LASER-INDUCED FLUORESCENCE MEASUREMENT
OF THE NASCENT ROTATIONAL DISTRIBUTION OF $N_2^+$ ($X^2Σ^+_{g}$)
FORMED BY ELECTRON IMPACT ON $N_2$

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The internal state distribution of ground state $N_2^+$ ions formed from $N_2$ by electron impact ionization is measured under collision-free conditions using laser-induced fluorescence. Analysis of the B–X (0, 0) band shows the rotational distribution to be characterized by a temperature which increases slightly with decreasing electron energy (60–100 eV). Cascade contributions are unimportant.

1. Introduction

The spectroscopy of molecular ions is undergoing a renaissance. Whereas formerly almost all studies relied upon the high resolution analysis of emission spectra [1], new techniques are being developed for investigating the ground states of molecular ions. For example, molecular ions have been studied using microwave spectroscopy [2], using their differential reactivity as a function of internal state to generate an infrared or visible absorption spectrum [3], using ion photofragment detection as a function of excitation wavelength [4], and using laser-induced fluorescence [5,6]. In the latter technique, all published accounts report ion generation methods which involve collisional relaxation with the possible exception of ref. [6].

We present here a demonstration of a simple technique for investigating molecular ions by laser-induced fluorescence under collision-free conditions. The molecular ions are formed by electron impact on target molecules at pressures of $10^{-4}–10^{-5}$ Torr using a pulsed electron gun of variable energy. Results are presented for the nascent internal state distribution of $N_2^+$ ($X^2Σ^+_g$), the rotational levels of the $v'' = 0$ state follow a Boltzmann distribution whose temperature appears to increase very weakly with decreasing electron energy over the range studied (60–100 eV).

2. Experimental

Fig. 1 presents a schematic layout of the experiment.

![](image)

**Fig. 1.** Schematic diagram of the experiment.
A trigger pulse from the nitrogen laser turns off the electron gun and initiates the nitrogen laser pulse after a fixed internal delay. The nitrogen laser (1 MW, Molecron model UV 24) pumps a tunable dye laser having an oscillator—amplifier configuration (Molecron model DL 14 P). The output of the dye laser (0.3 Å bandwidth, 10 ns duration, 20 pps) passes through the interaction zone where the ions are formed. A photomultiplier (S-20 response, Centronic model Q4283) detects the fluorescence and its output is signal averaged using gated detection electronics (boxcar integrator PAR model 162 with a 164 plug-in, 50 ns gate, 0 ns delay). A blue filter (Corning S-60 isolates the (0, 0) band of the N$_2^+$ B$^2\Sigma_u^+ - X^2\Sigma_g^+$ system. The dye used is 4', 4''-bis-butylacetylonyoxy-querterphenyl (BBQ). The electrons are supplied by a pulsed electron gun (10-100 eV, 10 µA-1 mA, variable pulse duration) in a differentially pumped chamber. The electrons are fired into the interaction region where N$_2$ gas is flowing at pressures of 10$^{-4}$-10$^{-5}$ Torr. The experiment is performed in the pulsed mode since electron impact on N$_2$ gives copious emission, and laser-induced fluorescence cannot be detected in its presence. The rate at which this emission is turned off is not limited by the switching electronics but rather by the radiative lifetime [7] of N$_2^+$ B$^2\Sigma_u^+$ (6.6 × 10$^{-8}$ s). Thus we employ a timing sequence as shown in the lower portion of fig. 1 so that the ions are probed by the pulsed dye laser after fluorescence has largely decayed away. The experiment is very sensitive to this electrons-off/laser-on delay. If the delay is too long, Coulombic repulsions deplete ion concentrations to below detectable limits. Within this time window where the laser-induced fluorescence experiment can be carried out, the excitation spectrum is not found to change, indicating that cascade processes do not affect our results. To minimize background light from the hot cathode of the electron gun, the interaction chamber was lined with thick black felt, which pumped down to ≈1 × 10$^{-6}$ Torr. These experiments were performed at 313 K due to heating of the chamber from the presence of the electron gun.

3. Discussion and results

Fig. 2 presents a fluorescence excitation spectrum of the N$_2^+$ ions produced by 100 eV electron impact on N$_2$. In the B$-X$ system the most prominent band is the (0, 0), but the (1, 1) band is also discernible. In the (0, 0) band the rotational lines are well resolved and the intensity alternation due to the nuclear spin statistics (I = 1) is apparent. A rotational temperature may be extracted from the relative rotational line intensities, I, by plotting the logarithm of the quantity $I_{N''N'' + 1}$ versus $N''(N'' + 1)$, where $N'$, $N''$ refers to the upper, lower rotational quantum numbers of the transition. Only even $N''$ values are used, since they are associated with the most intense rotational lines. The plot yields a straight line for a Boltzmann distribution whose slope is proportional to the reciprocal of the absolute temperature [8]. A least squares fit to the data in fig. 2 yields a rotational temperature of $T_R = 323 \pm 5$ K, where the uncertainty represents only the statistical scatter (one standard deviation). The (0, 0) band occurs over a relatively flat portion of the BBQ dye power curve where it changes by about 2%. Consequently, no correction was made for the variation of laser intensity with wavelength.

Excitation spectra were recorded as a function of electron energy. Fig. 3 shows the R branch of the (0, 0) band from which a rotational temperature is derived to be $T_R = 342 \pm 10$ K at 60 eV incident electron energy. A comparison of fig. 3 to fig. 2 shows that the signal-to-noise ratio decreases with decreasing electron energy.
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