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VIBRATION-ROTATION INTERACTION FACTORS FOR DIATOMIC MOLECULES CALCULATED BY NUMERICAL METHODS

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J. K. Cashion

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J. K. Cashion

Department of Chemistry and Lawrence Radiation Laboratory, University of California, Berkeley, California

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Abstract

The influence of vibration-rotation interaction on transition probabilities for diatomic molecules has been studied through numerical solution of the Schrodinger radial equation. The numerical method described is readily applicable to any choice of potential and dipole moment functions for the molecule, its accuracy considerably exceeds the requirements of practical applications, and it is very economical in terms of computer-time requirements. Its use is demonstrated here in two applications. First, it has been used to check the accuracy of the approximate formulae for the F-factors of a rotating Morse oscillator with a linear dipole moment function, derived by Herman, Rothery, and Rubin.[4] It was found that their formulae were very accurate for $\Delta v = 1$ transitions, but that the two formulae given by them for the first and second overtones could introduce errors of several percent at moderate J values. Secondly, quadratic and cubic terms were added to the dipole moment function in order to estimate the sensitivity of F-factors to changes in this

function. The results indicate that for all transitions in which $\Delta v > 1$, the higher terms can have considerable significance. For example, F-factors for the lines R(19) and R(20) of the 3-0 band of LiH were changed by factors of more than 3 when the dipole moment function employed was carried from a linear to a cubic approximation in a Taylor's series expansion.

Introduction

In order to relate the observed intensity of a spectral line to the population of its state of origin it is necessary to know the absolute value of R^{nm}, the matrix element of the dipole moment between the two states. For electric dipole transitions in general R^{nm} is given by

$$R^{nm} = \int \psi_n \bar{M} \psi_m \, d\tau, \tag{1}$$

where ψ_n and ψ_m are the eigenfunctions of the two states and $\bar{M}$ is the dipole moment operator. For the particular case of vibration-rotation transitions within a given electronic state of a diatomic molecule, it is customary to assume separability of the wave equation and to replace the dipole moment operator by an algebraic function of the intermuclear distance only. Under these assumptions the matrix element of the dipole moment is given by

$$R^{nm} = \int \psi_n M(r) \psi_m \, dr \tag{2}$$

where now ψ is the radial equation solution multiplied by r, and M(r) is called the dipole moment function. The functions

ψ are fixed by the choice of a functional form U(r) to represent the variation of the potential energy with internuclear distance. Hence, the value calculated for R^{nm} depends essentially on the choice of the functions U(r) and M(r).

If Eq. (2) is to be evaluated in closed form the functions U(r) and M(r) must be relatively simple and usually numerous mathematical approximations will be required. On the other hand numerical methods suffer from no such limitations. In principle they can be used to evaluate R^{nm} to any desired degree of accuracy for any choice whatsoever of the potential and dipole moment functions. The advent of high speed computers has brought this from the realm of principle to the practical. Using an IBM 7090 or comparable machine, less than a minute is required to evaluate Eq. (2) for each of the 41 transitions allowed between the rotational levels J = 0,1,...,20 of a given vibrational state and those of any lower vibrational state.

Since the choice of elaborate functional forms for U(r) and M(r) does not affect the efficiency of the numerical method to any significant degree, the ideal procedure would be to use potential and dipole moment functions which are known to give accurate representations of those properties. Unfortunately this is not possible at the present time, either for U(r) or M(r).

The best potential function for a diatomic molecule would be that derived from the Rydberg-Klein-Rees procedure. There has been a considerable revival of interest in this method of late, notably through the work of Jarmain[1] and of Vanderslice[2] et al. It employs observed term values to calculate the

classical turning points of the vibrational levels. By interpolation a complete potential curve can be constructed from these points and can be used to solve the radial equation for the vibrational-rotational eigenfunctions. It can be called the "true" or "experimental" potential in the sense that its eigenvalues reproduce the observed term values. The present limitation on its utility is chiefly the lack of sufficiently extensive spectroscopic data on most heteronuclear diatomic molecules. However, the use of approximate potential functions in calculating vibration-rotation intensities is probably not a major source of error, especially for the lower vibrational eigenstates. Such approximate potentials usually are fitted from experimental data derived from these lower states and from the observed dissociation energy. Hence, they tend to approximate the RKR curve well in the region about the potential minimum and generally do not lead to markedly different eigenfunctions for the lower states. The result is that transition probabilities are much more sensitive to the choice of dipole moment function than to the potential model assumed. This is borne out by the calculations of Benedict, Herman, Silverman and Moore[3] on the vibrational transition probabilities for HCl and also by those Herman, Rothery and Rubin[4] on vibration-rotation interaction. In both these studies Morse eigenfunctions and perturbed harmonic oscillator eigenfunctions were successively combined with the same dipole moment function. The resulting transition probabilities were not greatly different for the two potential models.

In regard to their sensitivity to the choice of potential functions, the calculation of electronic transition probabilities differs so markedly from the corresponding vibrational-rotational problem that the matter deserves mention here. Zare* has shown recently that eigenfunctions derived from RKR

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*R. N. Zare, to be published. The author is grateful to Mr. Zare for making the results of his studies available to him prior to their publication.

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potentials predict intensity distributions in good agreement with experiment for all bands of the iodine fluorescence spectrum which have been measured to date. On the other hand, Morse eigenfunctions applied to the same problem give qualitative agreement only over a limited range of transitions. The principal reason for this difference is the following. In vibration-rotation spectra, where one is dealing with a single potential curve, an approximate potential generally will deviate more and more from reality with increasing vibrational quantum number. This will be reflected in the eigenfunctions by an increasing shift of the approximate ones relative to the true eigenfunctions. For states of high v, the approximate eigenfunction may be completely out of phase with the true one. Nevertheless, two such approximate eigenfunctions for nearby states will have a relative nodal structure very similar to that between the corresponding true eigenfunctions. Since the product of the two is involved in Eq. (2) the approximate pair can give

much the same value for the integral as would the true eigenfunctions when combined with same function $M(r)$. On the other hand, the intensity distribution in electronic spectra depends on the overlap of eigenfunctions belonging to two different potential curves. Errors in approximating these two potentials may cancel to some extent but only fortuitously. They may just as easily add and produce a pattern of overlap integrals which is entirely spurious. Zare's work gives a very striking illustration of the sensitivity of electronic intensities to changes in the potential functions. In this writer's view it forces one to accept only with extreme reserve electronic intensities calculated from approximate potential models.

In regard to the choice of dipole moment function, at present neither theory nor experiment can provide one which is adequate over the whole range of internuclear separation. The approach most commonly used in the past has been to expand $M(r)$ in a Taylor's series about the equilibrium internuclear separation, r_e.

$$M(r) = \sum_{i=0}^{\infty} M_i \rho^i \tag{3}$$

where

$$M_i = \frac{1}{i!} \frac{d^i M(r)}{dr^i}$$

and

$$\rho = r - r_e.$$

This expansion is substituted in Eq. (2) to give the matrix element as a sum of integrals, each multiplied by the appropriate Taylor coefficient.

$$R^{nm} = \sum_{i=0}^{\infty} M_i \int \psi_n \rho^i \psi_m dr. \tag{4}$$

When the ψ's are the Morse eigenfunctions for rotationaless vibrational states, the first term is zero and the linear integral can be evaluated in closed form to yield a rather simple algebraic expression.[5] Approximate formulae for the quadratic integral have been derived by Heaps and Herzberg,[5] and for the cubic by Garvin.[6] These apply only to the (forbidden) pure vibrational transitions. When the effects of rotation are included the Morse eigenfunctions are considerably more difficult to manipulate algebraically. Herman and Rubin[7] have derived general expressions for Eq. (4), using the eigenfunctions of the rotating Morse oscillator and retaining as many terms in the summation as are desired. However, these expressions are not suitable for practical computation. Herman, Rothery and Rubin[4] carried out the formidable algebraic task of reducing the first two terms to a more tractable form, thus obtaining in closed form the transition probabilities for the model of a rotating Morse oscillator with a linear dipole moment function. [The integral $\int \psi_n \psi_m dr$ is non-zero when either ψ belongs to a $J \neq 0$ state. Hence the ratio M_1/M_0 must be known in order to use this model.] These formulae are not exact, and a secondary purpose of this paper is to determine the magnitude of the errors introduced by the mathermatical approximations used in their development.

The main purpose of this paper is twofold. First, we wish to outline a numerical method which is applicable to any combination of potential and dipole moment function. It will attain its maximum utility only when good RKR potentials are available and especially when better dipole moment functions are found. At present it affords a more accurate and an easier method of evaluating the vibrational-rotational transition probabilities for models in current use than does the approach of algebraic solution in closed form. Secondly, we wish to indicate the extent to which reasonable variations in the dipole moment function will affect the transition probabilities for a given potential model. For this latter purpose it is convenient to choose Morse eigenfunctions combined with two different dipole moment functions. One will be the linear model already mentioned. The second will be a model proposed recently by the author[8] in connection with the calculation of pure vibrational transition probabilities. A brief description of this dipole moment function will be followed by an outline of the numerical method and its application to the problems just enumerated.

A Non-linear Dipole Moment Function

It has been shown[8] that pure vibrational transition probabilities more accurate than those calculated from the Morse-linear dipole model can be obtained from the postulate that

$$\frac{R^{v',0}}{R^{v'-1,0}} = \frac{(v')^{1/2} - C_1^{v'}(v'-1)}{C_1^{v'}(v')}$$

$$+ \frac{(v'+1)^{1/2} - C_1^{v'}(v'+1)}{C_1^{v'}(v')} \frac{R^{v'+1,0}}{R^{v'-1,0}}, \quad v' \geq 2. \qquad (5)$$

In Eq. (5) the symbol $C_v^{v'}(i) = \int (\psi_{v'}\psi_v/\psi_0)\psi_i dr$, where the ψ's are Morse eigenfunctions for the rotationless states. Explicit formulae for the C's occuring in Eq. (5) are given in the reference cited, together with the detailed basis for the above postulate. Since Eq. (5) gives a unique set of relative vibrational transition probabilities it implicitly defines the dipole moment function to within a multiplicative constant (the value of $R^{1,0}$) and an additive one ($R^{0,0}$, the permanent dipole moment). If Eq. (5) is to be applied to the calculation of vibration-rotation transition probabilities it is necessary to have experimental values for these two quantities. This is virtually the same requirement which was noted above for the linear model, since for the latter the ratio M_1/M_0 is usually determined from observed values of $R^{1,0}$ and $R^{0,0}$ through the approximate relations $M_1 \simeq R^{1,0}/\int \psi_1 \rho \psi_0 \, dr$ and $M_0 \simeq R^{0,0}$. Each of these relations is usually accurate to within one or two percent. A plot of the dipole moment function versus r can be constructed from the relation

$$M(r) = \sum_{i=0}^{n} R^{i,0} \psi_i/\psi_0 + \int_{E>D_e} a(E)\psi(E)dE/\psi_0 \qquad (6)$$

where n is the ordinal number of the highest bound vibrational

state, D_e is the dissociation energy and a(E) is a function which gives the probability of a radiative transition from the ground vibrational state to the continuum. Eq. (6) is derived simply by expanding the function $M(r)\psi_0$ in terms of the vibrational eigenfunctions, a technique first suggested by Trischka and Salwen.[9] As explained in reference 8, for most cases of physical interest one can neglect contributions to M(r) made by the continuum states and by the higher bound states.

Figure 1 shows a plot of M(r) versus r for the lithium hydride molecule. Contributions to Eq. (6) from all bound states up to and including the fifteenth are included. The value used for $R^{0,0}$ was 5.882 debyes, as measured by Wharton, Gold and Klemperer.[10] These same authors reported a value of $R^{1,1} = 5.990$ debyes. From these two values and the ratio $R^{1,0}/R^{2,0}$ one can calculate the absolute value of $R^{1,0}$ through a relation discussed previously by the author,[8]

$$R^{1,1} = R^{0,0} + R^{1,0}\int(\psi_1^2/\psi_0)\psi_1 dr + R^{2,0}\int(\psi_1^2/\psi_0)\psi_2 dr. \tag{7}$$

This leads to a value of $R^{1,0} = -0.254$ debyes. The vibrational eigenfunctions used in Eqs. (5) and (7) were those for a Morse potential

$$U(r) = D_e[1-e^{-\beta(r-r_e)}]^2 - D_e \tag{8}$$

defined by $D_e = 20288\ cm^{-1}$, $\beta = 1.128\ Å^{-1}$ and $r_e = 1.5954$ Å. These are based on the dissociation energy reported by Velasco[11] and the spectroscopic constants given by Herzberg.[12]

Figure 1 also shows the linear dipole moment function derived from the same experimental data. Using the same Morse eigenfunctions the solid curve leads to a ratio $R^{1,0}/R^{3,0}$ which is 30% higher than that given by the broken line. For both of these transitions the eigenfunctions are so small outside the range $r_e \pm 0.5$ Å that the only significant contributions to the integrals come from within this range, where the two M(r) functions differ by a maximum of 1%. This provides a rather striking illustration of the sensitivity of vibrational transition probabilities to variations in the dipole moment function.

The Vibration-Rotation Interaction Factor

From the computational viewpoint the most direct means of relating line intensities to populations is through the evaluation of $R_{v,J}^{v',J'}$ as defined by Eq. (2). However, it is instructive to express each matrix as a product of two factors,

$$R_{v,J}^{v',J'} = R_v^{v'} \; F(m)^{1/2} \tag{9}$$

where $R_v^{v'}$ is the matrix element for the (forbidden) transition $v',0 \leftrightarrow v,0$ and F(m) is called the vibration-rotation interaction factor. In accord with customary spectroscopic notation the symbol m designates a particular line of the v',v band and takes the values

$$m = \begin{cases} J+1 & \text{, R-branch} \\ -J & \text{, P-branch} \end{cases} \tag{10}$$

The F-factor is a function of the four quantum numbers v', v, J' and J but for a given v', v band it shows the extent to which the interaction of vibration and rotations alters the intensity of a given line from that which the pure vibrational line would have if it were allowed. A number of formulae for F-factors have been derived using various potential models, usually coupled with a linear dipole moment function. Besides the papers of Herman at al[4,7] referred to previously one should note the work of Herman and Wallis.[13] This last reference contains a good summary of the earlier literature on this subject.

For purposes of comparison with earlier work, the results of this investigation will be reported in terms of F-factors rather than in terms of the matrix elements $R_{vJ}^{v'J'}$. The additional computational labor which this entails is relatively minor since the F-factors are given by

$$F = [\int \psi_{v',J'} M(r) \psi_{v,J} dr / \int \psi_{v',0} M(r) \psi_{v,0} dr]^2, \qquad (11)$$

where the denominator is the same for every line of a given band. Replacing M(r) in Eq. (11) by the expansion for it given in Eq. (3) leads to the working equation for the calculations reported below

$$F = [\int \psi_{v',J'} \sum_{i=0}^{\infty} M_i \rho^i \psi_{v,J} dr / \int \psi_{v',0} \sum_{i=0}^{\infty} M_i \rho^i \psi_{v,0} dr]^2. \qquad (12)$$

In making use of this expansion for M(r) it is important to note a general property of the integrals $\int \psi_{v'} \rho^i \psi_v dr$ first pointed out by Dunham.[14] For all $i \leq \Delta v$ these integrals will

be appreciably larger than those for which $i > \Delta v$. Hence to evaluate $R_v^{v'}$ from the relation

$$R_v^{v'} = M_1 \sum_{i=0}^{\infty} \psi_{v'} \rho^i \psi_v \, dr \tag{13}$$

it is necessary to include in the summation all terms with $i \leq \Delta v$. Each of them will make a first order contribution to the sum unless its expansion coefficient M_1 is extremely small. This generalization was made for the case of pure vibrational transitions but is valid also for rotation-vibration lines with moderate J values. As a specific example the integral $\int \psi_{1,0} \rho \psi_{0,0} \, dr$ for LiH is thirteen times larger than the corresponding quadratic integral and twenty-one times larger than the cubic. As J increases these ratios decrease steadily. For the P(21) line the integral $\int \psi_{1,20} \rho \psi_{0,21} \, dr$ exceeds its quadratic and cubic analogues by factors of four and eleven, respectively. Hence for low values of J, and F-factor for any $\Delta v = 1$ transition should be approximated very well by the expression

$$F = \left[\int \psi_{v',J'} \psi_{v,J} dr + \frac{M_1}{M_0} \int \psi_{v',J'} \rho \psi_{v,J} dr\right]^2 \Big/ \left[\frac{M_1}{M_0} \int \psi_{v',0} \rho \psi_{v,0} dr\right]^2 \tag{14}$$

For high values of J, and more especially, for bands with $\Delta v > 1$, the neglect of higher terms in Eq. (12) will tend to decrease the accuracy of Eq. (14). The formulae for F-factors derived by Herman, Rothery, and Rubin[4] (referred to hereafter as HRH) are all approximations to Eq. (14). Exact numerical solutions

for Eq. (14) will show what errors are introduced by their algebraic approximations. Carrying Eq. (12) to the quadratic and cubic terms will indicate the errors to be expected from the neglect of higher-order terms in the dipole moment expansion.

The Numerical Method

The heart of the numerical method used in this work is an efficient procedure developed by Cooley[15] for the solution of the radial Schrodinger equation. His paper should be consulted for a full description of the method, together with tests of its accuracy when up to 200 intervals are used in the numerical integration. Information on its use with up to 2000 intervals may be found in a recent paper by this writer.[16] A Fortran program embodying his procedure has been made available by Cooley to participants in the IBM SHARE program. It was written for use on an IBM 704 but can be adapted easily to the 7090. A detailed description of the necessary changes may be found in a recent report by Zare and the author.[17] This report also contains a few modifications which the authors found useful in their applications of this program. The following description of Cooley's procedure is limited to the working equations through which the results presented in this paper were derived.

Let $\psi(r)$ be the solution to the radial Schrodinger equation

$$d^2\psi/dr^2 + [E-U(r)]\psi(r) = 0, \tag{15}$$

where $U(r)$ is the effective potential energy. In the present

instance $U(r)$ is the Morse potential, given by Eq. (8) for rotationless states. For non-zero values of the rotational quantum number J, a term $J(J+1)/r^2$ must be added. Eq. (15) employs dimensionless units of energy and length. When length is measured in Bohr radii, $a_0 = 0.529172$ Å, the unit of energy is equivalent to $hN_0/8\pi^2 ca_0^2\mu_A$ wave numbers, where N_0 is Avagadro's number (physical scale) and μ_A is the reduced mass in Aston units. The numerical value of this factor is $60.2198/\mu_A$.

Values of $\psi(r)$ are obtained at n+2 equally-spaced values of r from the equation

$$Y_{i+1} + Y_{i-1} - 2Y_i = h^2(U_i - E)\psi_i \tag{16}$$

in which h is the separation between adjacent r values, E is a trial eigenvalue and

$$Y_i = [1 - (h^2/12)(U_i - E)]\psi_i. \tag{17}$$

The inward integration is begun by assigning a small arbitrary value to ψ_{n+1} and letting

$$\psi_n = \psi_{n+1}\exp[r_{n+1}(U_{n+1}-E)^{1/2} - r_n(U_n-E)^{1/2}]. \tag{18}$$

The inward integration is continued until ψ_i ceases to increase with decreasing i at some value of r, r_m. Then the outward integration is begun starting with the boundary condition $\psi_0 = 0$ and the assignment of a small arbitrary value to ψ_1 (the value of r_0 need not be zero). It is continued until the value of ψ_m^{out} has been obtained. Each ψ^{out} is divided by ψ_m^{out}, and each ψ^{in} by ψ_m^{in} to give curves normalized to the condition $\psi_m = 1$.

Next a correction to E is determined from the slopes of the two curves at the crossing-point r_m, using the relation

$$D(E) = [(-Y_{m-1} + 2Y_m - Y_{m+1})h^{-2} + (U_m - E)\psi_m] / \sum_{i=1}^{n} \psi_i^2. \tag{19}$$

The first trial eigenvalue E is replaced by $E' = E + D(E)$ and the process is repeated until the correction term is effectively zero. When this has been achieved the final values of ψ_i are normalized to the usual condition

$$\int \psi^2 dr = \sum_{i=1}^{n} \psi_i^2 = 1. \tag{20}$$

When both upper and lower state eigenfunctions have been obtained by this procedure, one has only to generate values of M(r) at the same r-values in order to calculate $R_{vJ}^{v'J'}$ from Eq. (2). The evaluation of the integral can be carried out conveniently by repeated applications of Simpson's rule, sometimes known as the parabolic rule,

$$\int_a^b f(x)dx = \frac{h}{3}[f_a + 4f_{a+h} + 2f_{a+2h} + \cdots + 2f_{b-2h} + 4f_{b-h} + f_b]. \tag{21}$$

The foregoing description covers the computational steps which would be necessary for the calculation of rotational-vibrational matrix elements for any specified U(r) and M(r) functions. As noted above, the present application combines a Morse potential with two different dipole moment functions. When the linear M(r) is used the F-factors are given by Eq. (14), the evaluation of which can be carried out by the procedure just described.

To employ the non-linear dipole moment described above one could carry out point-by-point evaluation of M(r) from Eq. (6), as was done for Fig. 1. An alternative procedure is available and is useful in the present context. The non-linear M(r) function can also be expressed in the form of a Taylor's expansion. It has been demonstrated[8] that for pure vibational transitions the retention of the terms through M_1 in such an expansion will give virtually the same value for $R^{v'}_{v'-1}$ as would the complete expansion. As noted above, this result can be extended to vibration-rotation transitions for moderate values of J. Hence, if one has the Taylor coefficients M_1 for any dipole model a very good approximation to the F-factors for the 2-0 band can be obtained from the relation,

$$F = \frac{\left[\int \psi_{2,J'}\psi_{0,J}dr + \frac{M_1}{M_0}\int \psi_{2,J'}\,\rho\,\psi_{0,J}dr + \frac{M_2}{M_0}\int \psi_{2,J'}\,\rho^2\psi_{0,J}dr\right]^2}{\left[\frac{M_1}{M_0}\int \psi_{2,0}\,\rho\,\psi_{0,0}dr + \frac{M_2}{M_1}\int \psi_{2,0}\,\rho^2\psi_{0,0}dr\right]^2} \qquad (22)$$

and similarly, for the 3-0 band,

$$F = \frac{\left[\int \psi_{3,J'}\psi_{0,J}dr + \frac{M_1}{M_0}\int \psi_{3,J'}\,\rho\psi_{0,J}dr + \frac{M_2}{M_0}\int \psi_{3,J'}\,\rho^2\psi_{0,J}dr + \frac{M_3}{M_0}\int \psi_{3,J'}\,\rho^3\psi_{0,J}dr\right]^2}{\left[\frac{M_1}{M_0}\int \psi_{3,0}\rho\psi_{0,0}dr + \frac{M_2}{M_0}\int \psi_{3,0}\rho^2\psi_{0,0}dr + \frac{M_3}{M_0}\int \psi_{3,0}\rho^3\psi_{0,0}dr\right]^2} \qquad (23)$$

The final computational equation applied in this work is that for deriving the Taylor coefficients M_i which correspond to the dipole moment function implicit in Eq. (5).

$$M_i = \frac{\beta^i}{i!} \sum_{v=0}^{n} R^{v,0} \frac{A_v}{A_0} \sum_{j=0}^{v} (-1)^j \frac{(v-j+1)_j (k-v-j)_j}{j!\, k^j} j^i \qquad (24)$$

where

$$A_v = [\beta(k-2v-1)/v!\Gamma(k-v)]^{1/2}$$

$$(a)_j = \begin{cases} 1 \text{ for } j = 0 \\ a(a+1)\cdots(a+j-1) \text{ for } j > 0 \end{cases}$$

$$k = 4D_e/\omega_e$$

and the remaining symbols have been defined previously. In the present calculations the first summation in Eq. (24) was carried through sixteen terms. This gives six-figure accuracy for the relative value of M_1 and at least four and three, respectively for M_2 and M_3.

It should be noted that the procedure just described for calculation of F-factors proper to the non-linear dipole model may lead to errors of a few percent for higher J values. However, this is of secondary importance. Eq. (24) yields M_i values which are physically reasonable. Therefore, when these are used in Eqs. (14), (22), and (23) we will obtain a good indication of the magnitude of the uncertainties to be expected in the use of the linear dipole model.

To complete this section a few words are necessary on the accuracy and time-requirements of the methods used. Regarding the solution of the radial equation using Cooley's program, the references cited earlier show that when 1000 points are used in the integration both eigenfunctions and eigenvalues are accurate to within the truncation errors of the 7090. Since

this machine carried just over 8 significant decimal digits, the eigenfunctions should have 7-figure accuracy. All the integrals involving these functions are oscillatory in character and hence there is the possibility of losing significant figures through cancellation of oppositely-signed contributions. One procedure for ascertaining whether or not this is a serious source of uncertainty is to evaluate a given integral in two parts. At the same time this checks the adequacy of the Simpson's rule integration formula, Eq. (21). For the linear integrals we have the relation

$$\int \psi' \rho \psi dr = \int \psi' r \psi dr - r_e \int \psi' \psi dr. \qquad (25)$$

For all linear integrals involved in the calculations reported here it was found that the two sides of Eq. (25) differed by less than one part in 10^6. The simplest and most significant test of the procedure as a whole is obtained by ascertaining the sensitivity of the final answers to variations in the computational parameters. In the present case the number of intervals used for the integration was varied between 400 and 1000. The F-factors most sensitive to these changes (those for J'=20) showed a maximum variation of less than one part in 10^4, and generally much less than this. In addition, the range of integration was varied in such a way that the values of the eigenfunctions at the end points decreased from about 10^{-25} to something less than 10^{-39} (a machine zero on the 7090). Maximum

variations in the F-factors were again less than a part in ten thousand. Hence we conclude that all results given below are accurate to within the limits imposed by their graphical representation.

The time required to compute F-factors for a band of forty-one rotational lines, using 1000 intervals in the integration, was slightly over one minute. This included the computation of a set of F's for each of Eqs. (14), (22), and (23) as well as certain other calculations for check purposes. A program omitting all but essential calculations and output, and using only 400 intervals for the integration would give a set of 41 F's in about one-half minute, accurate to at least 0.1%.

The Accuracy of the HRH Formulas

The exact F-factors for the rotating Morse oscillator-linear dipole model are given by Eq. (14). Herman, Rothery, and Rubin[4] have given an approximate general expression for this [their Eq. (50)] and have reduced it to a form more suitable for computation for the four vibrational bands 1-0, 2-0, 3-0, and 2-1 [their Eqs. (1A) through (4A), respectively]. It should be noted that typographical errors in their original paper affected all of these equations, directly or indirectly. However, the graphs given in that paper were calculated from the correct equations and they will be used for comparison with the present results.

Using the same Morse parameters for HF as were employed by HRH, the linear dipole F-factors for the four bands mentioned above were calculated numerically and compared with the HRH approximations given in their figure 2. For both the 1-0 and 2-1 bands the two results were identical to within about 1%, the accuracy to which the graphs could be read. This holds for all lines up to and including $m = \pm 12$, the highest m values for which the HRH results were given. For the 2-0 and 3-0 bands significant differences were found, as shown in figure 2. For the 3-0 band, only the R-branch lines are shown since differences for the P-branch lines were less than 1%.

The same comparisons were made for HCl (HRH, Fig. 1). The absolute values of the deviations were less but their pattern was entirely similar to the HF results. Reasons for relying on the high accuracy of the numerical results have been given above. In addition it might be noted that the eigenfunctions used to calculate F's for the 2-0 band are employed also for the 1-0 and 2-1 band. If either were in error one would expect that the results for either 1-0 or 2-1 would also be erroneous. This degree of internal consistency is not necessary in the HRH results since the F-factors for each band are calculated from a different formula. Each is a reduced form of their Eq. (50), appropriate to one band only since the indices of the thirteen summations in that equation all involve either v or Δv. (Some of the summations are multiple and the complexity of the

resultant formula increases very rapidly with each increase in v or Δv.) Hence we conclude that the HRH formulae for the 1-0 and 2-1 transitions are vitually exact at least up to $|m| = 12$, while their 2-0 and 3-0 formulae can introduce errors of several percent in this range. As will be shown below, these errors are less than the uncertainties which arise from the neglect of higher terms in the dipole moment expansion. Nevertheless, they are undesirable and can be avoided easily by using the numerical procedure.

F-factors for Quadratic and Cubic Dipole Moment Functions

The dipole moment function for LiH plotted in Fig. 1 can be represented by a Taylor series in ρ, the first four expansion coefficients of which have the values $M_0 = 5.830$ debyes, $M_1 = 2.148$ debyes/Å, $M_2 = 0.162$ debyes/Å^2, and $M_3 = -0.0475$ debyes/Å^3. Using these to evaluate the M_i/M_0 ratios in Eqs. (14), (22), and (23) one can calculate F-factors for a linear, a quadratic and a cubic approximation to Eq. (12). This has been done for each of the 1-0, 2-0, and 3-0 bands of LiH. The results are shown in Fig. 3.

As part a of the figure indicates it is only for the few highest $|m|$ values that differences in the three approximations for the 1-0 band can be shown on the scale used. In part b it is seen that the linear and quadratic approximations for the 2-0 band are significantly different, while the cubic is graphically indistinguishable from the quadratic. Finally,

part c shows that the F-factors for the 3-0 band are affected significantly both by the retention of quadratic and of cubic terms. All these results are in accord with the generalization discussed earlier, that a $\Delta v = 1$ transition probability will depend significantly on terms through M_1 in the Taylor expansion for $M(r)$. The F-factor will be affected much less by the neglect of higher terms that will the element $R_{vJ}^{v'J'}$ since there is a considerable cancellation of error in the terms neglected in both numerator and denominator of Eq. (12). For the range of J and i values studied here the integrals $\int \psi_{v',J\pm1} \rho^i \psi_{v,J}\, dr$ are always of the same sign as the integral $\int \psi_{v',0} \rho^i \psi_{v,0}\, dr$. Further, their relative magnitudes indicate that a reversal of sign would not occur until considerably higher J values were employed. Nevertheless, the differences between the linear and higher approximations for bands with $\Delta v > 1$ can be considerable. This is illustrated more clearly by Fig. 4, where the ratio of the cubic F to the linear for the 3-0 band of LiH is plotted against m.

Since initial state population is directly proportional to F, Fig. 4 may be taken as a rough index of the uncertainty introduced in relative rotational popultation calculations by the use of a linear dipole model for a $\Delta v = 3$ transition. In favorable cases the line intensities may be measured to within 10% or so. From the figure it is seen that the cubic to linear ratio exceeds this everywhere in the range $-6 > m > 4$. In fact, for the highest R-branch lines shown, the two approximations differ by a factor of more than 3.

It might be noted that LiH exhibits a greater sensitivity in this respect than do the other molecules investigated in this study, namely HF, HCl and CO. This is related to the greater strength of its vibration-rotation interaction, a good criterion for which is given by the magnitude of the parameter $\Theta = M_0/M_1 r_e$. From the data given earlier, Θ for LiH has a value of 1.71. For the other molecules the Θ values are, respectively, 1.18, 0.99 and 0.036 (see ref. 4 for original references). On the other hand, the dipole moment model being used here departs relatively little from linearity. The M(r) curve for LiH calculated by James, Norris, and Klemperer[18] shows much greater curvature over the range plotted in Fig. 1. It is quite possible that the true M_2 and M_3 coefficients would have greater magnitudes than those used here, thereby accentuating the differences between the linear, quadratic and cubic approximations. Hence it is not unreasonable to regard Fig. 4 as giving a fair indication of the sensitivity of F-factors for a $\Delta v = 3$ band to variations in the dipole moment function. That this sensitivity is so great for higher J values implies that a very accurate knowledge of the dipole moment function would be required in order to derive reliable populations from the line intensities of such a band. Conversely, it may be a useful property in determining the shape of the dipole moment function from the same data.

Conclusions

The numerical method proposed in this paper for the calculation of vibration-rotation transition probabilities offers many advantages over the approach of seeking algebraic formulae for these quantities. First, the method is extremely flexible and can make use of every improvement in potential and dipole moment function models with no essential increase in computational labor. Secondly, it gives highly accurate results for whatever models are chosen. It has been shown that approximate solutions, such as the HRH formulae for the Morse-linear dipole model, can introduce appreciable errors over and above those inherent in the choice of approximate models. Thirdly, the method can be applied easily and is very economical in terms of computer-time requirements. Approximate formulae can involve very tedious algebraic reductions, especially in the case of higher quantum numbers, and the possibility of errors arising in this procedure cannot be discounted lightly. On the other hand, the numerical method is no more difficult for high quantum numbers than for low, and the same simple procedures are available for checking the accuracy of the results. The foregoing remarks are not intended to deny the value of approximate algebraic solutions for problems which can be handled numerically. Numerical solutions are generally devoid of heuristic value for approaching more complex problems. However, for purposes of practical computation, such as deriving rotational populations from line intensity data, the use of

approximate formulae implies an introduction of error that now can be avoided easily.

Finally, it has been shown that for $\Delta v > 1$ bands the vibration-rotation interaction factors can be sufficiently sensitive to variations in the dipole moment function to introduce uncertainties from this source which are comparable to the uncertainties in line intensity measurements.

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Captions for Figures

1. Dipole moment functions for LiH. Solid curve: $M(r)$ curve implicit in Eq. (5) when $R^{0,0} = 5.882$ debyes and $R^{1,0} = -0.254$ debyes. Broken curve: the linear dipole $M(r) = 5.830 + 2.148\,(r-r_e)$.

2. Ratios of F-factors for the 2-0 and 3-0 bands of LiH calculated from the approximate formulae of Herman, Rothery and Rubin[4] to those calculated by the numerical method. Smoothed curves were drawn through points having an absolute uncertainty of about 1% from the graphical origin of the HRH data.

3. F-factors for the 1-0, 2-0 and 3-0 bands of LiH, each calculated for a linear, a quadratic and a cubic approximation to the dipole moment function.

4. Ratios of the cubic to the linear F factors for the 3-0 band of LiH. To a very good approximation the cubic F's are those given by the solid curve in Figure 1, while the linear F's are derived from the broken-line $M(r)$ of the same figure.

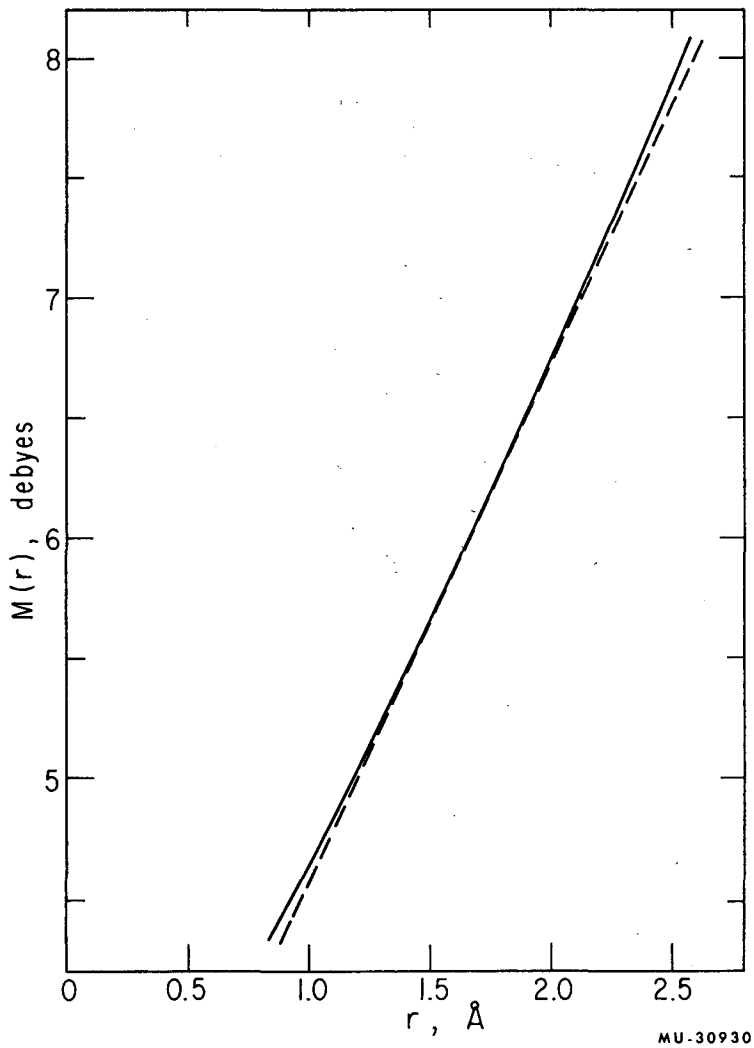
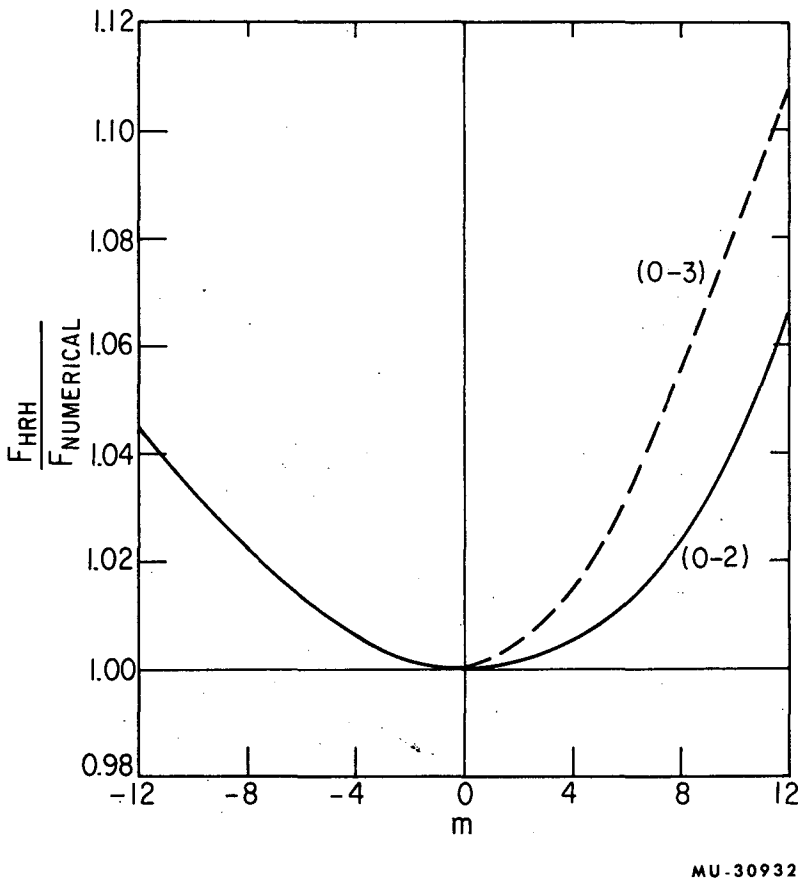


Fig. 1.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1.06
1.04
1.02
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(0-2)
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-8
-4
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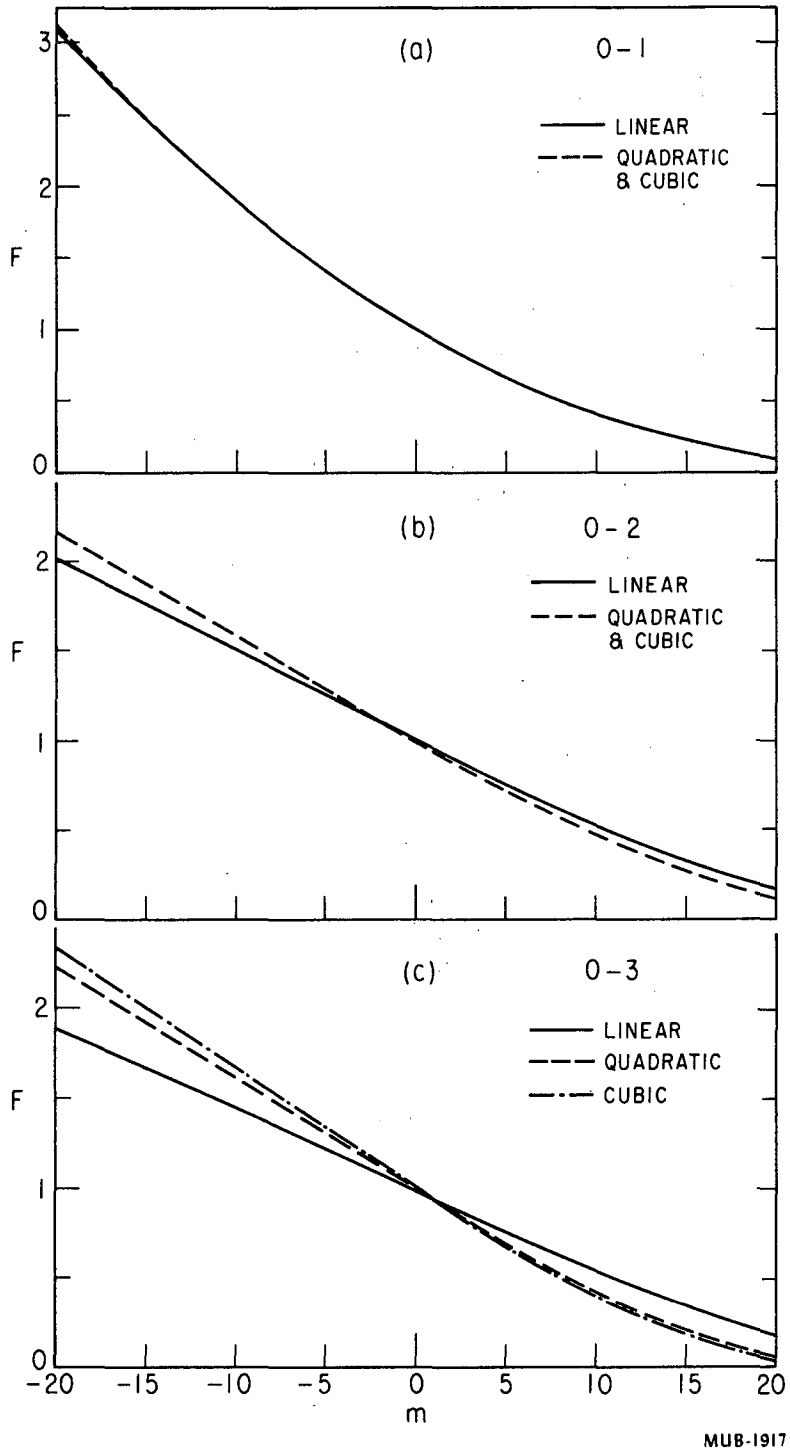
4
8
12
m
MU-30932

Fig. 2.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QUADRATIC & CUBIC
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3
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(b)
0-2
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F
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1
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(c)
0-3
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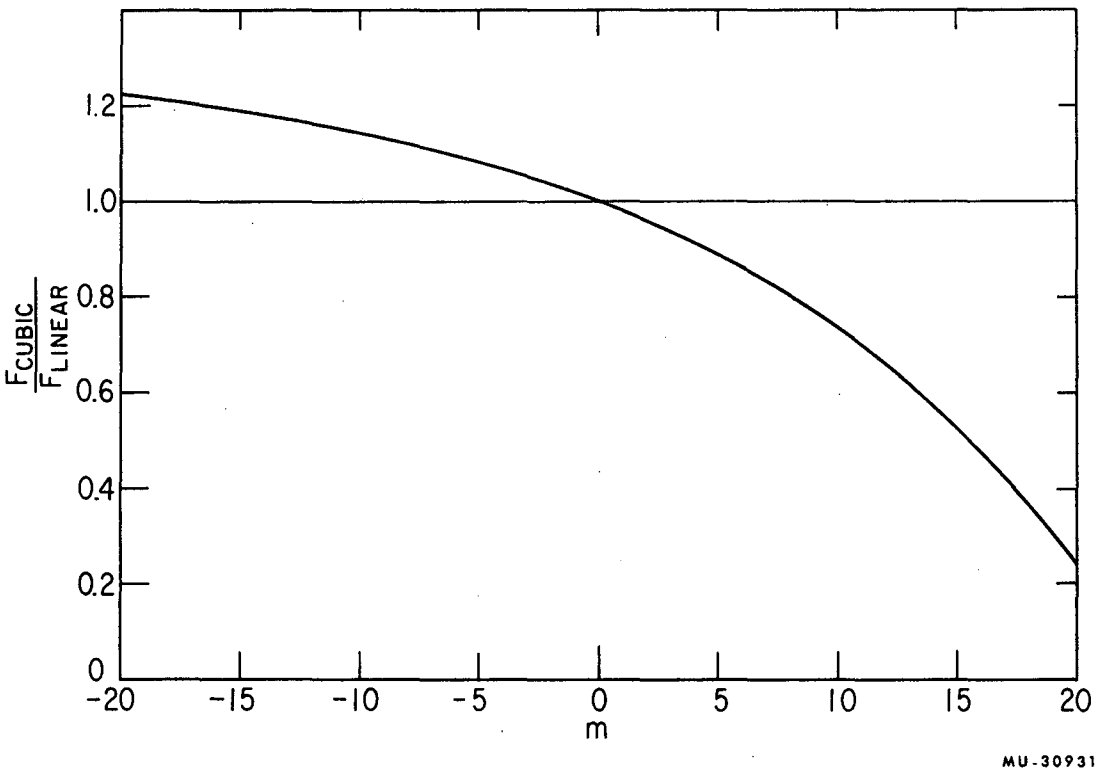
Fig. 3.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-20
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-10
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0
5
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Fig. 4.

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