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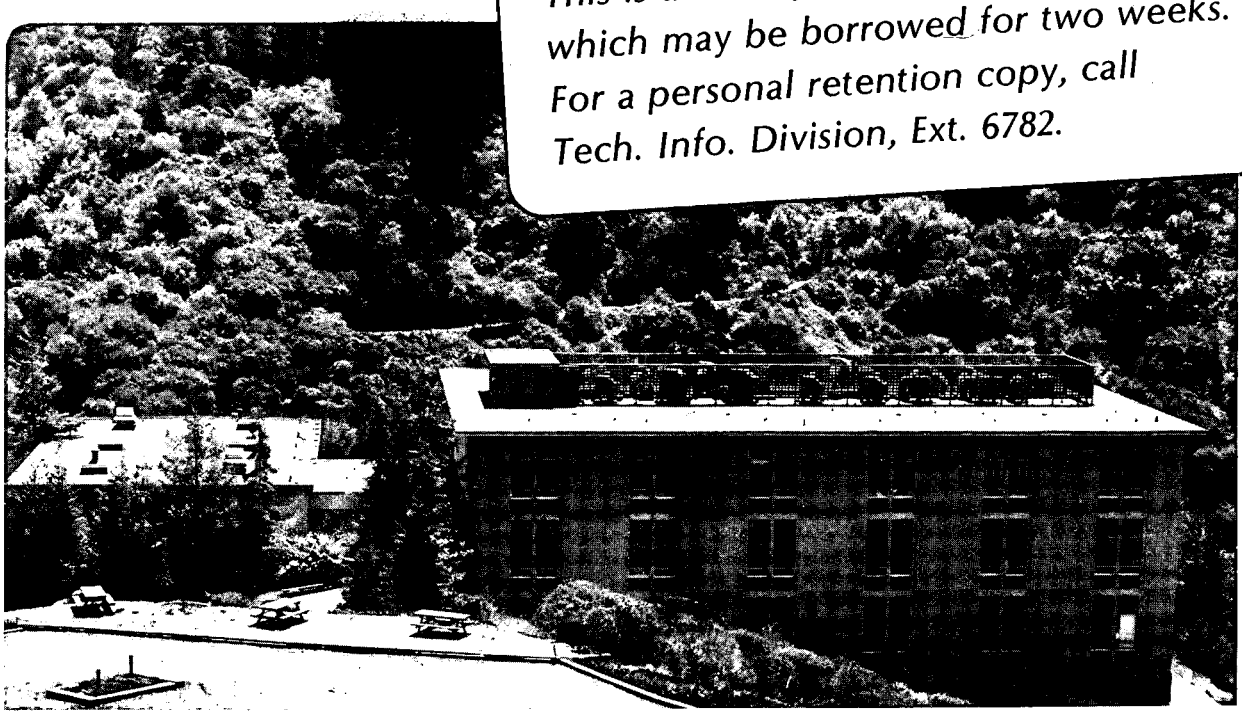

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# VELOCITY MODULATION ELECTRONIC ABSORPTION SPECTROSCOPY OF MOLECULAR IONS

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For several decades optical emission spectroscopy has been the only technique available for the investigation of electronic spectra and structures of molecular ions.[1-3] The inherently strong emission produced by electronic transitions at visible and ultraviolet wavelengths has been critically important to studies of charged species because the chemical reactivity and Coulomb repulsion of ions limit their steady-state densities to extremely low levels (typically 1 ppm of the total gas density). This high sensitivity of optical emission techniques is, however, compromised by several other factors,[4] including the strong interference from emissions of the far more abundant neutral molecular species, the unavailability of ro-vibronic population information on the lower state of the transition, the requirement that a rapid rate of production exists for the upper state, and a rather low resolution compared to that attainable in laser applications. Nevertheless, the majority of all rotationally resolved electronic spectra of molecular ions observed to date have been detected and measured by optical emission spectroscopy, and without this foundation the development of more sophisticated laser techniques would have been severely impeded.

Principally through rapid advances in the technology of tunable lasers, several new experimental approaches to molecular ion electronic spectroscopy have been devised.[2,3,5] The most powerful of these have been laser-induced fluorescence detection of charged molecules in discharge sources, ion beams, and RF quadrupole traps, and Doppler-tuned ion beam resonance experiments, all of which depend on <u>indirect</u> effects of the laser excitation for detection of the electronic transitions. Although these methods have been quite effective in overcoming some of the limitations of optical emission spectroscopy, the indirect detection schemes place rigid constraints on acceptable chemical and physical

properties of the charged species, and thus limit the generality of these otherwise sensitive and powerful approaches to electronic absorption spectroscopy. Moreover, these techniques generally require relatively high laser power levels in order to achieve good sensitivity; this, in turn limits the wavelengths that can be employed for high resolution measurements to the visible region. In this letter we describe a very simple new direct absorption technique for measurement of electronic spectra of molecular ions with Doppler limited resolution and with the imposition of minimal power requirements on the laser.

The technique of velocity modulation ion spectroscopy, which has proven to be highly successful in infrared vibration-rotation studies[6,7] of $HCO^+$, $HNN^+$, $H_3O^+$, and $NH_4^+$, has been extended to visible wavelengths by combining a single frequency tunable dye laser with an AC glow discharge molecular ion source. In these AC discharges the component of the ion drift velocity along the axis of the positive column is reversed each AC half-cycle, thereby Doppler shifting the electronic transition frequencies alternately to the red and to the blue. In predominantly He or $H_2$ discharges the electric field (E) of the positive column[8] and the ion mobility[9] (K) combine to yield drift velocities ($v_d = KE$) which are comparable to thermal random velocities. Thus the magnitude of the Doppler shift is comparable to the thermal Doppler linewidth, and the absorption of laser radiation which is tuned into resonance with an ionic transition is amplitude modulated at the discharge frequency. Phase sensitive detection then provides not only a narrow detection bandwidth, and therefore high sensitivity, but also very effectively suppresses absorptions due to neutrals, which are several orders of magnitude more abundant, but which remain unaffected by the electric field reversals.

The experiment (Fig. 1) is similar to those previously reported at infrared wavelengths,[6] but with two important differences. First, the color center laser has been replaced by a single mode dye laser (Spectra Physics 385), which was pumped with an $Ar^+$ laser and scanned in 390 MHz longitudinal cavity mode hop increments by ramping the PZT of an intracavity airgap etalon (FSR = 75 GHz). The intracavity solid etalon (FSR = 900 GHz) and the birefringent filter were manually tracked, permitting scan widths of ~10 $cm^{-1}$. Secondly, the ordinarily large amplitude fluctuations due to ion laser noise and dye jet instabilities were minimized by employing a spatial double beam configuration, providing a laser power reference which was balanced against the signal power with a rotatable polarizer and then subtracted. A thirty-fold noise reduction resulted, yielding a minimum detectable fractional absorption of 2 parts in $10^5$. Even with this subtraction scheme, laser power fluctuations limited this ultimate sensitivity.

The discharge cell used was a liquid nitrogen cooled 70 cm x 0.5 $cm^2$ pyrex tube operating with a flowing gas mixture consisting mainly of He (1-10 Torr) with 50-300 mTorr of Ar, CO, or $N_2$. The electrodes were watercooled coils of copper tubing, placed in sidearms so that the laser beam probed only the positive column of the discharge. The 30 mA, 1.5 kHz AC discharge was driven by a Bogen audio amplifier (Model MT 250, 250 watt), the output of which was stepped up to 3 kV rms in a neon sign transformer. Signal detection and background subtraction were performed by a bridge arrangement of two PIN photodiodes (HP 5082-4220). Lock-in detection at the discharge frequently (1.5 kHz) was used to demodulate the absorption signals, which were subsequently displayed on an X-Y recorder.

To demonstrate the effectiveness of this technique for electronic spectroscopy of ions, we have studied three fine-structure transitions in metastable $Ar^+$ ($^4F \rightarrow {}^4D$), the (2,0)[=(v",v')] band in the $X^2\Sigma^+ \rightarrow A^2\Pi$ system of $CO^+$, and the (1,5), (2,6), and (3,7) bands of the $N_2^+$ $X^2\Sigma_g^+ \rightarrow A^2\Pi_u$ system (Fig. 2), all of which fall in the dye wavelength region of rhodamine 640 (6200-6500 Å). The X-A $N_2^+$ system was first measured by optical emission spectroscopy[10] and has subsequently been investigated by several other spectroscopic methods.[3,11] In spite of this, these three particular vibrational bands of $N_2^+$ have never before been observed with resolved rotational structure, owing to the long radiative lifetime of the $A^2\Pi_u$ state[12] ($\tau \approx 10$ μsec) and the overlapping $A^3\Sigma_u^+$ - $B^2\Pi_g$ system of neutral $N_2$. The $CO^+$ and $Ar^+$ spectra are inherently stronger and less obscured by overlapping neutral bands, and have therefore been more completely characterized in conventional studies.[2,3,13]

Velocity modulated ion spectroscopy can also be used as a powerful non-intrusive probe of ion and discharge dynamics. For these preliminary studies, $N_2^+$ was the more convenient probe species, because $He/N_2$ mixtures do not produce the carbon deposits which form when organic compounds are discharged and thus necessitate frequent discharge cell cleaning. The vibrational and rotational temperatures for the $^2\Sigma$ ground state of $N_2^+$ have been estimated from the observed spectra to be 5000 K and 200 K, respectively. As these temperatures were determined from relative intensity measurements of $N_2^+$ transitions observed in liquid nitrogen cooled (77 K) discharges, the highly non-equilibrium nature of the plasma environment is evident. The linewidths of $N_2^+$ transitions were observed to be ~750 MHz (HWHM), which is considerably broader than those expected from thermal (77 K) Doppler broadening. It is not presently clear whether unresolved nitrogen hyperfine structure or a high translational temperature

(~560 K) is responsible. A quantitative study of $CO^+$ kinetic temperatures [X → A (0,1) band] is presently in progress, in which single mode scanning is employed, rather than the mode hopping method described above. Single mode scanning permits precise linewidth and relative intensity measurements to be made, and also provides for much more efficient laser noise subtraction. The high sensitivity (1 part in $10^6$ minimum detectable fractional absorption) which is realized in these experiments is illustrated in Figure 3, where a single mode scan ot the $R_{21}(2)$ line of the (0,1) $X^2\Sigma - A^2\Pi$ band is shown. Extensive $CO^+$ measurements suggest that not only are the rotation and translation degrees of freedom out of equilibrium, but also that the Doppler width is dependent upon the total He pressure and the rotational state. A complete treatment of $CO^+$ and $N_2^+$ dynamics in He discharges will be published separately.

By combining our absorbed power measurements on the (2,6) band with the radiative lifetime and Franck-Condon factors from optical emission measurements,[12] the absolute density of $X^2\Sigma$ $N_2^+$ is estimated to be $7 \times 10^{12}$ $cm^{-3}$. A large uncertainty (50%) in the number density arises from the uncertainties in several parameters, including rotational and vibrational partition functions, linewidth measurements, the ratio of Doppler shift to linewidth (modulation depth), unresolved hyperfine structure, and the measurement of these very weak absorption strengths (0.01%). Nonetheless, the spatial resolution and non-intrusive nature of this simple technique offers important advantages over conventional microwave phase shift and Langmuir probe density measurements for measuring ion densities in plasmas.

The development of this new technique for measuring electronic transitions in ions presents a variety of exciting possibilities for both spectroscopic and dynamical studies. Perhaps of greatest interest is the

exciting opportunity for measuring high resolution ultraviolet spectra of ions, which is created because of the low power requirements (~10 nW) of this direct absorption method, since cw powers of this magnitude can be generated in the ultraviolet by several nonlinear mixing processes with cw visible lasers.[14] Quantitative measurement of linewidths and Doppler shifts of ions in plasmas can illuminate the important collisional processes partitioning the ion translational energy into drift and random components. Transverse probing of a discharge can reveal the density and temperature (translational, rotational, and vibrational) profiles of the ionic species. Finally, and of the most obvious interest, velocity modulation electronic absorption spectroscopy will clearly be a powerful new tool for the discovery of new molecular ion spectra.

Acknowledgments

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Figure Captions

Figure 1. Diagram of velocity modulation spectrometer.
TDL = Tunable Dye Laser, S. A. = Spectrum Analyzer,

Figure 2. The $Q_2$, $R_2$, and $Q_{21}$ branches in the (2,6) band of the $N_2^+$ $X^2\Sigma_u^+ \rightarrow A^2\Pi_g$ system. The bandhead is at 15,530.29 $cm^{-1}$. The spin splitting between the $R_2$ and $Q_{21}$ branches is easily resolved for $N \geq 6$. This spectrum is a composite of three overlapping scans, each recorded with a lock-in time constant of 125 msec. Discharge conditions: 10 Torr He, 170 mTorr $N_2$, liquid nitrogen cooling, 30 mA, 1.5 kHz.

Figure 3. The $R_{21}(2)$ transition ($\tilde{\nu}$ = 22017.16 $cm^{-1}$) in the $X^2\Sigma^+ \rightarrow A^2\Pi_{\frac{1}{2}}$ (0,1) band of $CO^+$. Factional absorption = .06%, lock-in time constant = 400 msec, 100 mTorr CO, 7 Torr He, 46 mA, 15 KHz discharge.

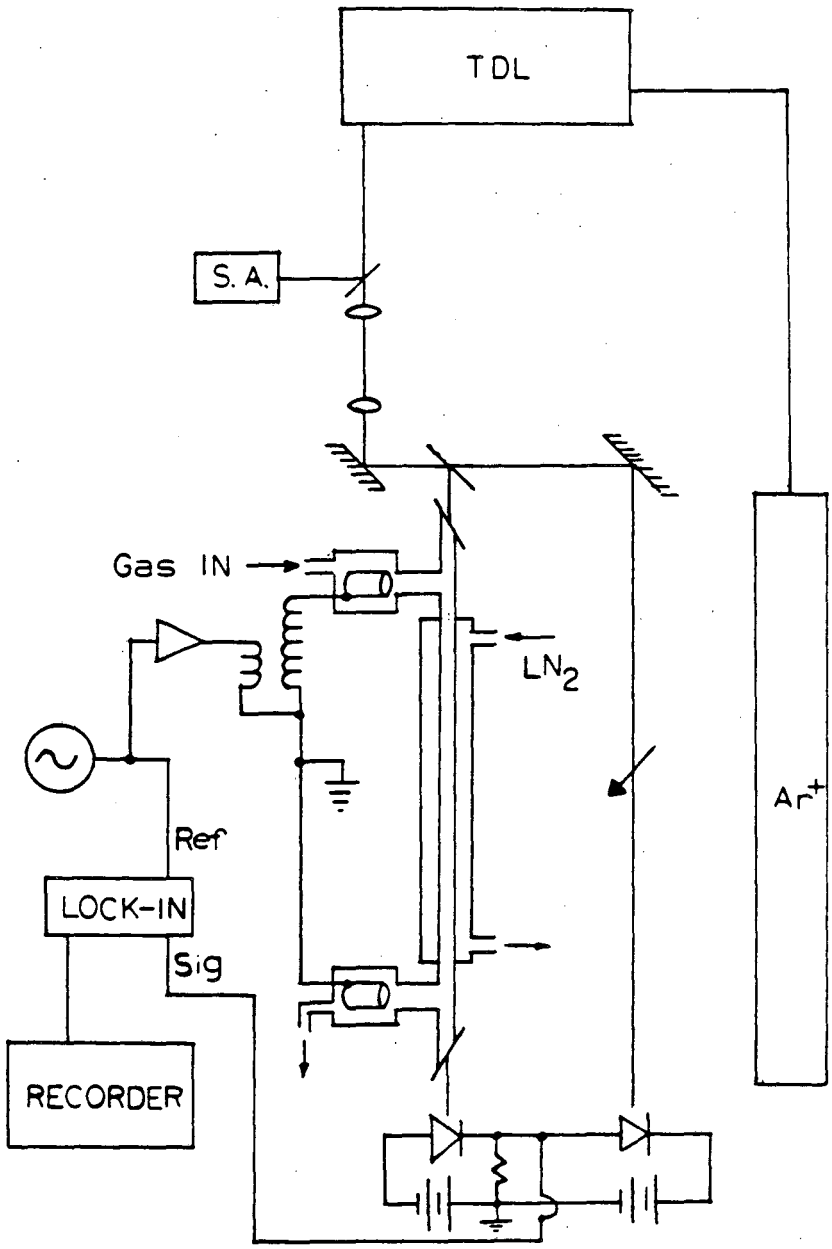


Figure 1

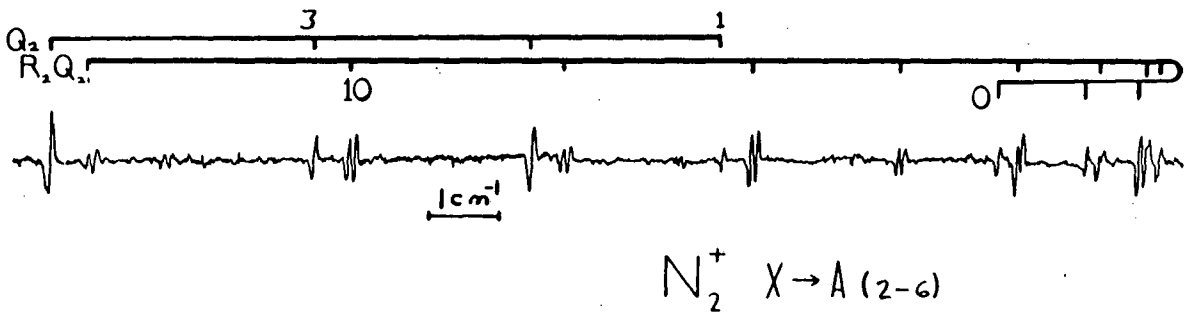


Figure 2

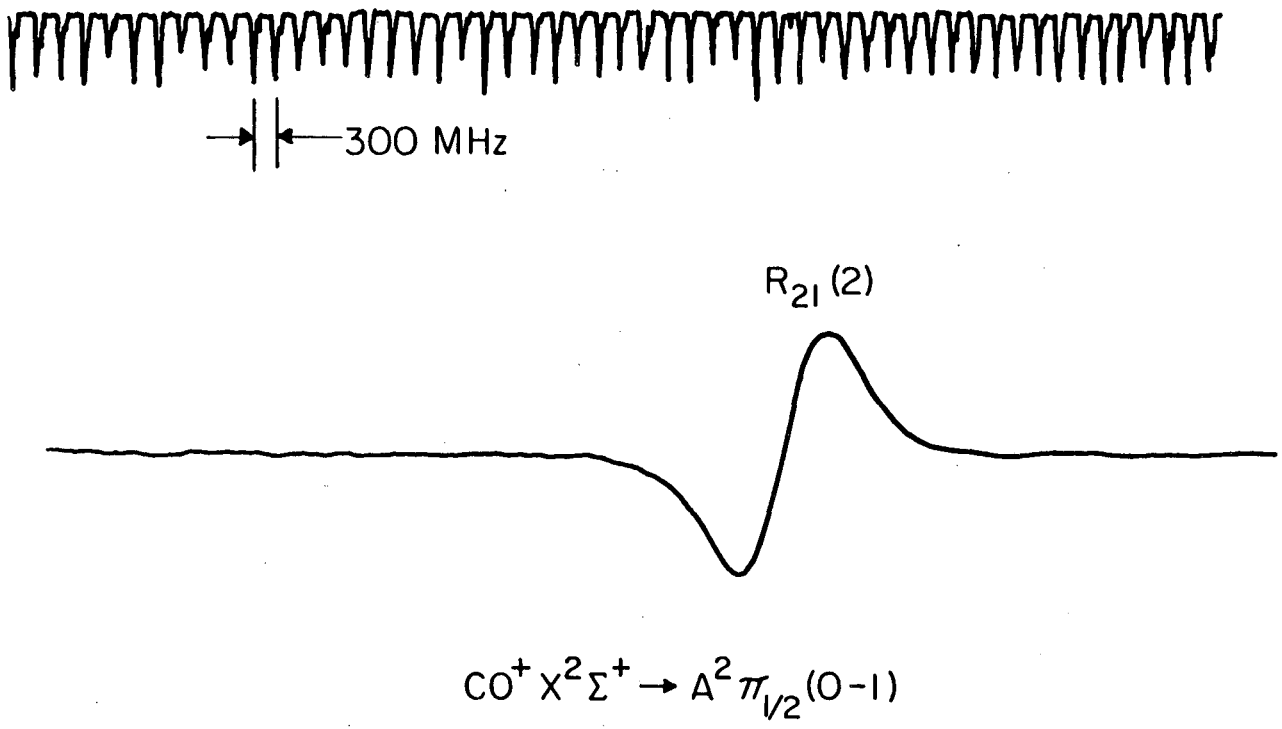


Figure 3

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