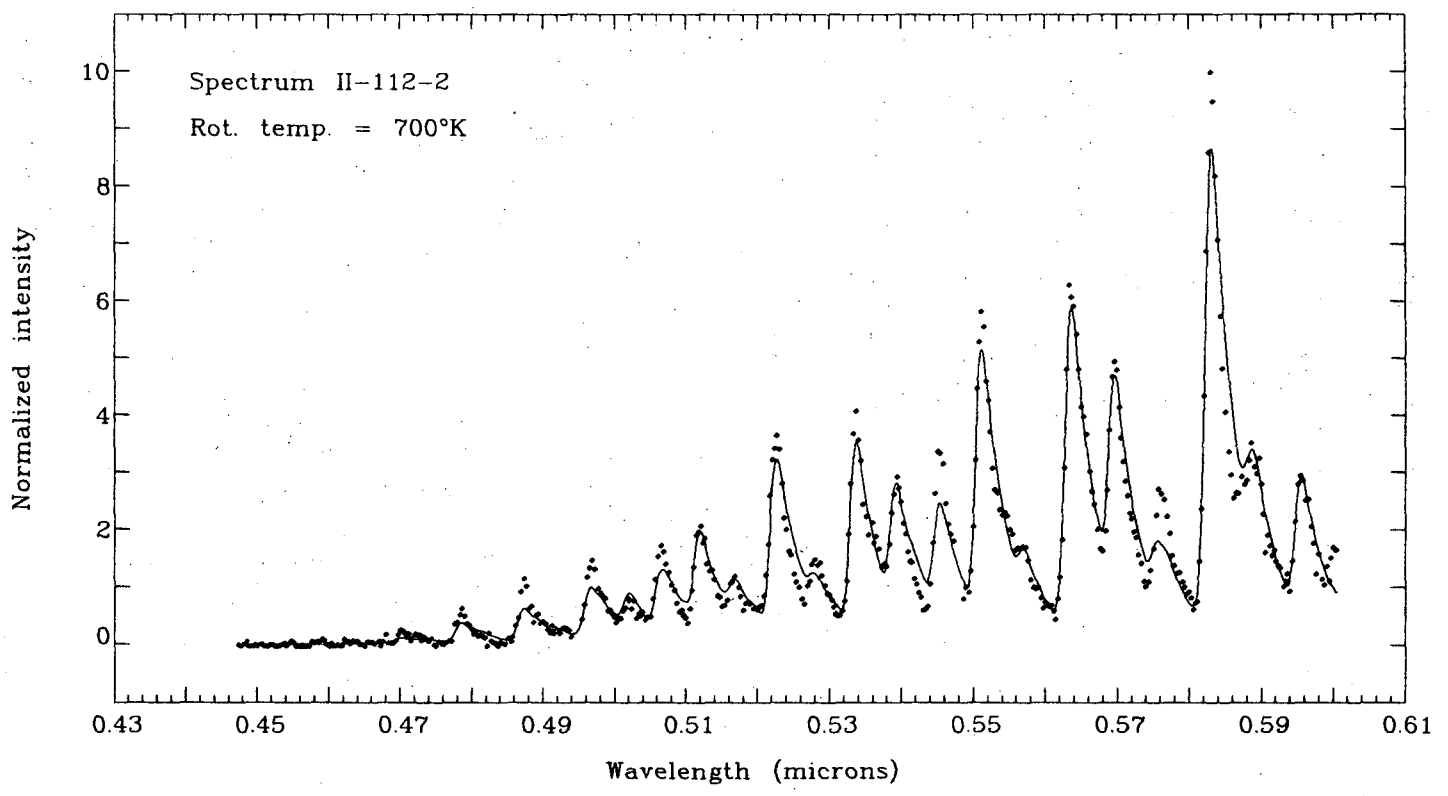

Spectrum II-112-2
Rot. temp. = 700°K
Normalized intensity
0
2
4
6
8
10
0.43
0.45
0.47
0.49
0.51
0.53
0.55
0.57
0.59
0.61
Wavelength (microns)
XBL 6812-6400

Fig. 141

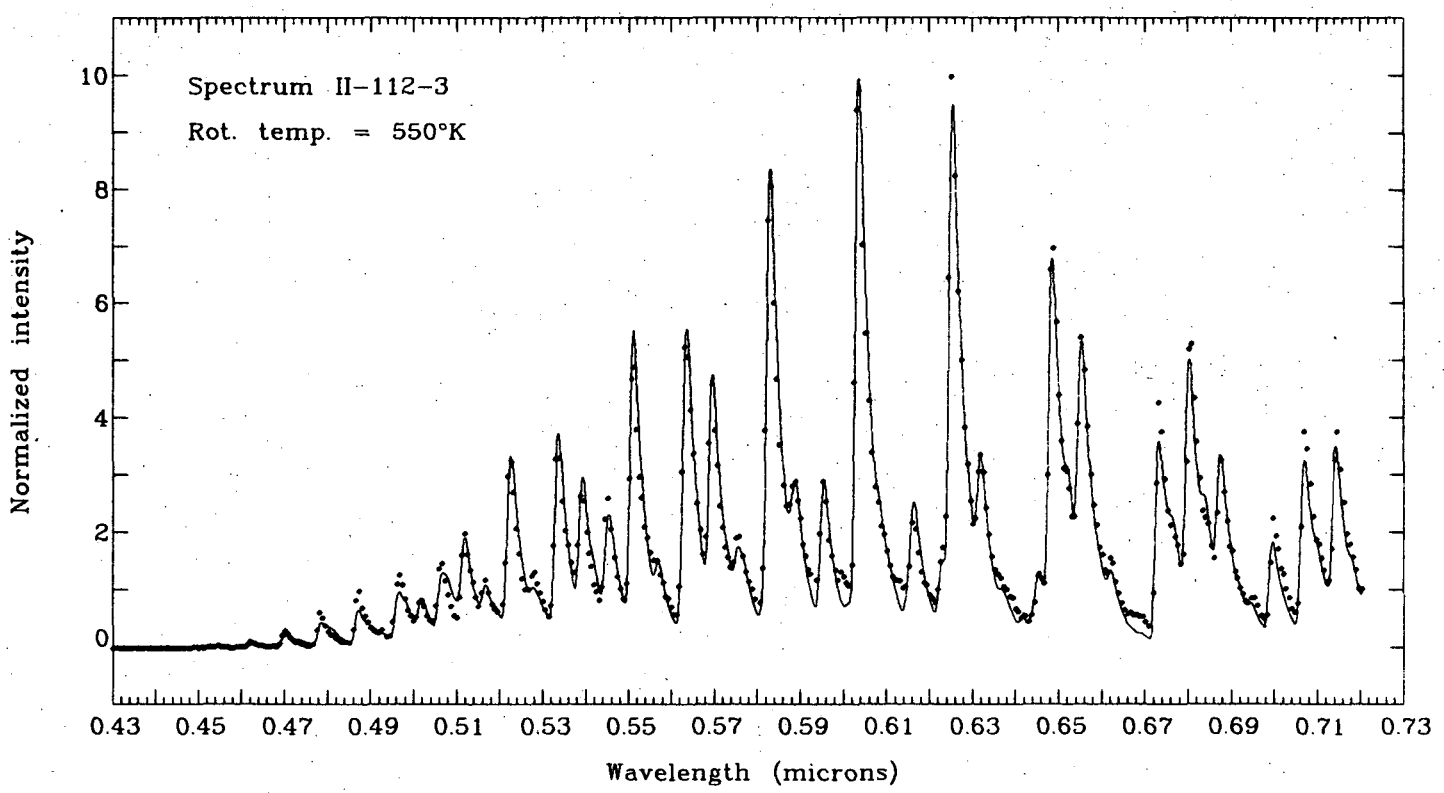
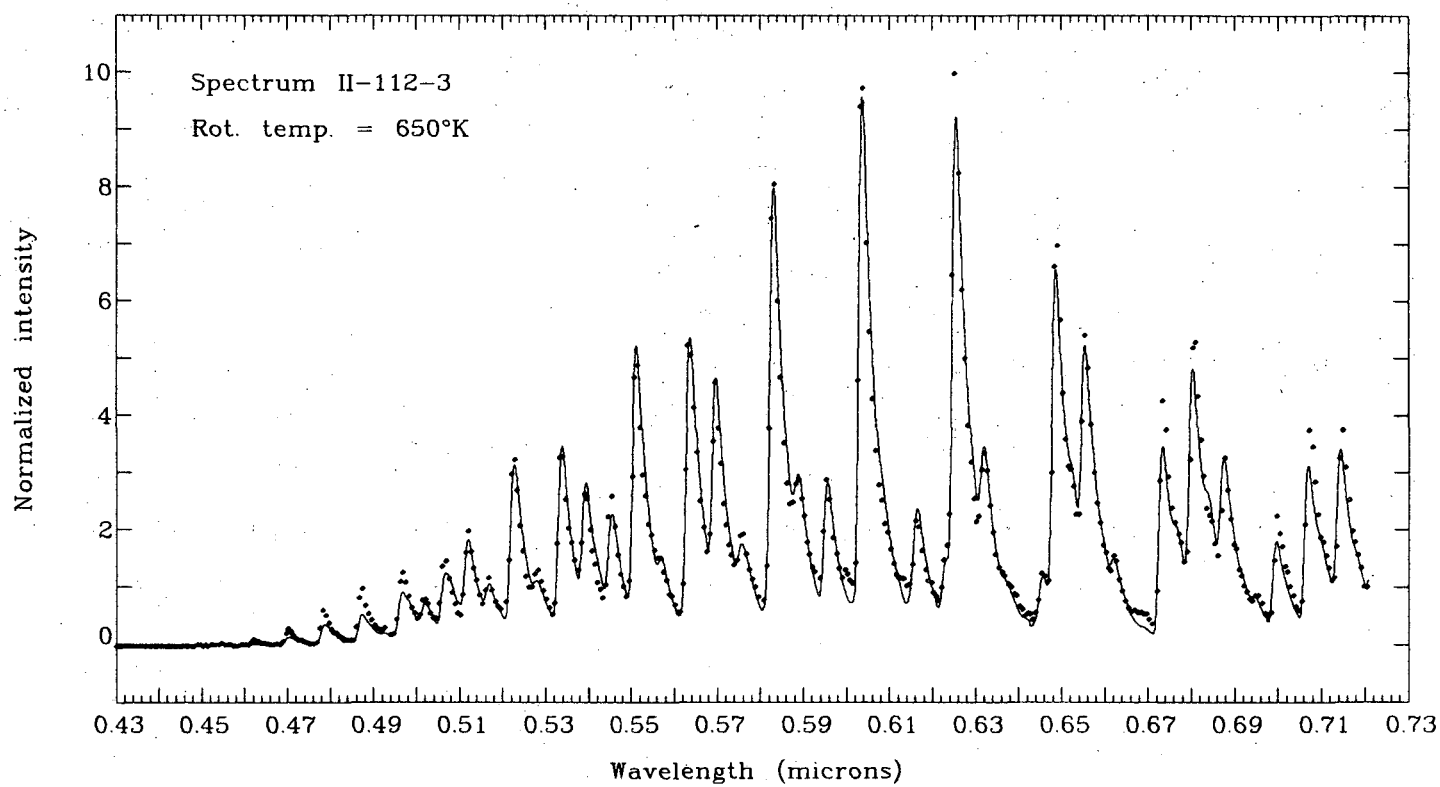
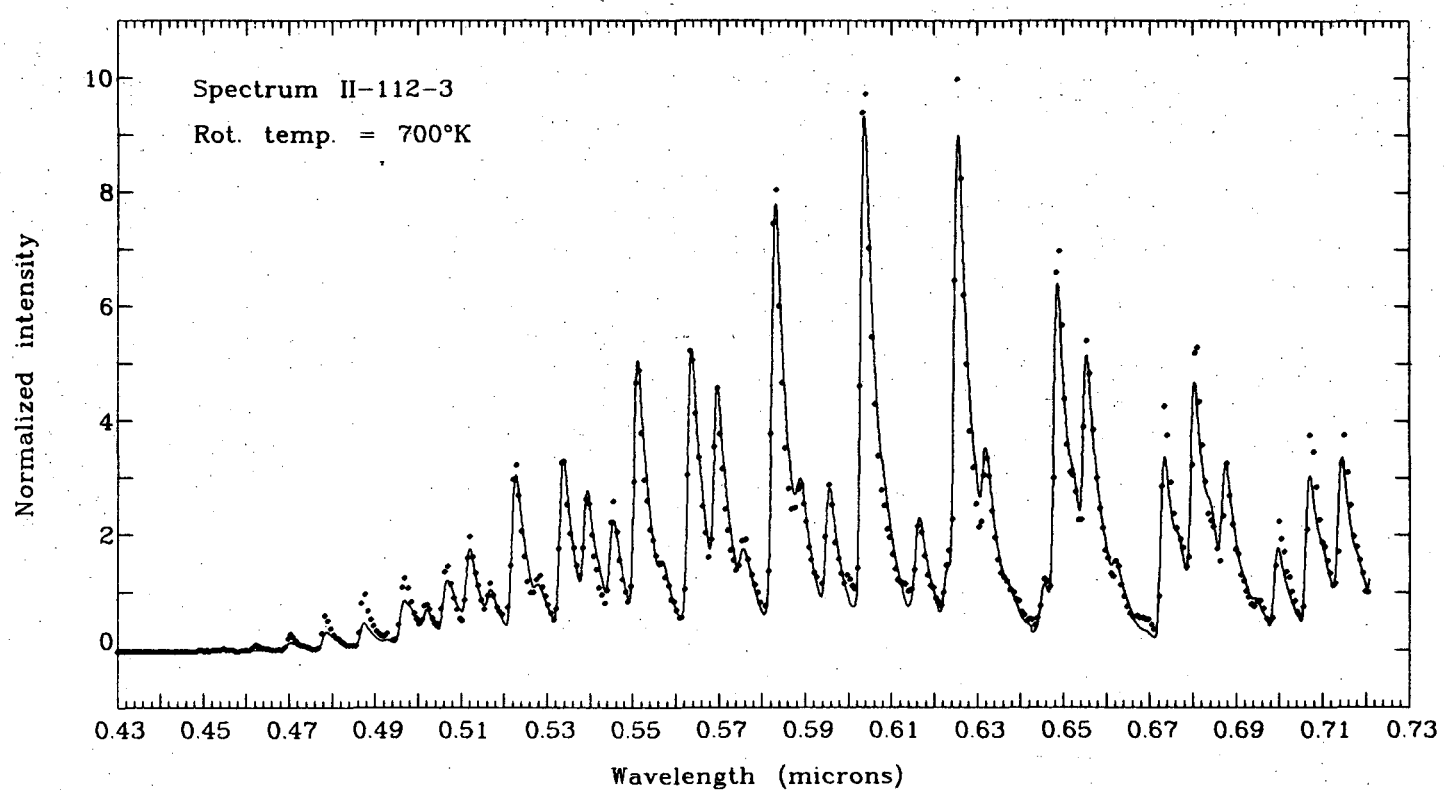

Spectrum II-112-3
Rot. temp. = 550°K
Normalized intensity
0
2
4
6
8
10
0.43
0.45
0.47
0.49
0.51
0.53
0.55
0.57
0.59
0.61
0.63
0.65
0.67
0.69
0.71
0.73
Wavelength (microns)

Fig. 14m



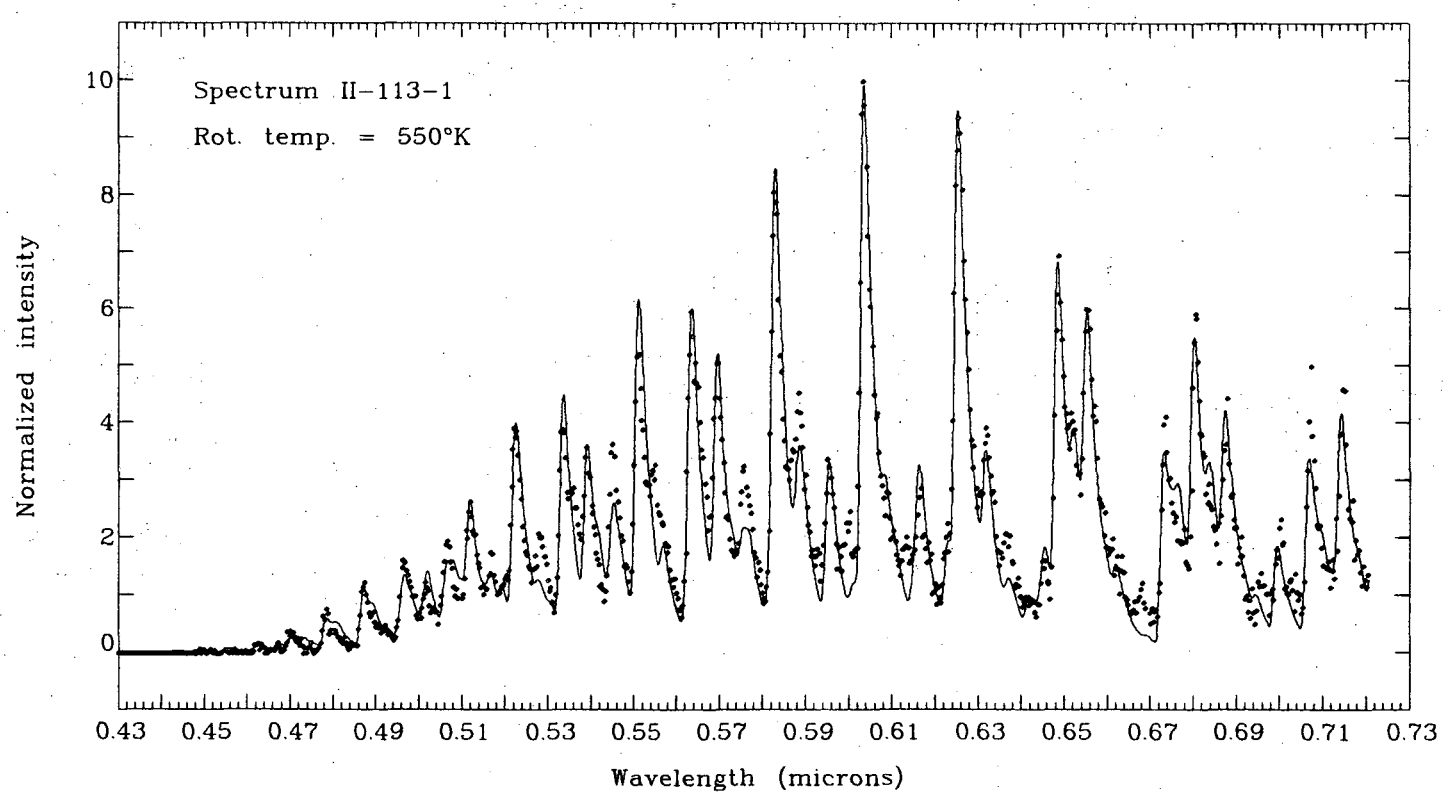
XBL 6812-6397

Fig. 14n



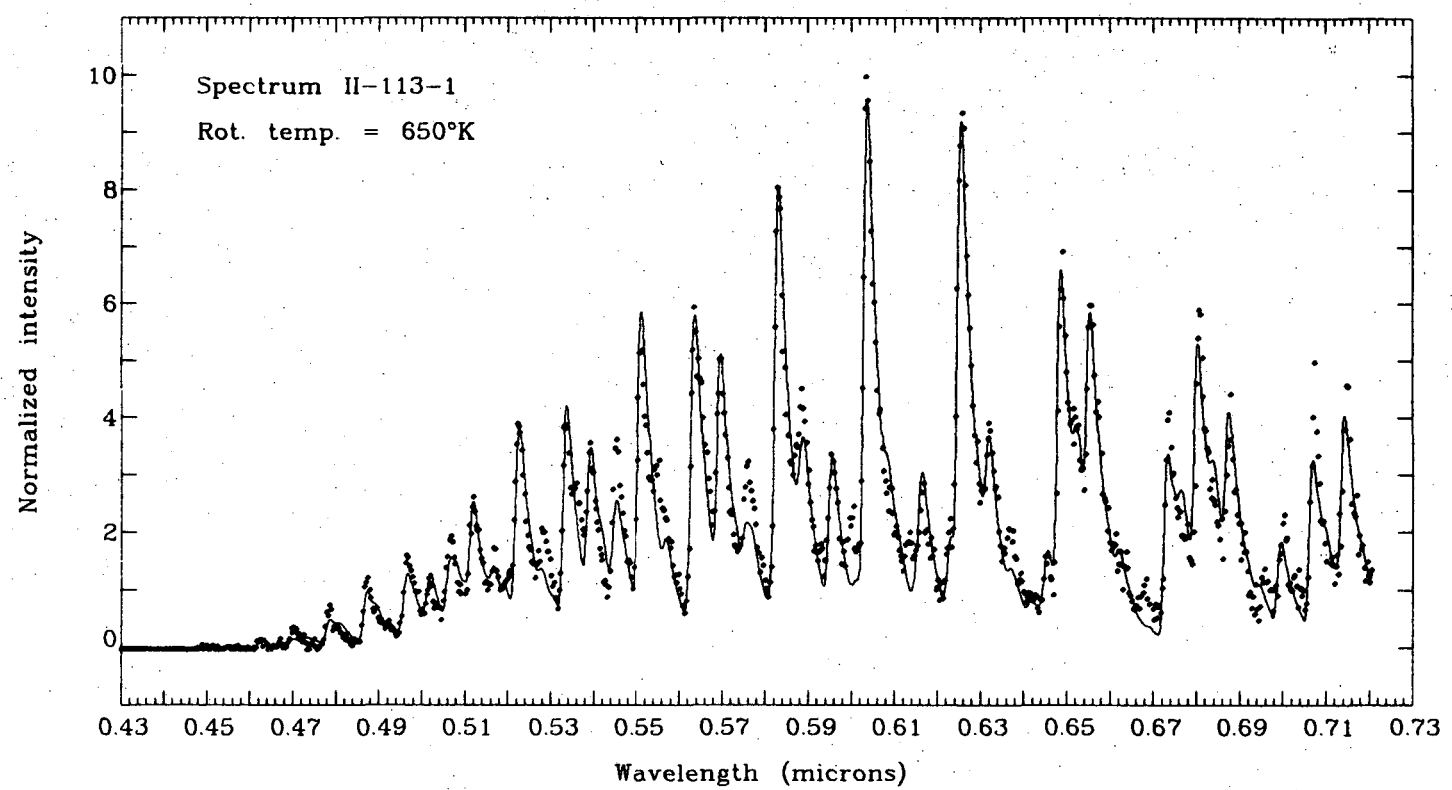
XBL 6812-6396

Fig. 14o



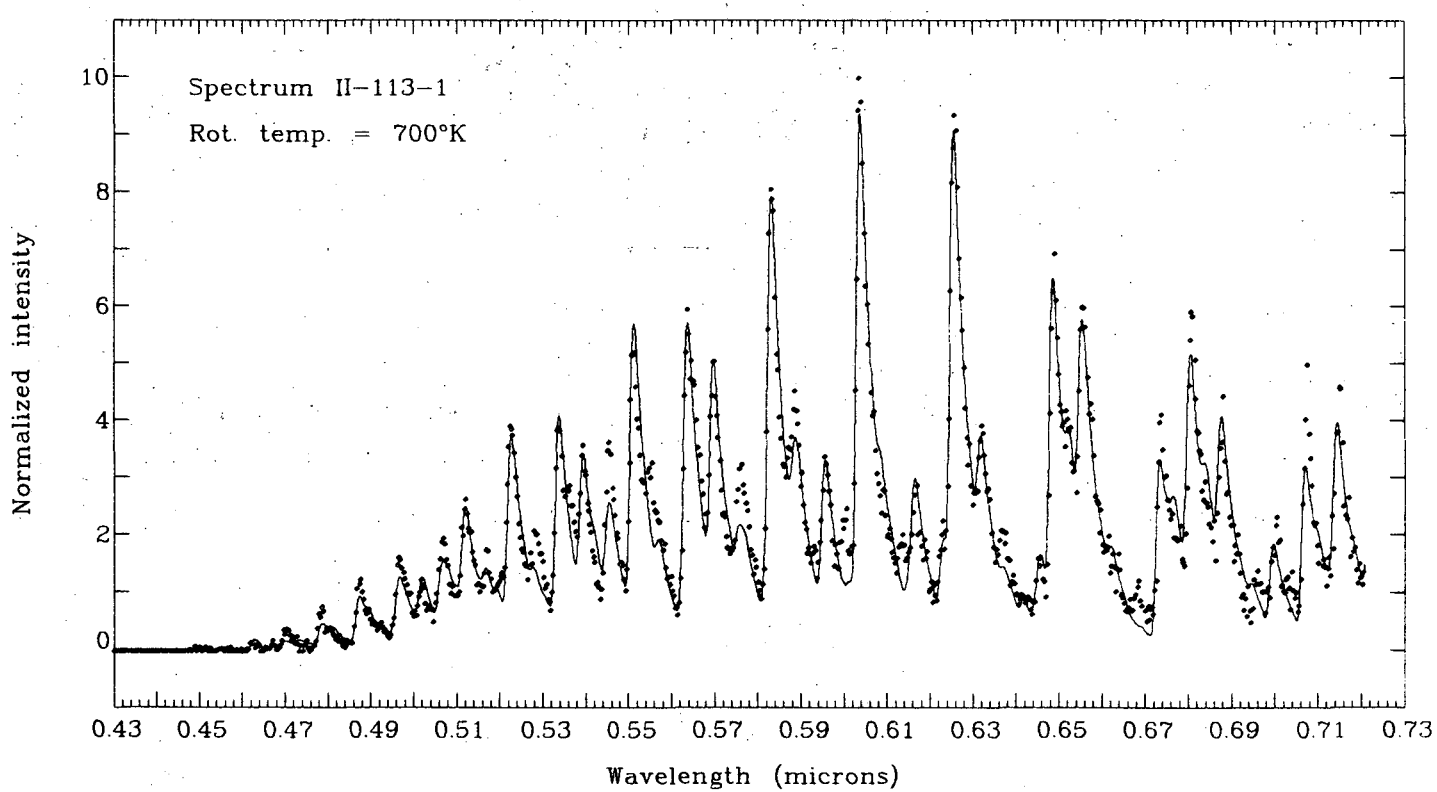
XBL 6812-6395

Fig. 14p



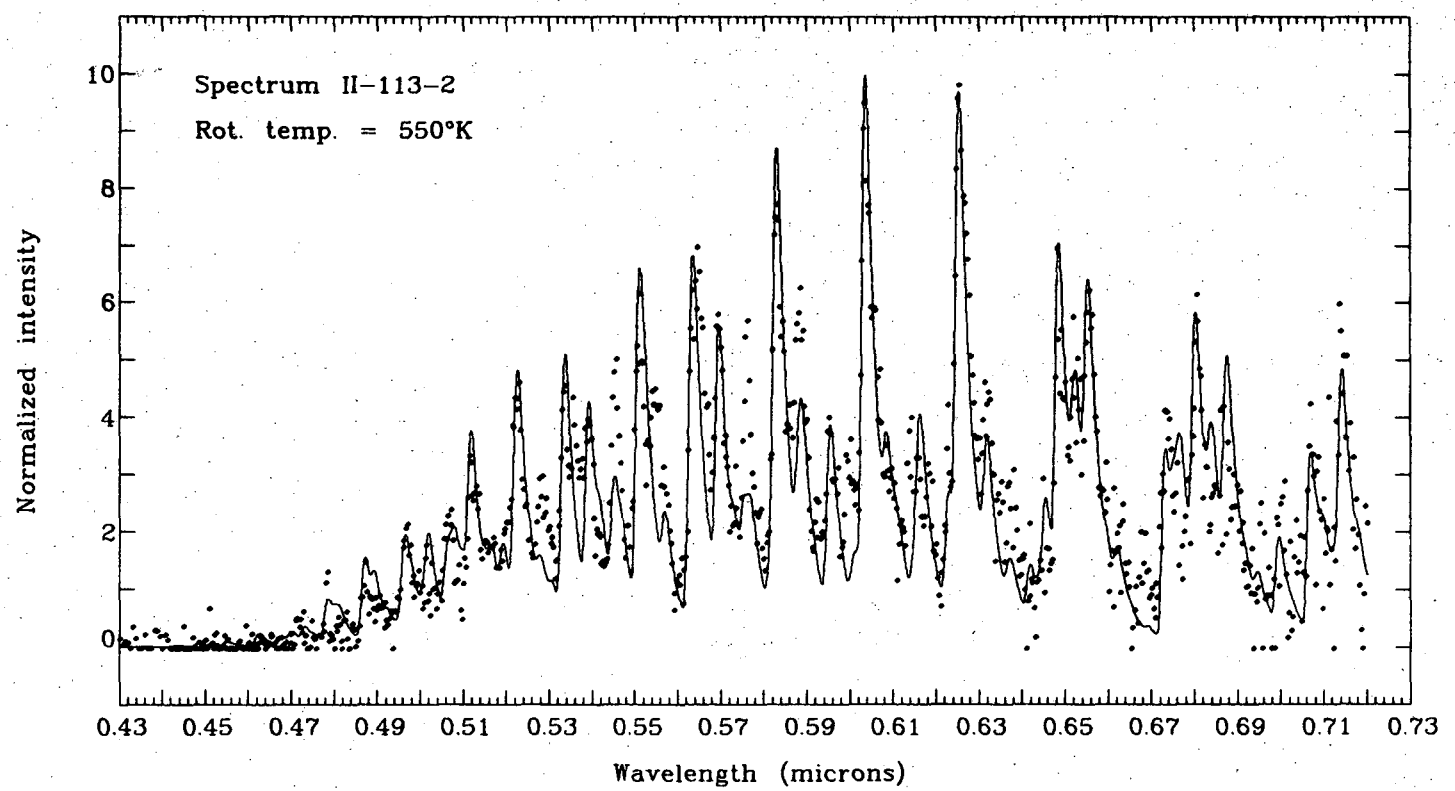
XBL 6812-6394

Fig. 14q



XBL 6812-6393

Fig. 14r



XBL 6812-6392

Fig. 14s

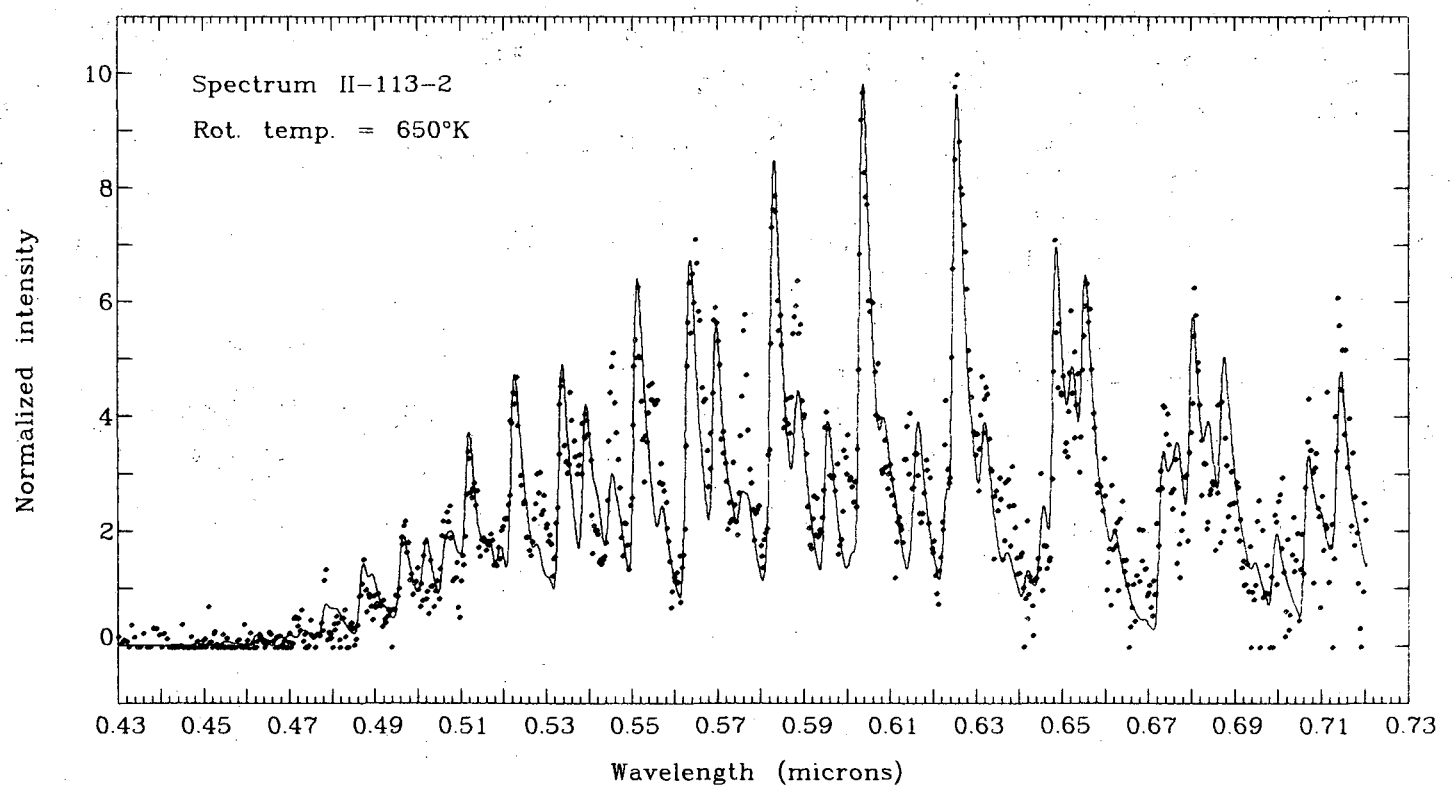

Spectrum II-113-2
Rot. temp. = 650°K
Normalized intensity
10
8
6
4
2
0
0.43
0.45
0.47
0.49
0.51
0.53
0.55
0.57
0.59
0.61
0.63
0.65
0.67
0.69
0.71
0.73
Wavelength (microns)

Fig. 14t

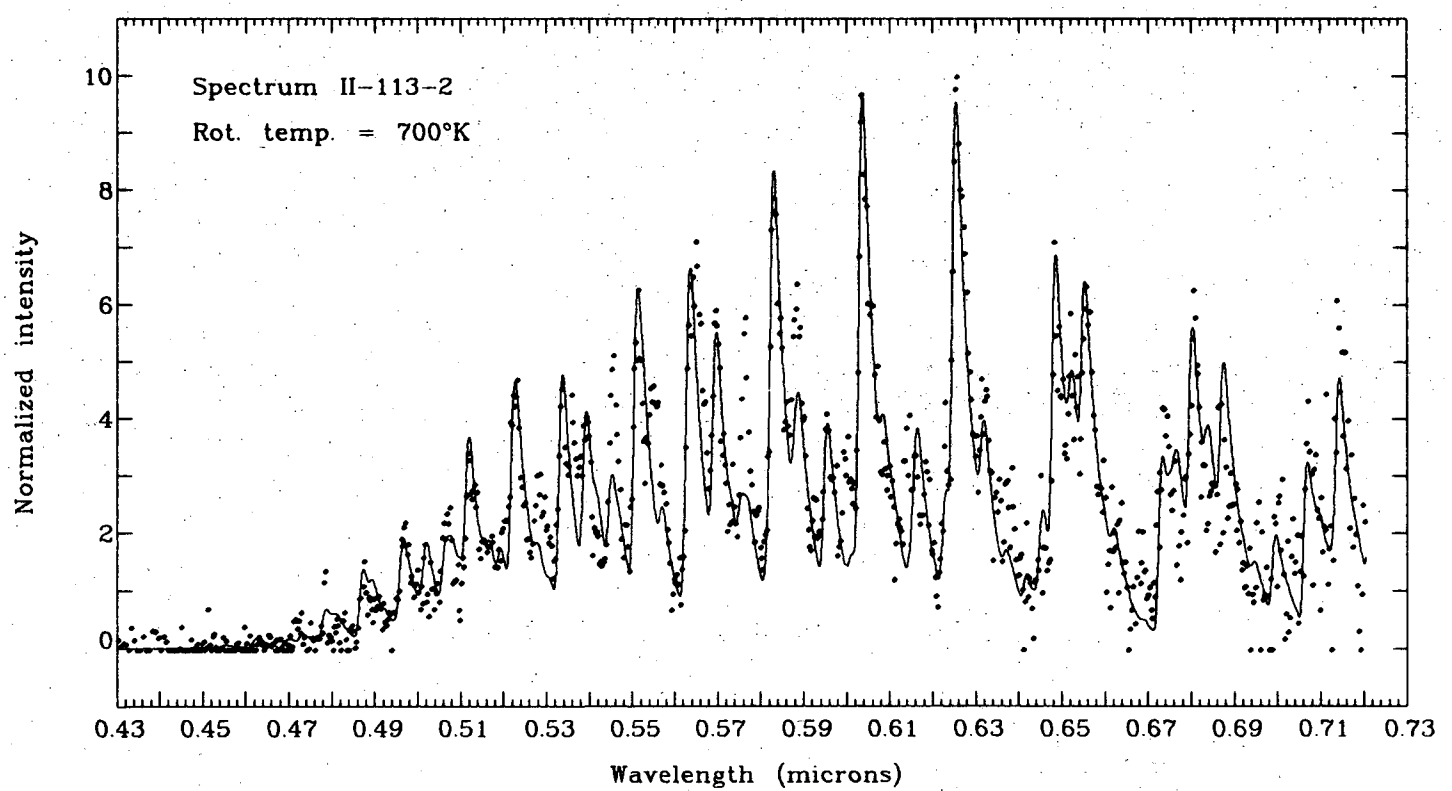
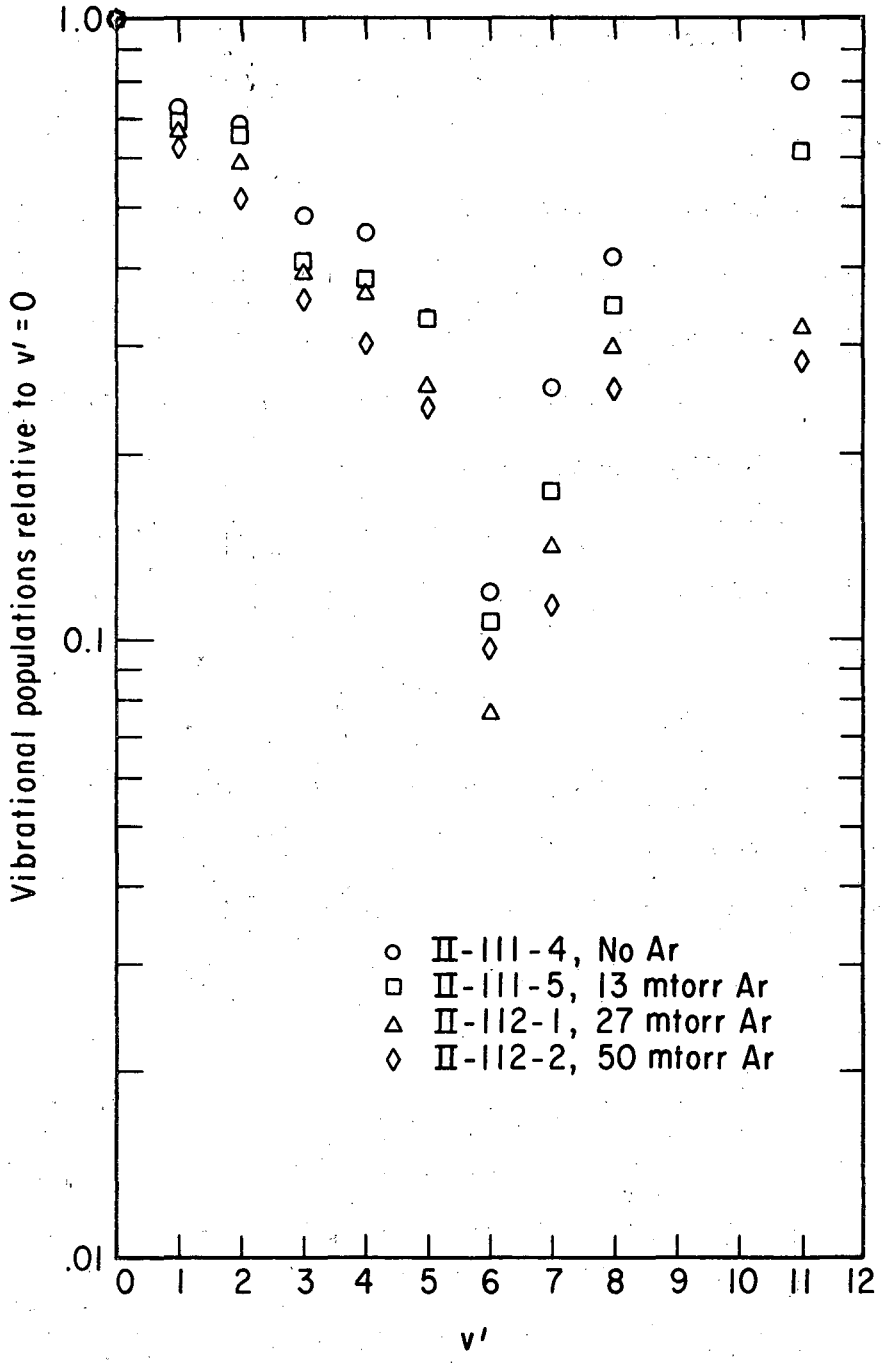

Spectrum II-113-2
Rot. temp. = 700°K
Normalized intensity
0
2
4
6
8
10
0.43
0.45
0.47
0.49
0.51
0.53
0.55
0.57
0.59
0.61
0.63
0.65
0.67
0.69
0.71
0.73
Wavelength (microns)

Fig. 14u



XBL 6812-6454

Fig. 15

V. DISCUSSION

A. Reliability of the Transition Moment and Vibrational Population Determinations

1. General Remarks

The methods derived in Section III-B-4 can be expected to yield excellent results when 1) transitions occur from and give rise to vibrational levels which are low or intermediate in quantum number, and 2) the S/N ratio is great enough so that uncertainties in the measured intensities of even small peaks are on the order of not more than ten percent. The first condition is a restatement of the necessity of knowing the Franck-Condon factors to a high degree of precision; the second condition assures that noise peaks are not mistaken in the calculations for actual peaks.

In the present investigations, these criteria are met with only partial success. Of great chemical interest is the behavior of the distribution functions over quantum levels of products and intermediates in chemical reactions. The closer in time the observation takes place to the formation of the excited species, the less uncertainty there is in the history of that species, or the simplerthe analysis of the kinetics becomes. In the case of atom recombination, then, one would like to make observations of populations of the highly excited vibrational levels. It is precisely here that we have the least confidence (Sec. III-B-3) in the RKR (or other) wave functions and resultant Franck-Condon overlaps. For the $^3\Pi_{0^+}$ state of IF, the dissociation limit occurs at v' = 16. Significant deviation between the Morse and RKR potentials (Fig. 12) begins to occur beyond v' = 10, 11; thus, applying the criterion of (56) we should expect Franck-Condon factors for these and higher levels to

be somewhat inaccurate. Furthermore, the electronic state responsible for the onset of predissociation at v' = 11, J' = 45 (Sec. III-A) can be assumed to give rise to further perturbations of the wavefunctions for v' = 11 and possibly for v' = 10. Thus accurate analysis of portions of the spectrum below 4450A becomes extremely difficult.

Difficulty in meeting the second condition results from the nature of the quantity we are trying to determine, viz. the transition moment. From Fig. 13 it is seen that the value of $R_e(r)$ ranges over two orders of magnitude, falling off rather rapidly at $\bar{r}$-centroids less than 1.95A. The strongest transitions from v' = 4 and higher occur at these values of the $\bar{r}$-centroid and consequently have only low to moderate intensity. Increasing their intensity relative to peaks emanating from v' = 0, 1, 2, 3 can be accomplished by lowering the pressure in the cell by reducing flow rates of I_2 and F_2 (see following section). However, at the same time, the overall intensity is diminished (see Spectra II-112-3, II-113-1 and II-113-2). The low intensities in this region occur in spite of the fact that the wavelength sensitivity is highest in this region (Fig. 6) and the ν^3 factor in the intensity expression [Eq. (37)] is favorable. Thus, the very fact that $R_e(r)$ is small in this region gives rise to only a moderate signal-to-noise ratio and ultimately to lower precision in its determination than at values of $\bar{r}$-centroid greater than 1.95A.

Two possible methods of obtaining a more accurate evaluation of the transition moment in this region suggest themselves. First, use of a larger cell having a longer optical pathlength would increase the light intensity while retaining the possibility of maintaining similar chemical conditions. Secondly, repeated multiple scans of the spectrum, time averaged, could greatly increase the S/N ratio while using the present

apparatus.

An added difficulty in the determination of $R_e(r)$ at small $\bar{r}$ is that no prominent peaks having $v' = 4$ or higher occur in the region of the spectrum where the transition moment takes on higher values. This results from either the fact that Franck-Condon factors for these peaks are generally quite small or that the peaks coincide with bands of large intensity having $v' = 0,1,2,3$. Again the importance of having accurate intensity data must be stressed, for the separation of the contributions to the intensity of the transition moment and the population for the (4,0), (5,0) .....(9,0) bands will depend on the precision to which the spectra at higher wavelengths can be decomposed. In this regard every effort was made to calibrate all aspects of instrumentation which would effect either the position of a band or its intensity (Sec. II).

2. Effect of Pressure on the Observed Spectra

The radiative lifetime for the $^3\Pi_{0+}$ state of IF may be assumed to take on an intermediate value between that of I_2 (7×10^{-7} sec)(70) and that of F_2 which has not been measured but can be considered as very large due to the forbiddenness of the transition for light molecules. Measurement of vibrational relaxation times for homonuclear halogens, made by Millikan and White (71), indicate typical values of $p\tau_v$ of about 10^{-7} at 500-1000°K where p is the pressure in atmospheres and τ_v is the vibrational relaxation time. At pressures of 100 m torr, this relation yields a relaxation time of about 8×10^{-4} seconds. A radiative lifetime much shorter than this would drain the population of the excited molecular state before the effects of collisional deactivation could take place. A very long radiative lifetime would make the transition too weak to observe. Study of the molecule IF is of particular interest because its radiative

lifetime falls in an intermediate range such that the effects of pressure on the spectra are readily seen; i.e. the rates of radiative decay and vibrational energy transfer are competitive.

Application of this effect was made in an effort to help evaluate the transition moment by increasing the prominence of some of the shoulders observed on the sides of larger peaks. The results were encouraging on the one hand, but disconcerting on the other. Variation of the relative vibrational populations was readily accomplished and will be discussed in further detail in a later section. As seen from Fig. 13 the transition moments obtained from spectra taken at total pressures of 55 m torr (II-112-3), 26 m torr (II-113-1) and 18 m torr (II-113-2) are in good agreement.

The disconcerting aspect of the pressure effect is that although a comparison of the observed spectra and the calculated spectra at higher pressures yields good agreement, at the lowest pressures noticeable discrepancies at certain wavelength regions are quite evident. A list of these discrepancies is given in Table X. Many of these differences coincide with positions of known bands having low v' [e.g. (1,4), (2,4), (0,1)]. However, the effect of pressure on the intensities at these wavelengths is much more pronounced than can be attributed to change in population of these low-lying vibrational levels as inferred from intensity changes in other regions of the spectrum. The conclusion that must be drawn is that these peaks, although appearing to have only one predominant contributing band, are the composite of at least two and perhaps several strong bands emanating from states having widely different upper quantum levels. The fact that agreement is good for the 55 m torr spectrum would indicate that the Franck-Condon factors are not in significant error.

Table X. Wavelengths of unexplained band intensities

5070 A	5760
5200	5880-90
5170	5930
5280-90	5990-6000
5360	6130-40
5450-60	6370-80
5550-60	6520-30
5650-60	6680
	6960

See Spectrum II-113-2

Indeed, there is no reason to believe that the RKR wave functions for the low quantum levels involved are in any way inaccurate.

Examination of Table VIII shows that in many of these regions, one should expect contributions from bands having moderate values of v' (i.e. 5-8). Yet, the calculated Franck-Condon factors for these bands, e.g., the (5,6) at 5751A or the (7,8) at 5885A and the (3,3) at 5446A (where large discrepancies occur at low pressure) do not have sufficiently large magnitudes to account for the observed intensity when compared to that of their respective transitions to v" = 0. The sharp decrease in the transition moment toward small values of the $\bar{r}$-centroid is in part caused by an attempt to increase contributions of peaks from moderate v' 's in the region of the discrepancies. The argument may be restated as follows: given the low intensity of say the (5,0) band which has a relatively high Franck-Condon overlap and favorable ν^3 term, in order to account for the large intensity at (5,6) which has a Franck-Condon factor down by a factor of 5 and a less favorable ν^3 term, the transition moment must be greatly different at the two wavelengths (or, more precisely, at their respective values of $\bar{r}$-centroid). The value of R_e at $\bar{r}_{5,6}$, however, is fixed quite well by intensity variations in neighboring bands having v' = 0. Thus, R_e $(\bar{r}_{5,0})$ is calculated to be quite small.

Of direct bearing in these considerations is the fact that some of the unexplained observed bands, notably those at 6000 and 6130A do not correspond in wavelength to any of the band heads listed in Table VIII. Even when the list is extended to include bands from v' = 13-16 (by taking ΔG (v'+1/2) values from Fig. 9), no band heads are found at these wavelengths. These observations strongly suggest the possibility of transitions from another excited electronic state of IF since emission

from the recombination of iodine atoms would be expected to occur at significantly higher wavelengths,* while emission from the recombination of fluorine atoms has not been reported. Thus, it would seem possible that these unexplained bands are due to the IF ($^3\Pi_1 \rightarrow {}^1\Sigma^+$) system analogous to that observed for ICl and IBr (see section III-A). At higher pressures, the only levels abundantly populated would give rise to transitions too far to the red to be observed in the present studies. At lower pressures, however, higher v' 's would have significant populations and these could give rise to bands in the region being studied.

This hypothesis could be tested in the future by looking in the red and near infrared with a red sensitive photomultiplier tube for the remainder of the $^3\Pi_1 \rightarrow {}^1\Sigma^+$ system.

In brief, the results of calculations of the transition moment function based on three independently measured spectra are in general agreement. The possibility of systematic errors caused by the overlapping of transitions from two excited electronic states to the ground state is suggested in the case of the low pressure spectra. Nevertheless, the closeness of agreement of the results indicates that this error is not of great magnitude. Yet, it is to be remembered that any error in the calculation of the transition moment will have direct effects on subsequent calculations of vibrational populations and temperatures.

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* Because of the rapid deactivation of ($^2P_{1/2}$) iodine atoms by I_2(72), the concentration of I^* would be expected to be very small if, indeed, any $I(^2P_{1/2})$ atoms are formed to begin with. Thus chemiluminescence from iodine atom recombination would have to occur through ($^3\Pi_1 \rightarrow {}^1\Sigma^+$) transitions. Nearly all reported bands in this system (observed in absorption experimentally) lie well to the red of the spectral region being studied in the present investigation [see, e.g., ref. (73)].

3. Explanation of the Behavior of the Transition Moment

In the summary of the systems for which determinations of the transition moment have been made given in (12), one finds both systems for which the derivative of R_e with respect to $\bar{r}$ is positive and those for which it is negative. For the $^3\Pi_{0^+} \rightarrow {}^1\Sigma^+$ system of the halogens, one would expect, in all cases, that the transition moment decrease for large internuclear separations since in the separated atom limit the transition is forbidden ($^2P_{1/2} \not\rightarrow {}^2P_{3/2}$). The range of $\bar{r}$ for which observations have been made in the present studies has not extended to large enough values of $\bar{r}$ for this consideration to have come into play. A second consideration on the projected behavior of the transition moment is that all of the halogen (and interhalogen) diatomic molecules are somewhere between Hund's coupling case a and case c (25). The character of the $^3\Pi_{0^+}$ state is determined by the extent to which the electric field along the internuclear axis breaks down the spin-orbit coupling of the electrons. When the field is weak (large internuclear separations) the (L,S) coupling is strong (Hund's case c is applicable) and the transition is allowed. Conversely, for strong fields (short internuclear distances) the field is strong, and the individual atomic (L,S) coupling is broken down such that the projections of the spin angular momentum Σ and the orbital angular momentum Λ along the internuclear axis become good quantum numbers. In this limit, transitions to the ground $^1\Sigma^+$ state are spin forbidden. I_2 and F_2 are respective examples of the two cases.

As indicated above, IF is intermediate in its properties between I_2 and F_2 with regard to its radiative lifetime. It is to be expected then that small changes in internuclear distance may have profound changes on the coupling characteristics of the emitting state. The

continuously increasing case a character concomitant with smaller values of the $\bar{r}$-centroid gives rise to the sharp fall off in the $R_e(r)$. At first it might seem that the above hypothesis should predict an increase in the transition moment for higher vibrational levels since the average internuclear distance increases with vibrational quantum number. However, an examination of the potential curves (Fig. 8) shows that the strongest transitions to ($^1\Sigma^+$, v"=0) should come from the left side of the $^3\Pi_{0^+}$ potential curve, i.e. the Franck-Condon vertical transition principle holds. This is further quantitatively evidenced by the fact that the $\bar{r}$-centroids decrease for a given v' progression.

The present determination of the transition moment function seems to follow the predictions of Zare, Larsson and Berg (74) who have proposed that only small charges (a factor of 2) in the transition moment with internuclear distance are to be expected for strong transitions ($\tau \sim 10^{-6}$ to 10^{-9} sec) but much larger charges are to be expected for weak or partially forbidden transitions ($\tau > 10^{-6}$ sec). This hypothesis has been further confirmed by observations of Joshi, Parthasarathi, and Sastri (75).

4. Validity of the $\bar{r}$-centroid Approach

As pointed out in Sec. III-B-3 and by James (76), present day computer technology is such that the $\bar{r}$-centroid approximation need no longer be relied upon for the evaluation of transition matrix elements. The variational method of obtaining the transition moment discussed in Sec. III-B-4 can readily be adapted such that trial $R_e(r)$ is integrated over the vibrational coordinate and the resulting matrix elements $\langle v'|R_e(r)|v''\rangle$ used in the calculation of the best set of vibrational populations. The form of $R_e(r)$ would then be adjusted until the best

fit to the spectrum is obtained. However, since many adjustments of the transition moment function are necessary before a final solution is converged upon, the repeated calculation of the transition matrix elements could use up so much time as to become prohibitive. Thus, although somewhat "outdated" the $\bar{r}$-centroid approach can nevertheless be a useful and perhaps necessary approximation. Its validity is easily tested by comparing the quantities $R_e(\bar{r}_{v'v''})^2 \langle v'|v''\rangle^2$ with the transition matrix elements obtained with this best $R_e(r)$. Such a comparison is made in Table XI. As can be seen, the two forms are in moderately good agreement, and the $\bar{r}$-centroid approach justified. Such agreement cannot be presupposed in all cases, however, and each molecular system must be examined independently.

A note of caution should be added with regard to the comparison of the two forms of the transition matrix elements. For bands having $\bar{r}$-centroids towards the extremes of the range for which $R_e(\bar{r})$ has been determined, accurate evaluation of the integrals $\langle v'|R_e(r)|v''\rangle$ would necessitate a knowledge of $R_e(r)$ beyond this range. Thus, matrix elements based upon the extrapolation of the determined $R_e(\bar{r})$ are expected to be somewhat in error. The fact that agreement is good for bands having $\bar{r}$-centroids in the middle of the range covered by the calculations strongly suggests that Eq. (33) holds for a sufficiently high value of n. Where discrepancies do exist then, it is expected that the quantities $R_e(\bar{r}_{v'v''}) \langle v'|v''\rangle$ are more accurate than the integrals $\langle v'|R_e(r)|v''\rangle$.

Table XI. Test of r-centroid approximation

v" \ v'	0	1	2	3	4	5	6
0	4.861-4	1.861-3	3.639-3	4.842-3	4.843-3	3.646-3	2.134-3
	4.557-4	1.734-3	3.373-3	4.511-3	4.586-3	3.678-3	2.367-3
1	3.605-3	9-363-3	1.169-2	9.076-3	4.408-3	1.075-3	1.780-5
	3.466-3	9.090-3	1.149-2	9.073-3	4.600-3	1.256-3	5.051-5
2	1.220-2	1.861-2	1.070-2	1.774-3	2.571-4	2.715-3	3.809-3
	1.192-2	1.848-2	1.105-2	2.106-3	1.254-4	2.228-3	3.351-3
3	2.512-2	1.699-2	9.980-4	2.961-3	7.631-3	4.971-3	8.600-4
	2.496-2	1.720-2	1.173-3	2.660-3	7.502-3	5.294-3	1.154-3
4.	3.584-2	4.884-3	4.512-3	1.164-2	3.737-3	1.298-4	3.549-3
	3.606-2	5.121-3	4.271-3	1.163-2	4.110-3	4.443-5	3.088-3
5	3.819-2	5.624-4	1.625-2	4.365-3	1.530-3	7.838-3	4.483-3
	3.846-2	5.026-4	1.630-2	4.579-3	1.380-3	7.791-3	4.889-3
6	3.138-2	1.327-2	1.222-2	1.409-3	1.131-2	3.413-3	6.900-4
	3.158-2	1.314-2	1.258-2	1.302-3	1.142-2	3.698-3	5.490-4
7	2.024-2	3.043-2	6.848-4	1.437-2	4.865-3	2.228-3	8.688-3
	2.050-2	3.034-2	8.883-4	1.427-2	5.117-3	2.111-3	8.876-3
8	1.047-2	3.581-2	6.425-3	1.423-2	1.457-3	1.182-2	1.730-3
	1.066-2	3.592-2	6.223-3	1.441-2	1.323-3	1.186-2	1.895-3
9	4.406-3	2.832-2	2.567-2	1.363-3	1.518-2	3.342-3	4.703-3
	4.447-3	2.842-2	2.565-2	1.458-3	1.500-2	3.500-3	4.546-3
10	1.522-3	1.644-2	3.654-2	5.721-3	1.353-2	3.279-3	1.182-2
	1.490-3	1.652-2	3.662-2	5.620-3	1.377-2	3.113-3	1.183-2
11	4.287-4	7.361-3	3.117-2	2.624-2	6.128-4	1.715-2	1.007-3
	4.195-4	7.355-3	3.126-2	2.616-2	6.778-4	1.726-2	1.098-3
12	9.672-5	2.528-3	1.860-2	3.774-2	8.439-3	1.066-2	7.371-3
	1.077-4	2.578-3	1.854-2	3.757-2	8.255-3	1.099-2	7.286-3
13.	1.805-5	6.849-4	7.902-3	3.129-2	3.040-2	8.966-6	1.844-2
	2.363-5	7.383-4	8.131-3	3.111-2	2.979-2	2.113-6	1.876-2
14	2.796-6	1.507-4	2.581-3	1.693-2	3.824-2	1.448-2	6.086-3
	2.878-6	1.716-4	2.745-3	1.742-2	3.790-2	1.369-2	6.414-3
15	3.709-7	2.673-5	6.674-4	6.756-3	2.763-2	3.486-2	1.798-2
	1.051-7	2.770-5	7.208-4	7.051-3	2.814-2	3.148-2	1.550-3
16	3.843-8	3.889-6	1.373-4	2.071-3	1.375-2	3.594-2	2.197-2
	3.598-8	2.566-6	1.351-4	2.132-3	1.408-2	3.626-2	2.131-2
17	2.440-9	4.794-7	2.291-5	5.001-4	5.065-3	2.296-2	3.715-2
	4.151-8	2.880-7	1.619-5	4.745-4	5.099-3	2.336-2	3.734-2

Table XI - continued

v'' \ v'	7	8	9	10	11	12
0	9.969-4	3.411-4	8.443-5	1.473-5	2.549-6	5.356-7
	1.210-3	4.684-4	1.147-4	7.649-6	4.561-6	2.047-5
1	1.856-4	4.200-4	3.791-4	1.992-4	7.173-5	1.903-5
	1.516-4	4.861-4	5.681-4	4.158-4	2.165-4	7.982-5
2	2.656-3	1.039-3	1.765-4	1.521-7	3.323-5	4.723-5
	2.430-3	9.844-4	1.535-4	5.409-6	1.192-4	1.975-4
3	1.213-4	1.297-3	1.851-3	1.333-3	6.028-4	1.843-4
	2.638-5	9.210-4	1.494-3	1.148-3	5.265-4	1.313-4
4	4.625-3	2.230-3	2.479-4	1.159-4	6.479-4	8.217-4
	4.415-3	2.360-3	3.746-4	4.108-5	4.669-4	6.848-4
5	1.429-4	1.260-3	3.165-3	2.597-3	1.018-3	1.307-4
	3.074-4	8.660-4	2.651-3	2.361-3	1.020-3	1.670-4
6	5.438-3	4.424-3	7.328-4	1.960-4	1.497-3	1.969-3
	5.274-3	4.711-3	1.032-3	5.783-5	1.055-3	1.560-3
7	2.745-3	2.757-4	3.666-3	3.974-3	1.489-3	7.253-5
	3.102-3	1.588-4	3.369-3	4.029-3	1.752-3	1.822-4
8	2.635-3	6.892-3	2.476-3	2.853-5	1.943-3	2.969-3
	2.519-3	7.106-3	2.873-3	2.870-7	1.604-3	2.766-3
9	8.562-3	5.916-4	2.465-3	5.439-3	2.613-3	1.468-4
	8.754-3	7.057-4	2.342-3	5.609-3	2.994-3	2.919-4
10	1.388-4	6.083-3	6.074-3	3.148-4	1.550-3	3.780-3
	1.757-4	6.014-3	6.345-3	4.155-4	1.416-3	3.799-3
11	8.701-3	6.277-3	2.054-4	5.671-3	4.678-3	6.266-4
	8.501-3	6.361-3	1.738-4	5.685-3	4.960-3	7.798-4
12	9.463-3	7.635-4	9.145-3	3.054-3	3.881-4	3.894-3
	9.659-3	6.998-4	9.051-3	3.128-3	3.563-4	3.915-3
13	4.459-5	1.222-2	2.389-3	2.900-3	7.202-3	2.326-3
	2.577-5	1.234-2	2.506-3	2.811-3	7.197-3	2.383-2
14	1.325-2	4.958-3	4.739-3	8.979-3	4.173-4	2.559-3
	1.313-2	5.306-3	4.603-3	9.170-3	4.686-4	2.510-3
15	1.680-2	2.676-3	1.264-2	4.651-5	6.771-3	5.977-3
	1.687-2	2.436-3	1.292-2	8.778-5	6.678-3	6.106-3
16	1.640-3	1.854-2	8.630-4	9.926-3	5.898-3	1.947-4
	1.788-3	1.798-2	1.012-3	9.759-3	6.214-3	1.391-4
17	7.060-3	1.161-2	8.916-3	9.208-3	1.171-3	8.915-3
	6.698-3	1.169-2	8.326-3	9.376-3	1.010-3	8.904-3

upper value: $R_e^2(\bar{r})\langle v'|v''\rangle^2$; lower value: $\langle v'|R_e|v''\rangle^2$

B. Rotational Temperatures

1. Determination and Influence on Calculation of Vibrational Populations and Temperatures

Examination of Fig. 11 shows that large changes in rotational temperature have pronounced effects on the band width of the integrated rotation-vibration envelope or band shape. For a change from 400 to 800°K the full width at half maximum integrated intensity is increased by 50%. The position of the intensity maximum is shifted only slightly and consequently the low wavelength sides of the three bands are nearly superimposed. Despite the fact that the widening appears exclusively on one side of the band, visual examination of the spectra does not offer a very satisfactory method of evaluating the best rotational temperature as can be seen from a comparison of fits of Spectrum II-112-2 at rotational temperatures 550, 650 and 700°K. The presence of overlapping bands and scatter in the data points tend to obscure the effects of small changes in the rotational temperature. Attempts to fit spectra at temperatures ranging from 300 to 900°K have been attempted; visual inspection of fits at the extremes of this range point out their inaccuracies-band widths much too narrow in the former case and washed out resolution of neighboring peaks in the latter. However, in the above mentioned spectra, only in the case of the (0,3) band at 5826A and its neighboring (1,4) band at 5888A can some visual influence of the rotational spectra perhaps be observed. For this reason, more reliance has been placed on the value of the weighted sum of the squares of deviations between the computed and observed spectra - the "goodness-of-fit" parameter or χ^2 value.

The results of calculations of vibrational populations and

temperatures for the series of 4 runs II-111-4, II-111-5, II-112-1, II-112-2 and for the 3 spectra from which $R_e(r)$ calculations have been made show χ^2 values varying by about 20% at the best and worst fits. The vibrational populations (and temperatures) are only slightly affected by the different rotational temperatures, however. In no case is a determination of a vibrational population including the range covered by its standard deviation, found not to overlap the range of a determination based on a different rotational temperature. Of course, the better the overall fit, the smaller the standard deviation associated with each vibrational population [Eq. (56)].

The best fit does not occur for the same value of the rotational temperature in all cases. For low pressure spectra with no or small amounts of M gas, (II-111-4, II-111-5) the lowest standard deviations occur for 700°K rotational temperature fits. For slightly higher partial pressures of argon (27 mtorr), other conditions being kept the same, (II-112-1), fits for rotational temperatures of 650 and 700°K give nearly identical values of χ^2. For still higher pressures of argon (50 m torr), the best rotational temperature is 550°K (II-112-2). Similar trends are noted for the other three above-mentioned spectra. In these instances, no M gas was added, but flow rates of I_2 and F_2 were adjusted so as to change the total pressure in the cell. For II-113-2 (18 mtorr), the best fit occurs for a rotational temperature of 700°K; for II-113-1 (26 mtorr), at 650°K, and for II-112-3 (58 mtorr) at 550°K.

Additional confirmation of this trend was obtained for these three spectra by measurement of the band width at half intensity of the (0,4) peak which is relatively isolated partly because of the anomalously low Franck-Condon factor for the (1,5) band. Measurements of 27.7A, 32.9A

and 38.5A were obtained from the recorder tracings for Spectra II-112-3, II-113-1 and II-113-2, respectively, corresponding to rotational temperatures of 450, 600 and 750°K (see Fig. 11).

These results are somewhat surprising in that rotational relaxation processes are expected to be rather fast. Although Steinfeld and Klemperer (3) observed changes in rotational quantum number of up to 50 (both positive and negative) in their study of vibrational relaxation in I_2, one would expect changes to be considerably less for IF since the rotational spacings are nearly a factor of 8 greater. In their study of the NO^* system, Broida and Carrington (77) found changes in J of up to 5 only. It must be remembered, however, that the radiative lifetime of IF is considerably longer than that of I_2 and therefore many more relaxing collisions are undergone before emission takes place. This should have the effect of bringing the system closer to thermal equilibrium.

Brennen and Carrington (78) have observed non-equilibrium rotational distributions in a study of CH chemiluminescence, the system being characterized by two rotational temperatures, one at the reactor temperature (360°K) and one at ~1200-1400°K. It was assumed that the lower characteristic temperature resulted when initially excited molecules suffered relatively few relaxing collisions, however. Moore (79) has discussed the probability of vibrational to rotational energy transfer (a possible means of obtaining rotational temperatures different from translational temperatures) but concluded that the effect is most significant for hydrogen containing molecules.

The possibility of a contribution to the decrease in rotational temperature with increased pressure (at least in the case of added M gas) from the fact that the equilibrium translational temperature is

also being lowered by the added heat capacity of the higher concentrations of M gas is doubtful. Although such an effect would occur in the case of adiabatic heating of the gases in the cell, a more realistic treatment would have to include conduction by these gases to the cell walls. This type of calculation is carried out in the next section.

2. Comparison of Rotational and Translational Temperatures

An estimate of the maximum temperature in the interior of the cell has been made using the formula of Benson (80), viz.

$$T(0, \infty) - T_0 = \frac{RHr^2}{6\kappa} \qquad (63)$$

where $T(0,\infty)$ is the temperature (°K) in the center of a spherical cell of radius r (cm) after an "infinite" induction period, T_0 is the temperature of the cell wall, R is the rate of reaction per unit volume (moles/cm^3 sec), H is the heat of reaction (cal/mole) and κ, the coefficient of thermal conductivity (cal/cm deg). This model assumes that the cell walls act as an infinite heat sink.

The heat of reaction was assumed to be that of

$$I_2 + F_2 \rightarrow 2IF \qquad \Delta H = -60 \text{ kcal/mole.}$$

Coefficients of thermal conductivity were calculated for I_2, F_2 and Ar according to the relation (81),

$$\kappa = 1.989\times10^{-4} \frac{(T/M)^{1/2}}{\sigma^2 \Omega^{(2,2)*}(T^*)} \left(\frac{4}{15} \frac{C_v}{R} + \frac{3}{5}\right) \qquad (64)$$

where T is the temperature, M the molecular weight, σ the Lennard-Jones collision diameter, T^* the L-J reduced temperature, and $\Omega^{(2,2)*}(T^*)$ a correction factor tabulated in the reference. Values of κ for the three

molecules were 8×10^{-6}, 7.5×10^{-5} and 4.2×10^{-5} cal/cm deg, respectively. Because F_2 was usually present in some excess, the concentration of I_2 is expected to be small. Therefore, the value of κ was approximated as 6×10^{-5}, resulting in a maximum temperature rise at the interior of the cell of ~20°K above the wall temperature. This estimate is based on a flow rate of fluorine of 2.2×10^{-3} μmoles/cm^3 sec and a cell radius of 6 cm in addition to the previously mentioned quantities.

In order to obtain κ for a binary or ternary mixture, the exact molar concentrations of all the species must be known. Since the values of the individual thermal conductivity coefficients lie very close in value (with the exception of I_2 which is thought to be present in only small quantities) the increasing concentration of Ar in the series of runs II-111-4 to II-112-2 would not be expected to change the overall coefficient of thermal conductivity significantly, and consequently, the internal translational temperature would remain unchanged.

From these considerations, it seems more plausible that the role of the added Ar is to increase the rate at which equilibrium between rotational and translational degrees of freedom is achieved, rather than to actually affect the translational temperature itself. More detailed studies of this phenomenon are being undertaken.

C. Possible Mechanisms for Formation of $IF(^3\Pi_0+)$

Knowledge of the mechanism of formation of the excited electronic state of IF is desirable for the subsequent analysis of vibrational relaxation processes. If, on the one hand, the formation step is a four center reaction involving the combination of an iodine and a fluorine molecule to form transition state complex which breaks up into a ground state If and an electronically excited IF^*, the kinetics become quite

complicated since the IF^* may be initially formed in any bound vibrational quantum state. However, if the formation step is that of atom recombination, all IF^* molecules are formed at the top of the energy "ladder," and population of low lying vibrational levels proceeds only through collisional deactivation.

Formulations of two such mechanisms under steady state flow conditions are given below:

Mechanism I

$$\xrightarrow{R_I} I_2$$

$$\xrightarrow{R_F} F_2$$

$$I_2 + F_2 \xrightarrow{a} IF(^1\Sigma^+) + IF(^3\Pi_{0+}) \quad \Delta H = +6 \text{ kcal to } -7 \text{ kcal}$$

$$IF^* \xrightarrow{f} IF + h\nu$$

$$IF^* + M \xrightarrow{g} IF + M$$

$$F_2, I_2, IF^* \xrightarrow{R_o}$$

where R_I, R_F input flow rates of I_2 and F_2, respectively, and R_0 is the pump-out rate. Solution of the steady state rate equations yield

$$(IF^*) = \frac{a(I_2)(F_2)}{f + g(M)} \tag{65}$$

and (I_2) and (F_2) are independent of (M) and are functions simple of the constants R_I, R_F, R_0, and a.

Mechanism II

$$\xrightarrow{R_I} I_2$$

$$\xrightarrow{R_F} F_2$$

$$I_2 + F_2 \xrightarrow{a} IF + I + F \quad \Delta H = +6 \text{ kcal}$$

$$I + F_2 \xrightarrow{b} IF + F$$

$$F + I_2 \xrightarrow{c} IF + I$$

$$I + F \underset{d_2}{\overset{d_1}{\rightleftharpoons}} IF^{\dagger}$$

$$IF^{\dagger} + M \xrightarrow{e} IF^* + M$$

$$IF^* \xrightarrow{f} IF + h\nu$$

$$IF^* + M \xrightarrow{g} IF + M$$

$$I_2, F_2, I, F \xrightarrow{R_0}$$

Recombinations steps of I atoms and F atoms to form I_2 and F_2, respectively, have been omitted because they are negligibly small compared to the input flow rates of I_2 and F_2. Steady state rate equations for $(IF^\ddagger)$ and (IF^*) straightforwardly yield

$$(IF^\ddagger) = \frac{d_1(I)(F)}{d_2 + e(M)} \text{ and } (IF^*) = \frac{e(M)(IF^\ddagger)}{[f + g(M)]} \qquad (66)$$

The expression for $(IF^\ddagger)$ simplifies because the rate constant $d_2 \gg e(M)$. One expects d_2 to correspond to the time for one vibration (10^{13}/sec). Assuming reaction e to be gas kinetic (10^{-10} cm^3/mol sec), any reasonable concentration of M gas still causes negligible contribution. Thus, we may write

$$(IF^*) = \frac{d_1 e(I)(F)(M)}{d_2[f + g(M)]} \qquad (67)$$

Further steady state rate expressions for (I_2), (F_2), (I) and (F) lead to the result that concentrations of (I) and (F) and also (I_2) and (F_2) are not dependent on M gas concentration but solely on the parameters R_I, R_F, R_0 and other constants. No further assumptions have been made to reach these conclusions.

It is quite evident, then, that the total concentration of IF^* $(^3\Pi_{0+})$, i.e. the sum of all vibrational populations, is expected to exhibit different behavior as a function of M gas concentration depending upon which of these mechanisms is correct. From Mechanism I, a plot of (IF^*) vs (M) should be flat at 0 pressure, and gradually begin to decrease as (M) increases. On other other hand, from Mechanism II, one expects

a possible slope at low pressures of M gas, and a gradual flattening out for higher concentrations of M gas.

The total concentrations of IF^* have been obtained from Table IX. Unfortunately, the results are not completely clear. If populations from all thirteen states are counted, the total population appears to remain constant (5.28, 5.18, 5.21, 5.14, in arbitrary units) for runs II-111-4 (30 m torr F_2 + I_2, no Ar), II-111-5 (13 m torr Ar added), II-112-1 (27 m torr Ar), and II-112-2 (50 m torr Ar). This would indicate that either the low pressure regime of Mechanism I or the high pressure region of Mechanism II had obtained. It must be remembered, however, (Sec. V-A), that the populations for high v' as well as having generally high statistical errors, are also subject to large systematic errors due to the presence of the unassigned and related peaks most likely coming from the $^3\Pi_1$ electronic state. Counting vibrational populations up to v' = 9 only, the total population of $IF(^3\Pi_{0+})$ shows a gradual increase with increasing (M) gas concentration (4.39, 4.51, 4.87, 4.76 in arbitrary units). Such a trend could not be explained in terms of Mechanism I. That we are in the low pressure regime of Mechanism II (as opposed to the high pressure regime) is highly likely since achieving the high pressure limit at the pressures encountered would imply a radiative lifetime of 10^{-1} sec assuming $g \approx 10^{-13}$ cm^3/mol sec. g cannot be much greater otherwise the excited IF molecules would be electronically quenched before being vibrationally deactivated.

Mechanism II is further in agreement with that postulated by Kapralova et al. (82) for the reaction of HI and F_2, viz.

$$HI + F_2 \longrightarrow HF + I + F$$

$$I + F + M \longrightarrow IF^{*} + M$$

This second step is simply a combination of steps (d) and (e) in Mechanism II. It should be noted, however, that no detailed reasoning was advanced by the authors for their choice of the above mechanism.

On theoretical grounds, however, Mechanism I would seem highly unlikely. Even though IF^{*} has only limited triplet character, according to the Woodward-Hoffman rules (83), one would not expect the initiating step to proceed through a four-center (trapezoidal) transition state complex due to the poor correlation of molecular orbitals of the reactants and products. Similar arguments have been proposed by Hoffman and Cusachs et al. (84) concerning the reaction of H_2 and I_2 to yield 2HI, reactants and products all being in their ground electronic state. They concluded that the orbital correlations again were such that it would be unlikely for the reaction to proceed through a four center complex.

D. Vibrational Energy Transfer

In this concluding section, a brief analysis of the vibrational population distributions obtained from Spectra II-111-4 to II-112-2 is presented. The model discussed is that of the step ladder - all electronically excited molecules are assumed to be formed in the highest bound quantum vibrational state. Each lower lying level is populated by collisional deactivation of higher levels and collisional excitation from lower levels. For the sake of simplicity (and the uncertainties in the calculated populations do not warrant other than a simplified treatment) only one quantum vibrational jump will be considered.

For a given vibrational level i, we may write the steady state equation

$$\frac{dN_i}{dt} = k_{i+1,i}\,(N_{i+1})(M) + k_{i-1,i}(N_{i-1})(M) - k_{i,i+1}(N_i)(M) - k_{i,i-1}(N_i)(M)$$

$$-(N_i)f - (N_i)(M)g = 0 \qquad (68)$$

where N_j is the population of level j, M is the concentration of the collision partner (Ar in the present case), f is the fluorescence rate constant, g the quenching rate constant, and $k_{\ell,m}$ is the probability upon collision of a molecule in initial state ℓ being transferred to final state m. From the principle of microscopic reversibility we have (1)

$$\frac{k_{\ell,m}}{k_{m,\ell}} = \frac{g_\ell}{g_m}\; e^{-(E_m - E_\ell)/kT} \qquad (69)$$

where the g's are the degeneracies of their respective states (unity in the present case) and the E's are their vibrational energies. Thus,

$$\frac{k_{i,i+1}}{k_{i+1,i}} = e^{-(E_{i+1}-E_i)/kT} = e^{-\Delta G(i+1/2)/kT} \qquad (70)$$

Further, a relation between collisional vibrational energy transfer rate constants $k_{i+1,i}$ and $k_{i,i-1}$ can be written (85)

$$\frac{k_{i+1,i}}{k_{i,i-1}} = \frac{\langle\psi_{i+1}|V(r)|\psi_i\rangle^2}{\langle\psi_i|V(r)|\psi_{i-1}\rangle^2}$$

where V(r) is the form of the perturbation bringing about the transition. For an exponential field and harmonic oscillator wave functions we find (85,86)

$$\frac{k_{i+1,i}}{k_{i,i-1}} = \frac{i+1}{i} \qquad (71)$$

If we now write $k_{1,0} \equiv k_1$ we have $k_{i+1,i} = (i+1)\, k_1$. Substituting these relations into Eq. (68) yields

$$\frac{dN_i}{dt} = (i+1)\, k_1\, (N_{i+1})(M) + ie^{-h\nu/kT}\, k_1(N_{i-1})(M) - (i+1)\, e^{-h\nu/kT}\, k_1(N_i)(M)$$

$$- k_1(N_i)(M) - (N_i)f - g(N_i)(M) = 0 \qquad (72)$$

where $\Delta G(i + 1/2)$ is set equal to $h\nu$ for all i (a sufficiently good approximation since we are restricting this discussion to low values of i). Eq. (72) can be arranged to yield

$$\frac{(i+1)(N_{i+1}) + ie^{-h\nu/kT}(N_{i-1})}{N_i} = [(i+1)\, e^{-h\nu/kT} + i + g/k_1] + \frac{f}{k_1[M]} \qquad (73)$$

A plot of the left side of Eq. (73) vs. 1/[M] should yield a straight line, the slope of which is proportional to the ratio of the fluorescence and vibrational deactivation rate constants, and from the intercept of which can be extracted the ratio of the electronic quenching and vibrational deactivation rate constants. Such a plot is presented in Fig. 15, for i = 0,3. Higher values of i have not been included because of the increasing uncertainties in the populations N_i.

The results are only qualitative in nature due to the large amount of scatter in the plotted points. This could reflect either the uncertainties in the vibrational populations or the inappropriateness of the chosen model. An average of these results yields $g/k_1 = 0.14$ and $f/k_1 = 5\times10^{14}$ mol/cc. Thus, for a reasonable estimate of the vibrational relaxation time of $\sim10^{-7}$ seconds at 1 atm (71), a radiative lifetime for $IF(^3\Pi_{0^+} \rightarrow {}^1\Sigma^+)$ of $\sim10^{-2}$ sec is implied.

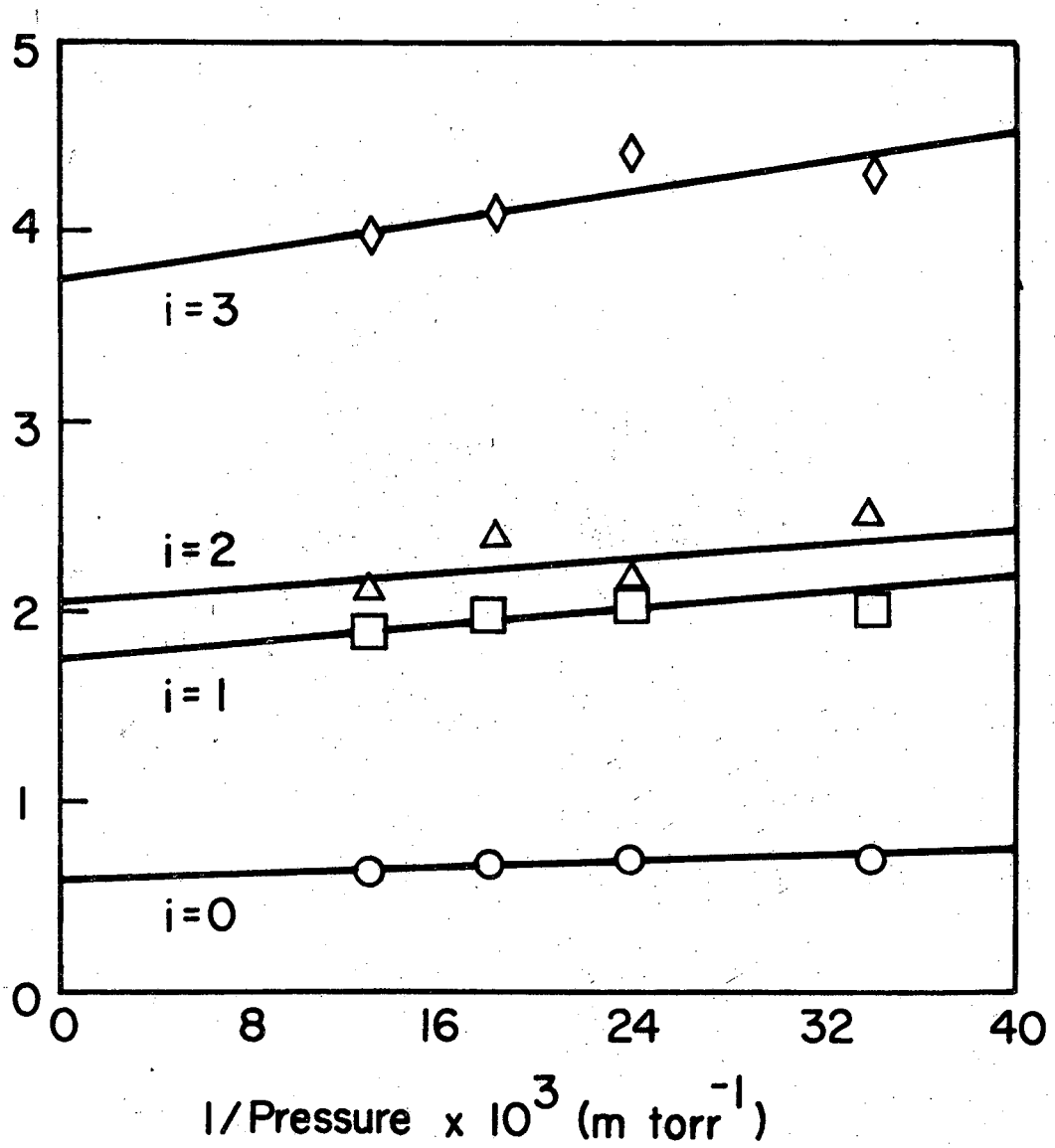

Fig. 16 Left hand side of Eq. (73) vs. inverse pressure

APPENDIX A

Intensity Data and Table

Appendix A. Corrected intensities vs wavelength for observed spectra

Flow rates (std cc/min)			Pressures (mtorr)			Remarks		
Spectrum	F_2	I_2	I_2	I_2+F_2	I_2+F_2+M	τ(sec)	Filtering (db)	Scan Speed (A/min)
II-109-1	8.2	3.8	28	60	60	2.06	6	100
II-109-2	8.2	3.8	28	62	104	2.06	6	100
II-109-3	8.2	3.8	28	61	126	2.06	6	100
II-109-4	8.2	3.8	28	61	154	2.06	6	100
II-109-5	8.2	3.8	28	61	192	2.06	6	100
II-110-1	2.5	1.1	8	28	28	2.06	6	100
II-110-3	2.5	1.4	10	29	33	2.06	6	100
II-111-1	2.5	1.4	10	29	48	2.06	6	100
II-111-2	2.5	1.4	10	29	72	2.06	6	100
II-111-3	2.5	1.4	10	29	99	2.06	6	100
II-111-4	2.5	.95	7	30	30	3.14	6	40
II-111-5	2.5	.95	7	29	42	3.14	6	40
II-112-1	2.5	.95	7	29	56	3.14	6	40
II-112-2	2.5	.95	7	28	78	3.14	6	40
II-112-3	8.2	3.8	28	58	58	3.14	6	40
II-113-1	2.5	.8	6	26	26	3.14	6	40
II-113-2	2.5	.5	4	18	18	3.14	6	40

SPECTRUM II-109-1

4479	0.	4699	.235	4931	.203	5151	.693	5389	2.299	5608	.488
4485	0.	4704	.196	4936	.200	5156	.732	5394	2.232	5613	.582
4490	0.	4709	.173	4941	.182	5162	.901	5399	1.949	5617	.802
4495	.011	4713	.148	4946	.226	5167	1.007	5403	1.667	5621	1.417
4500	.007	4718	.109	4951	.310	5173	.885	5408	1.428	5626	2.585
4505	.013	4722	.103	4957	.653	5178	.746	5412	1.130	5631	3.973
4509	.010	4727	.078	4962	.974	5184	.613	5417	1.004	5635	4.601
4514	.022	4731	.079	4968	1.074	5189	.574	5421	.948	5640	4.096
4518	0.	4736	.080	4973	.980	5194	.552	5426	.812	5646	3.527
4522	0.	4741	.042	4979	.796	5213	1.226	5431	.747	5651	2.872
4527	.008	4746	.046	4984	.709	5217	1.933	5435	.714	5656	2.451
4532	.038	4751	.042	4989	.564	5221	2.534	5440	1.128	5662	2.071
4536	.010	4757	.036	4994	.476	5226	2.647	5446	1.841	5667	1.807
4541	.017	4762	.039	4999	.429	5231	2.430	5451	2.261	5673	1.581
4546	.026	4768	.083	5004	.381	5235	2.079	5456	2.087	5678	1.524
4552	.039	4773	.214	5008	.478	5240	1.649	5462	1.682	5684	2.044
4557	.014	4779	.431	5013	.610	5246	1.350	5467	1.405	5689	3.105
4563	.022	4784	.538	5017	.738	5251	1.200	5473	1.175	5694	3.776
4568	.024	4789	.447	5022	.748	5256	.942	5478	.962	5699	3.653
4574	.026	4794	.329	5026	.648	5262	.815	5484	.867	5703	3.122
4579	.012	4799	.275	5031	.553	5267	.883	5489	.840	5708	2.621
4585	.019	4804	.235	5036	.422	5273	.977	5494	.955	5713	2.360
4590	.017	4809	.206	5041	.396	5278	1.014	5499	1.718	5717	1.964
4595	0.	4813	.176	5046	.381	5284	1.005	5503	3.074	5721	1.698
4600	0.	4817	.130	5051	.555	5289	.915	5508	3.977	5726	1.575
4604	.014	4822	.112	5056	.874	5294	.877	5512	4.050	5731	1.379
4609	.008	4826	.107	5062	1.192	5299	.741	5517	3.585	5735	1.229
4613	.034	4831	.078	5067	1.243	5303	.662	5521	2.579	5740	1.127
4618	.073	4836	.081	5073	1.100	5308	.553	5526	2.519	5746	1.268
4622	.056	4857	.165	5078	.898	5313	.524	5531	2.120	5751	1.543
4627	.074	4862	.422	5084	.739	5317	.514	5535	1.982	5756	1.597
4631	.067	4868	.729	5089	.588	5321	.835	5540	1.846	5762	1.604
4636	.056	4873	.821	5094	.541	5326	1.594	5546	1.711	5767	1.422
4641	.067	4879	.727	5099	.485	5331	2.554	5551	1.541	5773	1.143
4646	.045	4884	.593	5104	.544	5335	2.838	5556	1.318	5778	1.055
4652	.021	4889	.500	5108	.845	5340	2.561	5562	1.309	5784	.918
4657	.025	4894	.439	5113	1.358	5346	2.214	5567	1.258	5789	.811
4662	.016	4899	.375	5117	1.639	5351	1.833	5573	1.164	5794	.703
4668	.015	4904	.318	5122	1.621	5356	1.645	5578	1.057	5799	.657
4674	.015	4908	.281	5126	1.422	5362	1.466	5584	.872	5817	2.182
4679	.006	4913	.240	5131	1.204	5367	1.284	5589	.787	5822	4.080
4684	.019	4917	.245	5136	1.038	5373	1.174	5594	.680	5826	6.196
4690	.096	4922	.249	5140	.873	5378	1.298	5599	.644	5831	6.734
4695	.155	4926	.249	5146	.747	5384	1.822	5603	.579	5836	6.020

5841	4.884	6068	2.880	6313	2.549	6537	2.130	6780	1.297	7006	1.708
5846	3.977	6073	2.500	6318	2.893	6542	2.262	6786	1.267	7011	1.416
5851	3.304	6079	2.276	6322	2.870	6547	3.346	6791	1.398	7015	1.192
5856	2.715	6084	2.067	6327	2.617	6552	4.546	6796	2.224	7020	1.154
5862	2.297	6089	1.892	6331	2.160	6558	4.518	6801	3.686	7024	.987
5868	2.195	6094	1.633	6336	1.833	6563	3.771	6805	4.486	7029	.924
5873	2.223	6099	1.544	6341	1.545	6569	3.206	6810	4.288	7033	.726
5879	2.364	6104	1.401	6346	1.332	6574	2.853	6815	3.663	7038	.789
5884	2.449	6108	1.209	6352	1.313	6580	2.292	6819	3.324	7043	.665
5889	2.441	6113	1.159	6357	1.192	6585	1.900	6824	2.888	7049	.570
5894	2.260	6117	1.096	6363	1.108	6590	1.702	6828	2.505	7054	.693
5899	2.041	6122	1.009	6368	1.049	6595	1.588	6833	2.287	7059	1.192
5904	1.658	6126	.964	6374	.946	6600	1.378	6838	1.933	7065	2.145
5908	1.493	6131	.919	6379	.936	6605	1.216	6843	1.856	7070	3.238
5913	1.365	6136	.903	6385	.802	6609	1.204	6848	1.668	7076	3.236
5917	1.210	6141	.851	6390	.726	6614	1.206	6853	1.506	7081	2.733
5922	1.144	6146	.890	6395	.737	6618	1.212	6859	1.390	7087	2.181
5926	1.104	6151	1.156	6400	.703	6623	1.255	6864	1.477	7092	1.889
5931	.973	6157	1.612	6404	.603	6627	1.234	6870	1.957	7097	1.616
5936	1.013	6162	1.813	6409	.609	6632	1.156	6875	2.768	7102	1.614
5941	1.134	6168	1.744	6413	.496	6637	.875	6881	2.644	7107	1.407
5946	1.671	6174	1.588	6418	.472	6642	.728	6886	2.250	7111	1.423
5951	2.350	6179	1.221	6422	.467	6647	.703	6891	1.914	7116	1.217
5957	2.343	6184	1.106	6427	.473	6653	.544	6896	1.643	7120	1.111
5962	2.026	6190	1.034	6432	.460	6658	.604	6901	1.567	7125	1.030
5968	1.684	6195	.899	6437	.470	6664	.516	6906	1.300	7129	1.097
5973	1.421	6199	.783	6442	.576	6669	.508	6910	1.260	7134	1.254
5979	1.295	6204	.709	6447	.797	6675	.545	6915	1.038	7139	2.085
5984	1.106	6209	.693	6452	1.132	6680	.601	6919	.920	7144	3.018
5989	.949	6213	.720	6457	1.079	6685	.495	6924	.797	7149	3.009
5994	1.042	6218	.779	6463	1.073	6691	.439	6928	.811	7154	2.686
5999	1.119	6241	2.740	6469	1.218	6696	.406	6933	.849	7160	2.500
6004	1.370	6246	5.365	6474	2.086	6701	.423	6938	.615	7165	1.856
6008	1.018	6252	7.870	6480	4.107	6705	.389	6943	.702	7171	1.710
6013	.992	6257	7.982	6485	6.007	6723	1.309	6948	.681	7176	1.457
6017	1.198	6263	6.491	6490	5.897	6728	2.395	6954	.679	7182	1.450
6022	1.965	6268	5.438	6495	4.856	6732	3.430	6959	.721	7187	1.254
6026	4.261	6274	4.362	6500	4.190	6737	3.352	6965	.582	7192	1.001
6031	7.272	6279	3.717	6505	3.594	6742	2.918	6970	.550	7197	.978
6036	8.683	6285	3.222	6509	3.018	6748	2.412	6976	.627	7202	.742
6041	7.622	6290	2.649	6514	2.697	6753	2.086	6981	.569	7207	.801
6046	6.288	6295	2.367	6518	2.649	6758	1.892	6986	.775		
6051	5.068	6300	2.015	6523	2.563	6764	1.791	6992	1.322		
6057	4.051	6304	1.896	6527	2.302	6769	1.629	6997	1.824		
6062	3.488	6309	1.992	6532	2.234	6775	1.476	7001	1.887		

SPECTRUM II-109-2

4479	.007	4699	.282	4931	.249	5162	1.106	5399	2.295	5617	.902
4485	.011	4704	.275	4936	.205	5167	1.232	5403	1.870	5621	1.886
4490	.002	4709	.227	4941	.159	5173	1.031	5408	1.559	5626	3.917
4495	.021	4713	.175	4946	.190	5178	.854	5412	1.441	5631	6.167
4500	.002	4718	.131	4951	.391	5184	.778	5417	1.128	5635	6.937
4505	.010	4722	.105	4957	.847	5189	.725	5421	1.023	5640	6.245
4509	0.	4727	.104	4962	1.262	5194	.669	5426	.855	5646	4.924
4514	.027	4746	.043	4968	1.294	5199	.610	5431	.757	5651	3.999
4518	.012	4751	.023	4973	1.072	5204	.646	5435	.919	5656	3.212
4522	.006	4757	.036	4979	.934	5208	.806	5440	1.534	5662	2.510
4527	0.	4762	.059	4984	.777	5213	1.426	5446	2.510	5667	2.093
4532	.004	4768	.114	4989	.632	5217	2.437	5451	3.043	5673	1.810
4536	.009	4773	.238	4994	.526	5221	3.278	5456	2.761	5678	1.752
4541	0.	4779	.475	4999	.471	5226	3.401	5462	2.112	5684	2.524
4546	.011	4784	.565	5004	.442	5231	2.916	5467	1.688	5689	4.070
4552	.016	4789	.524	5008	.527	5235	2.404	5473	1.383	5694	4.917
4557	.047	4794	.408	5013	.673	5240	2.025	5478	1.130	5699	4.686
4563	.025	4799	.340	5017	.817	5246	1.569	5484	.900	5703	3.992
4568	.012	4804	.267	5022	.869	5251	1.170	5489	.910	5708	3.321
4574	.034	4809	.232	5026	.697	5256	1.045	5494	1.098	5713	2.860
4579	.018	4813	.225	5031	.603	5262	.916	5499	2.288	5717	2.449
4585	.009	4817	.138	5036	.472	5267	.949	5503	4.175	5721	1.947
4590	.002	4822	.131	5051	.659	5273	1.254	5508	5.409	5726	1.722
4595	.008	4826	.126	5056	1.130	5278	1.318	5512	5.316	5731	1.545
4600	0.	4831	.096	5062	1.523	5284	1.190	5517	4.683	5735	1.276
4604	.013	4836	.061	5067	1.445	5289	1.048	5521	3.907	5740	1.230
4609	.029	4841	.061	5073	1.212	5294	.909	5526	3.272	5746	1.411
4613	.027	4846	.083	5078	.989	5299	.752	5531	2.705	5751	1.683
4618	.086	4851	.122	5084	.853	5303	.651	5535	2.300	5756	1.881
4622	.078	4857	.193	5089	.659	5308	.630	5540	2.129	5762	1.839
4627	.078	4862	.534	5094	.619	5326	2.123	5546	1.829	5767	1.553
4631	.076	4868	.947	5099	.540	5331	3.398	5551	1.604	5773	1.251
4636	.063	4873	1.009	5104	.591	5335	3.891	5556	1.489	5778	1.133
4641	.038	4879	.830	5108	.937	5340	3.421	5562	1.480	5784	.936
4646	.039	4884	.662	5113	1.461	5346	2.729	5567	1.390	5789	.894
4652	.011	4889	.529	5117	1.920	5351	2.121	5573	1.234	5794	.685
4657	.030	4894	.520	5122	1.875	5356	1.860	5578	1.085	5799	.638
4662	.022	4899	.400	5126	1.589	5362	1.505	5584	.958	5804	.685
4668	.026	4904	.364	5131	1.328	5367	1.317	5589	.812	5808	.821
4674	.049	4908	.273	5136	1.173	5373	1.247	5594	.692	5813	1.377
4679	.023	4913	.216	5140	.913	5378	1.421	5599	.584	5817	3.133
4684	.035	4917	.254	5146	.818	5384	2.043	5603	.542	5822	6.700
4690	.093	4922	.254	5151	.742	5389	2.711	5608	.566	5826	10.208
4695	.207	4926	.288	5156	.842	5394	2.699	5613	.572	5831	10.778

5836	9.275	6062	4.590	6304	2.284	6527	3.042	6753	3.028	6997	2.950
5841	7.205	6068	3.784	6309	2.549	6532	2.523	6758	2.622	7001	3.003
5846	5.545	6073	3.157	6313	3.029	6537	2.417	6764	2.471	7006	2.614
5851	4.341	6079	2.766	6318	3.706	6542	2.799	6769	2.009	7011	2.267
5856	3.504	6084	2.430	6322	3.662	6547	4.323	6791	2.075	7015	1.818
5862	2.877	6089	2.145	6327	3.152	6552	5.811	6796	3.240	7020	1.513
5868	2.546	6094	1.946	6331	2.558	6558	5.788	6801	4.844	7024	1.352
5873	2.523	6099	1.716	6336	2.151	6563	4.612	6805	5.973	7029	1.205
5879	2.805	6104	1.508	6341	1.830	6569	3.747	6810	5.892	7033	.974
5884	2.865	6108	1.376	6346	1.512	6574	3.220	6815	4.897	7038	.817
5889	2.884	6113	1.290	6352	1.320	6580	2.767	6819	4.138	7043	.696
5894	2.621	6117	1.048	6357	1.167	6585	2.364	6824	3.455	7049	.742
5899	2.246	6122	1.045	6363	1.223	6590	1.967	6828	3.033	7054	.935
5904	1.905	6126	1.042	6368	1.146	6595	1.696	6833	2.524	7059	1.560
5908	1.736	6131	1.009	6374	1.047	6600	1.455	6838	2.436	7065	3.149
5913	1.439	6136	.824	6379	.980	6605	1.316	6843	2.244	7070	4.280
5917	1.316	6141	.839	6385	.857	6609	1.295	6848	2.027	7076	4.232
5922	1.149	6146	.988	6390	.810	6614	1.265	6853	1.725	7081	3.323
5926	1.088	6151	1.241	6395	.733	6618	1.341	6859	1.573	7087	2.930
5931	1.053	6157	1.723	6400	.600	6623	1.353	6864	1.758	7092	2.442
5936	.949	6162	2.115	6404	.610	6627	1.322	6870	2.527	7097	2.095
5941	1.220	6168	1.948	6409	.564	6632	1.039	6875	3.341	7102	1.962
5946	1.962	6174	1.613	6413	.545	6637	1.016	6881	3.150	7107	1.839
5951	2.691	6179	1.400	6418	.536	6642	.851	6886	2.688	7111	1.423
5957	2.799	6184	1.286	6422	.455	6647	.708	6891	2.378	7116	1.285
5962	2.363	6190	1.115	6427	.419	6653	.692	6896	2.256	7120	1.202
5968	1.902	6195	.999	6432	.402	6658	.595	6901	1.680	7125	1.034
5973	1.580	6199	.864	6437	.462	6664	.530	6906	1.503	7129	1.047
5979	1.383	6204	.785	6442	.568	6669	.532	6910	1.365	7134	1.436
5984	1.156	6209	.724	6447	.824	6675	.554	6915	1.321	7139	2.597
5989	1.055	6213	.619	6452	1.187	6680	.488	6919	1.050	7144	3.491
5994	1.070	6231	1.806	6457	1.201	6685	.530	6924	.952	7149	3.771
5999	1.130	6236	2.256	6463	1.235	6691	.596	6928	.786	7154	3.239
6004	1.089	6241	4.341	6469	1.464	6696	.406	6933	.729	7160	2.826
6008	.996	6246	9.229	6474	3.331	6701	.432	6938	.711	7165	2.339
6013	1.111	6252	12.981	6480	6.890	6705	.434	6943	.793	7171	2.012
6017	1.413	6257	12.869	6485	9.769	6710	.361	6948	.844	7176	1.656
6022	2.882	6263	10.353	6490	9.382	6714	.510	6954	.751	7182	1.560
6026	6.837	6268	8.006	6495	7.794	6719	.771	6959	.705	7187	1.327
6031	11.952	6274	6.441	6500	6.467	6723	1.978	6965	.718	7192	1.150
6036	13.925	6279	5.354	6505	5.162	6728	4.156	6970	.694	7197	1.078
6041	11.876	6285	4.344	6509	4.396	6732	5.713	6976	.724	7202	.892
6046	9.263	6290	3.455	6514	3.817	6737	5.711	6981	.705	7207	.931
6051	7.556	6295	2.955	6518	3.307	6742	4.642	6986	1.087		
6057	5.639	6300	2.548	6523	3.127	6748	3.834	6992	2.003		

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4474	.020	4695	.176	4922	.281	5151	.629	5373	1.160	5594	.580
4479	.009	4699	.250	4926	.219	5156	.703	5378	1.369	5599	.564
4485	.011	4704	.214	4931	.193	5162	.997	5384	1.994	5603	.532
4490	.009	4709	.203	4936	.161	5167	1.183	5389	2.531	5617	.889
4495	.016	4713	.122	4941	.165	5173	1.064	5394	2.556	5621	1.944
4500	0.	4718	.091	4946	.192	5178	.801	5399	2.059	5626	4.114
4505	.014	4722	.116	4951	.326	5184	.651	5403	1.811	5631	6.571
4509	.017	4727	.065	4957	.712	5189	.600	5408	1.468	5635	7.581
4514	0.	4731	.058	4962	1.124	5194	.578	5412	1.227	5640	6.448
4518	.006	4736	.049	4968	1.213	5199	.575	5417	1.018	5646	5.037
4522	.009	4741	.028	4973	.928	5204	.585	5421	.877	5651	3.926
4527	0.	4746	.054	4979	.808	5208	.734	5426	.735	5656	3.116
4532	0.	4762	.069	4984	.691	5213	1.333	5431	.707	5662	2.533
4536	.000	4768	.094	4989	.625	5217	2.357	5435	.812	5667	1.987
4541	.016	4773	.241	4994	.499	5221	2.990	5440	1.455	5673	1.608
4546	.033	4779	.395	4999	.445	5226	3.001	5446	2.559	5678	1.669
4552	.044	4784	.508	5004	.398	5231	2.575	5451	3.229	5684	2.473
4557	.030	4789	.468	5008	.478	5235	2.160	5456	2.837	5689	3.963
4563	.034	4794	.363	5013	.609	5240	1.744	5462	2.218	5694	4.772
4568	.009	4799	.264	5017	.699	5246	1.367	5467	1.699	5699	4.629
4574	.009	4804	.235	5022	.686	5251	1.112	5473	1.306	5703	3.719
4579	.007	4809	.174	5026	.591	5256	.897	5478	1.058	5708	3.161
4585	.017	4813	.143	5031	.540	5262	.822	5484	.871	5713	2.728
4590	.016	4817	.143	5036	.445	5267	.865	5489	.840	5717	2.236
4595	.017	4822	.136	5041	.374	5273	1.041	5494	1.129	5721	1.833
4600	.022	4826	.116	5046	.399	5278	1.191	5499	2.373	5726	1.551
4604	.022	4831	.083	5051	.578	5284	1.081	5503	4.215	5731	1.330
4609	.026	4836	.040	5056	.986	5289	.919	5508	5.432	5735	1.257
4613	.043	4841	.091	5062	1.423	5294	.754	5512	5.445	5740	1.159
4618	.074	4846	.083	5067	1.345	5299	.703	5517	4.670	5746	1.238
4622	.090	4851	.118	5073	1.121	5303	.581	5521	3.856	5751	1.462
4627	.079	4857	.168	5078	.945	5308	.531	5526	3.096	5756	1.765
4631	.044	4862	.441	5084	.787	5313	.488	5531	2.575	5762	1.626
4636	.062	4868	.776	5089	.616	5317	.617	5535	2.077	5767	1.359
4641	.049	4873	.838	5104	.558	5321	1.094	5540	1.905	5773	1.125
4646	.030	4879	.731	5108	.867	5326	2.176	5546	1.707	5778	.957
4652	.010	4884	.565	5113	1.390	5331	3.507	5551	1.436	5784	.808
4657	.010	4889	.498	5117	1.802	5335	3.784	5556	1.305	5789	.713
4662	.018	4894	.386	5122	1.724	5340	3.348	5562	1.274	5794	.651
4668	.011	4899	.343	5126	1.494	5346	2.625	5567	1.207	5799	.598
4674	.009	4904	.286	5131	1.217	5351	2.130	5573	1.100	5804	.531
4679	.032	4908	.245	5136	1.028	5356	1.680	5578	.951		
4684	.039	4913	.211	5140	.841	5362	1.470	5584	.781		
4690	.086	4917	.263	5146	.698	5367	1.229	5589	.656		

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4474	.005	4695	.100	4922	.147	5140	.639	5373	.814	5603	.300
4479	0.	4699	.165	4926	.159	5146	.544	5378	.943	5608	.327
4485	0.	4704	.170	4931	.163	5151	.456	5384	1.452	5613	.355
4490	0.	4709	.148	4936	.133	5156	.570	5389	1.847	5617	.582
4495	.001	4713	.095	4941	.096	5162	.846	5394	1.820	5621	1.413
4500	0.	4718	.085	4946	.128	5167	1.006	5399	1.600	5626	3.341
4505	.006	4722	.046	4951	.237	5173	.871	5403	1.209	5631	5.782
4509	.014	4727	.045	4957	.514	5178	.633	5408	1.033	5635	6.739
4514	.013	4731	.036	4962	.845	5184	.536	5412	.917	5640	5.861
4518	.010	4736	.029	4968	.860	5189	.462	5417	.728	5646	4.435
4522	0.	4741	.025	4973	.740	5194	.383	5421	.562	5651	3.459
4527	0.	4746	.021	4979	.607	5208	.519	5426	.510	5656	2.706
4532	0.	4751	.027	4984	.494	5213	1.055	5431	.475	5662	2.071
4536	.000	4768	.054	4989	.416	5217	1.792	5435	.590	5667	1.661
4541	.016	4773	.148	4994	.330	5221	2.399	5440	1.136	5673	1.387
4546	0.	4779	.291	4999	.281	5226	2.424	5446	2.111	5678	1.313
4552	.000	4784	.385	5004	.230	5231	2.075	5451	2.731	5684	1.977
4557	.014	4789	.319	5008	.326	5235	1.644	5456	2.342	5689	3.115
4563	.016	4794	.265	5013	.444	5240	1.288	5462	1.727	5694	3.963
4568	0.	4799	.192	5017	.489	5246	1.010	5467	1.290	5699	3.790
4574	.019	4804	.156	5022	.511	5251	.804	5484	.646	5703	3.173
4579	.010	4809	.149	5026	.461	5256	.669	5489	.644	5708	2.613
4585	0.	4813	.131	5031	.348	5262	.630	5494	.806	5713	2.085
4590	0.	4817	.086	5036	.302	5267	.657	5499	1.769	5717	1.729
4595	0.	4822	.074	5041	.253	5273	.864	5503	3.138	5721	1.481
4600	0.	4826	.052	5046	.254	5278	.949	5508	4.360	5726	1.256
4604	.001	4831	.041	5051	.367	5284	.869	5512	4.537	5731	1.025
4609	.013	4836	.038	5056	.810	5289	.745	5517	3.780	5735	.889
4613	.006	4841	.047	5062	1.114	5294	.623	5521	3.093	5740	.809
4618	.038	4846	.046	5067	1.128	5299	.517	5526	2.360	5746	.921
4622	.061	4851	.064	5073	.856	5303	.459	5531	1.984	5751	1.120
4627	.078	4857	.110	5078	.698	5308	.371	5535	1.652	5756	1.312
4631	.052	4862	.317	5084	.554	5313	.358	5540	1.398	5762	1.268
4636	.040	4868	.527	5089	.432	5317	.424	5546	1.194	5767	1.044
4641	.040	4873	.629	5094	.382	5321	.787	5551	.997	5773	.901
4646	.022	4879	.542	5099	.360	5326	1.684	5556	.918	5778	.703
4652	.019	4884	.444	5104	.411	5331	2.762	5562	.878	5784	.588
4657	.002	4889	.315	5108	.663	5335	3.122	5567	.807	5789	.506
4662	.010	4894	.258	5113	1.106	5340	2.805	5573	.848	5794	.458
4668	0.	4899	.209	5117	1.325	5346	1.995	5578	.677	5799	.396
4674	.013	4904	.198	5122	1.324	5351	1.561	5584	.588	5804	.387
4679	.025	4908	.176	5126	1.075	5356	1.296	5589	.467		
4684	.012	4913	.154	5131	.911	5362	1.073	5594	.390		
4690	.059	4917	.144	5136	.755	5367	.924	5599	.365		

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4474	.022	4695	.048	4913	.069	5140	.272	5362	.482	5594	.163
4479	0.	4699	.109	4917	.072	5146	.215	5367	.414	5599	.125
4485	0.	4704	.082	4922	.070	5151	.204	5373	.366	5603	.112
4490	0.	4709	.079	4926	.064	5156	.260	5378	.430	5617	.222
4495	.000	4713	.044	4931	.057	5162	.349	5384	.618	5621	.584
4500	.006	4718	.049	4936	.013	5167	.441	5389	.821	5626	1.355
4505	.014	4722	.047	4941	.039	5173	.413	5394	.770	5631	2.184
4509	.011	4727	.042	4946	.051	5178	.283	5399	.617	5635	2.596
4514	.013	4731	.020	4951	.103	5184	.230	5403	.476	5640	2.202
4518	.009	4736	.011	4957	.254	5189	.200	5408	.434	5646	1.733
4522	0.	4741	0.	4962	.370	5194	.228	5412	.345	5651	1.307
4527	0.	4746	.002	4968	.403	5199	.179	5417	.246	5656	1.039
4532	0.	4751	0.	4973	.316	5204	.213	5431	.152	5662	.764
4536	0.	4757	.004	4979	.252	5208	.256	5435	.244	5667	.574
4541	.008	4762	.023	4984	.209	5213	.527	5440	.510	5673	.484
4546	.013	4768	.032	4989	.160	5217	.879	5446	.959	5678	.509
4552	.014	4773	.063	4994	.161	5221	1.182	5451	1.072	5684	.761
4557	.016	4779	.166	4999	.145	5226	1.169	5456	.950	5689	1.201
4563	.007	4784	.184	5004	.101	5231	.988	5462	.695	5694	1.510
4568	.007	4789	.138	5008	.107	5235	.767	5467	.539	5699	1.388
4574	.011	4794	.120	5013	.166	5240	.619	5473	.400	5703	1.097
4579	0.	4799	.107	5017	.196	5246	.473	5478	.312	5708	.877
4585	.001	4804	.075	5022	.201	5251	.363	5484	.277	5713	.709
4590	0.	4809	.041	5026	.171	5256	.286	5489	.224	5717	.578
4595	0.	4813	.036	5031	.113	5262	.286	5494	.300	5721	.475
4600	0.	4817	.041	5036	.105	5267	.293	5499	.720	5726	.366
4604	.001	4822	.037	5051	.212	5273	.377	5503	1.322	5731	.334
4609	.003	4826	.017	5056	.346	5278	.422	5508	1.790	5735	.296
4613	.017	4831	.011	5062	.474	5284	.362	5512	1.749	5740	.268
4618	.027	4836	.024	5067	.471	5289	.299	5517	1.504	5746	.355
4622	.031	4841	.026	5073	.390	5294	.269	5521	1.164	5751	.438
4627	.014	4846	.012	5078	.300	5299	.229	5526	.960	5756	.550
4631	0.	4851	.032	5084	.214	5303	.198	5531	.823	5762	.498
4636	.018	4857	.059	5089	.159	5308	.138	5535	.658	5767	.432
4641	0.	4862	.164	5094	.122	5313	.163	5540	.619	5773	.360
4646	.009	4868	.260	5099	.137	5317	.217	5546	.530	5778	.278
4652	.009	4873	.296	5104	.152	5321	.398	5551	.510	5784	.220
4657	.028	4879	.263	5108	.285	5326	.826	5556	.402	5789	.192
4662	.000	4884	.172	5113	.432	5331	1.379	5562	.373	5794	.217
4668	.004	4889	.153	5117	.568	5335	1.443	5567	.343	5799	.153
4674	.010	4894	.146	5122	.566	5340	1.142	5573	.318	5804	.134
4679	.009	4899	.104	5126	.458	5346	.883	5578	.305		
4684	.011	4904	.090	5131	.367	5351	.731	5584	.208		
4690	.030	4908	.065	5136	.324	5356	.535	5589	.173		

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4474	0.	4695	.036	4913	.039	5146	.211	5368	.337	5589	.213
4480	.008	4700	.055	4918	.039	5151	.207	5373	.320	5594	.192
4485	0.	4705	.059	4922	.064	5157	.206	5379	.335	5599	.168
4490	.007	4709	.047	4927	.067	5162	.236	5384	.435	5604	.159
4495	0.	4714	.056	4931	.061	5168	.274	5389	.543	5608	.149
4500	.001	4718	.031	4936	.053	5174	.200	5394	.532	5613	.139
4505	.013	4722	.028	4941	.057	5179	.185	5399	.405	5617	.174
4510	.005	4727	.023	4946	.044	5184	.155	5404	.358	5622	.330
4514	0.	4732	.041	4952	.083	5189	.171	5408	.307	5626	.568
4518	.004	4736	.007	4957	.142	5194	.162	5413	.284	5631	.863
4523	.003	4741	.014	4963	.242	5199	.168	5417	.261	5636	.919
4527	0.	4747	.014	4968	.247	5204	.172	5422	.190	5641	.876
4532	.014	4752	.044	4974	.184	5209	.200	5426	.178	5646	.813
4537	0.	4757	0.	4979	.184	5213	.321	5431	.172	5651	.761
4542	.008	4763	.006	4984	.129	5217	.466	5436	.217	5657	.655
4547	0.	4768	.018	4990	.104	5222	.603	5441	.300	5662	.470
4552	.013	4774	.075	4995	.109	5226	.624	5446	.480	5668	.438
4558	.006	4779	.094	4999	.101	5231	.551	5451	.634	5673	.417
4563	.001	4785	.106	5004	.107	5236	.452	5457	.522	5679	.381
4569	0.	4790	.096	5009	.105	5241	.343	5462	.414	5684	.486
4574	0.	4795	.075	5013	.164	5246	.306	5468	.335	5689	.625
4580	0.	4800	.066	5018	.184	5251	.235	5473	.268	5694	.817
4585	.012	4804	.057	5022	.171	5257	.224	5479	.251	5699	.758
4590	.003	4809	.050	5027	.156	5262	.213	5484	.207	5704	.662
4595	.011	4813	.060	5031	.124	5268	.239	5489	.189	5709	.570
4600	0.	4818	.047	5036	.134	5273	.283	5494	.206	5713	.533
4605	0.	4822	.037	5041	.103	5279	.307	5499	.391	5717	.484
4609	.008	4827	.017	5046	.092	5284	.284	5504	.667	5722	.389
4614	0.	4832	.019	5052	.134	5289	.274	5508	.892	5726	.329
4618	.007	4836	.011	5057	.224	5294	.266	5513	.906	5731	.317
4623	.012	4841	.020	5062	.304	5299	.195	5517	.752	5736	.323
4627	.017	4846	.015	5068	.315	5304	.179	5522	.694	5741	.292
4632	.026	4852	.031	5074	.230	5308	.182	5526	.574	5746	.331
4637	.007	4857	.038	5079	.224	5313	.146	5531	.465	5751	.410
4642	.009	4863	.090	5084	.169	5317	.152	5536	.474	5757	.473
4647	.012	4868	.183	5090	.163	5322	.219	5541	.430	5762	.442
4652	.013	4874	.174	5109	.211	5326	.399	5546	.497	5768	.419
4658	.012	4879	.178	5113	.296	5331	.591	5551	.399	5774	.283
4663	0.	4885	.127	5118	.373	5336	.653	5557	.402	5779	.319
4669	0.	4890	.103	5122	.402	5341	.575	5562	.354	5784	.273
4674	.002	4895	.100	5127	.321	5346	.461	5568	.371	5790	.223
4680	0.	4900	.074	5131	.302	5351	.458	5573	.357	5795	.228
4685	0.	4904	.077	5136	.244	5357	.407	5579	.262	5799	.311
4690	.016	4909	.090	5141	.224	5362	.353	5584	.227	5804	.179

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4474	.025	4695	.027	4913	.070	5146	.195	5367	.317	5589	.170
4479	.016	4699	.053	4917	.065	5151	.148	5373	.296	5594	.177
4485	0.	4704	.042	4922	.071	5156	.166	5378	.354	5599	.175
4490	.004	4709	.025	4926	.057	5162	.200	5384	.432	5603	.124
4495	.006	4713	.040	4931	.054	5167	.217	5389	.508	5608	.135
4500	.002	4718	.035	4936	.038	5173	.251	5394	.469	5613	.128
4505	.004	4722	.024	4941	.059	5178	.165	5399	.432	5617	.131
4509	.001	4727	.018	4946	.049	5184	.147	5403	.329	5621	.282
4514	.006	4731	.014	4951	.074	5189	.140	5408	.333	5626	.481
4518	0.	4736	.022	4957	.149	5194	.152	5412	.263	5631	.766
4522	.000	4741	.005	4962	.188	5199	.161	5417	.231	5635	.828
4527	0.	4746	.027	4968	.196	5204	.168	5421	.193	5640	.839
4532	0.	4751	.017	4973	.204	5208	.193	5426	.167	5646	.740
4536	.003	4757	.011	4979	.196	5213	.292	5431	.133	5651	.670
4541	.009	4762	.010	4984	.169	5217	.433	5435	.190	5656	.631
4546	0.	4768	.025	4989	.151	5221	.580	5440	.269	5662	.517
4552	.001	4773	.052	4994	.124	5226	.596	5446	.422	5667	.386
4557	0.	4779	.078	4999	.080	5231	.502	5451	.528	5673	.359
4563	0.	4784	.093	5004	.097	5235	.461	5456	.491	5678	.351
4568	.011	4789	.106	5008	.128	5240	.360	5462	.389	5684	.488
4574	.001	4794	.074	5013	.155	5246	.295	5467	.342	5689	.674
4579	.005	4799	.069	5017	.149	5251	.228	5473	.294	5694	.750
4585	0.	4804	.059	5022	.127	5256	.199	5478	.242	5699	.697
4590	.010	4809	.042	5026	.124	5262	.187	5484	.207	5703	.633
4595	.021	4813	.040	5031	.116	5267	.195	5489	.182	5708	.565
4600	.022	4817	.046	5036	.103	5273	.277	5494	.232	5713	.460
4604	.016	4822	.024	5041	.104	5278	.302	5499	.356	5717	.396
4609	0.	4826	.030	5046	.087	5284	.305	5503	.634	5721	.362
4613	.012	4831	.031	5051	.135	5289	.223	5508	.897	5726	.327
4618	.006	4836	.037	5056	.216	5294	.200	5512	.878	5731	.341
4622	.022	4841	.029	5062	.266	5299	.208	5517	.743	5735	.301
4627	.027	4846	.025	5067	.279	5303	.191	5521	.612	5740	.245
4631	.022	4851	.036	5073	.198	5308	.174	5526	.490	5746	.289
4636	.018	4857	.040	5078	.192	5313	.157	5531	.432	5751	.361
4641	.006	4862	.081	5084	.176	5317	.108	5535	.443	5756	.467
4646	0.	4868	.143	5104	.160	5321	.192	5540	.478	5762	.517
4652	.013	4873	.172	5108	.194	5326	.344	5546	.475	5767	.417
4657	0.	4879	.144	5113	.309	5331	.532	5551	.422	5773	.367
4662	0.	4884	.112	5117	.366	5335	.633	5556	.378	5778	.324
4668	0.	4889	.108	5122	.360	5340	.558	5562	.381	5784	.235
4674	.016	4894	.089	5126	.359	5346	.424	5567	.347	5789	.208
4679	.005	4899	.113	5131	.262	5351	.371	5573	.313	5794	.132
4684	.008	4904	.078	5136	.244	5356	.387	5578	.272	5799	.101
4690	.009	4908	.046	5140	.226	5362	.356	5584	.213	5804	.195

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4473	0.	4694	.030	4912	.073	5145	.182	5367	.402	5588	.183
4479	0.	4699	.069	4917	.065	5151	.141	5372	.349	5594	.204
4484	.006	4704	.055	4921	.080	5156	.203	5378	.383	5598	.139
4490	.001	4708	.045	4926	.064	5161	.216	5383	.510	5603	.127
4495	0.	4713	.059	4931	.072	5167	.239	5388	.563	5608	.146
4499	0.	4717	.035	4951	.071	5173	.215	5393	.539	5612	.120
4504	0.	4722	.026	4956	.196	5178	.182	5398	.482	5617	.160
4509	0.	4726	.022	4962	.296	5183	.168	5403	.358	5621	.340
4513	0.	4731	.017	4967	.283	5189	.171	5408	.328	5626	.685
4518	0.	4736	.007	4973	.239	5194	.209	5412	.300	5630	.932
4522	0.	4741	.009	4978	.199	5198	.188	5417	.257	5635	1.025
4527	0.	4746	.020	4983	.179	5203	.180	5421	.238	5640	.970
4531	0.	4751	.025	4989	.125	5208	.192	5426	.202	5645	.855
4536	0.	4756	.006	4994	.141	5212	.349	5430	.209	5650	.728
4541	.010	4762	.001	4999	.104	5217	.530	5435	.211	5656	.679
4546	.010	4767	.018	5003	.109	5221	.682	5440	.297	5661	.573
4551	.013	4773	.069	5008	.138	5226	.692	5445	.498	5667	.452
4557	0.	4778	.108	5012	.149	5230	.616	5450	.589	5673	.357
4562	.008	4784	.143	5017	.190	5235	.513	5456	.541	5678	.403
4568	.009	4789	.108	5021	.186	5240	.443	5461	.452	5683	.563
4573	.012	4794	.045	5026	.167	5245	.310	5467	.359	5689	.812
4579	.020	4799	.054	5030	.114	5250	.241	5472	.327	5694	.873
4584	.009	4804	.060	5035	.111	5256	.223	5478	.274	5698	.870
4589	0.	4808	.065	5040	.128	5261	.219	5483	.218	5703	.656
4594	0.	4813	.060	5045	.134	5267	.222	5488	.205	5708	.574
4599	.000	4817	.033	5051	.147	5272	.267	5493	.252	5712	.539
4604	0.	4822	.028	5056	.233	5278	.312	5498	.444	5717	.453
4608	.008	4826	.025	5062	.294	5283	.281	5503	.710	5721	.437
4613	0.	4831	0.	5067	.304	5288	.269	5508	.948	5726	.367
4617	.016	4835	.016	5073	.290	5294	.245	5512	1.010	5730	.349
4622	.025	4840	.022	5078	.212	5298	.235	5517	.853	5735	.291
4626	.034	4846	.019	5083	.146	5303	.193	5521	.673	5740	.307
4631	.031	4851	0.	5089	.146	5308	.167	5526	.603	5745	.366
4636	.024	4856	.056	5094	.109	5312	.145	5530	.499	5751	.438
4641	.003	4862	.111	5099	.101	5317	.150	5535	.486	5756	.492
4646	0.	4867	.184	5103	.143	5321	.222	5540	.474	5761	.521
4651	.006	4873	.194	5108	.215	5326	.455	5545	.483	5767	.396
4657	.022	4878	.169	5112	.357	5330	.653	5550	.414	5773	.352
4662	.001	4884	.124	5117	.427	5335	.715	5556	.418	5778	.353
4668	0.	4889	.121	5121	.405	5340	.674	5561	.394	5783	.295
4673	0.	4894	.097	5126	.333	5345	.526	5567	.412	5789	.273
4679	0.	4899	.090	5130	.294	5350	.479	5572	.299	5794	.211
4684	.024	4903	.085	5135	.250	5356	.453	5578	.274	5798	.194
4689	.024	4908	.073	5140	.225	5361	.429	5583	.217	5803	.155

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4474	.005	4695	.055	4936	.040	5173	.288	5394	.594	5613	.126
4480	.010	4700	.047	4941	.049	5179	.215	5399	.525	5617	.192
4485	.010	4704	.069	4946	.070	5184	.193	5404	.473	5622	.415
4490	.005	4709	.046	4951	.125	5189	.178	5408	.370	5626	.845
4495	0.	4713	.020	4957	.202	5194	.185	5413	.316	5631	1.316
4500	.003	4718	.032	4962	.311	5199	.167	5417	.278	5636	1.425
4505	.000	4722	.024	4968	.313	5204	.177	5422	.243	5641	1.269
4509	0.	4727	.016	4973	.250	5208	.239	5426	.196	5646	1.061
4514	0.	4731	.025	4979	.203	5213	.398	5431	.207	5651	.891
4518	.002	4736	.009	4984	.190	5217	.641	5436	.203	5657	.751
4523	0.	4741	.004	4989	.135	5222	.812	5441	.334	5662	.590
4527	0.	4746	0.	4994	.123	5226	.858	5446	.574	5668	.505
4532	0.	4752	.010	4999	.114	5231	.708	5451	.708	5673	.477
4537	.007	4757	.015	5004	.108	5236	.636	5457	.664	5679	.377
4542	.012	4763	.011	5009	.122	5241	.457	5462	.520	5684	.572
4547	.025	4768	.015	5013	.172	5246	.394	5468	.424	5689	.980
4552	.023	4774	.041	5017	.223	5251	.295	5473	.341	5694	1.175
4557	.016	4779	.111	5022	.202	5257	.263	5479	.257	5699	1.030
4563	.008	4784	.133	5026	.148	5262	.220	5484	.218	5704	.878
4569	0.	4790	.132	5031	.096	5268	.237	5489	.201	5708	.757
4574	0.	4795	.087	5051	.177	5273	.277	5494	.273	5713	.644
4580	.014	4800	.062	5057	.254	5279	.334	5499	.526	5717	.533
4585	0.	4804	.056	5062	.301	5284	.338	5504	.983	5722	.437
4590	0.	4809	.064	5068	.360	5289	.255	5508	1.301	5726	.405
4595	.002	4813	.040	5073	.312	5294	.189	5513	1.246	5731	.318
4600	.008	4818	.039	5079	.210	5299	.230	5517	1.040	5736	.295
4605	0.	4822	.036	5084	.194	5304	.171	5522	.850	5741	.300
4609	.003	4827	.034	5089	.158	5308	.165	5526	.709	5746	.296
4614	.023	4831	.038	5094	.143	5313	.115	5531	.576	5751	.419
4618	.003	4836	.008	5099	.138	5317	.182	5536	.486	5757	.543
4622	.030	4841	.015	5104	.141	5322	.284	5541	.501	5762	.568
4627	.026	4846	.023	5108	.241	5326	.532	5546	.481	5768	.464
4632	.010	4852	.018	5113	.376	5331	.773	5551	.413	5773	.388
4636	.010	4857	.064	5117	.484	5336	.891	5557	.395	5779	.331
4641	.010	4862	.121	5122	.423	5341	.805	5562	.380	5784	.289
4647	.010	4884	.164	5126	.390	5346	.621	5568	.383	5789	.190
4652	0.	4895	.096	5131	.304	5351	.549	5573	.312	5794	.131
4657	.004	4904	.074	5136	.286	5357	.455	5579	.262	5799	.173
4663	.000	4909	.061	5141	.233	5362	.404	5584	.218	5804	.135
4668	.007	4913	.066	5146	.211	5368	.375	5589	.151		
4674	.013	4918	.057	5151	.189	5373	.308	5594	.099		
4679	.022	4922	.072	5157	.182	5379	.358	5599	.115		
4685	.021	4927	.062	5162	.240	5384	.494	5604	.125		
4690	.024	4931	.061	5168	.268	5389	.587	5608	.122		

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4474	.013	4695	.033	4913	.035	5146	.166	5384	.438	5604	.120
4480	.010	4700	.068	4918	.053	5151	.179	5389	.558	5608	.103
4485	.003	4704	.072	4922	.051	5157	.188	5394	.590	5613	.085
4490	0.	4709	.059	4927	.063	5162	.229	5399	.464	5617	.168
4495	0.	4713	.051	4931	.067	5168	.274	5404	.383	5622	.359
4500	0.	4718	.026	4951	.084	5173	.255	5408	.295	5626	.776
4505	0.	4722	.010	4957	.154	5179	.189	5413	.277	5631	1.305
4509	.014	4727	.039	4962	.259	5184	.142	5417	.150	5636	1.478
4514	.003	4731	.014	4968	.276	5189	.163	5422	.177	5641	1.283
4518	0.	4736	.004	4973	.242	5194	.160	5426	.159	5646	1.054
4523	0.	4741	0.	4979	.234	5199	.158	5431	.123	5651	.843
4527	0.	4746	0.	4984	.148	5204	.138	5436	.148	5657	.658
4532	0.	4752	0.	4989	.138	5208	.180	5441	.295	5662	.514
4537	0.	4757	.001	4994	.096	5213	.308	5446	.531	5668	.456
4542	.024	4763	.018	4999	.080	5217	.539	5451	.622	5673	.362
4547	.019	4768	0.	5004	.076	5222	.697	5457	.610	5679	.363
4552	.007	4774	.033	5009	.076	5226	.688	5462	.488	5684	.497
4557	0.	4779	.089	5013	.151	5231	.632	5468	.380	5689	.805
4563	.021	4784	.106	5017	.145	5236	.463	5473	.320	5694	1.059
4569	0.	4790	.116	5022	.136	5241	.360	5479	.227	5699	.970
4574	0.	4795	.071	5026	.136	5246	.288	5484	.190	5704	.771
4580	0.	4800	.052	5031	.123	5251	.238	5489	.162	5708	.644
4585	.017	4804	.056	5036	.097	5257	.182	5494	.248	5713	.512
4590	.002	4809	.052	5041	.071	5262	.169	5499	.496	5717	.437
4595	.003	4813	.033	5046	.087	5268	.200	5504	.892	5722	.359
4600	0.	4818	.019	5051	.146	5273	.283	5508	1.184	5726	.278
4605	0.	4822	.015	5057	.232	5279	.305	5513	1.166	5731	.262
4609	0.	4827	.033	5062	.314	5284	.227	5517	.982	5736	.228
4614	0.	4831	0.	5068	.252	5289	.224	5522	.830	5741	.218
4618	.010	4836	0.	5073	.254	5294	.187	5526	.666	5746	.267
4622	.012	4841	.013	5079	.222	5299	.141	5531	.529	5751	.367
4627	.026	4846	0.	5084	.144	5304	.145	5536	.452	5757	.380
4632	.009	4852	.018	5089	.136	5308	.137	5541	.480	5762	.417
4636	.008	4857	.041	5094	.109	5313	.098	5546	.431	5768	.382
4641	.022	4862	.091	5099	.087	5317	.133	5551	.355	5773	.309
4647	.012	4868	.182	5104	.105	5322	.220	5557	.297	5779	.247
4652	.004	4874	.186	5108	.200	5326	.453	5562	.322	5784	.188
4657	.001	4879	.154	5113	.359	5331	.802	5568	.304	5789	.184
4663	.014	4884	.115	5117	.393	5336	.816	5573	.262	5794	.180
4668	.003	4890	.111	5122	.405	5341	.734	5579	.229	5799	.062
4674	0.	4895	.064	5126	.332	5346	.604	5584	.184	5804	.118
4679	0.	4899	.068	5131	.286	5351	.497	5589	.146		
4685	.006	4904	.050	5136	.238	5373	.286	5594	.106		
4690	.010	4909	.067	5141	.195	5379	.319	5599	.120		

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4473	0.	4619	.014	4766	.009	4912	.034	5058	.157	5215	.256
4477	.007	4622	.018	4769	.025	4915	.043	5062	.205	5218	.342
4481	.008	4625	.019	4773	.027	4918	.039	5065	.206	5221	.453
4484	.010	4628	.009	4777	.043	4921	.049	5069	.212	5224	.470
4488	0.	4631	0.	4780	.076	4924	.048	5073	.200	5227	.456
4491	0.	4634	.025	4784	.089	4927	.045	5076	.161	5230	.417
4495	0.	4637	.017	4787	.080	4931	.049	5080	.155	5233	.404
4498	0.	4641	.018	4791	.061	4934	.049	5083	.139	5237	.340
4501	0.	4644	.029	4794	.063	4937	.049	5087	.111	5240	.309
4504	0.	4648	.010	4797	.060	4940	.019	5090	.123	5243	.293
4507	.008	4651	.009	4800	.049	4944	.036	5094	.109	5247	.236
4510	0.	4655	.011	4804	.044	4947	.028	5097	.115	5250	.192
4513	0.	4658	0.	4807	.038	4951	.054	5100	.087	5254	.186
4516	0.	4662	.004	4810	.036	4954	.079	5103	.100	5258	.151
4519	.002	4666	.013	4813	.034	4958	.124	5106	.113	5261	.160
4522	0.	4669	.008	4816	.033	4962	.159	5109	.173	5265	.169
4525	0.	4673	0.	4819	.033	4965	.183	5112	.205	5269	.175
4528	.027	4677	.006	4822	.031	4969	.192	5115	.273	5272	.177
4531	.016	4680	.002	4825	.019	4973	.168	5118	.304	5276	.236
4534	0.	4684	.009	4828	.026	4976	.151	5121	.318	5280	.296
4538	.005	4687	0.	4831	.017	4980	.157	5124	.298	5283	.256
4541	.000	4691	.011	4834	.024	4983	.145	5127	.262	5287	.224
4544	0.	4694	.015	4837	.012	4987	.132	5130	.236	5290	.221
4548	0.	4697	.028	4840	.016	4990	.096	5134	.228	5294	.203
4551	.004	4701	.054	4844	.005	4994	.089	5137	.202	5297	.227
4555	.002	4704	.047	4847	.004	4997	.106	5140	.187	5300	.193
4559	0.	4707	.032	4851	.012	5000	.072	5143	.186	5303	.163
4562	.006	4710	.030	4854	.017	5003	.094	5147	.135	5306	.166
4566	.003	4713	.010	4858	.028	5006	.091	5151	.136	5309	.136
4570	.012	4716	.014	4862	.039	5009	.101	5154	.128	5312	.114
4573	.008	4719	.018	4865	.094	5012	.096	5158	.162	5315	.128
4577	.007	4722	.026	4869	.127	5015	.101	5161	.156	5318	.124
4581	0.	4725	.026	4873	.126	5018	.128	5176	.150	5321	.117
4584	.003	4728	.011	4876	.133	5021	.140	5180	.115	5324	.190
4588	.014	4731	.020	4880	.118	5024	.125	5183	.095	5327	.260
4591	0.	4734	.002	4884	.114	5027	.120	5187	.127	5330	.407
4594	.008	4737	.003	4887	.083	5030	.110	5190	.124	5333	.475
4598	.006	4741	.012	4891	.096	5034	.090	5194	.151	5337	.480
4601	.006	4744	.002	4894	.073	5037	.095	5197	.162	5340	.455
4604	.006	4747	.004	4897	.071	5040	.100	5200	.153	5343	.398
4607	0.	4751	.004	4900	.084	5044	.069	5203	.165	5347	.359
4610	.006	4755	.004	4903	.049	5047	.077	5206	.141	5350	.310
4613	.006	4758	.005	4906	.062	5051	.092	5209	.158	5354	.322
4616	.023	4762	.015	4910	.059	5054	.137	5212	.213	5358	.340

5361	.366	5472	.254	5583	.207	5694	.584	5803	.156	5912	.260
5365	.308	5476	.232	5587	.153	5697	.575	5806	.131	5915	.238
5369	.266	5480	.209	5590	.136	5700	.550	5809	.146	5918	.210
5372	.261	5483	.182	5594	.157	5703	.532	5812	.145	5921	.231
5376	.261	5487	.175	5597	.133	5706	.472	5815	.222	5924	.223
5380	.263	5490	.155	5600	.119	5709	.395	5818	.301	5927	.227
5383	.349	5493	.155	5603	.081	5712	.385	5821	.434	5930	.188
5387	.396	5497	.157	5606	.107	5715	.333	5824	.682	5934	.165
5390	.418	5500	.282	5609	.108	5718	.289	5827	.874	5937	.187
5393	.398	5503	.426	5612	.088	5721	.274	5830	.971	5940	.192
5397	.405	5506	.595	5615	.114	5724	.287	5834	.959	5944	.233
5400	.359	5509	.683	5618	.105	5727	.266	5837	.838	5947	.321
5403	.326	5512	.696	5621	.167	5730	.275	5840	.759	5951	.353
5406	.277	5515	.617	5624	.254	5733	.223	5844	.663	5954	.384
5409	.252	5518	.565	5627	.380	5737	.212	5847	.544	5958	.385
5412	.253	5521	.503	5630	.528	5740	.215	5851	.506	5962	.403
5415	.205	5524	.416	5633	.608	5743	.192	5854	.487	5965	.328
5418	.201	5527	.427	5637	.691	5747	.199	5858	.429	5969	.296
5421	.160	5530	.359	5640	.676	5751	.301	5862	.358	5973	.260
5424	.150	5533	.371	5643	.650	5754	.363	5865	.346	5976	.229
5427	.162	5537	.358	5647	.617	5758	.394	5869	.373	5980	.187
5430	.130	5540	.351	5650	.585	5761	.416	5873	.401	5984	.159
5433	.120	5543	.394	5654	.570	5765	.411	5876	.491	5987	.193
5437	.112	5547	.416	5658	.490	5769	.374	5880	.473	5990	.200
5440	.154	5550	.395	5661	.463	5773	.318	5883	.480	5994	.236
5443	.246	5554	.364	5665	.423	5776	.301	5887	.521	5997	.264
5447	.342	5558	.322	5669	.354	5780	.277	5890	.505	6000	.269
5450	.433	5561	.320	5673	.304	5783	.215	5894	.454	6003	.278
5454	.449	5565	.309	5676	.293	5787	.229	5897	.417		
5458	.414	5569	.277	5680	.264	5790	.182	5900	.396		
5461	.367	5572	.266	5683	.300	5794	.195	5903	.362		
5465	.340	5576	.234	5687	.390	5797	.172	5906	.290		
5469	.289	5580	.218	5690	.519	5800	.153	5909	.293		

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4473	0.	4619	.016	4766	0.	4912	.049	5058	.159	5215	.270
4477	0.	4622	.014	4769	.014	4915	.045	5062	.207	5218	.348
4481	0.	4625	.019	4773	.040	4918	.049	5065	.230	5221	.459
4484	0.	4628	.014	4777	.079	4921	.043	5069	.217	5224	.488
4488	0.	4631	.024	4780	.089	4924	.052	5073	.192	5227	.530
4491	.022	4634	.008	4784	.088	4927	.049	5076	.198	5230	.484
4495	0.	4637	.009	4787	.089	4931	.037	5080	.179	5233	.459
4498	0.	4641	.004	4791	.076	4934	.035	5083	.158	5237	.397
4501	.002	4644	.011	4794	.049	4937	.027	5087	.126	5240	.328
4504	0.	4648	0.	4797	.054	4940	.025	5090	.105	5243	.264
4507	0.	4651	0.	4800	.036	4944	.023	5094	.098	5247	.233
4510	0.	4655	0.	4804	.036	4947	.027	5097	.101	5250	.234
4513	.005	4658	.014	4807	.039	4951	.040	5100	.093	5254	.177
4516	0.	4662	.000	4810	.030	4954	.097	5103	.085	5258	.165
4519	.007	4666	.004	4813	.034	4958	.106	5106	.103	5261	.156
4522	.006	4669	.010	4816	.034	4962	.163	5109	.142	5265	.149
4525	.005	4673	0.	4819	.029	4965	.174	5112	.181	5269	.182
4528	.005	4677	0.	4822	.027	4969	.195	5115	.265	5272	.214
4531	0.	4680	.003	4825	0.	4973	.175	5118	.274	5276	.252
4534	.013	4684	0.	4828	.024	4976	.178	5121	.325	5280	.275
4538	.011	4687	.003	4831	.008	4980	.154	5124	.281	5283	.243
4541	0.	4691	.008	4834	.013	4983	.139	5127	.247	5287	.220
4544	0.	4694	.026	4837	.021	4987	.114	5130	.225	5290	.200
4548	.007	4697	.038	4840	0.	4990	.112	5134	.198	5294	.206
4551	.004	4701	.034	4844	.007	4994	.086	5137	.195	5297	.158
4555	.001	4704	.035	4847	.017	4997	.082	5140	.189	5300	.176
4559	.015	4707	.054	4851	.003	5000	.059	5143	.150	5303	.164
4562	.008	4710	.031	4854	0.	5003	.074	5147	.134	5306	.158
4566	.014	4713	.033	4858	.028	5006	.063	5151	.133	5309	.153
4570	.011	4716	.020	4862	.059	5009	.082	5154	.106	5312	.130
4573	.006	4719	.028	4865	.091	5012	.106	5158	.138	5315	.112
4577	.012	4722	.023	4869	.115	5015	.112	5161	.177	5318	.101
4581	0.	4725	.021	4873	.152	5018	.115	5165	.187	5321	.134
4584	0.	4728	.006	4876	.122	5021	.129	5169	.174	5324	.194
4588	0.	4731	0.	4880	.122	5024	.125	5173	.154	5327	.273
4591	.004	4734	.007	4884	.111	5027	.108	5176	.154	5330	.400
4594	.000	4737	.026	4887	.084	5030	.102	5180	.124	5333	.476
4598	0.	4741	.012	4891	.080	5034	.082	5183	.127	5337	.523
4601	.004	4744	.009	4894	.073	5037	.078	5187	.161	5340	.458
4604	.005	4747	.013	4897	.078	5040	.070	5190	.118	5343	.397
4607	0.	4751	.016	4900	.064	5044	.070	5194	.124	5347	.356
4610	.002	4755	.006	4903	.051	5047	.074	5197	.142	5350	.306
4613	0.	4758	.010	4906	.050	5051	.088	5209	.132	5354	.314
4616	.004	4762	0.	4910	.031	5054	.118	5212	.185	5358	.310

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5361	.326	5472	.249	5583	.199	5694	.590	5803	.144	5912	.245
5365	.348	5476	.217	5587	.165	5697	.676	5806	.131	5915	.218
5369	.290	5480	.211	5590	.159	5700	.628	5809	.137	5918	.241
5372	.281	5483	.179	5594	.135	5703	.607	5812	.126	5921	.219
5376	.260	5487	.174	5597	.141	5706	.509	5815	.186	5924	.216
5380	.283	5490	.131	5600	.134	5709	.437	5818	.316	5927	.212
5383	.350	5493	.111	5603	.121	5712	.368	5821	.499	5930	.164
5387	.411	5497	.151	5606	.107	5715	.372	5824	.736	5934	.185
5390	.450	5500	.303	5609	.098	5718	.332	5827	.964	5937	.184
5393	.425	5503	.423	5612	.088	5721	.291	5830	1.084	5940	.187
5397	.388	5506	.575	5615	.092	5724	.279	5834	1.069	5944	.245
5400	.350	5509	.649	5618	.120	5727	.240	5837	.957	5947	.318
5403	.315	5512	.677	5621	.158	5730	.222	5840	.782	5951	.401
5406	.292	5515	.678	5624	.284	5733	.219	5844	.755	5954	.444
5409	.254	5518	.600	5627	.397	5737	.238	5847	.634	5958	.441
5412	.207	5521	.530	5630	.533	5740	.182	5851	.551	5962	.368
5415	.181	5524	.447	5633	.653	5743	.185	5854	.475	5965	.346
5418	.174	5527	.388	5637	.674	5747	.244	5858	.416	5969	.312
5421	.180	5530	.382	5640	.709	5751	.245	5862	.379	5973	.287
5424	.144	5533	.375	5643	.660	5754	.321	5865	.362	5976	.241
5427	.132	5537	.334	5647	.687	5758	.407	5869	.385	5980	.255
5430	.133	5540	.364	5650	.570	5761	.414	5873	.443	5984	.211
5433	.129	5543	.395	5654	.611	5765	.457	5876	.469	5987	.177
5437	.150	5547	.439	5658	.507	5769	.398	5880	.522	5990	.181
5440	.162	5550	.399	5661	.414	5773	.307	5883	.468	5994	.229
5443	.260	5554	.389	5665	.408	5776	.303	5887	.473	5997	.255
5447	.379	5558	.300	5669	.347	5780	.274	5890	.503	6000	.319
5450	.476	5561	.298	5673	.300	5783	.255	5894	.485	6003	.330
5454	.484	5565	.304	5676	.281	5787	.202	5897	.431		
5458	.448	5569	.293	5680	.252	5790	.176	5900	.406		
5461	.370	5572	.259	5683	.298	5794	.160	5903	.376		
5465	.376	5576	.245	5687	.431	5797	.146	5906	.284		
5469	.292	5580	.238	5690	.525	5800	.161	5909	.297		

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4473	.012	4619	.004	4766	.017	4912	.039	5058	.135	5215	.296
4477	.009	4622	.018	4769	.004	4915	.049	5062	.241	5218	.369
4481	.003	4625	.015	4773	.015	4918	.051	5065	.238	5221	.481
4484	0.	4628	.008	4777	.045	4921	.038	5069	.263	5224	.559
4488	0.	4631	.012	4780	.079	4924	.046	5073	.228	5227	.568
4491	.008	4634	.014	4784	.111	4927	.036	5076	.187	5230	.474
4495	0.	4637	.013	4787	.086	4931	.033	5080	.151	5233	.456
4498	0.	4641	.015	4791	.069	4934	.034	5083	.156	5237	.389
4501	0.	4644	.013	4794	.068	4937	.033	5087	.117	5240	.358
4504	0.	4648	.021	4797	.051	4940	.032	5100	.076	5243	.279
4507	.006	4651	.016	4800	.040	4944	.027	5103	.084	5247	.237
4510	0.	4655	.003	4804	.033	4947	.041	5106	.091	5250	.210
4513	.006	4658	.002	4807	.043	4951	.068	5109	.142	5254	.200
4516	0.	4662	.003	4810	.036	4954	.065	5112	.204	5258	.169
4519	0.	4666	.000	4813	.031	4958	.115	5115	.278	5261	.155
4522	0.	4669	0.	4816	.042	4962	.184	5118	.341	5265	.144
4525	0.	4673	.003	4819	.020	4965	.211	5121	.330	5269	.174
4528	0.	4677	.010	4822	.013	4969	.223	5124	.336	5272	.202
4531	0.	4680	.019	4825	.020	4973	.182	5127	.301	5276	.242
4534	0.	4684	.016	4828	.023	4976	.173	5130	.246	5280	.266
4538	.009	4687	.004	4831	.037	4980	.157	5134	.215	5283	.255
4541	.006	4691	.009	4834	.010	4983	.153	5137	.181	5287	.227
4544	.002	4694	.015	4837	.016	4987	.132	5140	.187	5290	.215
4548	0.	4697	.035	4840	.015	4990	.103	5143	.156	5294	.213
4551	.001	4701	.039	4844	.006	4994	.094	5147	.156	5297	.197
4555	0.	4704	.045	4847	.023	4997	.070	5151	.120	5300	.181
4559	0.	4707	.039	4851	0.	5000	.080	5154	.107	5303	.155
4562	0.	4710	.027	4854	.002	5003	.069	5158	.119	5306	.154
4566	0.	4713	.035	4858	.023	5006	.065	5161	.154	5309	.129
4570	0.	4716	.038	4862	.050	5009	.086	5165	.184	5312	.116
4573	.003	4719	.024	4865	.092	5012	.090	5169	.193	5315	.108
4577	.013	4722	.023	4869	.140	5015	.103	5173	.184	5318	.099
4581	0.	4725	.014	4873	.163	5018	.128	5176	.140	5321	.107
4584	0.	4728	.005	4876	.154	5021	.114	5180	.132	5324	.156
4588	.001	4731	.008	4880	.130	5024	.139	5183	.118	5327	.277
4591	.004	4734	.010	4884	.101	5027	.121	5187	.118	5330	.474
4594	0.	4737	0.	4887	.092	5030	.105	5190	.129	5333	.528
4598	0.	4741	.009	4891	.075	5034	.080	5194	.130	5337	.596
4601	0.	4744	.016	4894	.063	5037	.080	5197	.122	5340	.529
4604	0.	4747	.014	4897	.072	5040	.068	5200	.132	5343	.470
4607	.004	4751	.009	4900	.057	5044	.071	5203	.140	5347	.381
4610	.007	4755	.003	4903	.050	5047	.089	5206	.130	5350	.357
4613	.007	4758	.008	4906	.048	5051	.098	5209	.156	5354	.327
4616	.008	4762	.009	4910	.050	5054	.110	5212	.214	5358	.326

5361	.354	5472	.256	5583	.221	5694	.764	5803	.140	5912	.260
5365	.313	5476	.231	5587	.175	5697	.682	5806	.132	5915	.268
5369	.317	5480	.197	5590	.173	5700	.699	5809	.137	5918	.243
5372	.258	5483	.169	5594	.132	5703	.613	5812	.119	5921	.249
5376	.227	5487	.146	5597	.141	5706	.560	5815	.202	5924	.190
5380	.261	5490	.171	5600	.123	5709	.501	5818	.324	5927	.187
5383	.324	5493	.145	5603	.112	5712	.441	5821	.571	5930	.162
5387	.444	5497	.199	5606	.103	5715	.385	5824	.863	5934	.175
5390	.464	5500	.304	5609	.077	5718	.367	5827	1.181	5937	.179
5393	.484	5503	.507	5612	.083	5721	.328	5830	1.305	5940	.195
5397	.430	5506	.689	5615	.098	5724	.254	5834	1.263	5944	.250
5400	.397	5509	.789	5618	.117	5727	.283	5837	1.106	5947	.295
5403	.343	5512	.790	5621	.194	5730	.240	5840	.944	5951	.423
5406	.300	5515	.768	5624	.307	5733	.257	5844	.865	5954	.491
5409	.294	5518	.713	5627	.470	5737	.191	5847	.740	5958	.464
5412	.262	5521	.605	5630	.692	5740	.209	5851	.709	5962	.405
5415	.197	5524	.534	5633	.831	5743	.215	5854	.566	5965	.318
5418	.196	5527	.429	5637	.699	5747	.232	5858	.492	5969	.345
5421	.193	5530	.400	5640	.696	5751	.280	5862	.413	5973	.289
5424	.146	5533	.378	5643	.759	5754	.331	5865	.394	5976	.252
5427	.142	5537	.379	5647	.753	5758	.399	5869	.388	5980	.230
5430	.137	5540	.401	5650	.727	5761	.412	5873	.474	5984	.180
5433	.104	5543	.385	5654	.606	5765	.464	5876	.517	5987	.190
5437	.149	5547	.398	5658	.575	5769	.394	5880	.529	5990	.189
5440	.186	5550	.421	5661	.515	5773	.355	5883	.543	5994	.237
5443	.266	5554	.332	5665	.409	5776	.276	5887	.530	5997	.229
5447	.419	5558	.330	5669	.380	5780	.270	5890	.556	6000	.279
5450	.517	5561	.272	5673	.316	5783	.213	5894	.511	6003	.281
5454	.530	5565	.281	5676	.308	5787	.198	5897	.474		
5458	.417	5569	.266	5680	.295	5790	.194	5900	.404		
5461	.369	5572	.287	5683	.319	5794	.169	5903	.384		
5465	.330	5576	.231	5687	.406	5797	.150	5906	.370		
5469	.279	5580	.205	5690	.621	5800	.138	5909	.308		

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4473	.001	4619	0.	4766	.009	4912	.055	5069	.254	5215	.276
4477	0.	4622	.017	4769	.013	4915	.034	5073	.222	5218	.407
4481	.003	4625	.010	4773	.011	4918	.047	5076	.200	5221	.504
4484	.012	4628	.012	4777	.059	4921	.042	5080	.166	5224	.535
4488	0.	4631	.005	4780	.064	4924	.034	5083	.150	5227	.570
4491	0.	4634	.013	4784	.085	4927	.049	5087	.115	5230	.533
4495	0.	4637	.012	4787	.101	4931	.048	5090	.093	5233	.441
4498	.001	4641	.011	4791	.080	4934	.047	5094	.097	5237	.346
4501	0.	4644	.001	4794	.060	4937	.043	5097	.084	5240	.315
4504	.000	4648	.000	4797	.054	4940	.024	5100	.075	5243	.257
4507	.006	4651	0.	4800	.044	4954	.072	5103	.062	5247	.247
4510	0.	4655	.011	4804	.032	4958	.112	5106	.100	5250	.195
4513	0.	4658	.009	4807	.038	4962	.187	5109	.151	5254	.173
4516	0.	4662	.009	4810	.025	4965	.211	5112	.212	5258	.159
4519	.003	4666	.004	4813	.031	4969	.233	5115	.301	5261	.127
4522	.001	4669	.011	4816	.026	4973	.207	5118	.308	5265	.113
4525	0.	4673	0.	4819	.023	4976	.156	5121	.325	5269	.164
4528	0.	4677	.012	4822	0.	4980	.143	5124	.279	5272	.176
4531	0.	4680	.030	4825	.034	4983	.133	5127	.291	5276	.222
4534	.003	4684	.007	4828	.015	4987	.129	5130	.221	5280	.234
4538	.008	4687	.008	4831	.009	4990	.094	5134	.203	5283	.219
4541	0.	4691	.007	4834	.008	4994	.098	5137	.205	5287	.225
4544	.006	4694	.014	4837	0.	4997	.087	5140	.180	5290	.190
4548	.014	4697	.030	4840	.010	5000	.078	5143	.136	5294	.163
4551	.009	4701	.042	4844	.007	5003	.063	5147	.132	5297	.143
4555	0.	4704	.041	4847	.005	5006	.075	5151	.106	5300	.138
4559	0.	4707	.035	4851	.019	5009	.074	5154	.110	5303	.125
4562	0.	4710	.024	4854	.012	5012	.094	5158	.124	5306	.108
4566	0.	4713	.033	4858	.024	5015	.103	5161	.170	5309	.089
4570	0.	4716	.014	4862	.055	5018	.131	5165	.173	5312	.083
4573	0.	4719	.024	4865	.076	5021	.124	5169	.188	5315	.083
4577	.011	4722	.033	4869	.147	5024	.101	5173	.160	5318	.094
4581	.007	4725	.028	4873	.181	5027	.125	5176	.135	5321	.121
4584	.011	4728	.027	4876	.162	5030	.076	5180	.096	5324	.176
4588	.008	4731	.014	4880	.098	5034	.088	5183	.115	5327	.302
4591	.018	4734	.025	4884	.108	5037	.080	5187	.120	5330	.441
4594	.014	4737	.018	4887	.064	5040	.090	5190	.112	5333	.576
4598	.001	4741	.011	4891	.085	5044	.071	5194	.100	5337	.638
4601	0.	4744	.020	4894	.086	5047	.078	5197	.102	5340	.558
4604	.007	4747	.000	4897	.061	5051	.077	5200	.098	5343	.503
4607	0.	4751	0.	4900	.065	5054	.127	5203	.106	5347	.385
4610	0.	4755	.012	4903	.059	5058	.179	5206	.109	5350	.351
4613	.002	4758	.005	4906	.046	5062	.243	5209	.137	5354	.301
4616	0.	4762	.001	4910	.037	5065	.271	5212	.193	5358	.334

5361	.279	5469	.303	5587	.155	5694	.732	5800	.147	5906	.253
5365	.297	5472	.284	5590	.157	5697	.773	5803	.129	5909	.301
5369	.264	5487	.128	5594	.129	5700	.749	5806	.098	5912	.271
5372	.214	5490	.157	5597	.102	5703	.648	5809	.118	5915	.244
5376	.225	5493	.145	5600	.119	5706	.565	5812	.120	5918	.259
5380	.215	5497	.203	5603	.112	5709	.500	5815	.229	5921	.231
5383	.277	5500	.323	5606	.105	5712	.447	5818	.371	5924	.216
5387	.360	5503	.505	5609	.110	5715	.407	5821	.676	5927	.212
5390	.411	5506	.701	5612	.096	5718	.359	5824	1.075	5930	.162
5393	.458	5509	.827	5615	.071	5721	.345	5827	1.343	5934	.175
5397	.427	5512	.910	5618	.129	5724	.309	5830	1.560	5937	.197
5400	.389	5515	.868	5621	.186	5727	.295	5834	1.481	5940	.148
5403	.331	5518	.719	5624	.289	5730	.246	5837	1.279	5944	.229
5406	.303	5521	.667	5627	.483	5733	.224	5840	1.105	5947	.337
5409	.254	5524	.581	5630	.752	5737	.175	5844	.897	5951	.438
5412	.229	5527	.482	5633	.984	5740	.161	5847	.754	5954	.462
5415	.226	5530	.424	5637	.950	5743	.173	5851	.635	5958	.449
5418	.183	5533	.415	5640	.925	5747	.206	5854	.526	5962	.395
5421	.166	5537	.369	5643	.849	5751	.262	5858	.464	5965	.396
5424	.145	5540	.355	5647	.752	5754	.354	5862	.401	5969	.323
5427	.132	5543	.361	5650	.650	5758	.425	5865	.414	5973	.277
5430	.097	5547	.353	5654	.622	5761	.413	5869	.413	5976	.194
5433	.098	5550	.316	5658	.573	5765	.396	5873	.458	5980	.249
5437	.106	5554	.303	5661	.472	5769	.350	5876	.437	5984	.181
5440	.167	5558	.259	5665	.419	5773	.304	5880	.449	5987	.165
5443	.279	5561	.264	5669	.385	5776	.245	5883	.502	5990	.215
5447	.413	5565	.261	5673	.315	5780	.217	5887	.550	5994	.177
5450	.528	5569	.270	5676	.261	5783	.197	5890	.485	5997	.238
5454	.522	5572	.267	5680	.258	5787	.198	5894	.467	6000	.266
5458	.495	5576	.231	5683	.310	5790	.173	5897	.509	6003	.259
5461	.386	5580	.180	5687	.422	5794	.158	5900	.438		
5465	.330	5583	.160	5690	.587	5797	.141	5903	.356		

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4300	0.	4528	.003	4822	.136	5121	1.664	5421	.921	5715	2.067
4305	0.	4534	.002	4828	.113	5127	1.363	5427	.813	5721	1.748
4309	0.	4541	.002	4834	.086	5134	1.131	5433	.700	5727	1.467
4314	0.	4548	.035	4840	.086	5140	.952	5440	.886	5733	1.316
4318	0.	4555	.021	4847	.083	5147	.742	5447	1.871	5740	1.173
4323	0.	4562	.016	4854	.074	5154	.611	5454	2.181	5747	1.237
4327	0.	4570	.014	4862	.277	5161	.811	5461	1.734	5754	1.603
4332	0.	4577	0.	4869	.699	5169	.987	5469	1.320	5761	1.619
4336	0.	4584	0.	4876	.827	5176	.803	5476	1.046	5769	1.329
4341	0.	4591	.001	4884	.584	5183	.640	5483	.867	5776	1.111
4346	0.	4598	.006	4891	.457	5190	.559	5490	.721	5783	.958
4352	0.	4604	.002	4897	.370	5197	.524	5497	.942	5790	.842
4357	0.	4610	.007	4903	.282	5209	.642	5503	2.466	5797	.712
4363	0.	4616	.047	4910	.252	5215	1.244	5509	3.909	5809	.667
4368	0.	4622	.096	4915	.233	5221	2.499	5515	4.089	5815	1.160
4374	0.	4628	.078	4921	.220	5227	2.706	5521	3.181	5821	3.167
4379	0.	4634	.063	4927	.257	5233	2.263	5527	2.484	5827	6.237
4385	0.	4641	.036	4940	.166	5240	1.742	5533	2.185	5834	6.727
4390	0.	4648	.042	4947	.172	5247	1.371	5540	1.768	5840	5.016
4395	0.	4655	.026	4954	.386	5254	1.011	5547	1.607	5847	3.904
4400	0.	4662	.020	4962	.927	5261	.839	5554	1.389	5854	2.953
4404	0.	4669	.016	4969	1.062	5269	.850	5561	1.269	5862	2.363
4409	0.	4677	.027	4976	.922	5276	1.038	5569	1.279	5869	2.069
4413	0.	4684	.014	4983	.721	5283	1.100	5576	1.071	5876	2.087
4418	0.	4691	.062	4990	.554	5290	.935	5583	.947	5883	2.356
4422	0.	4697	.183	4997	.470	5297	.800	5590	.755	5890	2.423
4427	0.	4704	.254	5003	.394	5303	.674	5597	.715	5897	2.139
4431	0.	4710	.204	5009	.446	5309	.552	5603	.590	5903	1.889
4436	0.	4716	.151	5015	.657	5315	.456	5609	.480	5909	1.505
4441	0.	4722	.111	5021	.672	5321	.621	5615	.484	5915	1.336
4446	0.	4728	.081	5027	.609	5327	1.489	5621	.897	5921	1.138
4452	0.	4734	.078	5034	.477	5333	2.747	5627	2.570	5927	1.073
4457	0.	4741	.056	5040	.402	5340	2.760	5633	4.377	5940	.986
4462	0.	4747	.054	5047	.394	5347	2.136	5640	4.231	5947	1.668
4468	0.	4755	.031	5054	.615	5354	1.712	5647	3.470	5954	2.417
4470	0.	4762	.032	5062	1.154	5361	1.499	5654	2.825	5962	2.130
4477	0.	4769	.054	5069	1.235	5369	1.240	5661	2.106	5969	1.578
4484	0.	4777	.262	5076	.973	5376	1.095	5669	1.723	5976	1.342
4491	.017	4784	.513	5083	.769	5383	1.499	5676	1.359	5984	1.127
4498	.002	4791	.444	5090	.606	5390	2.208	5683	1.619	5990	.988
4504	0.	4797	.323	5097	.469	5397	2.141	5690	2.983	5997	1.113
4510	.005	4804	.243	5103	.439	5403	1.685	5697	3.832	6003	1.041
4516	0.	4810	.198	5109	.738	5409	1.379	5703	3.167	6009	.952
4522	.001	4816	.188	5115	1.350	5415	1.184	5709	2.657	6015	.903

6021	1.206	6222	.854	6422	.474	6623	1.306	6829	2.462	7030	.857
6027	3.873	6228	1.257	6428	.458	6629	1.227	6836	1.999	7036	.732
6034	7.862	6234	1.461	6434	.388	6635	.958	6842	1.895	7043	.564
6040	8.137	6241	1.918	6441	.480	6642	.799	6849	1.812	7050	.515
6047	5.882	6248	5.400	6448	.666	6649	.647	6856	1.488	7057	.650
6054	4.581	6255	8.350	6455	1.050	6656	.546	6864	1.311	7064	1.765
6062	3.606	6262	6.899	6463	1.010	6663	.492	6871	1.954	7072	3.144
6069	2.846	6270	5.198	6470	.946	6671	.519	6879	2.733	7079	2.905
6077	2.348	6277	4.184	6477	2.522	6678	.483	6886	2.265	7086	2.384
6084	2.124	6284	3.212	6485	5.527	6685	.486	6893	1.846	7093	1.915
6091	1.780	6291	2.682	6491	5.842	6692	.464	6899	1.476	7100	1.578
6097	1.650	6298	2.142	6498	4.734	6699	.457	6905	1.393	7106	1.508
6104	1.403	6304	1.804	6504	3.676	6705	.379	6912	1.103	7112	1.310
6110	1.196	6310	1.882	6510	3.007	6711	.322	6917	1.018	7118	1.135
6116	1.036	6316	2.569	6516	2.615	6723	.798	6923	.879	7124	.953
6122	.992	6322	2.815	6522	2.571	6729	2.402	6930	.784	7130	.980
6128	.983	6328	2.551	6528	2.323	6735	3.572	6936	.688	7137	1.437
6134	.978	6334	2.047	6535	1.913	6742	3.141	6943	.647	7143	2.737
6141	.873	6341	1.657	6541	1.914	6749	2.459	6950	.733	7150	3.140
6147	.898	6348	1.331	6548	3.266	6756	1.999	6957	.732	7157	2.594
6155	1.189	6355	1.140	6555	4.529	6763	1.783	6964	.617	7165	2.120
6162	1.825	6362	1.080	6563	4.047	6771	1.624	6972	.477	7172	1.661
6169	1.728	6370	1.015	6570	3.219	6778	1.497	6979	.429	7180	1.504
6177	1.381	6377	.895	6578	2.524	6785	1.217	6986	.485	7187	1.315
6184	1.104	6384	.853	6585	2.079	6792	1.366	6993	1.236	7194	1.119
6191	.949	6391	.756	6592	1.786	6799	2.705	6999	1.890	7200	.866
6197	.921	6398	.728	6598	1.466	6805	4.343	7006	1.635	7207	.851
6204	.774	6404	.562	6605	1.348	6811	4.424	7012	1.442		
6210	.722	6410	.528	6611	1.115	6817	3.625	7018	1.149		
6216	.664	6416	.441	6617	1.090	6823	2.998	7024	1.079		

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4300	0.	4504	.003	4648	.002	4797	.049	4940	.032	5090	.138
4305	0.	4507	0.	4651	0.	4800	.043	4944	.028	5094	.119
4309	0.	4510	0.	4655	.008	4804	.049	4947	.034	5103	.119
4314	0.	4513	.003	4658	.004	4807	.049	4951	.056	5106	.127
4318	0.	4516	.007	4662	.007	4810	.042	4954	.070	5109	.163
4323	0.	4519	.002	4666	.005	4813	.035	4958	.121	5112	.266
4327	0.	4522	0.	4669	.014	4816	.035	4962	.186	5115	.249
4332	0.	4525	.007	4673	.023	4819	.026	4965	.203	5118	.307
4336	0.	4528	0.	4677	.011	4822	.028	4969	.197	5121	.329
4341	0.	4531	0.	4680	.002	4825	.021	4973	.178	5124	.296
4346	0.	4534	0.	4684	.002	4828	.034	4976	.167	5127	.265
4352	0.	4538	0.	4687	.005	4831	.023	4980	.156	5130	.256
4357	0.	4541	0.	4691	.014	4834	.018	4983	.142	5134	.257
4363	0.	4544	.001	4694	.022	4837	.011	4987	.124	5137	.213
4368	0.	4548	.004	4697	.046	4840	.007	4990	.123	5140	.196
4374	0.	4551	.004	4701	.037	4844	.023	4994	.123	5143	.185
4379	0.	4555	.003	4704	.048	4847	.016	4997	.083	5147	.142
4385	0.	4559	0.	4707	.043	4851	.018	5000	.075	5151	.145
4390	0.	4562	0.	4710	.042	4854	.017	5003	.086	5154	.127
4395	0.	4566	.006	4713	.033	4858	.016	5006	.076	5158	.140
4400	0.	4570	0.	4716	.024	4862	.053	5009	.097	5161	.139
4404	0.	4573	.008	4719	.030	4865	.082	5012	.117	5165	.168
4409	0.	4577	0.	4722	.021	4869	.134	5015	.127	5169	.219
4413	0.	4581	0.	4725	.016	4873	.144	5018	.153	5173	.215
4418	0.	4584	0.	4728	.031	4876	.154	5021	.142	5176	.168
4422	0.	4588	.003	4731	.015	4880	.127	5024	.135	5180	.156
4427	0.	4591	0.	4734	0.	4884	.110	5027	.102	5183	.126
4431	0.	4594	0.	4737	.011	4887	.087	5030	.088	5187	.132
4436	0.	4598	.005	4741	0.	4891	.079	5034	.092	5190	.131
4441	0.	4601	0.	4744	.011	4894	.084	5037	.097	5194	.140
4446	0.	4604	0.	4747	.014	4897	.090	5040	.090	5197	.146
4452	0.	4607	0.	4751	.023	4900	.067	5044	.090	5200	.151
4457	0.	4610	.003	4755	.005	4903	.057	5047	.062	5203	.162
4462	0.	4613	0.	4758	0.	4906	.062	5051	.104	5206	.167
4468	0.	4616	.003	4762	.001	4910	.056	5054	.124	5209	.159
4473	0.	4619	.017	4766	.009	4912	.056	5058	.175	5212	.181
4477	.001	4622	.017	4769	.011	4915	.044	5062	.199	5215	.279
4481	0.	4625	.017	4773	.021	4918	.049	5065	.235	5218	.362
4484	0.	4628	.020	4777	.049	4921	.057	5069	.243	5221	.444
4488	.000	4631	.006	4780	.080	4924	.060	5073	.231	5224	.488
4491	.009	4634	.020	4784	.072	4927	.051	5076	.196	5227	.482
4495	0.	4637	.014	4787	.095	4931	.041	5080	.184	5230	.468
4498	.002	4641	.010	4791	.085	4934	.042	5083	.144	5233	.431
4501	.008	4644	0.	4794	.040	4937	.038	5087	.124	5237	.377

5240	.334	5390	.425	5533	.367	5683	.299	5827	.910	5976	.184
5243	.275	5393	.447	5537	.364	5687	.382	5830	1.005	5980	.230
5247	.245	5397	.390	5540	.342	5690	.509	5834	.983	5984	.211
5250	.220	5400	.382	5543	.389	5694	.555	5837	.957	5987	.179
5254	.214	5403	.321	5547	.397	5697	.630	5840	.769	5990	.235
5258	.189	5406	.304	5550	.376	5700	.629	5844	.646	5994	.238
5261	.184	5409	.273	5554	.408	5703	.553	5847	.612	5997	.283
5265	.154	5412	.257	5558	.321	5706	.511	5851	.508	6000	.265
5269	.182	5415	.216	5561	.304	5709	.463	5854	.462	6003	.283
5272	.211	5418	.204	5565	.300	5712	.413	5858	.405	6006	.308
5276	.189	5421	.193	5569	.283	5715	.349	5862	.400	6009	.217
5280	.260	5424	.145	5572	.278	5718	.296	5865	.374	6012	.209
5283	.251	5427	.148	5576	.239	5721	.299	5869	.418	6015	.219
5287	.250	5430	.139	5580	.219	5724	.290	5873	.442	6018	.228
5290	.232	5433	.112	5583	.233	5727	.247	5876	.437	6021	.228
5294	.208	5437	.134	5587	.180	5730	.224	5880	.465	6024	.363
5297	.208	5440	.167	5590	.156	5733	.220	5883	.525	6027	.566
5300	.193	5443	.273	5594	.160	5737	.211	5887	.565	6031	.809
5303	.159	5447	.345	5597	.143	5740	.217	5890	.522	6034	1.176
5306	.136	5450	.435	5600	.163	5743	.224	5894	.493	6037	1.247
5309	.144	5454	.453	5603	.131	5747	.239	5897	.447	6040	1.195
5312	.111	5458	.426	5606	.119	5751	.323	5900	.357	6044	1.062
5315	.106	5461	.353	5609	.095	5754	.350	5903	.387	6047	.911
5318	.088	5465	.328	5612	.095	5758	.394	5906	.317	6051	.794
5321	.125	5469	.293	5615	.077	5761	.405	5909	.279	6054	.754
5324	.163	5472	.255	5618	.104	5765	.359	5912	.264	6058	.667
5327	.255	5476	.243	5621	.157	5769	.341	5915	.213	6062	.562
5330	.397	5480	.188	5624	.217	5773	.320	5918	.223	6066	.512
5333	.480	5483	.192	5627	.394	5776	.304	5921	.208	6069	.519
5337	.485	5487	.186	5630	.555	5780	.269	5924	.191	6073	.434
5340	.478	5490	.155	5633	.650	5783	.219	5927	.210	6077	.385
5343	.423	5493	.131	5637	.742	5787	.207	5930	.227	6080	.363
5347	.349	5497	.178	5640	.689	5790	.165	5934	.217	6084	.336
5350	.335	5500	.280	5643	.591	5794	.198	5937	.157	6087	.298
5354	.350	5503	.408	5647	.630	5797	.180	5940	.193	6091	.350
5358	.346	5506	.546	5650	.586	5800	.149	5944	.236	6094	.346
5361	.358	5509	.644	5654	.578	5803	.130	5947	.284	6097	.292
5365	.315	5512	.645	5658	.500	5806	.119	5951	.348	6100	.246
5369	.316	5515	.649	5661	.442	5809	.113	5954	.422	6104	.250
5372	.278	5518	.574	5665	.425	5812	.144	5958	.406	6107	.265
5376	.258	5521	.504	5669	.368	5815	.178	5962	.381	6110	.242
5380	.247	5524	.485	5673	.341	5818	.266	5965	.346	6113	.213
5383	.297	5527	.425	5676	.267	5821	.477	5969	.317	6116	.203
5387	.341	5530	.371	5680	.297	5824	.700	5973	.239	6119	.190

6122	.168	6270	.855	6416	.121	6563	.705	6717	.094	6864	.195
6125	.200	6273	.770	6419	.116	6567	.594	6720	.079	6867	.298
6128	.226	6277	.698	6422	.104	6570	.515	6723	.132	6871	.374
6131	.227	6281	.616	6425	.108	6574	.536	6726	.153	6875	.439
6134	.231	6284	.527	6428	.118	6578	.503	6729	.312	6879	.454
6137	.252	6288	.463	6431	.112	6581	.424	6732	.409	6882	.553
6141	.229	6291	.404	6434	.089	6585	.335	6735	.497	6886	.412
6144	.195	6294	.450	6438	.080	6588	.326	6739	.514	6889	.340
6147	.202	6298	.358	6441	.107	6592	.318	6742	.436	6893	.345
6151	.214	6301	.317	6445	.106	6595	.255	6745	.377	6896	.291
6155	.224	6304	.344	6448	.153	6598	.305	6749	.380	6899	.272
6158	.251	6307	.350	6452	.200	6601	.231	6752	.326	6902	.273
6162	.300	6310	.343	6455	.184	6605	.214	6756	.305	6905	.193
6166	.339	6313	.348	6459	.201	6608	.227	6760	.284	6909	.229
6169	.358	6316	.420	6463	.155	6611	.222	6763	.297	6912	.211
6173	.251	6319	.456	6466	.151	6614	.225	6767	.245	6915	.249
6177	.257	6322	.489	6470	.117	6617	.249	6771	.243	6917	.208
6180	.227	6325	.473	6474	.187	6620	.166	6775	.239	6920	.168
6184	.196	6328	.425	6477	.337	6623	.184	6778	.240	6923	.117
6187	.240	6331	.386	6481	.516	6626	.210	6782	.270	6926	.125
6191	.200	6334	.347	6485	.701	6629	.183	6785	.199	6930	.088
6194	.215	6338	.352	6488	.780	6632	.129	6789	.193	6933	.114
6197	.129	6341	.328	6491	.866	6635	.179	6792	.183	6936	.075
6201	.133	6344	.254	6495	.762	6638	.208	6796	.254	6939	.140
6204	.151	6348	.224	6498	.680	6642	.176	6799	.354	6943	.088
6207	.106	6351	.190	6501	.601	6645	.123	6802	.576	6946	.062
6210	.142	6355	.219	6504	.535	6649	.116	6805	.676	6950	.093
6213	.120	6359	.206	6507	.520	6652	.105	6808	.738	6953	.155
6216	.110	6362	.240	6510	.488	6656	.087	6811	.727	6957	.146
6219	.148	6366	.260	6513	.495	6659	.085	6814	.634	6960	.175
6222	.205	6370	.258	6516	.444	6663	.094	6817	.548	6964	.146
6225	.219	6373	.232	6519	.522	6667	.112	6820	.478	6968	.148
6228	.250	6377	.255	6522	.503	6671	.088	6823	.473	6972	.130
6231	.282	6381	.200	6525	.477	6674	.114	6826	.436	6975	.128
6234	.220	6384	.195	6528	.484	6678	.122	6829	.426	6979	.082
6237	.261	6388	.143	6532	.408	6681	.138	6832	.347	6982	.128
6241	.357	6391	.151	6535	.388	6685	.152	6836	.327	6986	.140
6244	.505	6395	.163	6538	.390	6689	.109	6839	.367	6989	.115
6248	.785	6398	.145	6541	.343	6692	.097	6842	.320	6993	.194
6251	1.020	6401	.123	6545	.421	6702	.087	6846	.311	6996	.225
6255	1.097	6404	.120	6548	.565	6705	.064	6849	.276	6999	.206
6258	1.165	6407	.101	6552	.700	6708	.097	6853	.266	7003	.272
6262	1.134	6410	.113	6555	.748	6711	.067	6856	.237	7006	.291
6266	1.011	6413	.122	6559	.746	6714	.090	6860	.282	7009	.235

7012	.240	7043	.133	7079	.472	7118	.183	7150	.573	7187	.223
7015	.141	7046	.115	7083	.416	7121	.143	7154	.569	7190	.175
7018	.144	7050	.125	7086	.359	7124	.179	7157	.453	7194	.147
7021	.131	7053	.085	7090	.278	7127	.204	7161	.313	7197	.188
7024	.126	7057	.099	7093	.273	7130	.162	7165	.291	7200	.158
7027	.156	7061	.156	7097	.277	7133	.294	7169	.286	7203	.144
7030	.160	7064	.319	7100	.229	7137	.222	7172	.332	7207	.170
7033	.138	7068	.397	7103	.191	7140	.342	7176	.204		
7036	.091	7072	.503	7112	.186	7143	.475	7180	.244		
7040	.173	7076	.623	7115	.199	7147	.476	7183	.215		

SPECTRUM II-113-2

4305	.006	4516	.003	4662	.002	4810	.011	4954	.033	5103	.043
4311	.002	4519	.003	4666	.004	4813	.020	4958	.038	5106	.059
4317	.004	4522	0.	4669	0.	4816	.016	4962	.071	5109	.053
4323	.003	4525	.009	4673	.006	4819	.005	4965	.066	5112	.072
4329	0.	4528	.010	4677	0.	4822	0.	4969	.079	5115	.099
4335	.014	4531	.002	4680	.007	4825	.019	4973	.081	5118	.126
4341	.006	4534	0.	4684	.002	4828	.019	4976	.061	5121	.122
4348	0.	4538	0.	4687	0.	4831	.024	4980	.068	5124	.100
4355	0.	4541	0.	4691	.004	4834	.006	4983	.043	5127	.097
4363	.009	4544	.001	4694	0.	4837	0.	4987	.047	5130	.102
4370	0.	4548	.008	4697	0.	4840	0.	4990	.034	5134	.106
4377	0.	4551	0.	4701	.003	4844	.014	4994	.041	5137	.091
4385	.012	4555	.006	4704	.009	4847	.016	4997	.042	5140	.101
4391	.012	4559	0.	4707	0.	4851	.012	5000	.051	5143	.065
4398	.008	4562	0.	4710	.002	4854	.001	5003	.037	5147	.058
4404	0.	4566	0.	4713	.018	4858	.005	5006	.026	5151	.069
4410	.009	4570	0.	4716	.019	4862	.014	5009	.041	5154	.071
4416	.005	4573	0.	4719	.019	4865	.033	5012	.030	5158	.069
4422	0.	4577	0.	4722	.014	4869	.033	5015	.059	5161	.062
4428	0.	4581	.004	4725	.019	4873	.041	5018	.067	5165	.067
4435	0.	4584	.005	4728	.010	4876	.056	5021	.031	5169	.066
4438	0.	4588	.001	4731	.024	4880	.037	5024	.036	5173	.073
4441	0.	4591	0.	4734	.003	4884	.022	5027	.021	5176	.069
4445	0.	4594	0.	4737	.008	4887	.034	5030	.056	5180	.053
4448	.000	4598	.015	4741	0.	4891	.032	5034	.039	5183	.053
4452	.015	4601	0.	4744	0.	4894	.026	5037	.039	5187	.053
4455	0.	4604	.004	4747	.000	4897	.017	5040	.026	5190	.065
4459	0.	4607	0.	4751	.018	4900	.033	5044	.036	5194	.057
4462	0.	4610	.009	4755	.008	4903	.025	5047	.043	5197	.075
4466	0.	4613	0.	4758	.006	4906	.028	5051	.031	5200	.078
4470	0.	4616	.003	4762	0.	4910	.034	5054	.051	5203	.083
4473	.007	4619	0.	4766	.008	4912	.027	5058	.072	5206	.083
4477	0.	4622	0.	4769	.008	4915	.026	5062	.081	5209	.083
4481	0.	4625	0.	4773	.007	4918	.013	5065	.071	5212	.092
4484	0.	4628	.003	4777	.016	4921	.030	5069	.087	5215	.098
4488	.004	4631	.008	4780	.011	4924	.018	5073	.081	5218	.147
4491	0.	4634	.007	4784	.043	4927	.015	5076	.091	5221	.145
4495	.001	4637	.005	4787	.050	4931	.020	5080	.071	5224	.165
4498	0.	4641	.003	4791	.005	4934	.024	5083	.043	5227	.157
4501	.004	4644	0.	4794	.010	4937	.023	5087	.044	5230	.164
4504	.005	4648	.002	4797	.008	4940	0.	5090	.045	5233	.174
4507	0.	4651	.003	4800	.006	4944	.024	5094	.055	5237	.143
4510	.001	4655	.009	4804	0.	4947	.024	5097	.025	5240	.111
4513	.026	4658	.008	4807	.015	4951	.033	5100	.019	5243	.105

5247	.093	5397	.146	5540	.151	5690	.164	5834	.292	5984	.066
5250	.094	5400	.138	5543	.169	5694	.212	5837	.281	5987	.070
5254	.071	5403	.121	5547	.160	5697	.219	5840	.224	5990	.088
5258	.071	5406	.085	5550	.170	5700	.209	5844	.205	5994	.127
5261	.062	5409	.061	5554	.159	5703	.197	5847	.214	5997	.123
5265	.059	5412	.078	5558	.157	5706	.182	5851	.195	6000	.112
5269	.068	5415	.075	5561	.159	5709	.134	5854	.142	6003	.137
5272	.083	5418	.075	5565	.107	5712	.125	5858	.147	6006	.108
5276	.093	5421	.073	5569	.119	5715	.139	5862	.160	6009	.109
5280	.112	5424	.055	5572	.106	5718	.119	5865	.144	6012	.104
5283	.099	5427	.057	5576	.101	5721	.107	5869	.138	6015	.094
5287	.113	5430	.054	5580	.094	5724	.076	5873	.161	6018	.107
5290	.086	5433	.056	5583	.077	5727	.093	5876	.202	6021	.091
5294	.088	5437	.059	5587	.069	5730	.080	5880	.213	6024	.128
5297	.098	5440	.068	5590	.056	5733	.082	5883	.220	6027	.179
5300	.077	5443	.095	5594	.025	5737	.119	5887	.237	6031	.255
5303	.080	5447	.133	5597	.036	5740	.092	5890	.202	6034	.342
5306	.069	5450	.165	5600	.045	5743	.081	5894	.208	6037	.359
5309	.073	5454	.181	5603	.043	5747	.073	5897	.159	6040	.307
5312	.066	5458	.190	5606	.048	5751	.099	5900	.148	6044	.292
5315	.046	5461	.158	5609	.042	5754	.136	5903	.150	6047	.286
5318	.057	5465	.139	5612	.059	5758	.162	5906	.125	6051	.224
5321	.058	5469	.122	5615	.029	5761	.205	5909	.091	6054	.217
5324	.080	5472	.103	5618	.052	5765	.215	5912	.077	6058	.223
5327	.090	5476	.071	5621	.060	5769	.176	5915	.066	6062	.222
5330	.125	5480	.059	5624	.076	5773	.140	5918	.063	6066	.178
5333	.157	5483	.080	5627	.130	5776	.115	5921	.083	6069	.150
5337	.168	5487	.080	5630	.182	5780	.106	5924	.098	6073	.183
5340	.172	5490	.066	5633	.210	5783	.089	5927	.073	6077	.148
5343	.130	5493	.050	5637	.235	5787	.069	5930	.096	6080	.115
5347	.120	5497	.092	5640	.203	5790	.086	5934	.072	6084	.112
5350	.112	5500	.096	5643	.241	5794	.089	5937	.076	6087	.134
5354	.118	5503	.143	5647	.223	5797	.091	5940	.074	6091	.117
5358	.165	5506	.182	5650	.264	5800	.066	5944	.084	6094	.103
5361	.147	5509	.199	5654	.247	5803	.058	5947	.101	6097	.112
5365	.133	5512	.187	5658	.217	5806	.051	5951	.142	6100	.118
5369	.123	5515	.233	5661	.210	5809	.069	5954	.152	6104	.098
5372	.112	5518	.188	5665	.167	5812	.074	5958	.141	6107	.109
5376	.118	5521	.187	5669	.158	5815	.076	5962	.111	6110	.092
5380	.124	5524	.159	5673	.160	5818	.124	5965	.109	6113	.045
5383	.112	5527	.134	5676	.127	5821	.127	5969	.111	6116	.068
5387	.145	5530	.107	5680	.104	5824	.196	5973	.101	6119	.081
5390	.135	5533	.137	5683	.115	5827	.272	5976	.118	6122	.084
5393	.151	5537	.133	5687	.138	5830	.283	5980	.060	6125	.079

6128	.076	6277	.256	6422	.034	6570	.179	6717	.034	6864	.156
6131	.067	6281	.231	6425	.046	6574	.151	6720	.080	6867	.068
6134	.121	6284	.192	6428	.043	6578	.142	6723	.102	6871	.159
6137	.121	6288	.179	6431	.027	6581	.105	6726	.066	6875	.074
6141	.143	6291	.161	6434	.007	6585	.100	6729	.114	6879	.135
6144	.112	6294	.139	6438	.043	6588	.104	6732	.103	6882	.117
6147	.151	6298	.138	6441	.045	6592	.103	6735	.156	6886	.084
6151	.103	6301	.124	6445	.058	6595	.088	6739	.155	6889	.092
6155	.103	6304	.138	6448	.051	6598	.122	6742	.137	6893	.113
6158	.125	6307	.101	6452	.111	6601	.098	6745	.150	6896	.093
6162	.125	6310	.128	6455	.037	6605	.037	6749	.131	6899	.093
6166	.111	6313	.150	6459	.066	6608	.055	6752	.100	6902	.107
6169	.086	6316	.175	6463	.065	6611	.064	6756	.089	6905	.077
6173	.080	6319	.139	6466	.051	6614	.027	6760	.102	6909	.103
6177	.086	6322	.160	6470	.056	6617	.105	6763	.121	6912	.069
6180	.099	6325	.168	6474	.058	6620	.063	6767	.054	6915	.082
6184	.121	6328	.163	6477	.109	6623	.075	6771	.066	6917	.051
6187	.114	6331	.135	6481	.178	6626	.066	6775	.045	6920	.056
6191	.080	6334	.115	6485	.263	6629	.080	6778	.075	6923	.040
6194	.109	6338	.114	6488	.203	6632	.036	6782	.086	6926	.041
6197	.064	6341	.057	6491	.167	6635	.083	6785	.110	6930	.054
6201	.061	6344	.098	6495	.209	6638	.094	6789	.111	6933	.036
6204	.068	6348	.101	6498	.164	6642	.055	6792	.068	6936	.065
6207	.046	6351	.088	6501	.163	6645	.049	6796	.126	6939	0.
6210	.034	6355	.109	6504	.175	6649	.056	6799	.139	6943	.036
6213	.027	6359	.096	6507	.126	6652	.040	6802	.157	6946	.031
6216	.049	6362	.057	6510	.132	6656	0.	6805	.201	6950	.040
6219	.058	6366	.069	6513	.123	6659	.013	6808	.232	6953	.081
6222	.081	6370	.107	6516	.152	6663	.025	6811	.214	6957	.095
6225	.076	6373	.109	6519	.177	6667	.040	6814	.184	6960	0.
6228	.131	6377	.091	6522	.217	6671	.016	6817	.178	6964	.075
6231	.160	6381	.066	6525	.164	6674	.046	6820	.156	6968	.032
6234	.115	6384	.117	6528	.135	6678	.076	6823	.098	6972	.035
6237	.106	6388	.092	6532	.191	6681	.042	6826	.134	6975	.053
6241	.110	6391	.077	6535	.156	6685	.056	6829	.119	6979	.034
6244	.187	6395	.057	6538	.176	6689	.075	6832	.118	6982	0.
6248	.244	6398	.047	6541	.113	6692	.050	6836	.076	6986	.045
6251	.316	6401	.048	6545	.136	6695	.051	6839	.081	6989	0.
6255	.362	6404	.058	6548	.179	6699	.033	6842	.099	6993	.085
6258	.371	6407	.061	6552	.201	6702	.035	6846	.101	6996	.081
6262	.327	6410	.038	6555	.220	6705	.040	6849	.107	6999	.040
6266	.297	6413	0.	6559	.234	6708	.025	6853	.105	7003	.094
6270	.293	6416	.031	6563	.210	6711	.020	6856	.062	7006	.099
6273	.273	6419	.081	6567	.218	6714	.043	6860	.100	7009	.063

7012	.110	7043	.056	7079	.113	7112	.077	7143	.208	7180	.097
7015	.048	7046	.073	7083	.041	7115	.165	7147	.167	7183	.074
7018	.007	7050	.017	7086	.116	7118	.042	7150	.192	7187	.041
7021	.023	7053	.050	7090	.125	7121	.064	7154	.138	7190	.012
7024	.070	7057	.073	7093	.090	7124	.079	7157	.192	7194	0.
7027	.011	7061	.047	7097	.084	7127	0.	7161	.116	7197	.036
7030	.020	7064	.103	7100	.026	7130	.057	7165	.148	7200	.093
7033	.060	7068	.133	7103	.098	7133	.149	7169	.078	7203	.082
7036	.084	7072	.160	7106	.062	7137	.127	7172	.125		
7040	.049	7076	.127	7109	.079	7140	.226	7176	.065		

APPENDIX B

COMPUTER PROGRAM LISTINGS

1. Program FCFACT calculates Franck-Condon overlap factors based on Morse potential functions. The format of the input deck, as well as the function of the subroutines, is described by the comment cards. The gamma functions used in the normalization factors for the wave functions are evaluated by subroutine GAMLOG[1] (not listed).

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[1] Subroutine GAMLOG, LRL Identification C3 BKY GAMLOG (FORTRAN), written by J. D. Lawrence, (February, 1965) and modified by D. H. Wilber, (November 1965).

```
      PROGRAM FCFACT(INPUT,OUTPUT,PUNCH)
      DIMENSION WE(2),WEXE(2),RE(2),PSI(2,20),SUM(20,20),SUM2(20,20),RMI
     1N(2),RMAX(2),LABEL(20),ALPHA1(2),K1(2),GAMLG1(2),SUMR(20,20),RCENT
     2(20,20)
      REAL MUA,K1
      INTEGER VMAXU,VMAXL,VM
      COMMON/RNGPSI/ALPHA1,K1,RE
      COMMON/PSIG/GAMLG1
    1 FORMAT (8F10.3)
    2 FORMAT (10I5)
    3 FORMAT (1H1,40X,*OVERLAP INTEGRALS FOR UPPER ELECTRONIC STATE*//)
    4 FORMAT (1H1,40X,*OVERLAP INTEGRALS FOR LOWER ELECTRONIC STATE*//)
    5 FORMAT(6H V$  =I4,10X,7H V$$  =I4,10X,*OVERLAP INTEGRAL  =*,E12.3)
    6 FORMAT (1H1,40X,*FRANCK-CONDON OVERLAP INTEGRALS*)
    7 FORMAT (1H1,44X,*R - CENTROIDS (ANGSTROMS)*)
    8 FORMAT (F10.2,(10E12.3))
  151 FORMAT (2H0*/3H  */8H   * V$$,I9,9I12)
  152 FORMAT (4X,1H*/6H  V$ */6X,1H*/7X,1H*)
  153 FORMAT (1H0,I3,5X,10E12.3)
  154 FORMAT (1H1,20X,*WAVE FUNCTIONS FOR UPPER ELECTRONIC STATE*//)
  155 FORMAT (1H1,20X,*WAVE FUNCTIONS FOR LOWER ELECTRONIC STATE*//)
  156 FORMAT (1H1,46X,2HWE,11X,4HWEXE,13X,2HRE,12X,2HMU)
  157 FORMAT (1H0,13X,*UPPER ELECTRONIC STATE*,F15.3,F15.5,F15.4,F15.5)
  158 FORMAT (1H0,13X,*LOWER ELECTRONIC STATE*,F15.3,F15.5,F15.4)
 1000 READ 1, WE(1),WEXE(1),RE(1),WE(2),WEXE(2),RE(2),MUA
      IF (WE(1).EQ.0.) STOP
      READ 2, VMAXU,VMAXL,ITEST,IWAVEF,IRCENT
      PRINT 156
      PRINT 157,WE(1),WEXE(1),RE(1),MUA
      PRINT 158,WE(2),WEXE(2),RE(2)
      DO 9 NA=1,2
      K1(NA)=WE(NA)/WEXE(NA)
      ALPHA1(NA)=0.2435586*SQRT(MUA*WEXE(NA))
    9 GAMLG1(NA)=GAMLOG((K1(NA)-1.),1)
      CALL RANGE(VMAXU,VMAXL,RMIN,RMAX)
C.....IF ITEST EQUALS 1, THE INTEGRAL OF PSI(V1)*PSI(V2) WILL BE CALCULATED
C.....FOR ALL VALUES OF V FOR EACH ELECTRONIC STATE.
C.....IF IWAVEF EQUALS 1, THE VALUES OF THE WAVE FUNCTIONS PSI(V,R) WILL BE
C.....TABULATED AS A FUNCTION OF THE INTERNUCLEAR DISTANCE R.
C.....IF IRCENT EQUALS 1, THE INTEGRAL OF PSI(V1)*PSI(V2)*R (THE R-CENTROID)
C.....WILL BE CALCULATED FOR ALL VALUES OF V FOR EACH ELECTRONIC STATE.
      IF (ITEST.NE.1) GO TO 100
C.....TEST TO SEE WHETHER WAVE FUNCTIONS ARE ORTHO-NORMAL FOR EACH
C.....ELECTRONIC STATE
      DO 90 N=1,2
      IF (N.EQ.1) VM=VMAXU
      IF (N.EQ.2) VM=VMAXL
      DO 10 I=0,VM
      DO 10 J=0,VM
      SUM(I+1,J+1)=0.
   10 CONTINUE
      IF (VM.GE.9) 11,12
   11 IVM=9
      GO TO 13
   12 IVM=VM
   13 CONTINUE
      IF (N.EQ.1.AND.IWAVEF.EQ.1) PRINT 154
      IF (N.EQ.2.AND.IWAVEF.EQ.1) PRINT 155
      IRMIN=RMIN(N)*100
```

```
      IRMAX=RMAX(N)*100
      DO 20 IR=IRMIN,IRMAX
      CALL PHI(VM,N,IR*.01,PSI)
      IF (IWAVEF.NE.1) GO TO 15
      R1=IR/100.
      PRINT 8,R1,(PSI(N,I+1),I=0,IVM)
   15 DO 20 II=0,VM
      DO 20 JJ=0,VM
      SUM(II+1,JJ+1)=SUM(II+1,JJ+1)+PSI(N,II+1)*PSI(N,JJ+1)*.01
   20 CONTINUE
      IF (N.EQ.1) PRINT 3
      IF (N.EQ.2) PRINT 4
      DO 40 MK=1,20
   40 LABEL(MK)=MK-1
      IF (VM.LE.9) 50,65
   50 PRINT 151,(LABEL(NK+1),NK=0,VM)
      PRINT 152
      DO 60 MI=0,VM
   60 PRINT 153,MI,(SUM(MI+1,MJ+1),MJ=0,VM)
      GO TO 90
   65 PRINT 151,(LABEL(NK+1),NK=0,9)
      PRINT 152
      DO 70 MI=0,VM
   70 PRINT 153,MI,(SUM(MI+1,MJ+1),MJ=0,9)
      PRINT 151,(LABEL(NK+1),NK=10,VM)
      PRINT 152
      DO 80 MI=0,VM
   80 PRINT 153,MI,(SUM(MI+1,MJ+1),MJ=10,VM)
   90 CONTINUE
C.....THIS PART OF THE PROGRAM COMPUTES THE ACTUAL FRANCK-CONDON FACTORS.
  100 DO 110 I=0,VMAXU
      DO 110 J=0,VMAXL
      SUM(I+1,J+1)=0.
      SUMR(I+1,J+1)=0.
  110 CONTINUE
      IRMIN=AMIN1(RMIN(1),RMIN(2))*100
      IRMAX=AMAX1(RMAX(1),RMAX(2))*100
      DO 120 IR=IRMIN,IRMAX
      CALL PHI(VMAXU,1,IR*.01,PSI)
      CALL PHI(VMAXL,2,IR*.01,PSI)
      DO 120 II=0,VMAXU
      DO 120 JJ=0,VMAXL
      SUM(II+1,JJ+1)=SUM(II+1,JJ+1)+PSI(1,II+1)*PSI(2,JJ+1)*.01
      IF (IRCENT.NE.1) GO TO 120
      SUMR(II+1,JJ+1)=SUMR(II+1,JJ+1)+PSI(1,II+1)*PSI(2,JJ+1)*IR*.0001
  120 CONTINUE
      PRINT 6
      DO 130 MI=0,VMAXU
      DO 130 MJ=0,VMAXL
      SUM2(MI+1,MJ+1)=SUM(MI+1,MJ+1)**2
      PUNCH 159,MJ,MI,SUM2(MI+1,MJ+1)
  159 FORMAT (2I4,3X,E11.4)
  130 CONTINUE
      DO 140 MK=1,20
  140 LABEL(MK)=MK-1
      IF (VMAXL.LE.9) 150,165
  150 PRINT 151,(LABEL(NK+1),NK=0,VMAXL)
      PRINT 152
      DO 160 MI=0,VMAXU
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```
  160 PRINT 153,MI,(SUM2(MI+1,MJ+1),MJ=0,VMAXL)
      GO TO 200
  165 PRINT 151,(LABEL(NK+1),NK=0,9)
      PRINT 152
      DO 170 MI=0,VMAXU
  170 PRINT 153,MI,(SUM2(MI+1,MJ+1),MJ=0,9)
      PRINT 151,(LABEL(NK+1),NK=10,VMAXL)
      PRINT 152
      DO 180 MI=0,VMAXU
  180 PRINT 153,MI,(SUM2(MI+1,MJ+1),MJ=10,VMAXL)
  200 IF (IRCENT.NE.1) GO TO 300
      PRINT 7
      DO 230 MI=0,VMAXU
      DO 230 MJ=0,VMAXL
      RCENT(MI+1,MJ+1)=SUMR(MI+1,MJ+1)/SUM(MI+1,MJ+1)
  230 CONTINUE
      IF (VMAXL.LE.9) 250,265
  250 PRINT 151,(LABEL(NK+1),NK=0,VMAXL)
      PRINT 152
      DO 260 MI=0,VMAXU
  260 PRINT 153,MI,(RCENT(MI+1,MJ+1),MJ=0,VMAXL)
      GO TO 1000
  265 PRINT 151,(LABEL(NK+1),NK=0,9)
      PRINT 152
      DO 270 MI=0,VMAXU
  270 PRINT 153,MI,(RCENT(MI+1,MJ+1),MJ=0,9)
      PRINT 151,(LABEL(NK+1),NK=10,VMAXL)
      PRINT 152
      DO 280 MI=0,VMAXU
  280 PRINT 153,MI,(RCENT(MI+1,MJ+1),MJ=10,VMAXL)
  300 GO TO 1000
C.....PROGRAM IS SET TO RECYCLE. IN ORDER TO STOP PROGRAM, INSERT BLANK CARD
C.....AFTER LAST DATA DECK.
      END


      SUBROUTINE RANGE(VMAXU,VMAXL,RMIN,RMAX)
C.....THIS SUBROUTINE CALCULATES THE LIMITS OF R BETWEEN WHICH THE WAVE
C.....FUNCTION PSI(V,R) IS APPRECIABLE.
      INTEGER VMAXU,VMAXL
      REAL K1
      DIMENSION RMIN(2),RMAX(2),V(2)
      COMMON/RNGPSI/ALPHA1(2),K1(2),RE(2)
      V(1)=(VMAXU+.5)/K1(1)
      V(2)=(VMAXL+.5)/K1(2)
      DO 10 N=1,2
      RMIN(N)=RE(N)-.1-1/ALPHA1(N)*ALOG(1+2*SQRT(V(N)-V(N)**2))
      RMAX(N)=RE(N)+.2-1/ALPHA1(N)*ALOG(1-2*SQRT(V(N)-V(N)**2))
   10 CONTINUE
      RETURN
      END


      SUBROUTINE PHI(VMAX,STATE,R,PSI)
C  THIS SUBROUTINE CALCULATES THE VALUES OF PSI(V) FOR A GIVEN INTERNUCLEAR
C  DISTANCE R USING THE ASSOCIATED LAGUERRE POLUNOMIALS GENERATED BY
C  SUBROUTINE LAGUER.
```

```
      INTEGER STATE,VMAX,V
      REAL K,L,K1
      DIMENSION L(20),PSI(2,20)
      COMMON/RNGPSI/ALPHA1(2),K1(2),RE(2)
      COMMON/PSIG/GAMLG1(2)
      K=K1(STATE)
      ALPHA=ALPHA1(STATE)
      Z=K*EXP(-ALPHA*(R-RE(STATE)))
      PSI(STATE,1)=EXP(.5*(ALOG(ALPHA)-GAMLG1(STATE))+((K-1.)/2.)*ALOG(Z
     1)-Z/2.)
      IF (VMAX.EQ.0) RETURN
      CALL LAGUER(Z,K,L,VMAX)
      PSI(STATE,2)=PSI(STATE,1)*SQRT(K-3)*L(2)/(Z*L(1))
      IF (VMAX.EQ.1) RETURN
      DO 20 V=2,VMAX
      IF (ABS(L(V+1)/L(V)).GT.500.) GO TO 10
      PSI(STATE,V+1)=PSI(STATE,V)*SQRT((K-V)*(K-2*V-1)/(V*(K-2*V+1)))*L(
     1V+1)/(Z*L(V))
      GO TO 20
   10 PSI(STATE,V+1)=PSI(STATE,V-1)*SQRT((K-V)*(K-2*V-1)*(K-V+1)/(V*(V-1
     1)*(K-2*V+3)))*L(V+1)/(Z**2*L(V-1))
   20 CONTINUE
      RETURN
      END


      SUBROUTINE LAGUER(Z,K,Y,VMAX)
C  THIS SUBROUTINE CALCULATES THE VALUES OF THE ASSOCIATED LAGUERRE
C  POLYNOMIALS LSUBV(Z) THROUGH A RE-ITERATIVE PROCESS AND STORES THEM
C  IN AN ARRAY WHOSE INDEX IS (V+1).
      REAL K
      INTEGER VMAX,V,R
      DOUBLE PRECISION SUM,L
      DIMENSION L(20),Y(20)
      L(1)=1.
      Y(1)=1.
      L(2)=Z-(K-2)
      Y(2)=Z-(K-2)
      IF (VMAX.EQ.1) RETURN
      DO 30 V=2,VMAX
      IV=V-1
      SUM=0.
      DO 20 R=0,IV
      SUM=SUM+FACT(V-1)*FACT(2*R)/(FACT(V-1-R)*FACT(R)*FACT(R+1))*L(V-R)
   20 CONTINUE
      L(V+1)=Z*L(V)-(K-2.*V)*SUM
      Y(V+1)=L(V+1)
   30 CONTINUE
      RETURN
      END


      FUNCTION FACT(I)
C  THIS SUBPROGRAM COMPUTES THE VALUE OF I FACTORIAL WHERE I IS AN INTEGER.
      IF (I.EQ.0.OR.I.EQ.1) 10,15
   10 FACT=1.
      RETURN
   15 FACT=1.
      DO 20 J=2,I
   20 FACT=FACT*J
      RETURN
      END
```

2. Program IFSHAPE determines the integrated band shapes given the vibrational and rotational spectroscopic constants T_e, ω_e, $\omega_e x_e$, $\omega_e y_e$, B_e, α_e, γ_e, and D for each electronic state as well as the values of the assumed rotational temperature (T), the spectral slit width (SPSW), the time to scan the spectral slit width (TE) and the RC time constant (TAU). The program, as listed, performs calculations for single section filtering only. Also needed are the values of v' (JUBEG to JUEND) and v" (JLBEG to JLEND) for which the band shapes are to be calculated. The profile is printed out for each band and a list of wavelengths, intensities, and code for the band, sorted in order of increasing wavelength, is stored on magnetic tape for further calculations.

The vibrational levels are calculated by function VIB and the sorting performed by subroutine SORTR[2] (not listed). Subroutine LOOKUP[3] is used to determine the indices of the P and R branch lines at the limits of the non-zero range of the spectral slit function for a particular observation wavelength.

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[2] Subroutine SORTR, LRL Identification MI BKY SORTR (ASCENTF), written by Robert Downs (August 1966). The method is described in a paper by P. Hildebrandt and H. Isbitz, "Radix-Exchange- an Internal Sorting Method for Digital Computers," J.A.C.M. 6, 156 (1959).

[3] Subroutine LOOKUP, LRL Identification EI BKY LOOKUP (ASCENTF), written by William Dempster (July, 1967).

```
      PROGRAM IFSHAPE(INPUT,OUTPUT,TAPE5)
      DIMENSION EM(300),WLA(300),SUMA(200),L(200),REXP(150),PEXP(150),
     1X(11)
      DIMENSION A(2,200,177),INTA(2,200,177)
      DIMENSION MASK1(3)
      COMMON A
      COMMON/V/X
      EQUIVALENCE (A,INTA)
      INTEGER RB,RE,PB,PE
      SPEC1(Z)=(Z-1.+EXP(-Z))/TI
      SPEC2(Z)=(2*TI-Z+1.+(1.-2*EXTI)*EXP(-Z))/TI
      SPEC3(Z)=(1.-EXTI)**2*EXP(-Z)/TI
      CORR(Z)=1./(1.+2.68068E-4+122.78E-16*Z**2+3.3E-24*Z**4)
      ROT(M)=(BVU+BVL)*M+(BVU-BVL-DVU+DVL)*M**2-2*(DVU+DVL)*M**3-(DVU-DV
     1L)*M**4
    1 FORMAT (8E10.0)
    2 FORMAT (I1,I4,3I5)
    3 FORMAT (I5,E12.3,5(I10,E12.3))
    4 FORMAT (* V$ =*I3,5X,*V$$ =*I3//)
    6 FORMAT (///)
    7 FORMAT (1H1,19X,*THE FOLLOWING BAND SHAPES ARE FOR A SPECTRAL SLIT
     1 WIDTH EQUAL TO*F6.2* ANGSTROMS AND ASSUME*/20X,*A ROTATIONAL TEMP
     1ERATURE OF*F5.0* DEGREES KELVIN*)
  401 FORMAT (I1,I9,5F10.0)
      MASK1(1)=77777B
      MASK1(2)=0
      MASK1(3)=0
      READ 1,(X(I),I=1,7)
      READ 1,BEU,AEU,GEU,DVU,BEL,AEL,GEL,DVL
      NL=120
      NLL=2*NL
0  75 READ 401,JSTOP,IFILE,SPSW,T,TE,TAU
      IF (JSTOP.EQ.1) STOP
      PRINT 7,SPSW,T
      PRINT 77,TE,TAU
   77 FORMAT (1H0,19X*TIME TO SCAN SPECTRAL SLIT WIDTH =*F5.1* SECONDS A
     1ND RC TIME CONSTANT =*F5.2* SECONDS*/20X*SINGLE SECTION FILTERING*
     2)
      TI=TE/TAU
      EXTI=EXP(TI)
      INDX=0
    8 READ 2,JLAST,JUBEG,JUEND,JLBEG,JLEND
      DO 300 JU=JUBEG,JUEND
      BVU=BEU-AEU*(JU+.5)+GEU*(JU+.5)**2
      PEXP(1)=1.
      REXP(NL)=EXP((-BVU*NL*(NL+1)+DVU*(NL*(NL+1))**2)/(.695029*T))
      DO 50 N=2,NL
      PEXP(N)=EXP((-BVU*N*(N-1)+DVU*(N*(N-1))**2)/(.695029*T))
      REXP(N-1)=PEXP(N)
   50 CONTINUE
      DO 300 JL=JLBEG,JLEND
      BVL=BEL-AEL*(JL+.5)+GEL*(JL+.5)**2
      VI=VIB(JU+.5,JL+.5)
      DO 100 N=1,NL
C.....P BRANCH INTENSITIES AND WAVELENGTHS (CORRECTED FOR AIR)
      EM(N)=(VI+ROT(-N))**3*N*PEXP(N)*BVU/T
      WLA(N)=1.E8/(VI+ROT(-N))*CORR(VI+ROT(-N))
C.....R BRANCH INTENSITIES AND WAVELENGTHS (CORRECTED FOR AIR)
      EM(N+NL)=(VI+ROT(N))**3*N*REXP(N)*BVU/T
```

```
      WLA(N+NL)=1.E8/(VI+ROT(N))*CORR(VI+ROT(N))
  100 CONTINUE
      MVER=-(BVU+BVL)/(2*(BVU-BVL))
      IBEG=WLA(MVER+NL)-SPSW*2.
      IEND=IBEG+199
      IWL=0
      INDX=INDX+1
      IND=JL*13+JU+1
      DO 210 IW=IBEG,IEND
      IWL=IWL+1
      L(IWL)=IW
      INTA(1,IWL,INDX)=IW
      WL=IW
      SUMA(IWL)=0.
      CALL LOOKUP(WLA,NL,WL-SPSW,PB,MYB)
      CALL LOOKUP(WLA,NL,WL+2*SPSW,PE,MYB)
      CALL LOOKUP(WLA(NL+MVER+1),NL-MVER,WL-SPSW,RB,MYB)
      CALL LOOKUP(WLA(NL+MVER+1),NL-MVER,WL+2*SPSW,RE,MYB)
      IF (RB+RE.EQ.0) GO TO 150
      IF (RB.EQ.0.AND.RE.NE.0) 117,118
  117 RB=1
      GO TO 119
  118 RB=RB+1
  119 DO 120 J=RB,RE
      JJ=J+NL+MVER
      TT=(WLA(JJ)-WL)/SPSW+1.
      ISPEC=IFIX(TT)-1
      TT=TT*TI
      IF(ISPEC) 1191,1192,1193
 1191 SUMA(IWL)=SUMA(IWL)+SPEC1(TT)*EM(JJ)
      GO TO 120
 1192 SUMA(IWL)=SUMA(IWL)+SPEC2(TT)*EM(JJ)
      GO TO 120
 1193 SUMA(IWL)=SUMA(IWL)+SPEC3(TT)*EM(JJ)
  120 CONTINUE
      IF(PB.GE.1) GO TO 125
      IRB=NL+1
      IRE=NL+MVER
      DO 110 I=IRB,IRE
      TT=(WLA(I)-WL)/SPSW+1.
      IF (TT.LE.0..OR.TT.GT.2.) GO TO 110
      ISPEC=IFIX(TT)-1
      TT=TT*TI
      IF (ISPEC)1091,1092,1093
 1091 SUMA(IWL)=SUMA(IWL)+SPEC1(TT)*EM(I)
      GO TO 110
 1092 SUMA(IWL)=SUMA(IWL)+SPEC2(TT)*EM(I)
      GO TO 110
 1093 SUMA(IWL)=SUMA(IWL)+SPEC3(TT)*EM(I)
  110 CONTINUE
  125 IF (PB+PE.EQ.0) GO TO 150
      IF (PB.EQ.0.AND.PE.NE.0) 127,128
  127 PB=1
      GO TO 129
  128 PB=PB+1
  129 DO 130 J=PB,PE
      TT=(WLA(J)-WL)/SPSW+1.
      ISPEC=IFIX(TT)-1
      TT=TT*TI
```

```
      IF (ISPEC) 1291,1292,1293
 1291 SUMA(IWL)=SUMA(IWL)+SPEC1(TT)*EM(J)
      GO TO 130
 1292 SUMA(IWL)=SUMA(IWL)+SPEC2(TT)*EM(J)
      GO TO 130
 1293 SUMA(IWL)=SUMA(IWL)+SPEC3(TT)*EM(J)
  130 CONTINUE
  150 CONTINUE
      A(2,IWL,INDX)=(SUMA(IWL).AND..NOT.777B).OR.IND
  210 CONTINUE
      PRINT 6
      PRINT 4,JU,JL
      DO 280 I=1,34
      JEND=I+170
  280 PRINT 3,(L(J),SUMA(J),J=I,JEND,34)
  300 CONTINUE
      IF (JLAST.NE.1) GO TO 8
C.....ARRAYS ARE REORDERED IN ORDER OF INCREASING WAVELENGTH
      CALL SORTR(A,-35400,2,MASK1)
      NAME=7HIFSHAPE
      IF (IFILE.EQ.0) GO TO 360
      NFILE=1
      NAME=7HIFSHAPE
      READ (5) NNAME
      IF (NNAME.NE.7HIFSHAPE)301,305
  301 PRINT 302
  302 FORMAT (1H1,*WRONG TAPE*)
      STOP
  305 IF (IFILE.EQ.1) GO TO 365
  310 DO 350 I=1,1000
      READ (5)
      IF (ENDFILE 5) 355,350
  350 CONTINUE
  355 NFILE=NFILE+1
      IF (IFILE.EQ.NFILE) 360,310
  360 WRITE (5) NAME
  365 WRITE (5) SPSW,T
      DO 370 J=1,177
      IA=200*(J-1)+1
      IB=IA+199
      WRITE(5)(INTA(1,I),A(2,I),I=IA,IB)
  370 CONTINUE
      END FILE 5
      GO TO 75
      END
```

```
      FUNCTION VIB(A,B)
      DIMENSION C(3)
      COMMON/V/X(11)
      DATA C/319.,295.,265./
      IF (A.GT.9.6) GO TO 20
      VIB=X(1)+X(2)*A+X(3)*A**2+X(4)*A**3-X(5)*B-X(6)*B**2-X(7)*B**3
      RETURN
   20 I=A-9.5
      VIB=X(1)+X(2)*9.5+X(3)*9.5**2+X(4)*9.5**3-X(5)*B-X(6)*B**2-X(7)*B*
     1*3
      DO 25 J=1,I
      VIB=VIB+C(J)
   25 CONTINUE
      RETURN
      END
```

3. Program IFVMT, using the band shapes computed by program IFSHAPE, calculates the set of vibrational populations giving the best fit to the observed spectrum. It assumes that the Franck-Condon factors have been multiplied by $R_e^2(\bar{r}_{v'v''})$. Details concerning the input parameters are given in the comment cards. The wavelength response correction factors begin at λ = 4300A and are supplied at 50A intervals.

Input-output is performed by the main program as well as corrections of the raw intensity data. The A array is calculated in subroutine FUNCTA. In subroutine CALC the setting up of the least squares problem and calculation of the standard deviations in relative populations and temperatures, based upon the variance-covariance matrix supplied by subroutine VARIA, takes place. Vibrational temperatures are calculated in subroutines VIBTEMP and spectrometer wavelength corrections in subroutine LAMCOR. Subroutines ARRAY and TPREAD read the band shapes from the magnetic tape and set up preliminary arrays from which the A matrix is calculated.

The center of this program, the least squares calculation, is performed by subroutine package LSQVMT[4] (not listed) which has been modified for use as a subroutine rather than as a main program. The fitting function is defined in subroutine TABLE.

Calculation of the complete computed spectrum is performed by subroutine GRPREP. It and the plotting subroutines GRAPH 1 and GRAPH 2 have not been listed.

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[4] Program LSQVMT, LRL identification E2 BKY LSQVMT (FORTRAN), written by Eric Beals (November 1966). The method is due to W. C. Davidon, as described in "Variable Metric Minimization," Argonne National Laboratory Report ANL 5990 (Rev. 1959).

```
      PROGRAM IFVMT(INPUT,OUTPUT,TAPE3=OUTPUT,TAPE1,TAPE4,TAPE5,TAPE6)
C.....                GENERAL COMMENTS
C.....
C.....THE PURPOSE OF THIS PROGRAM (WHEN USED IN CONJUNCTION WITH PROGRAM
C..... IFSHAPE) IS TO DETERMINE THE RELATIVE VIBRATIONAL POPULATIONS (AND
C..... TEMPERATURES) OF THE FIRST EXCITED ELECTRONIC STATE OF IODINE MONO-
C..... FLUORIDE.  THE GENERAL METHOD IS TO SOLVE THE MATRIX EQUATION AX=B BY
C..... USE OF A VARIATIONAL METHOD LEAST SQUARES LIBRARY ROUTINE.  THE A MATRIX
C..... IS ASSOCIATED WITH THE EXPECTED CONTRIBUTION FROM EACH VIBRATIONAL BAND
C..... AT A PARTICULAR WAVELENGTH.  THE SHAPE OF THE BANDS IS DEPENDENT ON BOTH
C..... THE SPECTRAL SLITWIDTH AND THE ROTATIONAL TEMPERATURE OF THE EMITTING
C..... MOLECULES.  THESE INDIVIDUAL BAND SHAPES ARE GENERATED BY PROGRAM
C..... IFSHAPE.  THE B VECTOR IS COMPOSED OF THE OBSERVED INTENSITIES AT
C..... VARIOUS WAVELENGTHS AFTER THE RAW INTENSITIES HAVE BEEN CORRECTED FOR THE
C..... RESPONSE OF THE SYSTEM.  THE X VECTOR IS THE SOLUTION VECTOR, I.E.
C..... THE DESIRED RELATIVE POPULATIONS OF THE VIBRATIONAL LEVELS OF THE
C..... A STATE OF IODINE MONOFLUORIDE.
      DIMENSION RELINT(35400),INDXWL(3000),A(13,850),X(13),B(850,1),
     1PARCOR(10),WLRSPNS(70),DAT(850),ILAM(850),JLAM(850),PAR(850),
     2BB(850),SIGMA1(13),SIGMA2(13),FACT(273)
      DIMENSION VIBPOP(13),TITLEA(13),TITLEB(13),XPLOT(3000),YPLOT(3000)
      DIMENSION NU(5),TVIB(13)
      REAL NU,ILAM
      INTEGER PAR
      EQUIVALENCE (B,BB)
      COMMON/1/RELINT,INDXWL,A,X,FACT,ASTART
      COMMON/2/XPLOT,YPLOT,N,JLAM,BB,M
      COMMON/4/LTP,MTP,IFILE
      COMMON/5/IBEST,TITLEB,DAT
      COMMON/SGMA/SIGMA1
      DATA PARCOR/953.3,480.1,195.9,98.26,48.93,19.77,10.07,4.897,2.004,
     11.000/
C.....READ FRANCK CONDON FACTORS FOR IODINE MONOFLUORIDE
      READ 3,(FACT(I),I=1,234)
C.....READ RELATIVE WAVELENGTH RESPONSE CORRECTION FACTORS FOR OPTICAL SYSTEM
      READ 3,(WLRSPNS(I),I=1,67)
    3 FORMAT (8E10.3)
C.....READ WE,WEXE,WEYE,WEZE,WETE FOR UPPER ELECTRONIC STATE OF IODINE MONO-
C..... FLUORIDE. THESE CONSTANTS ARE USED IN THE CALCULATION S OF VIBRATIONAL
C..... TEMPERATURES.
      READ 3,(NU(I),I=1,5)
C.....THE FOLLOWING CARD CONTAINS DATA AS FOLLOWS
C.....M EQUALS NUMBER OF DATA POINTS (NOT TO EXCEED 850)
C.....EITHER OF THE FOLLOWING OPTIONS MAY BE EXERCISED
C.....FOR ICHOICE = 1, WAVELENGTH MUST BE SPECIFIED FOR EACH INTENSITY
C.....READ IN.
C.....FOR ICHOICE = 2, FIRST INTENSITY DATA POINT IS FOR WAVELENGTH =
C.....LBEGIN AND SUBSEQUENT POINTS ARE SPACED AT INTRVL WAVELENGTH
C.....INTERVALS FOR A TOTAL OF M POINTS.
C.....FOR ICHOICE = 3, EXPERIMENTAL DATA KEPT SAME AS FOR PREVIOUS RUN -
C..... GRAPH OPTION MAY BE CHANGED.
C.....FOR ICHOICE = 4,ROTATIONAL TEMPERATURE KEPT SAME AS FOR PREVIOUS RUN
C.....FOR IGRAPH = 1, NO POINTS WILL BE PLOTTED.
C.....FOR IGRAPH = 2, THE EXPERIMENTAL POINTS AND POINTS CALCULATED AT ONE
C..... ANGSTROM WAVELENGTH INTERVALS WILL BE PLOTTED.
C.....FOR IGRAPH = 3, SAME AS FOR IGRAPH = 2 EXCEPT GRAPHS ARE LARGE
    4 READ 5,ISTOP,M,IFILE,ICHOICE,IGRAPH,WLPAP
    5 FORMAT (I1,I4,3I5,F10.3)
      IF (ISTOP.EQ.1) GO TO 110
```

```
      IF (ICHOICE.EQ.4) GO TO 7000
C.....SKIP TO THE IFILE TH FILE ON DATA TAPE
      IFILE=MOD(IFILE,7)
      REWIND IFILE
      READ(IFILE) NAME
      IF (NAME.NE.7HIFSHAPE) GO TO 100
      READ (IFILE) SPSW,T
      LTP=201
      MTP=35400
      CALL ARRAY(RELINT,INDXWL,ASTART)
    6 FORMAT (1H1)
 7000 READ 7,(TITLEA(I),I=1,8)
    7 FORMAT (13A10)
      CALL CENTER(TITLEA,8,TITLEB,80)
      GO TO (8,10,33,8) ICHOICE
    8 READ 9,(ILAM(I),DAT(I),PAR(I),I=1,M)
    9 FORMAT (5(F8.2,F6.3,I2))
      GO TO 14
   10 READ 1000,LBEGIN,INTRVL
 1000 FORMAT (2I5)
      ILAM(1)=LBEGIN
      DO 11 I=2,M
      ILAM(I)=ILAM(I-1)+INTRVL
   11 CONTINUE
      READ 12,(DAT(I),PAR(I),I=1,M)
   12 FORMAT (10(F7.4,I1))
C.....CORRECTION OF RAW DATA FOR RESPONSE OF PAR LOCK-IN AMPLIFIER AND
C.....FOR SPECTRAL RESPONSE OF OPTICAL SYSTEM
   14 DO 30 L=1,M
      ID=PAR(L)+1
   16 IWVL=IFIX(ILAM(L)-4250)/50
      KLAM=IFIX(ILAM(L))/50*50
      IF (KLAM-IFIX(ILAM(L))) 18,17,18
   17 WVLCOR=WLRSPNS(IWVL)
      GO TO 20
   18 WVLCOR=((50+KLAM-ILAM(L))*WLRSPNS(IWVL)+(ILAM(L)-KLAM)*WLRSPNS(IWV
     1L+1))/50
   20 DAT(L)=DAT(L)*PARCOR(ID)
      IF (DAT(L).LT.0.) DAT(L) = 0.
      B(L)=DAT(L)*WVLCOR*1.E-13
   30 CONTINUE
   33 CONTINUE
      CALL LAMCOR(M,ILAM,JLAM,WLPAP)
      IBEST=1
      CALL FUNCTA
   62 FORMAT (     19X,*SPECTRAL SLITWIDTH =*,F6.2,* ANGSTROMS*,10X,*ROTA
     1TIONAL TEMPERATURE =*,F5.0,* DEGREES KELVIN*///)
   70 IXMAX=0
      XMAX=X(1)
      DO 72 I=2,13
      IF (X(I).LE.XMAX) GO TO 72
      XMAX=X(I)
      IXMAX=I-1
   72 CONTINUE
      DO 75 I=1,13
      VIBPOP(I)=X(I)/XMAX
   75 CONTINUE
      PRINT 76,(TITLEB(I),I=1,8)
   76 FORMAT (1H1,26X,8A10)
```

```
      PRINT 77,IXMAX,XMAX
   77 FORMAT(1H0,42X,*ABSOLUTE POPULATION FOR V$ =*,I2,* EQUALS*,E10.3//
     1/)
      PRINT 62,SPSW,T
      CALL VIBTEMP(NU,VIBPOP,TVIB,SIGMA2,IXMAX)
      PRINT 80,IXMAX
   80 FORMAT (7X,*VIBRATIONAL POPULATIONS AND TEMPERATURES (RELATIVE TO
     1V$ =*,I2,*) FOR THE UPPER ELECTRONIC STATE OF IODINE MONOFLUORIDE*
     2///)
   85 FORMAT (22X,*V$ =*,I2,2(10X,E10.3),2(10X,F10.0)//)
      DO 90 I=1,13
      IX=I-1
   90 PRINT 85,IX,VIBPOP(I),SIGMA1(I),TVIB(I),SIGMA2(I)
      CALL GRPREP
   99 GO TO 4
  100 PRINT 101
  101 FORMAT (1H1,*TAPE NOT LABELED SHAPE - PROGRAM STOP*)
      PRINT 105,IFILE,NAME
  105 FORMAT (* IFILE =*,I4,*  NAME  =  *,O20)
  110 CONTINUE
  120 STOP
      END


      SUBROUTINE FUNCTA
      DIMENSION SIGMA1(13)
      COMMON/1/RELINT(35400),INDXWL(3000),A(13,850),X(13),FCFACT(273),
     1ASTART
      COMMON/2/XPLOT(3000),YPLOT(3000),N,JLAM(850),BB(850),M
      COMMON/5/IBEST,TITLEB(13),DAT(850)
      COMMON/SGMA/SIGMA1
C.....CALCULATION OF A ARRAY
      DO 5 J=1,13
      DO 5 I=1,850
      A(J,I)=0.
    5 CONTINUE
      DO 20 IM=1,M
      NBIN=JLAM(IM)-IFIX(ASTART)+1
      LOCN=MOD(INDXWL(NBIN),40000)
      KOUNT=INDXWL(NBIN)/40000
      IK=LOCN+KOUNT-1
      DO 10 IL=LOCN,IK
      K=RELINT(IL).AND.777B
      IV=K-(K-1)/13*13
      REL=RELINT(IL).AND..NOT.777B
   10 A(IV,IM)=A(IV,IM)+REL*FCFACT(K)*1.E-13
   20 CONTINUE
      CALL CALC(A,X,BB,M,TITLEB,DAT,SIGMA1,IBEST,FBEST,JLAM)
      RETURN
      END


      SUBROUTINE CALC(A,X,B,M,TITLEB,DAT,SIGMA,IBEST,FBEST,JLAM)
      DIMENSION A(13,850),X(13,1),XX(13),IOLD(13),B(850,1),TEST(13),
     1TITLEB(13),DAT(850),VAR(20,13),SIGMA(13),WEIGHT(850),BRAVAR(13),
     2YCALC(850),SIG(13),JLAM(850)
      COMMON/VIBA/BRAVAR
```

```
      COMMON/TABL/IORDER
      COMMON/BEST/FBE,FERR,XX,XERR(13),IB,ISAME
      COMMON/CALF/WEIGHT,YCALC,NA,NB,NC,CHAR(8)
    1 FORMAT (1X,*YOBS-YCALC-WEIGHT-INDEPENDENT VARIABLES*//)
    2 FORMAT (1H1,8A10//)
    3 FORMAT (I10,3X,13E9.2)
    4 FORMAT (///(10E12.3))
      IORDER=0
      DO 20 I=1,13
      TEST(I)=0.
      DO 5 J=1,M
      TEST(I)=TEST(I)+A(I,J)
    5 CONTINUE
      IF (TEST(I).EQ.0.) GO TO 20
      IORDER=IORDER+1
      DO 10 J=1,M
   10 A(IORDER,J)=A(I,J)
      IOLD(IORDER)=I
   20 CONTINUE
      DO 21 I=1,M
      WEIGHT(I)=1./(ABS(DAT(I))+.36)
   21 CONTINUE
      DO 6 I=1,8
      CHAR(I)=TITLEB(I)
    6 CONTINUE
      NA=IORDER $ NB=IORDER $ NC=M
      CALL LSQVMT
      DO 25 I=1,13
      XX(I)=XX(I)**2
      SIG(I)=0.
      SIGMA(I)=0.
   25 X(I)=0.
      IF (IBEST.NE.1) RETURN
      FBEST=FBE
      CALL VARIA(A,XX,B,WEIGHT,M,IORDER,YCALC,FBEST,VAR)
      DO 40 I=2,IORDER
      BRAVAR(I)=((XX(I)/XX(1))**2*VAR(1,1)+VAR(I,I)-2.*XX(I)/XX(1)*VAR(1
     1,I))/XX(1)**2
      SIG(I)=SQRT(BRAVAR(I))
   40 CONTINUE
      DO 30 JJ=1,IORDER
      J=IORDER+1-JJ
      II=IOLD(J)
      X(II)=XX(J)
      SIGMA(II)=SIG(J)
   30 CONTINUE
      PRINT 2,(TITLEB(I),I=1,8)
      PRINT 1

      DO 50 I=1,M
      PRINT 3,JLAM(I),(A(J,I),J=1,IORDER)
   50 CONTINUE
      PRINT 4,(B(I),YCALC(I),I=1,M)

      PRINT 55,FBEST
   55 FORMAT (1H0,*CHISQ = *,E10.3/1H0,*VARIANCE - COVARIANCE MATRIX*//)
      GO TO 66
      DO 65 J=1,IORDER
      PRINT 60,(VAR(J,K),K=1,IORDER)
```

```
   60 FORMAT (10E12.3)
   65 CONTINUE
   66 CONTINUE
      RETURN
      END
```

```
$.....SUBROUTINE VIBTEMP
      SUBROUTINE VIBTEMP(NU,X,TVIB,SIGMA2,IXMAX)
      DIMENSION NU(5),X(13),TVIB(13),BRAVAR(13),SIGMA2(13)
      COMMON/VIBA/BRAVAR
      REAL NU
      ENERGY(I)=NU(1)*(I+.5)+NU(2)*(I+.5)**2+NU(3)*(I+.5)**3+NU(4)*(I+.5
     1)**4+NU(5)*(I+.5)**5
      DO 10 J=1,13
      SIGMA2(J)=0.
   10 TVIB(J)=0.
      IF (IXMAX.NE.0) RETURN
      DO 30 J=1,12
      IF(X(J+1).LE.0.) GO TO 30
      EN=ENERGY(J)-ENERGY(0)
      TVIB(J+1)=-EN/(.695029*ALOG(X(J+1)))
      SIGMA2(J+1)=TVIB(J+1)**2*.695029*SQRT(BRAVAR(J+1))/(X(J+1)*EN)
   30 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE VARIA(TDATA,XBEST,YOBS,W,NDATA,NPARAM,YCALC,FBEST,VAR)
      DIMENSION XBEST(13),G(13)
      DIMENSION TDATA(13,850),W(850),YOBS(850),YCALC(850)
      DIMENSION VAR(20,13),B(20,1)
C     DIMENSION = 20 FOR COMPATIBILITY WITH MATINV
      DO 10 J=1,NPARAM
      DO 10 K=1,NPARAM
   10 VAR(J,K)=0.
      DO 100 I=1,NDATA
      DO 50 J=1,NPARAM
      DO 50 K=1,NPARAM
      VAR(J,K)=VAR(J,K)+TDATA(J,I)*TDATA(K,I)*W(I)
   50 CONTINUE
  100 CONTINUE
      CALL MATINV(VAR,NPARAM,B,0,DET)
      DO 200 J=1,NPARAM
      DO 200 K=1,NPARAM
      VAR(J,K)=VAR(J,K)*FBEST/(NDATA*5/6.-NPARAM)
  200 CONTINUE
      RETURN
      END
```

```
$.....SUBROUTINE LAMCOR
      SUBROUTINE LAMCOR(M,XLAM,JLAM,WLPAP)
```

```
      DIMENSION JLAM(850),XLAM(850),YLAM(850)
      DATA A,B,C,D,E,F/35.45,.987403,1.1561E-6,1.766,.0628637,-4.20202/
      DO 20 I=1,M
      XLAM(I)=XLAM(I)+WLPAP
      YLAM(I)=A+B*XLAM(I)+C*XLAM(I)**2+D*SIN(E*XLAM(I)+F)
      JLAM(I)=YLAM(I)
      IF (YLAM(I)-JLAM(I).GE..5) JLAM(I)=JLAM(I)+1
   20 CONTINUE
      RETURN
      END


      SUBROUTINE ARRAY(RELINT,INDXWL,ASTART)
      DIMENSION RELINT(35400),INDXWL(3000)
      KOUNT=0
      NOLD=1
      LOCN=1
      DO 10 I=1,35400
      CALL TPREAD(A,R)
      IF (A.EQ.1.) CALL ABORT
      IF (I.EQ.1) ASTART=A
      NBIN=A-ASTART+1
      IF (NBIN.LT.NOLD) CALL ABORT
      IF (NBIN.EQ.NOLD) GO TO 5
      IF (NBIN.NE.NOLD+1) CALL ABORT
      INDXWL(NOLD)=40000*KOUNT+LOCN
      KOUNT=0
      LOCN=I
      NOLD=NBIN
    5 RELINT(I)=R
      KOUNT=KOUNT+1
   10 CONTINUE
      RETURN
      END


      SUBROUTINE TPREAD(WL,REL)
      COMMON/4/L,M,IFILE
      DIMENSION LAMBDA(200),RELINT(200)
      IF (M.GT.0) GO TO 1
      A=1.
      RETURN
    1 IF (L.LE.200) GO TO 2
      II=200
      IF (M.LT.200) II=M
      READ (IFILE)(LAMBDA(I),RELINT(I),I=1,II)
      L=1
    2 WL=LAMBDA(L)
      REL=RELINT(L)
      L=L+1
      M=M-1
      RETURN
      END


      SUBROUTINE TABLE(F,G,X,T,M1)
```

```
      DIMENSION X(13),T(13),G(13)
      COMMON/TABL/IORDER
      IF (M1.EQ.1) RETURN
      F=0.
      DO 10 I=1,IORDER
      F=F+X(I)**2*T(I)
      G(I)=2*X(I)*T(I)
   10 CONTINUE
      RETURN
      END
```

4. Calculation of the electronic transition moment function is done by program SSRER. It is quite similar to the preceding program in operation, many of the subroutines used being the same (and therefore not listed a second time). Of course, the Franck-Condon factors are not assumed to be multiplied by $R_e^2(\bar{r}_{v'v''})$. The transition matrix elements based on a trial transition moment "function" (see Sec. III-B-4) are calculated in subroutine CALFUN. Subroutine SSQMIN[5] varies both the transition moment parameters and the vibrational populations so as to minimize the sums of the squares of deviations between the observed and best-fit computed spectra. Lagrangian interpolation of the transition moment function between selected points is performed by subroutine LAGINT.[6]

---

[5] Subroutine SSQMIN, LRL identification E4 BKY SSQMIN (FORTRAN), written by Eric Beals (November 1965). A detailed description of the method may be found in "A Method for Minimizing a Sum of Squares of Non-Linear Functions without Calculating Derivatives" by M. J. D. Powell, The Computer Journal (January 1965).

[6] Subroutine LAGINT, LRL identification E1 EO LAGT (FORTRAN), written by James Eusebio (July, 1964) and modified by S. Gabelnick and S. E. Schwartz (June, 1968).

```
      PROGRAM SSRER(INPUT,OUTPUT,TAPE3=OUTPUT,TAPE1)
      DIMENSION RELINT(35400),INDXWL(3000),A(850,13),B(850),DAT(850),
     1ILAM(850),JLAM(850),WEIGHT(850),PAR(851),WLRSPNS(70),FCFACT(273),
     2FACT(273),RCENT(273),PARCOR(10),F(850),X(30),E(30)
      REAL ILAM
      INTEGER PAR
      COMMON/CAL/FACT,RCENT,A,B,WEIGHT
      COMMON/1/RELINT,INDXWL,JLAM,ASTART
      COMMON/4/LTP,MTP,IFILE
      COMMON W(26000)
      DATA PARCOR/953.3,480.1,195.9,98.26,48.93,19.77,10.07,4.897,2.004,
     11.000/
C.....READ FRANCK CONDON FACTORS FOR IODINE MONOFLUORIDE
      READ 2,(FACT(I),RCENT(I),I=1,234)
    2 FORMAT (8X,2E14.4)
C.....READ RELATIVE WAVELENGTH RESPONSE CORRECTION FACTORS FOR OPTICAL SYSTEM
      READ 3,(WLRSPNS(I),I=1,67)
    3 FORMAT (8E10.3)
      READ 4,M,N,WLPAP
    4 FORMAT (2I5,F5.0)
C.....SKIP TO THE IFILE TH FILE ON DATA TAPE
      IFILE=1
      REWIND IFILE
      READ(IFILE) NAME
      IF (NAME.NE.7HIFSHAPE) GO TO 110
      READ (IFILE) SPSW,T
      LTP=201
      MTP=35400
      CALL ARRAY(RELINT,INDXWL,ASTART)
    8 READ 9,(ILAM(I),DAT(I),PAR(I),I=1,M)
    9 FORMAT (5(F8.2,F6.3,I2))
      READ 10,(X(I),I=1,N)
      READ 10,(E(I),I=1,N)
   10 FORMAT (8E10.3)
C.....CORRECTION OF RAW DATA FOR RESPONSE OF PAR LOCK-IN AMPLIFIER AND
C.....FOR SPECTRAL RESPONSE OF OPTICAL SYSTEM
   14 DO 30 L=1,M
      ID=PAR(L)+1
   16 IWVL=IFIX(ILAM(L)-4250)/50
      KLAM=IFIX(ILAM(L))/50*50
      IF (KLAM-IFIX(ILAM(L))) 18,17,18
   17 WVLCOR=WLRSPNS(IWVL)
      GO TO 20
   18 WVLCOR=((50+KLAM-ILAM(L))*WLRSPNS(IWVL)+(ILAM(L)-KLAM)*WLRSPNS(IWV
     1L+1))/50
   20 DAT(L)=DAT(L)*PARCOR(ID)
      IF (DAT(L).LT.0.) DAT(L) = 0.
      B(L)=DAT(L)*WVLCOR*1.E-13
      WEIGHT(L)=1./SQRT(ABS(DAT(L))+.36)
   30 CONTINUE
      CALL LAMCOR(M,ILAM,JLAM,WLPAP)
      IPRINT=0
      ESCALE=100
      MAXFUN=5000
      CALL SSQMIN(M,N,F,X,E,ESCALE,IPRINT,MAXFUN)
      DO 50 I=1,12
      X(I)=X(I)**2
   50 CONTINUE
      FBEST=0.
```

```
      DO 100 I=1,M
      FBEST=FBEST+F(I)**2
  100 CONTINUE
      PRINT 105,FBEST,(X(I),I=1,N)
  105 FORMAT (1H1,E10.3/(1H0,E10.3))
      PRINT 62,SPSW,T
   62 FORMAT (     19X,*SPECTRAL SLITWIDTH =*,F6.2,* ANGSTROMS*,10X,*ROTA
     1TIONAL TEMPERATURE =*,F5.0,* DEGREES KELVIN*///)
      STOP
  110 PRINT 115
  115 FORMAT (*1HERE WE GO AGAIN - BAD TAPE*)
      PRINT 120,NAME
  120 FORMAT (* NAME =* O20)
      STOP
      END


      SUBROUTINE CALFUN(M,N,F,X)
      DIMENSION F(850),X(30),XX(20),YY(20),FCFACT(273)
      COMMON/CAL/FACT(273),RCENT(273),A(850,13),B(850),WEIGHT(850)
      COMMON/1/RELINT(35400),INDXWL(3000),JLAM(850),ASTART
      DATA XX/1.84,1.86,1.87,1.89,1.91,1.93,1.95,1.97,1.99,2.03,2.07,
     12.12,2.16,2.19,2.21,2.23,2.30,2.65/
      DATA YY(1),YY(2),YY(17),YY(18)/-7.0,-6.9,-1.05,-.25/
      DO 1 I=1,14
      YY(I+2)=ALOG(ABS(X(I+12)))
    1 CONTINUE
      DO 2 I=1,234
      CALL LAGINT(18,XX,YY,1,K,RCENT(I),RF)
      FCFACT(I)=FACT(I)*EXP(RF)*19.44**2
    2 CONTINUE
C.....CALCULATION OF A ARRAY
      DO 5 J=1,13
      DO 5 I=1,850
      A(I,J)=0.
    5 CONTINUE
      DO 20 IM=1,M
      NBIN=JLAM(IM)-IFIX(ASTART)+1
      LOCN=MOD(INDXWL(NBIN),40000)
      KOUNT=INDXWL(NBIN)/40000
      IK=LOCN+KOUNT-1
      DO 10 IL=LOCN,IK
      K=RELINT(IL).AND.777B
      IV=K-(K-1)/13*13
      REL=RELINT(IL).AND..NOT.777B
   10 A(IM,IV)=A(IM,IV)+REL*FCFACT(K)*1.E-13
   20 CONTINUE
      DO 50 I=1,M
      F(I)=A(I,1)
      DO 40 J= =I2
      F(I)=F(I)+A(I,J+1)*X(J)**2
   40 CONTINUE
      F(I)=(F(I)-B(I))*WEIGHT(I)
   50 CONTINUE
      RETURN
      END
```

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