Experimental Observation of Rotational Doppler Broadening in a Molecular System

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The first experimental evidence of rotational Doppler broadening in photoelectron spectra, reported here, show good agreement with recently described theoretical predictions. The dependence of the broadening on temperature and photoelectron kinetic energy is quantitatively predicted by the theory. The experiments verify that the rotational contributions to the linewidth are comparable to those from translational Doppler broadening and must be considered in the analysis of high-resolution photoelectron spectra. A classical model accounting for this newly observed effect is presented.

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The Doppler effect is well known in physics. It is seen principally as the consequence of the linear motion of an object and is observed in many phenomena such as the redshift of radiation from receding stars, the measurement of velocities via radar, the broadening of lines in atomic and molecular spectroscopy, and the shifting of nuclear transition energies in Mössbauer spectroscopy. Less well known is the rotational Doppler effect, where the *rotational* motion of an object affects the energy of emitted radiation. This is seen primarily in astrophysics, where it is used to determine angular velocities of astronomical objects. To our knowledge, it has never been observed at the molecular level [1–3]. In a recent theoretical investigation of this phenomenon, Sun, Wang and Gel'mukhanov [4] have predicted that rotational Doppler broadening should be observable in high-resolution photoelectron spectroscopy and have presented expressions to describe its dependence on the kinetic energy of the photoelectron and on the temperature of the sample. Here we present the first experimental investigation of this recently predicted phenomenon.

In the 40+ years since Siegbahn and coworkers demonstrated the unique ability of electron spectroscopy to probe electronic structure and chemical environment in molecules and solids [5], impressive progress has been achieved in this field [6,7], and, in particular, in the instrumental resolution. However, there remains line broadening due to intrinsic sources, such as the Doppler effect, and, in the case of inner-shell electrons, the natural lifetime. With the possibility that the Auger-Resonant-Raman effect can be used to overcome lifetime broadening in some situations [8], it is the Doppler broadening that sets the ultimate limit to the narrowest obtainable linewidth in photoelectron spectroscopy [9]. For instance in a recent measurement of the $4p$ photoelectron spectrum of Kr [10] the observed linewidth of 66 meV arises from an instrumental resolution of 59 meV and a translational Doppler broadening of 30 meV. For molecules, there can be additional broadening. In the same experiment, the peaks arising from valence ionization of N_2 have widths of about 90 meV, which is more than can be accounted for by the instrumental resolution and the translational Doppler broadening (52 meV). There is an almost equal additional broadening of 45 meV, which can be attributed to the effect of rotational motion of the molecule. This rotational broadening is our concern here and we present the results of measurements covering a wide range of photoelectron kinetic energies on room-temperature samples. Combining these results with others from low-temperature experiments [11] allows us to confirm the dependence on both kinetic energy and temperature predicted by Sun *et al.* [4]. We also show that a simple classical model gives results that are in agreement with both the quantum-mechanical model of Sun *et al.* and with our experimental results.

These results are significant in a number of ways. First is the demonstration for the first time that Doppler broadening due to rotational motion can be seen in a molecule and that this effect can be observed via high-resolution photoelectron spectroscopy. Second, we find experimentally that if we have accounted for instrumental broadening, translational Doppler broadening, and rotational Doppler broadening, then we have accounted for *all* of the major sources of broadening. Third, as noted by Sun *et al.*, this broadening will be a common feature of such spectra, occurring whenever the site of photoemission differs from the center of mass of the molecule. Fourth, as the example of N_2 cited above and the examples given by Sun *et al.* indicate, the rotational Doppler broadening can be comparable to, and, in some cases, even greater than the translational Doppler broadening [12,13]. Thus any analysis of the line shape in such spectroscopy must take this effect into account. Fifth, we show that a simple classical model can account quantitatively for this effect, even at energies close to threshold. Finally, an excellent description of the phenomenon is obtained by assuming that the electron is emitted from a specific atom, even though the electronic wave function may be delocalized over the entire molecule.

Valence photoelectron spectra for N_2 were measured at the SPring-8, MAX II, and SOLEIL synchrotron radiation facilities for photon energies ranging from 60 to 900 eV. The procedures and equipment used at SPring-8 and MAX II have been described [10,14], and those used on the PLEIADES beam line at SOLEIL are similar. In each case, a mixture of nitrogen and krypton was allowed into the gas cell of an electrostatic electron-energy analyzer. The spectra were analyzed using least-squares to fit them with a set of Gaussian shapes [15]. From the fits of the krypton lines, the overall instrumental resolution was determined by correcting the measured widths for the effect of translational Doppler broadening. The values (FWHM) ranged from 5 to 150 meV. Using these values for the instrumental resolution we corrected the measured linewidths of the nitrogen peaks for instrumental resolution and translational Doppler broadening to extract the contribution that can be attributed to rotational broadening.

The rotational Doppler broadening is, as noted by Sun *et al.* [4], closely related to the recoil-induced rotational excitation, which we have discussed elsewhere [10,14]. To model the rotational Doppler broadening we follow a procedure similar to that described in these earlier works. Consider a linear molecule, and assume that a photoelectron with momentum $\vec{p}_e$ is emitted isotropically in the molecular framework from atom A, located at R_A from the center of mass. (SI units are used, except as otherwise indicated.) The molecule has initial angular momentum $\vec{J}_0$. There is no angular momentum along the axis of the molecule (the z axis), and we choose the coordinate system so that the components of $\vec{J}_0$ are $(0, J_0, 0)$. The kinetic energy associated with this angular momentum is $E_{\mathrm{rot}} = J_0^2/(2I)$, where I is the moment of inertia of the molecule. The emission of the electron leads to a change in the angular momentum and the rotational energy of the molecule.

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

$$J_x = -R_A p_e \sin\theta \sin\phi, \quad J_y = R_A p_e \sin\theta \cos\phi, \quad J_z = 0, \tag{1}$$

and the new angular-momentum components for the molecule are

$$J_x' = R_A p_e \sin\theta \sin\phi, \quad J_y' = J_0 - R_A p_e \sin\theta \cos\phi, \quad J_z' = 0. \tag{2}$$

The new rotational kinetic energy is

$$E_{\mathrm{rot}}' = (J_0^2 + R_A^2 p_e^2 \sin^2\theta - 2J_0 R_A p_e \sin\theta \cos\phi)/(2I') \tag{3}$$

where I' is the moment of inertia of the ion. The change in rotational energy associated with the electron ejection is thus

$$\Delta E_{\mathrm{rot}} = (R_A^2 p_e^2 \sin^2\theta - 2J_0 R_A p_e \sin\theta \cos\phi)/(2I') + \frac{J_0^2}{2}\left(\frac{1}{I'} - \frac{1}{I}\right). \tag{4}$$

Averaging over all emission directions and rearranging the second term results in

$$\langle \Delta E_{\mathrm{rot}} \rangle = \frac{2}{3}\frac{R_A^2 p_e^2}{2I'} + \frac{J_0^2}{2I}\left(\frac{I - I'}{I'}\right). \tag{5}$$

This equation gives the average recoil-induced rotational excitation [10,14]. The first term is independent of the initial rotational kinetic energy and the second term is independent of the energy of the photoelectron. In order to evaluate the latter, we note that the average rotational kinetic energy $\langle J_0^2/(2I)\rangle$ of an ensemble of linear molecules in thermal equilibrium is $k_B T$, 26 meV at room temperature. However, since the fractional change of the momentum of inertia upon ionization is typically quite small ($(I - I')/I' = 0.04$ for the B state in N_2^+ [16]), the second term is of the order of only 1 meV. For comparison, the values of the first term for the B state in N_2^+ range from 0 to 14 meV as the kinetic energy ranges from 0 to 1000 eV [10,14]. Although the second term is not negligible, it does not affect measurements of the kinetic energy dependence of $\langle \Delta E_{\mathrm{rot}} \rangle$.

The rotational Doppler broadening observed in the spectra is proportional to the variance of the distribution of ΔE_{rot}, or $\langle \Delta E_{\mathrm{rot}}^2 \rangle - \langle \Delta E_{\mathrm{rot}} \rangle^2$. Using Eq. (4) for ΔE_{rot}, we have, after averaging over angles,

$$\langle \Delta E_{\mathrm{rot}}^2 \rangle - \langle \Delta E_{\mathrm{rot}} \rangle^2 = \langle \Delta E_{\mathrm{rot}} \rangle^2/5 + 2\langle \Delta E_{\mathrm{rot}} \rangle J_0^2/(2I'). \tag{6}$$

To assess the relative importance of the terms in Eq. (6) we divide by $\langle \Delta E_{\mathrm{rot}} \rangle$ to give

$$[\langle \Delta E_{\mathrm{rot}}^2 \rangle - \langle \Delta E_{\mathrm{rot}} \rangle^2]/\langle \Delta E_{\mathrm{rot}} \rangle = \frac{\langle \Delta E_{\mathrm{rot}} \rangle}{5} + 2\frac{J_0^2}{2I'}. \tag{7}$$

If we now average over all values of J_0, we have that $\langle J_0^2/(2I')\rangle = (I/I')\langle J_0^2/(2I)\rangle = k_B T(I/I')$ for a linear molecule. Thus the right-hand term in Eq. (7) is approximately equal to $2k_B T$ or about 52 meV at room temperature. The numerator of the left-hand term is the recoil-induced shift in the centroid and in our experiments is always less than about 14 meV. Thus, the left-hand term is less than about 3 meV and we can conclude that the variance in the distribution of energies, accounting for the rotational Doppler broadening, is approximately given by the expression

$$\langle \Delta E_{\mathrm{rot}}^2 \rangle - \langle \Delta E_{\mathrm{rot}} \rangle^2 \approx 2k_B T \langle \Delta E_{\mathrm{rot}} \rangle (I/I'). \quad (8)$$

Except for the correction for the change in the moment of inertia between the neutral molecule and the molecular ions, Eq. (8) is essentially the same result as that given by Sun *et al.* [4]. A similar expression given by Domcke and Cederbaum [17] predicts a much smaller broadening and does not contain a dependence on temperature. Since $\langle \Delta E_{\mathrm{rot}} \rangle$ increases linearly with the kinetic energy of the photoelectron $\langle \Delta E_{\mathrm{rot}}^2 \rangle - \langle \Delta E_{\mathrm{rot}} \rangle^2$ is also expected to increase linearly with the kinetic energy.

One type of data that can be compared with these predictions comes from the fluorescence decay of the B state in N_2^+ [11] following the population of the B state by photoemission. From the rotationally resolved distributions for the B state (Fig. (5) of Ref. [11]) we can calculate the mean energy, the mean-square energy, and the variance. The expected linear variation of the variance is seen clearly in Fig. 1(a), where we have plotted the variance versus the photoelectron kinetic energy [18].

In addition, Eq. (8) indicates that the ratio of the variance to the centroid of the distribution should be a constant equal to $2k_B T(I/I')$, and we see in Fig. 1(b) that this ratio is, indeed, nearly constant, with a value of 2.2 meV. This corresponds to a temperature of 12 K, in good agreement with the value of 14 K given in Ref. [11].

A second type of data comes from the measurements of the valence photoelectron spectra of N_2 described above. The N_2 lines are broader than the Kr lines, and most of this additional width is due to the rotational Doppler broadening. From the measurements we obtain the rotational broadening W_{rot} with the expression $W_{\mathrm{rot}}^2 = W_{N_2}^2 - W_{\mathrm{Kr}}^2 + D_{\mathrm{Kr}}^2 - D_{N_2}^2$, where W_{N_2} and W_{Kr} are the measured widths for the nitrogen and krypton peaks, respectively, and D_{N_2} and D_{Kr} are the translational Doppler widths (which are readily calculated). The results of these measurements are shown in Fig. 2, where we have plotted the square of W_{rot} (FWHM) versus the electron kinetic energy. We have included in this graph an estimate close to threshold based on the He I measurements of Allen and Grimm [19]. The solid line shows a straight-line fit to all of the data.

We see that a linear relationship between W_{rot}^2 and the photoelectron data accounts well for the results. The slope of the line in Fig. 2 is 4.60 ± 0.05 μeV. We can use Eq. (8) together with our previous measurements [10] of the average rotational energy shift $\langle \Delta E_{\mathrm{rot}} \rangle$ to predict a value for this slope. For the B state in N_2^+, $\langle \Delta E_{\mathrm{rot}} \rangle$ is found to vary as $(1.4 \pm 0.08) \times 10^{-5}$ times the photoelectron kinetic energy [10]. Using the nominal temperature of the experiments, 298 K, and the known values of the rotational constants [16] we predict a slope of 4.1 ± 0.2 μeV close to the observed slope. Thus, the classical model accounts well for the widths observed in these room-temperature experiments.

These experimental results verify the recent predictions of Sun *et al.* [4], showing that the rotational Doppler broadening is a significant contributor to the width of high-resolution photoelectron spectra and follows closely the predicted dependence on temperature and electron kinetic energy. It is important to note that the experimental width that we have assigned to rotational Doppler broadening represents *all* of the observed contributions that cannot be attributed to either instrumental or to translational Doppler broadening. Thus the quantitative agreement between experiment and theory implies that there is

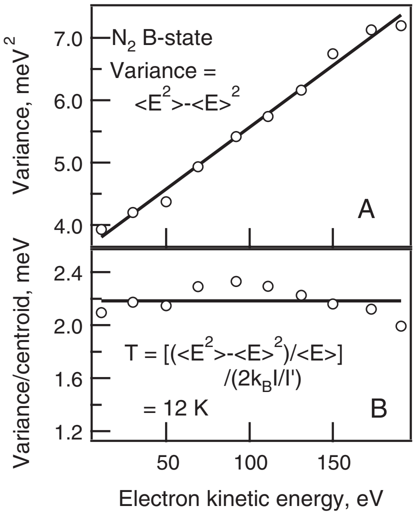

FIG. 1. (a) Variance of the distribution of rotational states populated in the ionization of N_2 to form the B state of N_2^+ plotted against the kinetic energy of the photoelectron. The solid line is a straight line fitted to the data. Data from Poliakoff *et al.* [11]. (b) Temperature derived from the ratio of the variance to the centroid.

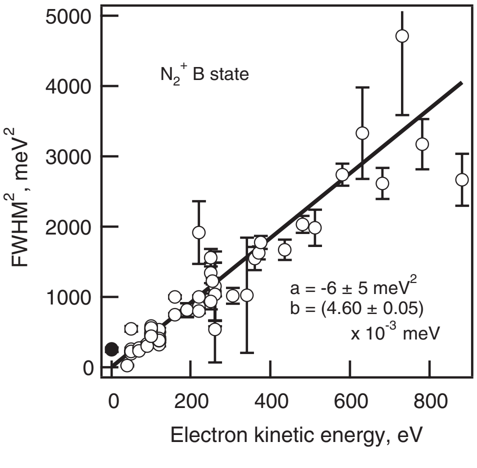

FIG. 2. Rotational contribution to the widths for the B-state peaks in the N_2 photoelectron spectrum. The square of the rotational component of the width (full width at half maximum) is plotted against the photoelectron kinetic energy. The solid point is based on He I data from Ref. [19]. The solid line is a straight line fitted to the data.

no other significant source of broadening that has not been accounted for.

The success of the classical model even at low energy in accounting for the dependence of the experimental widths on electron kinetic energy is surprising—the lowest kinetic energy for the data shown in Fig. 1 is only 11 eV. The classical theory ignores the angular-momentum change that is inherent in the absorption of the photon—± 1 (in atomic units) for the B state of N_2^+. We can, thus, expect the classical theory to fail when the angular-momentum change produced by the ejected electron is about equal to 1 au. For N_2 this would occur for an electron momentum of about 1 au, or a kinetic energy of about 14 eV. Nevertheless, the observed results appear to follow the classical prediction quite well. The reason for this is that the angular-momentum change (and hence the broadening) that arises from the recoil is generally large compared with the 1 unit of angular momentum associated with the photon. However, the classical theory cannot work at threshold, where there must still be broadening due to the photon angular momentum, and this is apparent in the nonzero intercept seen in Fig. 1(a) and in the slight disagreement between the He I point from Ref. [19] and our data in Fig. 2.

Problems for the future are to consider those situations where the molecular-frame angular distribution of the photoelectron is not expected to be isotropic, as for ionization to form the A state of N_2^+, or where there are inequivalent sites in the same molecule, as, for example, the valence photoionization of CO.

Just as there is rotational Doppler broadening associated with the recoil-induced rotational excitation, there is also vibrational Doppler broadening associated with the recoil-induced vibrational excitation ΔE_{vib} (discussed elsewhere [20–22]). In simplest approximation this broadening will be proportional to $\langle ke\rangle \Delta E_{\mathrm{vib}}$, where $\langle ke\rangle$ is the average vibrational kinetic energy. For a linear molecule at low temperature, $\langle ke\rangle$ is equal to half the zero-point energy, and the expression reduces to that given by Domcke and Cederbaum [17]. At high temperature $\langle ke\rangle = k_B T/2$, and we obtain an expression similar to that for the rotational Doppler broadening, Eq. (8). The temperature dependence of the vibrational Doppler broadening in solids has been discussed by Fujikawa *et al.* [23].

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[1] The term ‘‘rotational Doppler effect’’ has also been used with reference to changes in angular momentum parallel to the direction of propagation of the radiation [2,3]. This is different from the situation here, where the changes are perpendicular to the propagation direction.
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