ELECTRONIC SPECTROSCOPY OF MOLECULAR IONS BY VELOCITY MODULATION WITH cw DYE LASERS: 
A NON-INTRUSIVE, IN SITU STATE-SELECTIVE PROBE OF PLASMA DYNAMICS

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Translational and rotational population distributions were measured for the X \( ^2 \Sigma^+ \) ground states of \( \text{N}_2^+ \) and \( \text{CO}^+ \) in plasma environments by velocity modulation laser spectroscopy. These experiments reveal rotational state-dependent linewidths for \( \text{CO}^+ \) in low-pressure plasmas, while translational temperatures in excess of rotational temperatures, and non-Boltzmann rotational distributions were observed for both of these ions in low-pressure plasmas.

In this Letter we describe a simple new direct absorption technique for measurement of electronic spectra of molecular ions generated in ac plasmas with very high sensitivity, with Doppler-limited resolution, and with the imposition of minimal power requirements on the laser. We demonstrate the use of this method for the extraction of information on the translational, vibrational, and rotational population distributions of molecular ions in plasma environments. These experiments reveal a strong dependence of molecular ion translational energies on the rotational state of the ion and ion translational temperatures which exceed rotational temperatures, for certain plasma conditions.

The technique of velocity modulation laser absorption spectroscopy [1], which has proven to be highly successful in infrared vibration-rotation studies, of \( \text{HCO}^+ \), \( \text{HNN}^+ \) [2], \( \text{H}_3\text{O}^+ \) [3], \( \text{NH}_4^+ \) [4], \( \text{H}_2\text{F}^+ \) [5], \( \text{HCS}^+ \) [6,7], \( \text{HCNH}^+ \) [8], \( \text{OH} \) + [9], and \( \text{H}_2\text{O}^+ \) [9], has been extended to visible wavelengths by combining a single-frequency tunable dye laser with an ac glow discharge. 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 \( \text{H}_2 \) discharges the electric field \( (E) \) of the positive column and the ion mobility \( (K) \) combine to yield drift velocities \( (v_d = K E) \) which are comparable to random thermal 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 not only provides a narrow detection bandwidth, and therefore high sensitivity, but also very effectively suppresses absorptions due to neutral, which are orders of magnitude more abundant, but which remain unaffected by the electric field reversals [1].

The W-visible laser velocity modulation experiment, shown in fig.1, is very similar to those reported earlier at infrared wavelengths, but with two important differences: the color center laser has been replaced by a single-mode scanning dye laser, pumped by an \( \text{Ar}^+ \) laser, and a spatial double-beam power subtraction configuration [10] was employed to minimize the effects of the large amplitude fluctuations from the \( \text{Ar}^+ \) pump laser and the dye jet instabilities. With this system, proper balancing of the reference beam with the signal power resulted in a hundred-fold reduction in the amplitude noise, yielding a minimum detectable fractional absorption of 1 part in \( 10^6 \).

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The discharge cell used was a liquid-nitrogen-cooled 70 cm X 0.5 cm² Pyrex tube operating with a flowing gas mixture consisting mainly of He (1–10 Torr) with 50–300 mTorr of Ar, CO, or N₂. The electrodes were water-cooled coils of copper tubing, placed in side-arms so that the laser beam probed only the positive column portion of the discharge. The ac discharge was driven by an audio amplifier, the output of which was stepped up to about 3 kW rms in a neon sign transformer. Signal detection and background subtraction were performed by a bridge arrangement of two Si photodiodes (SGD-1GO A). Lock-in detection at the discharge frequency was used to demodulate the absorption signals, which were subsequently displayed on an X-Y recorder.

To evaluate the effectiveness of this new technique for electronic spectroscopy of ions, we first studied three fine-structure transitions in metastable Ar⁺(4F → 4D), the (2,0) band in the X²Σ⁺ → A ²Πu system of CO⁺, and the (1,5), (2,6), and (3,7) bands of the N₂⁺ X²Σ⁺ → A ²Πu system (Meinel bands), all of which fall in the wavelength region of rhodamine (6200–6500 Å). The X-A system of N₂⁺ was first measured by optical emission spectroscopy [11] and has subsequently been investigated by several other spectroscopic methods [12]. In spite of this, these three particular vibrational bands of N₂⁺ have only recently been observed with resolved rotational structure [13,14], owing to the long radiative lifetime of the A ²Πu state (=10μs) and the overlapping A 3Σ⁺u-B 3Πg system of neutral N₂. The CO⁺ and Ar⁺ spectra are inherently stronger and less obscured by overlapping neutral bands, and have therefore been more completely characterized in previous conventional studies [15].

A 10 cm⁻¹ portion of the At X(1-5,2-6, and 3-7) bands of N₂⁺, observed by velocity modulation, and therefore free of interference from neutral absorbers, is presented in fig. 2. For these measurements, the dye laser (Spectra Physics 385) was scanned in discrete 390 MHz cavity mode-hop increments by ramping the PZT of an intracavity airgap etalon (FSR = 75 GHz) and manually tracking the birefringent filter and solid etalon. This procedure could be used to make ≈10 cm⁻¹ scans, albeit with some difficulty.

The discharge, generated in 5 Torr of helium containing 100 mTorr of N₂, was driven at 1.5 kHz by a 250 W amplifier (Bogen MT-250), which produced about 30 mA of current. The smallest fractional absorption measurable with this arrangement was ≈2 x 10⁻⁵.

The vibrational temperature for this band of N₂⁺,

\[
\begin{align*}
\text{(1-5)} & \quad \text{[1]} \\
\text{(2-6)} & \quad \text{[1]} \\
\text{(3-7)} & \quad \text{[1]}
\end{align*}
\]

Fig. 2. The (1,5), (2,6), and (3,7) bands of the N₂⁺ X²Σ⁺ → A ²Πu system. The (2,6) bandhead is at 15530.29 cm⁻¹, while that for the (1,5) band occurred at 15875.7 cm⁻¹. This spectrum was recorded with a time constant of 125 ms. Discharge conditions/ 5 Torr He, 100 mTorr N₂, liquid nitrogen cooling, 30 mA, 1.5 kHz.
generated under these conditions, was estimated from the relative intensities of each band. In fig. 2 it is apparent that all three bands are essentially equal in intensity. Considering Franck–Condon factors and assuming a Boltzmann distribution, an effective vibrational temperature of 7000 ± 3000 K was determined. The rotational temperature was estimated from relative line intensity measurements, obtained from the peak-to-peak amplitudes of individual rotational components, adjusted for laser power and line strengths and graphed as a standard Boltzmann plot. The resulting rotational temperatures observed were 200 ± 50 K. Assuming the Doppler linewidth (Δν) to be greater than the Doppler shift (Δν), linewidth estimates were based on the maxima separation of the derivative lineshape and were calibrated against the laser mode-hop scan increment (390 MHz). Linewidths (hwhm) of 750 ± 200 MHz were obtained for the N₂⁺ transitions in this fashion, a very surprising result since the Doppler width at 77 K is only 280 MHz for these transitions. Unresolved hyperfine splitting could have been the cause of the broadening, although the experiments on CO⁺ described next instead suggest that the assumption that Δν > Δν may break down at low pressures. Linewidths corresponding to a translational temperature that is much higher than the rotational temperature have been observed by Walkup, Dreyfus, and Avouris [16] in their optogalvanic study of N₂⁺ in cathode sheath plasmas. In contrast to the positive column, ions in the sheath are virtually collision free, and the lack of equilibrium is therefore not surprising.

By combining the absorbed power measurements for the (2,6) band with radiative lifetimes and Franck–Condon factors from optical emission measurements, the absolute density of X²Σ⁺ N₂⁺ is estimated to be 7 X 10¹² cm⁻³. A large uncertainty (50%) in this number density arises from the corresponding 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 actual measurement of these weak absorption strengths (0.01%). Nevertheless, the high spatial resolution and non-intrusive nature of this simple technique offer interesting potential advantages over conventional microwave phase shift and Langmuir probe techniques for measuring ion densities in plasmas [17].

In order to make more precise linewidth and intensity measurements, and to further explore the interesting dynamical features of molecular ion transitions, the mode-hop scanning laser system was replaced with a continuous, single-mode scanning laser (Coherent 599-21), rented from the San Francisco Laser Center. The double-beam subtraction technique worked considerably better in this configuration, yielding a minimum detectable absorption of ≈1X10⁻⁶ for the A ← X(1-0) band of CO⁺. A 10 cm⁻¹ portion of the R₂₁ bandhead of this system, located near 420 nm, is shown in fig. 3. Several unassigned lines in this scan are probably due to the B ²Σ⁺ − X ²Σ⁺ system of N₂⁺, as determined by their behavior upon introduction of N₂ into the discharge, while the others are of unknown origin. Similar spectra were recorded over the range 22010-22021 cm⁻¹, using stilbene 420 dye pumped by 2.0 W in the UV lines of a Spectra Physics 171 Ar⁺ laser. In this work, the Bogen amplifier was replaced by an Altec (model 9440A), operating at 15 kHz, with ≈80 mA current output. The discharge was again cooled with liquid nitrogen. The laser frequency was measured with the use of Te₂ calibration lines and a 300 MHz marker etalon. The linewidth of a single rovibronic transition (again assuming Au > Δν) could be measured in this fashion with a precision of ±75 MHz.

The R₂₁ bandhead of the O-1 band of CO⁺ occurs in a very narrow wavelength interval. This enabled us to conveniently measure the linewidths of these transitions as a function of rotational state over a considerable range in rotational quantum numbers (ν = 0-12). The most interesting result of these measurements, as shown in fig. 4, is that for total pressures ≤1.0 Torr, the linewidth was observed to be a strong function of CO⁺ measured near 420 nm by velocity modulation laser absorption spectroscopy.
of rotational state increasing rapidly with $N$ for $N \gg 5$. Moreover, as discussed previously in connection with the measurements on $N_2^+$, the translational "temperature", as deduced from the Doppler widths (350 ± 10 K) of low-$N$ transitions, is higher than the rotational "temperature" (180 ± 4 K), and increases to approximately 700 K for $N = 11$. $T_{rot}$ was estimated from a Boltzmann plot, in which a rather obvious departure from linearity indicated that even the populations in rotational states of CO+ are not in thermal equilibrium in these low-pressure plasmas.

These "low-pressure" results can be contrasted with the linewidth measurements made at total pressures near 4 Torr, also shown in fig. 4. In this case, both the translational and rotational energy distributions are somewhat cooler (270 and 160 K, respectively), and no systematic variation of the linewidth with $N$ is evident. The Boltzmann plot for the $R_{21}$ bandhead members at this pressure exhibits a smaller, but still observable curvature. Hence, the translational and rotational quantum state distributions of CO+ in helium are also quite strongly dependent on the pressure.

The fact that the rotational temperatures of the ions exceed the wall temperature by 100-200 K can be understood simply on the following basis: The neutral gas (mainly He) in the center of the plasma tube is hotter than that immediately near the liquid nitrogen-cooled walls (77 K) because of the finite thermal conductivity of the gas. In fact, a simple calculation of the radial thermal gradient, based on the thermal conductivity of helium and a 100 W power input to the plasma, agrees very well with the ion rotational temperature measured in the center of the plasma. Hence, the rotational state populations of molecular ions sampled by the collimated laser beam in the center of the plasma are in equilibrium with the neutral gas translational motion in this region.

We currently do not have a definitive model which explains the dependence of the linewidth on rotational state observed at low pressures. These same observations of rotational state and pressure dependent "Doppler" linewidths have also been made in recent infrared studies of both HNN+ [18] and DNN+ [19]. In these experiments as well, the translational "temperature" of the ions was observed to exceed the approximate rotational "temperature", and the rotational states again exhibited non-Boltzmann populations. Similarly, the magnitude of the contribution to the observed linewidths made by the Doppler shifts is not quantitatively understood, but it appears that it may be substantial. In order to further examine these questions, extensive studies of infrared transitions of HNN+ in hydrogen, argon, and nitrogen plasmas have now been carried out, and 2 detailed analysis of these results is underway [18].

The development of the velocity modulation technique for measuring electronic transitions in ions presents a variety of exciting possibilities for both spectroscopic and dynamical studies. Certainly of great interest is the opportunity for measuring high-resolution ultraviolet absorption spectra of ions, which is created because of the low laser power requirements ($\approx 10$ mW) of this method, since cw powers of this magnitude can be generated in the ultraviolet by several possible non-linear mixing processes with cw visible lasers. 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, and transverse probing of a discharge can reveal the density and temperature (translational, rotational, and vibrational) profiles of the ionic species. Finally, and perhaps most obviously, velocity modulation electronic absorption spectroscopy will very likely be a powerful new tool for the discovery of new molecular ion electronic spectra.
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References