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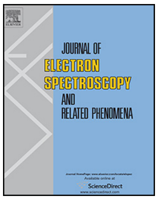

Small molecule photoelectron spectroscopy: Recoil effects, stoichiometric surprises, and double-core-hole ionization

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ABSTRACT

Three features of small-molecule photoelectron spectroscopy are considered (1) the atom from which a photoelectron is emitted must have a recoil momentum equal to that of the emitted electron. This is shared among the various modes of motion of the ion, leading to rotational and vibrational excitation. Furthermore, any initial velocity of the atom (due to either translational, rotational, or vibrational motion) will lead to Doppler broadening. These effects are observable and can, in general, be accounted for by simple models. In some cases, however, the simple models fail and a deeper insight is necessary. (2) Inner-shell photoionization is essentially an atomic process, and it is expected that the intensity for emission of a photoelectron from the core of an atom in a molecule will be independent of its chemical environment. Recent measurements on the carbon 1s photoelectron spectra of three chloroethanes show that this is not the case. At energies not far above the ionization threshold there are strong oscillations of the intensity ratio (C_{Cl}/C_H) with increasing photon energy. These are similar to those seen in EXAFS and can be accounted for by considering backscattering of the photoelectrons from the chlorine atoms. Moreover, even at high energies the cross section for ionization has been found to depend on the chemical environment of the atom. These results have important consequences for the use of inner-shell electron spectroscopy for quantitative analysis. (3) Single-core-hole ionization energies have long been used as a tool for investigating chemical phenomena. Double-core-hole ionization energies provide additional chemical information. By combining the single-hole and double-hole ionization energies it is possible to determine the effects of the initial-state charge distribution and final-state charge rearrangement on the chemical shifts and on other chemical properties. Until recently double-core-hole ionization energies have not been experimentally accessible for first-row elements. New experimental techniques have, however, made it possible to measure these not only for single sites in a molecule, but also for two different sites in the same molecule. The chemical information that can be obtained from such measurements is discussed.

1. Introduction

For more than 40 years, photoelectron spectroscopy has proved to be an important tool for studying a variety of phenomena in atoms, molecules, surfaces, and solids. As its name implies, the technique involves an incident photon and an ejected electron, whose kinetic energy is measured. For inner-shell photoelectron spectroscopy the kinetic energy reflects the elemental identity of the atom from which the electron is ejected, and, in more detail, it reflects the chemical environment of the atom. The intensity of a particular photoelectron peak in the spectrum depends on the number of atoms of that particular kind that are in the sample, but recent experiments [1] show that the intensities can differ markedly from those expected from the stoichiometry of the molecule. Relevant results are described in Section 3.

The chemical shifts of the kinetic energies between photoelectrons from the same element in different environments are well known and have long been exploited to provide insights into chemical properties and as an analytical tool to identify the chemical nature of a particular atom. Additional chemical information can be obtained if the one-hole ionization energies that are obtained in conventional photoelectron spectroscopy can be compared with measurements of two-hole ionization energies. Until recently, two-hole ionization energies were available only via core–core–core Auger spectroscopy, precluding the possibility of measurements of these quantities for first-row elements. Recently, however, new experimental techniques have opened up the possibility for such measurements in first-row elements. Some of the implications and opportunities of this newly acquired ability have been discussed in Refs. [2,3] and are reviewed briefly in Section 4.

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For ionization of an atom that is initially at rest the photon energy, $h\nu$, must be equal to the sum of the ionization energy, I, and the total kinetic energy, ϵ_{kin}, of the photoelectron and the ion. The total kinetic energy divides between the two particles according to conservation of momentum, with the consequence that each receives a kinetic energy that is proportional to the mass of the partner fragment. Thus we have

$$h\nu = I + \epsilon_{kin} = I + \epsilon_e + \epsilon_{ion} \tag{1}$$

$$= I + \frac{\epsilon_{kin}M_{ion}}{M_A} + \frac{\epsilon_{kin}m_e}{M_A} \tag{2}$$

where ϵ_e and ϵ_{ion} are the kinetic energies of the electron and the ion. M_A, M_{ion}, and m_e are the masses of the atom, ion, and electron. Since $M_A \approx M_{ion}$ and $m_e \ll M_A$, the electron kinetic energy is almost equal to the total kinetic energy and the ion kinetic energy (often referred to as the "recoil" energy) is small.

If the electron is ionized from an atom in a molecule, then conservation of momentum applies to both the atom and the molecule. The recoil energy for the atom is equal to $\epsilon_e m_e/M_A$, whereas that for the molecule is less, $\epsilon_e m_e/M_M$, where M_M is the mass of the molecule. The difference between these appears as internal excitation of the molecular ion – vibrational and rotational – and thus we have what may be referred to as "recoil-induced" vibrational and rotational excitation of the ion [4]. Although such effects were predicted theoretically many years ago [5], they have been observed experimentally only in the last few years [6–11].

In addition to the recoil effects just mentioned, the final energies of both the electron and the ion are affected by any initial kinetic energy that the atom may have. This appears as a Doppler broadening of the spectral lines. Doppler broadening due to translational motion is quite familiar, but in addition there can be broadening arising from the kinetic energy that the atom may have as a result of the rotational or vibrational motion of the molecule. Rotational Doppler broadening in molecular systems was predicted theoretically only recently [12] and observed experimentally only in 2011 [13]. The various recoil effects are discussed in more detail in Section 2.

2. Recoil effects

The difference, ΔE, between the recoil energy of the atom from which the electron is ejected and that of the molecular ion is equal to $\epsilon_e m_e(1/M_A - 1/M_M)$. This energy goes into internal (rotational and vibrational) excitation of the molecular ion. The division of this energy among the various normal modes of the ion depends on the direction of emission of the electron with respect to the molecular frame, on the location of the atom from which the electron is emitted in the ion, and on the normal-mode vectors of the ion [7]. For isotropic emission from a diatomic molecule one-third of the recoil excitation energy goes into vibrational excitation and two-thirds into rotational excitation. If the atom from which the electron is emitted is at the center of mass of the molecule (as in carbon 1s ionization of CH_4 and CF_4), then there is only vibrational excitation. Specific examples of recoil-induced rotational and vibrational excitation are discussed in the following sections.

2.1. Rotational effects

For most photoelectron spectroscopic measurements it is not possible to resolve the individual rotational states of the final ion. It is, therefore, necessary to consider the average effect of the recoil-induced rotational excitation. For this purpose, a classical model is sufficient to account for the features observed in currently available data. For emission of an electron with momentum k from atom A of a linear molecule, the change in rotational energy due to the recoil is given by the following expression [8,10].

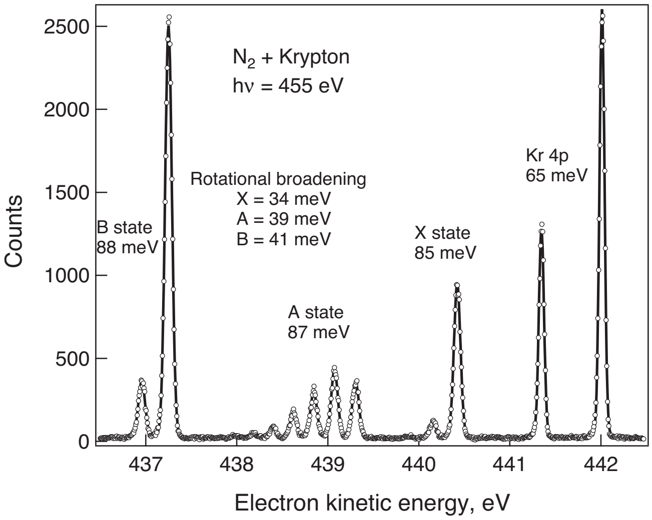

Fig. 1. Valence photoelectron spectrum of a mixture of N_2 and Kr at a photon energy of 455 eV. The numbers indicated for each group of peaks show the width of the peak (FWHM). The numbers indicated as "rotational broadening" show the widths corrected for instrumental and translational Doppler broadening.
Data from [15].

$$\Delta E_{rot} = \frac{k^2R_A^2 \sin^2\theta - 2kJ_0R_A \sin\theta \cos\phi}{2I} \tag{3}$$

R_A is the distance of atom A from the center of mass of the molecule, J_0 is the initial angular momentum of the molecule, and I the moment of inertia of the molecule [14]; θ and ϕ define the direction of emission with respect to the molecular frame. To average over the angles of emission it is necessary to know the angular distribution of the photoelectrons in the molecular framework. For a linear molecule this depends only on θ, and the normalized angular distribution $P(\theta)$ can be expressed as

$$P(\theta) = \sum_k \frac{A_k P_k(\theta)}{2A_0} \tag{4}$$

$P_K(\theta)$ is a Legendre polynomial and the A_k's are coefficients that describe the angular distribution. Combining Eqs. (3) and (4) and averaging over θ and ϕ gives

$$\left\langle \Delta E_{rot} \right\rangle = \left(\frac{2}{3} - \frac{A_2}{A_0}\frac{4}{15}\right)\frac{R_A^2k^2}{2I} \tag{5}$$

For a diatomic molecule Eq. (5) becomes

$$\left\langle \Delta E_{rot} \right\rangle = \left(\frac{2}{3} - \frac{A_2}{A_0}\frac{4}{15}\right)\epsilon_e m_e\left(\frac{1}{M_a} - \frac{1}{M_m}\right) \tag{6}$$

For an isotropic distribution ($A_2 = 0$), the factor represented by the first set of parentheses is 2/3. If $P(\theta) \propto \sin^2\theta$, it is 4/5, and if $P(\theta) \propto \cos^2\theta$ it is 2/5.

2.1.1. Rotational-recoil-induced shifts

Eq. (6) shows that the average rotational energy and, hence, the apparent ionization energy, increases linearly with the kinetic energy of the outgoing electron. The slope of the increase depends on the molecular-frame angular distribution of the photoelectrons. The apparent ionization energy can be measured from spectra such as shown in Fig. 1, which shows the valence photoelectron spectrum of a mixture of N_2 and Kr. The Kr, for which the ionization energy is well known, provides a reference line for both the energy scale and the resolution. The difference in positions between the