

Photoelectron-recoil-induced rotational excitation of the  $B^2\Sigma_u^+$  state in  $N_2^+$ 

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In the photoelectron spectrum of  $N_2$  the apparent ionization energy to form the  $B^2\Sigma_u^+$  state increases linearly with the photon energy. Rotationally resolved measurements of the fluorescent decay of this state show a linear increase of rotational heating with increasing photon energy. These results are in quantitative agreement with the prediction of the theory of recoil-induced rotational excitation, indicating that the rotational heating that has been observed previously arises primarily from such recoil-induced excitation. Together with other results that have been reported they show that recoil-induced internal excitation is significant in many situations, including near threshold.

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When a photoelectron is ejected from an atom, molecule, or solid the remaining ion has a recoil momentum that is equal and opposite to that of the electron. Although the first discussions of this effect [1] were limited to translational recoil, it was recognized by Domcke and Cederbaum [2] that the recoil effect could lead to internal excitation of the ion. However, this prediction remained unverified until recent observations in core-electron photoelectron spectra of recoil excitation of vibrations in molecules [3,4] and phonons in solids [5]. These experiments show that the recoil-induced internal excitation is quantitatively in accord with a model based on emission of the electron from a localized atom.

Although a model based on emission from a localized atom may be appropriate for core ionization, it is not apparent that such a model is appropriate for valence ionization, where the electrons are delocalized. This question has been recently addressed by Takata *et al.* [6] who showed that at a photon energy of 8 keV there is a shift in the apparent position of the Fermi edge of aluminum that is consistent with the recoil being taken up by a single atom.

The investigations mentioned above have been concerned with vibrational excitation. Here we consider recoil-induced rotational excitation during valence photoionization of  $N_2$ . Thus we extend the previous investigations by considering a different type of internal excitation and by considering valence excitation in a distinctly different system (a small molecule rather than a solid). Specifically we investigate rotational excitation during photoionization to produce the  $B^2\Sigma_u^+$  state of  $N_2^+$ . Using both photoelectron and fluorescence spectroscopy we show that there is recoil-induced rotational excitation in quantitative accord with a model based on emis-

sion of the electron from a localized atom. Moreover, we note that this effect is observable even within 100 eV of threshold. Thus it becomes apparent that significant recoil-induced internal excitation is widespread in terms of both the physical system (molecule or solid) and the energy range.

It has been previously noted that the distribution of rotational states produced during photoionization to form the  $B^2\Sigma_u^+$  state of  $N_2^+$  depends on the photon energy [7,8]. The distribution shifts to higher values of the rotational quantum number as the photon energy increases. This “rotational heating” was investigated in detail by Poliakoff *et al.* [7], who were able to account for it quantitatively. They did not, however, make a connection between the observed effect and recoil-induced excitation.

To investigate the possibility that the rotational heating arises from the recoil effect we have extended the energy range that has been previously studied. We have investigated the photoelectron spectrum of  $N_2$  to form the  $B$  state of  $N_2^+$  at photon energies up to 800 eV, and the fluorescence decay of the  $B$  state of  $N_2^+$  up to 450 eV. The fluorescence results (rotationally resolved) show an increase in the average rotational quantum number with photon energy, similar to that seen previously [7,8]. The centroids of both the rotational distributions and the photoelectron peaks (rotationally unresolved) shift to higher energies nearly linearly as the photon energy increases in accord with the predictions of the theory of the recoil effect. The rate of increase of the centroid energy is quantitatively in accord with these predictions. From this result it appears that the major source of rotational heating is recoil-induced rotational excitation. Thus, these results provide quantitative verification of the prediction of recoil-

induced rotational excitation [2] and better understanding of the physics underlying the rotational heating observed by Poliakoff *et al.* [7,8].

In addition to the experimental results, we present two theoretical descriptions of the recoil-induced excitation, one classical and one quantum mechanical, that account quantitatively and without adjustable parameters for the observed experimental results. The important result of the classical model is the prediction that the recoil-induced rotational heating should increase linearly with the kinetic energy of the ejected photon, just as we observe experimentally.

Valence photoelectron spectra for  $N_2$  were measured at the SPring-8 and MAX II synchrotron radiation centers. Beamline BL27SU at SPring-8 was used to provide photons from 300 to 800 eV, and beamline I411 at MAX II was used to cover the range from 60 to 360 eV. The photoelectron spectra were measured using either a Scienta SES-2002 (Spring-8) or a Scienta R4000 (MAX II) electron spectrometer. At SPring-8 the analyzer was positioned at  $0^\circ$  to the polarization direction of the beam and at MAX II the analyzer was positioned at  $54.7^\circ$ . The nitrogen gas was mixed with either argon (SPring-8) or krypton (MAX II) and the argon  $3p_{3/2}$  and krypton  $4p_{3/2}$  photoelectron lines were used for calibration of the energies. The linearity and slope of the analyzer energy scale were verified using measurements of the xenon  $N_{4,5}OO$  Auger spectrum [9]. The spacing between the argon and krypton calibration peaks and the peak corresponding to the  $v=0$   $B^2\Sigma_u^+$  state were determined by least-squares fitting of Gaussian shapes to the spectra [10]. The energy spacings were corrected for the different translational recoil of nitrogen and the calibration gases and then combined with the known ionization energies of the calibrants [11] to give absolute ionization energies. On the basis of the statistics of the fits, the reproducibility of duplicate measurements, and the scatter of the data with respect to a smooth curve, we estimate the uncertainty in these energies to be about 1 meV. The instrumental resolution was determined from the widths of the krypton and argon calibration lines, corrected for Doppler broadening, and was found to vary from 50 to 116 meV, depending on the photon energy and on where the experiments were done.

The measured centroids of the photoelectron peaks are plotted against the photoelectron kinetic energy as the solid circles in Fig. 1. We see that the centroid increases approximately linearly with the electron kinetic energy, as would be expected for recoil-induced rotational heating. The solid line in Fig. 1 shows a least-squares fit of a straight line to the data. The slope of this line is  $(1.30 \pm 0.08) \times 10^{-5}$ , in excellent agreement with the value predicted by the classical theory discussed below.

The original evidence for rotational heating [7,8] came from rotationally resolved fluorescence spectra for the deexcitation of the  $B$  state in  $N_2^+$ . We have made measurements of this fluorescence spectra and have expanded the upper end of the range of photon energies from 220 eV in Refs. [7,8] to 450 eV. Details of these experiments are presented elsewhere [12]. Briefly, a supersonic molecular gas jet of molecular nitrogen (stagnation pressure of 2 bar, nozzle temperature 150 K) was used to produce molecules with a rotational temperature of about 17 K. The gas jet was

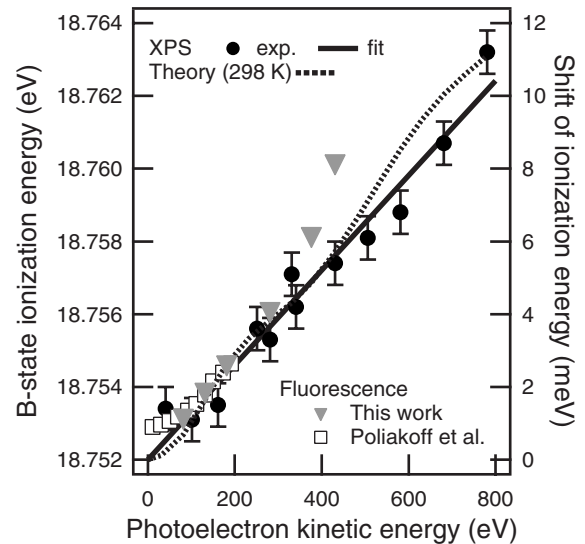


FIG. 1. Mean apparent ionization energy to produce the  $v=0$   $B$  state of  $N_2^+$  as a function of photoelectron kinetic energy. Solid circles, left-hand axis: From photoelectron spectroscopy. Squares and triangles, right-hand axis: From fluorescence measurements. Triangles are from this work and squares are from Ref. [7]. The solid line represents a least-squares fit of a straight line to the photoelectron data. The dotted line shows the predictions of a quantum-mechanical theoretical model.

crossed by monochromatic synchrotron radiation from the undulator beam line UE52-SGM at the synchrotron facility BESSY-II (Berlin, Germany) and the fluorescence was analyzed by a high-resolution secondary monochromator (Jobin-Yvon, HRS-460) [13] equipped with a 3600 1/mm (and 1800 1/mm) grating, which provides an ultimate wavelength resolution of 0.015 (0.03) nm corresponding to an energy resolution of 0.2 (0.4) meV. The rotationally resolved fluorescence measurements give the rotational distribution in the ionized state, and, from these distributions it is straightforward to calculate the centroid.

The fluorescence measurements give the centroids of the distribution relative to the energy of the  $J=0$  state at each photon energy, whereas the photoelectron measurements give the centroid of the apparent ionization energy relative to the ground state of  $N_2$ . To compare these we need the shifts in the centroids relative to what they would be for a measurement at threshold. For the photoelectron measurements we can estimate the threshold value from the intercept of the solid line shown in Fig. 1, and from this we can establish a scale of shifts, as indicated by the right-hand axis of Fig. 1. For our fluorescence results the data for photon energies of 100, 150, 200, and 300 eV follow a straight line very closely, deviating from it by at most 0.01 meV. The slope of this line,  $1.47 \times 10^{-5}$ , is in approximate agreement with the value we have determined in the photoelectron spectroscopy experiments. For photon energies of 395 and, more clearly, 450 eV, the fluorescence measurements give centroids that are higher than predicted by theory or indicated by the photoelectron spectroscopic measurements. Possibly the fluorescence results at high energies reflect other mechanisms than direct photoionization that populate the  $B$  state. This possibility

will be discussed in a future presentation [12]. For the data of Poliakoff *et al.* [7] there are deviations from linearity near threshold, and, therefore, we have used their data at photon energies above 100 eV for this extrapolation. The slope from this fit is  $1.34 \times 10^{-5}$ . The shifts relative to the threshold centroids are shown in Fig. 1. If we consider the fluorescence data at photon energies only between 100 eV and 350 eV we see that there is good agreement among the three experiments.

To provide a quantitative picture of recoil-induced rotational excitation, we consider first a classical model for a linear molecule. We assume that a photoelectron with momentum  $\vec{p}_e$  is emitted isotropically from atom  $A$ , located at  $R_A$  from the center of mass. The molecule has initial angular momentum,  $\vec{J}_0$ . There is no angular momentum along the axis of the molecule (the  $z$  axis), and, by choice of coordinate system, we can choose the component of initial angular momentum along the  $x$  axis of the molecule to be 0. Then the components of the angular momentum vector are  $(0, J_0, 0)$ . The kinetic energy associated with this angular momentum is  $T = J_0^2 / (2\mathcal{I})$ , where  $\mathcal{I}$  is the moment of inertia of the molecule.

The electron is emitted with momentum  $p_e$  from atom  $A$  in the direction defined by the angles  $\theta$  and  $\phi$ . Its angular momentum with respect to the molecule is given by the components

$$J_x = -R_A p_e \sin \theta \sin \phi, \quad J_y = R_A p_e \sin \theta \cos \phi, \quad J_z = 0 \quad (1)$$

and the new angular momentum components for the molecule are

$$J'_x = R_A p_e \sin \theta \sin \phi, \quad J'_y = J_0 - R_A p_e \sin \theta \cos \phi, \quad J'_z = 0. \quad (2)$$

The new rotational kinetic energy is

$$T_{\text{rot}} = (J_0^2 + R_A^2 p_e^2 \sin^2 \theta - 2J_0 R_A p_e \sin \theta \cos \phi) / (2\mathcal{I}) \quad (3)$$

and the change in rotational energy is

$$\Delta T_{\text{rot}} = (R_A^2 p_e^2 \sin^2 \theta - 2J_0 R_A p_e \sin \theta \cos \phi) / (2\mathcal{I}). \quad (4)$$

Averaging over angles gives  $\langle \Delta T_{\text{rot}} \rangle = (2/3) R_A^2 p_e^2 / (2\mathcal{I})$ , independent of the initial rotational kinetic energy.

For  $\text{N}_2$   $R_A = R/2$  and  $\mathcal{I} = m_N R^2 / 2$ , where  $m_N$  is the mass of the nitrogen atom and  $R$  is the bond length. Setting  $p_e^2 = 2m_e \epsilon_e$  we have  $\langle \Delta T_{\text{rot}} \rangle = \epsilon_e m_e / (3m_N)$  where  $\epsilon_e$  and  $m_e$  are the kinetic energy and mass of the electron [14]. Thus, we expect the average rotational energy of the ion to increase linearly with the kinetic energy of the photoelectron. For  $\text{N}_2$   $\langle \Delta T_{\text{rot}} \rangle = 1.31 \times 10^{-5} \epsilon_e$ , which, as noted, agrees well with the slope observed experimentally,  $(1.30 \pm 0.08) \times 10^{-5}$ .

In addition to the classical model, we consider a quantum mechanical prediction of the rotational population of the final  $B^2\Sigma_u^+$  state, which is created by the photoemission ( $2\sigma_u \rightarrow \psi_{\mathbf{k}}$ ) of the  $2\sigma_u = a(2s_1 - 2s_2) + b(2p_{\sigma_1} + 2p_{\sigma_2})$  electron. The cross section for photoionization is given by  $|\langle \mathbf{e} \cdot \mathbf{d}_{2\sigma_u, \psi_{\mathbf{k}}} \rangle|^2$ , where  $\mathbf{d}$  is the dipole matrix element and  $\mathbf{e}$  is a unit vector in the polarization direction. In high-energy

photoionization the wave function of the photoelectron near the  $n$ th nitrogen atom,

$$\psi_{\mathbf{k}}(\mathbf{r}) \approx \exp(i\mathbf{k} \cdot \mathbf{R}_n) \sum_{lm} R_l(r_n) Y_{lm}(\mathbf{r}_n), \quad (5)$$

is defined by the radial wave function  $R_l(r_n)$ , where  $\mathbf{k}$  is the electron momentum and  $\mathbf{R}_n$  is the radius vector of the atom. The formal mechanism of the photoionization is included in the phase factors

$$g_{\pm} = e^{i\mathbf{k} \cdot \mathbf{R}/2} \pm e^{-i\mathbf{k} \cdot \mathbf{R}/2} \quad (6)$$

of the amplitude of the photoionization written in the center of gravity of  $\text{N}_2$ ,

$$\langle \mathbf{e} \cdot \mathbf{d}_{2\sigma_u, \psi_{\mathbf{k}}} \rangle = s(\mathbf{e} \cdot \mathbf{k})g_- + [q(\mathbf{e} \cdot \mathbf{R}) + p(\mathbf{e} \cdot \mathbf{k})(\mathbf{k} \cdot \mathbf{R})]g_+. \quad (7)$$

Here the first term and the last two terms at the right-hand side of this equation correspond to the  $2s \rightarrow \epsilon p$  and  $2p \rightarrow \epsilon s, \epsilon d$  transitions, respectively,  $s, p,$  and  $q$  are weighting factors for these three channels, and  $\mathbf{R}$  is the internuclear radius vector. For example, for the photoionization channel  $2s \rightarrow \epsilon p$  we have

$$\sigma(J_0, J) \propto \sum_{M_0} \left| \sum_{l=|J-J_0|}^{J+J_0} \mathfrak{N}_{l0} j_l(L) \right|^2 \quad (8)$$

with

$$\mathfrak{N}_{l0} = \sqrt{(2J_0+1)(2J+1)} t^{l-1} [1 - (-1)^l] C_{J_0 0 J_0}^{l0} C_{J_0 - M_0 J M_0}^{l0}.$$

Here  $C_{J_0 M_0 J M}^{lm}$  is the Clebsh-Gordon coefficient and  $J_0$  and  $J$  refer to the initial and final angular momentum. In the spherical Bessel function  $j_l(L)$  the argument  $L = kR/2$  has the physical meaning of the angular momentum obtained by the molecule due to the recoil effect.

The normalized rotational distribution of the final  $B$  state is defined by the total cross section for the transition to the rotational levels of the final state

$$\rho(J) = \frac{\sigma(J)}{\sum_J \sigma(J)}, \quad \sigma(J) = \sum_{J_0=0}^{\infty} \frac{\sigma(J_0, J) \rho_0(J_0)}{2J_0 + 1}, \quad (9)$$

where  $\rho_0(J_0)$  gives the distribution of angular momentum in the initial state. From Eq. (9) and the known rotational spacings for the  $B$  state [11] we can calculate the centroids of the rotational distributions. The results of such a calculation for a temperature of 298 K are shown as the dotted line in Fig. 1, where we see that there is good agreement between the predicted and the observed shifts. Detailed comparisons of the predicted and experimental  $\rho(J)$  distributions are presented elsewhere [12].

The classical and quantum mechanical models differ, in particular, in that the quantum mechanical model takes into account interference between emission from the two nitrogen atoms. Inclusion of this interference is essential for understanding the details of the rotational distributions [12] and is essential for a complete description of recoil-induced internal excitation. However, it can be shown that the interference terms do not affect the centroids in the limit of  $kR \gg 1$

[15,16] or if the wavelength of the outgoing photoelectron is comparable to or shorter than the zero-point vibrational motion of the nuclei [2]. As a result, the two models are in reasonable agreement when we consider the centroids. In the absence of interference effects the recoil-induced excitation is just that expected from an ensemble of individual atoms, as has been seen both in our work and in that of Takata *et al.* [6].

Summarizing, we see that the prediction of photoelectron-recoil-induced rotational excitation predicted by Domcke and Cederbaum [2] is verified. The mean rotational heating that was observed by Poliakoff *et al.* [7,8] can be accounted for quantitatively in terms of this process, except very close to threshold. Both the photoelectron spectroscopic measurements and the fluorescence measurements can be understood quantitatively in terms of a model in which the photoelectron originates at a localized atom even though the valence orbital from which the electron is ejected is delocalized. These results, together with others [3–6], indicate that photoelectron-

recoil-induced internal excitation is a widespread phenomenon and can have a significant effect even for energies not far above threshold.

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