Photoelectron-recoil-induced rotational excitation

When a photoelectron is ejected from an atom or molecule, the remaining ion has a momentum that is equal and opposite to that of the ejected electron. For a free atom this so-called "recoil" momentum appears entirely as translational motion and the atomic ion has a kinetic energy (the "recoil" energy) that is easily calculated by conservation of momentum from the kinetic energy of the electron and the masses of the electron and the atom. In a molecule, however, the recoil energy can be shared among the various normal modes of the molecule – translational, rotational, and vibrational [1]. The fraction of the energy that goes into translational motion is easily calculated from the kinetic energy of the electron and the masses of the electron, the atom, and the molecule. The interesting point is that the division of the recoil energy between vibrational and rotational motion depends on the location of the atom in the molecule and the angular distribution of the photoelectron with respect to the molecular frame.

In the previous experiments, we have investigated the recoil-induced vibrational excitation in carbon 1*s* ionization of CH_4 [2] and CF_4 [3]. These were special cases where recoil-induced rotational excitation is completely suppressed and recoil-induced vibrational excitation is limited to the asymmetric modes. We then have investigated the recoil-induced rotational excitation of the B state in the valence ionization of N_2 [4]. We found that the photon energy dependence of the excitation was well described by a classical model in which the photoelectron is ejected isotropically from a localized atom. In this case the partitioning of the internal excitation between vibrational and rotational motion is given by the number of degrees of freedom for each mode, i.e., 1:2.

We have now extended these studies to include results for the X and A states in N_2, for which the angular distributions are not expected to be isotropic, and for the X, A, and B states of CO^+, where the photoelectron might originate from either the carbon or the oxygen atom [5]. The low-energy measurements were carried out on beamline I411 of the MAX II and the high energy measurements on beamline **BL27SU** of the SPring-8. The photoelectron spectrum of N_2 measured at SPring-8 at photon energy of 500 eV is shown in Fig. 1. We see that the widths are broader for the N_2 peaks (90–92 meV) than they are for the krypton peaks (66 meV). After correcting for the difference of Doppler broadening there remains about 45 meV of width in the N_2 peaks that is not accounted for by either instrumental width or Doppler broadening. This excess width presumably represents rotational broadening. The individual rotational lines cannot be resolved. In this case, the recoil-induced excitation is reflected in a shift in the centroid of the peak. Our analysis, therefore, involves determining the energy spacing between the centroid of the calibration line and the centroid of the $v=0$ peaks for the transitions to the X, A, and B states of the ions. This difference is corrected for the difference between translational recoil energies of the molecule and the reference atom to give the apparent differences in ionization energies between the molecule and the atom.

In the very simplest approximation, the molecular-frame angular distribution depends on the nature of the atomic orbital from which the electron is ejected. In the plane-wave approximation, ejection from an *s* orbital of a cylindrically symmetric molecule is isotropic in the molecular frame, ejection from a p_σ orbital has a distribution that goes as $\cos^2\theta$, and emission from a p_π orbital has a distribution that goes as $\sin^2\theta$, where θ is the angle between the electron emission direction and the molecular symmetry axis. Each of these angular distributions leads to a different sharing of the recoil-induced internal excitation between the vibrational and rotational modes, with the result that measurements of

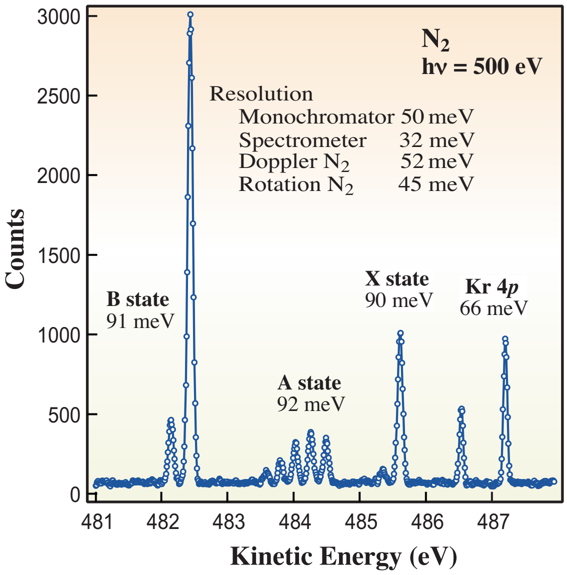

Fig. 1. Valence photoelectron spectrum of N_2/krypton mixture measured at a photon energy of 500 eV. Open circles show the data and the solid line shows a least-squares fit of Gaussian functions to the data. The widths (FWHM) determined from the fitting procedure for each group of peaks are shown. Also listed are the various components that contribute to the resolution.

the degree of recoil-induced rotational excitation can lead to information on the atomic orbital composition of the molecular orbital from which the electron is ejected.

The results of these measurements for the X, A, and B states of N_2^+ are shown in Fig. 2, where we have plotted the apparent ionization energy to form each of these states as a function of the kinetic energy of the photoelectron. The open circles show the experimental data and the solid lines show the results of weighted least-squares fits of straight lines to the data. The slopes of these lines are indicated in the figure. These slopes are generally in accord with a simple model that treats the electrons as if they were emitted from isolated atoms. This treatment takes into account the atom from which the electron is emitted, the molecular-frame angular distribution of the electron, and the dependence of the photoelectron cross section on photon energy, on atomic identity, and on the type of atomic orbital from which the electron is ejected. The results for the X and A states in N_2 and similar results for the X, A, and B states of CO^+ (not shown here) show that the degree of rotational excitation does depend on the type of molecular orbital, and that this technique can provide information on the atomic orbital composition of the molecular orbitals.

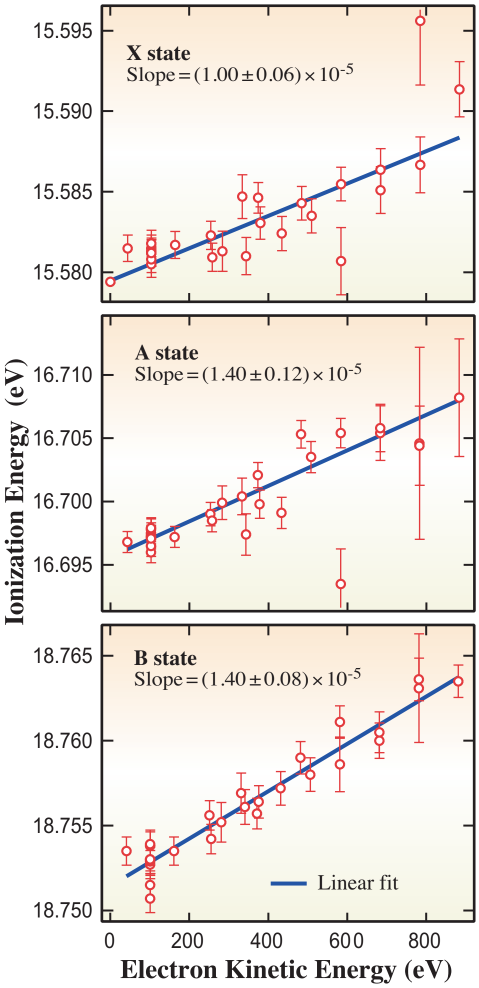

Fig. 2. Apparent energies for the X, A, and B states in N_2^+ (relative to N_2) as a function of photoelectron kinetic energy. The open circles show the data and the solid lines show straight lines fit to the data by weighted least-squares.

Additional information on the atomic orbital composition of the molecular orbitals can be obtained from the relative probabilities of ionization to form the X, A, and B states in N_2^+ and CO^+, that is, from the relative intensities of the lines observed in spectra such as that in Fig. 1. For example, at high photon energies the cross section for ionization of 2*s* electrons in a nitrogen atom is about nine times larger than the cross section for ionization of 2*p* electrons. In N_2 the X and A states are either predominantly or exclusively of 2*p* character, whereas the B state is predominantly of 2*s* character. As a consequence, the cross sections to form the X and A states are much smaller than the cross section to form the B state. In addition, the valence photoelectron spectrum of N_2 at high photon energy shows a stronger peak for the X state, which has some nitrogen 2*s* character, than for the A state, which is exclusively nitrogen 2*p*. Thus the measurement of these relative cross sections provides a potential additional tool for determining the atomic orbital character of the molecular orbitals. An analysis of these intensities to obtain such information is reported in Ref. [5].

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