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Polarized Laser Induced Fluorescence of $N_2^+(X^2\Sigma_g^+)$ Produced in the Electron Impact Ionization of N_2

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When nitrogen molecule was ionized in collision with electrons of 80 - 300 eV, the angular distribution of the rotation vector of $N_2^+(X^2\Sigma_g^+)$ was found to be slightly anisotropic with respect to the direction of the electron beam in the vicinity of 80 eV. This anisotropy indicates that the ejection of a π_u electron is the dominant channel in the ionization process in this energy range.

The electron-impact ionization of nitrogen molecule,

$$N_2(X^1\Sigma_g^+) + e \rightarrow N_2^+(X^2\Sigma_g^+) + 2e, \qquad (1)$$

is one of the fundamental processes investigated intensively as a prototype system in electron-molecule collisions. Recent measurements of the nascent rotational distribution of the product $N_2^+(X^2\Sigma_g^+)$ ion have revealed significant "rotational excitation" in process (1); the product $N_2^+(X^2\Sigma_g^+)$ ion is rotationally more excited than the parent $N_2(X^1\Sigma_g^+)$ molecule, and the degree of rotational excitation increases with decreasing impact energy.[1-5] The angular distribution of the rotation vector, **N**, of the product N_2^+ ion provides complementary information on the ionization dynamics, but little is known about it. An anisotropic angular distribution of **N** has been reported for $N_2^+(B^2\Sigma_u^+)$ produced in photoionization, where optical polarization of the resulting $N_2^+(B^2\Sigma_u^+ - X^2\Sigma_g^+)$ emission has been used as a probe of the rotational alignment.[6,7] In the present study, polarized laser induced fluorescence (LIF) was applied to process (1) to investigate the rotational alignment of the $N_2^+(X^2\Sigma_g^+)$ product. The observed alignment is accounted for in terms of the branching into two degenerate ionization continua.

The details of the experimental apparatus have been described elsewhere.[5] A pulsed supersonic beam of nitrogen molecule (≈100 μs duration, 2 atm stagnation pressure) was crossed by a pulsed electron beam (1.5 μs duration, ≈10 μA) under an ambient pressure of $\approx 4\times10^{-6}$ Torr. The output of a pulsed dye laser pumped by an excimer laser (Lambda Physik FL2002/EMG102) was introduced into the interaction zone through a linear polarizer and a double Fresnel rhomb prism, which selected the direction of the electric vector, $\boldsymbol{\varepsilon}_e$, of the probe laser. The $N' = 1 \leftarrow N'' = 2$ transition of the $N_2^+(B^2\Sigma_u^+ - X^2\Sigma_g^+)$ system was pumped by the probe laser pulse (≲30 μJ, ≈10 ns duration, ≈0.2 cm^{-1} bandwidth at 391.257 nm) with a delay time of 500 ns after the electron pulse was set off. Under these conditions the effect of collisional relaxation can be regarded as inessential.[5] The resulting fluorescence was focused onto a photomultiplier window (Hamamatsu R1398) through a sheet polarizer (Polaroid HNP'B), lenses and filters, which defined the wavelength and the polarization vector, ε_d, of the emitted photons. The output signal was stored digitally in a transient recorder (Iwatsu DM2350, 50 MHz sampling rate) and accumulated by a microcomputer. The LIF intensities for $\varepsilon_e /\!/ z$ and $\varepsilon_e \perp z$ were measured by rotating the Fresnel rhomb prism as a function of electron-impact energy of 80 - 300 eV. Mutually orthogonal geometry shown in Fig. 1 was employed in the measurement of the polarized LIF signal for the excitation-detection configuration. Namely, the electron beam was directed along the z axis. The probe laser was introduced along the y axis with its electric vector, ε_e, either parallel or perpendicular to the z axis. The fluorescence was monitored in the direction of the x axis. The polarizer was set on the detector axis so that the fluorescence component perpendicular to the z axis ($\varepsilon_d \perp z$) was allowed to pass through it and reach the detector.

In general, the intensities of the polarized LIF signal, $I_{/\!/}$ for $\varepsilon_e /\!/ z$ and $I_{\perp}$ for $\varepsilon_e \perp z$, can be written in terms of the state multipoles, $\mathcal{A}_0^{(n)}$, with ranks n = 2 and 4.[8] In the present case, where the N' = 1 ← N" = 2 transition is used for excitation, contributions of the terms with rank 4 are calculated to be at most 1.7% to $I_{/\!/}$ and 0.4% to $I_{\perp}$ with allowance for the depolarization due to the spin-rotation and hyperfine interactions.[8,9] Hence, $I_{/\!/}$ and $I_{\perp}$ can be expressed approximately only by $\mathcal{A}_0^{(2)}$ defined as

$$\mathcal{A}_0^{(2)} = \overline{\langle N''|(3|m_N|^2 - \mathbf{N}^2)/\mathbf{N}^2|N''\rangle}, \qquad (2)$$

where m_N is the projection of **N** onto the z axis and the average is taken over the ensemble of the $|N''\rangle$ rotational states. One set of the measurements of $I_{/\!/}$ and $I_{\perp}$ for a given direction of ε_d is sufficient to determine the value of $\mathcal{A}_0^{(2)}$, since $\mathcal{A}_0^{(2)}$ is given by

$$\mathcal{A}_0^{(2)} \simeq [a(1 - r)]/[b + cr], \qquad (3)$$

where r represents the intensity ratio, $I_{/\!/}/I_{\perp}$, and constants a, b and c are calculated to be 1.936×10^{-2}, 5.564×10^{-3}, and 3.024×10^{-3}, respectively.[9]

Figure 2 shows the observed intensity ratio, r, against electron energy. The value varies from 0.935±0.026 to 0.995±0.020 as the electron energy increases from 80 to 250 eV. It is shown from Eq. 3 that $\mathcal{A}_0^{(2)}$ is practically zero within experimental accuracy above 250 eV, because r ≃ 1 (see Fig. 2), and $\mathcal{A}_0^{(2)}$ has

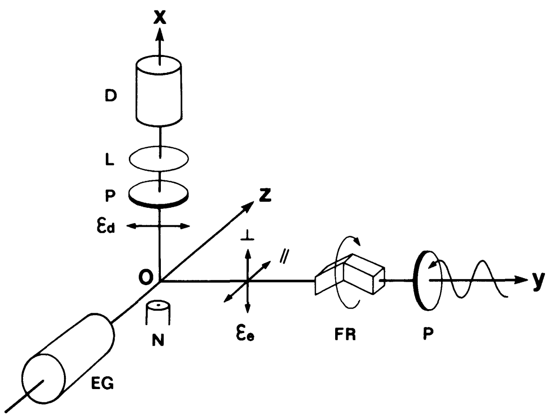

Fig. 1. A schematic drawing of the excitation-detection configuration. EG: electron gun; D: detector; FR: Fresnel rhomb prism; L: lens; N: nozzle; P: polarizer.

positive sign at lower energy; $A_0^{(2)}$ = 0.15±0.06 in the vicinity of 80 eV. This trend shows that the N" = 2 states of $N_2^+(X^2\Sigma_g^+)$ with different $|m_N|$ values are equally populated at high impact energy but that the states with higher $|m_N|$ are preferentially produced at low energy.

The partial alignment of the product ion results from competitive contributions of several ionization channels having different symmetries and oscillator strengths. The electron-impact energy is so much higher than the threshold that electron-exchange interaction can be ruled out. Accordingly, the dipole transition is likely to make a dominant contribution to the ionization process. In the framework of the dipole transition, the ionization channels that play a dominant role, are the transitions to the ionization continuum producing a σ_u electron and a π_u electron. For further discussion, we assume here that the dipole transition to the σ_u continuum can be identified with a $\Sigma_u^+ \leftarrow \Sigma_g^+$ transition and that to the π_u continuum with a $\Pi_u \leftarrow \Sigma_g^+$ transition, since the residual ion has Σ_g^+ symmetry. As the final states have different symmetries, ionization via each continuum generates a different anisotropy in the angular distribution of **N** of the residual ions with respect to the axis of symmetry. According to Dunn's symmetry argument,[10] the $\Sigma_u^+ \leftarrow \Sigma_g^+$ transition produces N_2^+ ions aligned with its internuclear axis parallel to the axis of symmetry while the $\Pi_u \leftarrow \Sigma_g^+$ transition makes their internuclear axis to align perpendicular to the symmetry axis. Hence, the alignment depends on the ratio of the dipole strengths (channel ratio) to each continuum.

In the limit of the Born approximation, the symmetry of the system should be referred to the axis along the momentum transfer vector, which is defined as $\mathbf{K} = \mathbf{k} - \mathbf{k}'$, where **k** and **k'** represent the momentum vectors of the incident and scattered electrons, respectively.[10] The direction of **K** relative to **k** is readily estimated in the following two limiting cases: In the limit of high energy, where the incident electron undergoes a small momentum change, one finds that $|\mathbf{K}| \ll |\mathbf{k}|$ and $\mathbf{k} \simeq \mathbf{k}'$. Hence, **K** is pointed in the direction perpendicular to **k**. On the other hand, at the threshold the incident electron transfers all the energy to the target; then $\mathbf{K} \simeq \mathbf{k}$, and **K** lies along the direction of **k**. In the medium energy range, **K** may have a certain angular distribution relative to **k**.

At the electron-impact energy of 80 eV, all the continua located below 80 eV are excited since the electrons act as a source of white light causing broad band

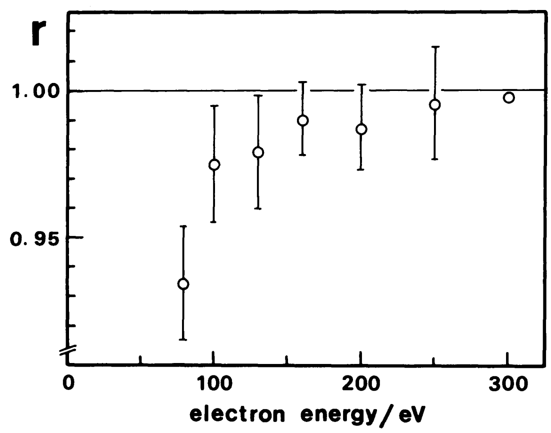

Fig. 2. Plots of the intensity ratio r as a function of electron energy. Error bars represent standard deviations estimated from 2 - 4 sets of measurements.

excitation. Since a sizable amount of energy should be transferred from the incident electron for the excitation to the continua just above the ionization threshold (15.58 eV), the average direction of **K** is expected to lie along the z axis. The continua just below 80 eV suffer near-threshold excitation, because the incident electron loses almost all the energy for the excitation (**K** ≃ **k**). The closer the continuum to the incident energy, the more is the relevant **K** directed preferentially to the z axis, thus resulting in the enhancement of anisotropy. The positive $\boldsymbol{A}_0^{(2)}$ observed in the present study indicates that the internuclear axis of the product ion is preferentially aligned perpendicular to the **K** direction. It then follows from the above symmetry argument that the π_u continuum located near 80 eV has a higher dipole strength than the σ_u continuum. This conclusion seems to be consistent with existing theoretical calculations, which predict a larger cross section for the vertical photoionization to the π_u continuum as the excitation energy is increased to 40 - 50 eV.[11] As the electron-impact energy is increased to the high-energy limit, the average direction of **K** deviates from that of **k** and the channel ratio approaches to unity.[6] This trend is indeed observed at energy higher than 250 eV, where the degree of alignment decreases.

In our previous study, the rotational excitation of $N_2^+(X^2\Sigma_g^+)$ was found to occur noticeably below 100 eV;[5] the electron-impact energy for the onset of the rotational excitation nearly coincides with that for the onset of the rotational alignment observed in the present study. As the transitions to the two different continua are expected to obey different selection rules for change in the rotational angular momentum of the residual ion, it is likely that a dominant contribution of the π_u continuum in the vicinity of 80 eV causes rotational excitation, as well as rotational alignment, with decreasing electron-impact energy.

References

1) J. Allison, T. Kondow, and R. N. Zare, Chem. Phys. Lett., 64, 202 (1979).
2) M. I. Lester, B. R. Zegarski, and T. A. Miller, J. Phys. Chem., 87, 5228 (1983).
3) H. Helvajian, B. M. Dekoven, and A. P. Baronavski, Chem. Phys., 90, 175 (1984).
4) H. Kawazumi, T. Uchida, and T. Ogawa, Bull. Chem. Soc. Jpn., 59, 937 (1986).
5) T. Nagata, A. Nakajima, T. Kondow, and K. Kuchitsu, J. Chem. Phys., submitted.
6) E. D. Poliakoff, J. L. Dehmer, D. Dill, A. C. Parr, K. H. Jackson, and R. N. Zare, Phys. Rev. Lett., 46, 907 (1981).
7) J. A. Guest, K. H. Jackson, and R. N. Zare, Phys. Rev. A, 28, 2217 (1983).
8) C. H. Greene and R. N. Zare, J. Chem. Phys., 78, 6741 (1983).
9) T. Nagata, A. Nakajima, T. Kondow, and K. Kuchitsu, unpublished data.
10) G. H. Dunn, Phys. Rev. Lett., 8, 62 (1962).
11) T. N. Rescigno, C. F. Bender, B. V. McKoy, and P. W. Langhoff, J. Chem. Phys., 68, 970 (1978).

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