Journal of Electron Spectroscopy and Related Phenomena 183 (2011) 53–58

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

Recoil effects in molecular photoemission

Edwin Kukk[a,b,*], T.Darrah Thomas[c], Kiyoshi Ueda[d]

[a] Dept. of Physics and Astronomy, University of Turku, FIN-20014 Turku, Finland
[b] Turku University Centre of Materials and Surfaces (MatSurf), Finland
[c] Department of Chemistry, Oregon State University, Corvallis, OR 97331, USA
[d] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

ARTICLE INFO

Article history:
Available online 15 March 2010

Keywords:
Photoemission
Recoil
Molecular

ABSTRACT

A departing photoelectron leaves the molecular ion with a recoil momentum that is distributed between translational motion and the excitation of vibrational and rotational energy levels. In this review, recent measurements of recoil induced effects in core- and valence level photoelectron spectra of free molecules are summarized. The experimental examples are preceded by the outline of a semiclassical model to treat the recoil effects in free molecules.

1. Introduction

One of the main historical challenges and goals of gas-phase soft X-ray electron spectroscopy has been accurate determination of the vibrational fine structure in molecular core-level photoemission [1]. Reliable values of vibrational constants and intensity ratios are a prerequisite for determining quantities of fundamental physical and chemical significance, such as ionization energies and chemical shifts. Core-level photoelectron spectra are an excellent source for this information. It has been customary to assume that well above the core-ionization threshold, the vibrational structure of the photoelectron spectrum is entirely determined by the well-known Franck–Condon principle, which states: "… the electron transition affects neither the position nor the momentum [of the nuclei] directly" [2]. However, the departing photoelectron has a certain linear momentum and by conservation of momentum the momentum of the molecular ion must differ from that of the neutral molecule by this amount. Recent photoemission measurements of gas-phase molecules have demonstrated that not only does this "recoil" momentum change the translational motion of the whole molecule (which is a trivial effect), but it also introduces additional vibrational and rotational excitations in the molecule.

The recoil excitations are observable already at relatively low kinetic energies of the departing photoelectrons—about 100 eV, and become stronger with increasing electron energy. Apart from the need to take these effects into account in analyzing the vibrational structure in core-level photoemission spectra, the study of recoil effects provokes rather fundamental questions of its own. Recoil excitations are a common phenomenon in photoelectron spectroscopy; they have been observed also in solids [3,4], and the ability to understand and predict them is especially important for a quickly developing branch of photoelectron spectroscopy—HIKE (high kinetic energy) spectroscopy.

Recoil effects in molecular photoemission were first predicted by Domcke and Cederbaum, who presented a quantum mechanical formalism for the effect [3]. A different theoretical approach is given by Gel'mukhanov et al. in the form of generalized Franck–Condon factors, which take into account also the recoil effects [4]. Photoelectron recoil effects are present also in solids. Quantitative estimates for the broadening and shifts of XPS line profiles due to photoelectron recoil were given already in a theoretical paper by Flynn [5]. Notably, effects very similar to the photoemission recoil are present in nuclear β-decay taking place in molecules. The quantum mechanical formulation including the vibrational and rotational recoil in β-decay is presented in Ref. [6].

2. The basis of the photoelectron recoil effects

2.1. Classical model

Let us first consider a simple case of core-level photoemission from a diatomic molecule. The assumptions on which the following treatment is based are:

(i) A bound core electron is coupled via the Coulombic interaction to essentially one atom in the molecule.
(ii) The momentum of the photon is negligibly small.

---

[*] Corresponding author at: Dept. of Physics and Astronomy, University of Turku, FIN-20014 Turku, Finland.
E-mail address: edwin.kukk@utu.fi (E. Kukk).

0368-2048/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.elspec.2010.03.006

In a photoemission event, the coupling between the core electron and the nucleus is broken. The electron and nucleus have at any moment equal but opposite momenta: $\vec{p}_e = -\vec{p}_N$. As the photoabsorption breaks this coupling and the electron departs, carrying the momentum $p_e = \sqrt{2m_e E_{kin}}$, the nucleus is left with the "recoil" momentum $\vec{p}_N = -p_e$. The term "photoelectron recoil" can thus be somewhat misleading, since neither the photoelectron nor the photon generates this momentum, but rather it is the unbalanced momentum remaining in the molecular ion. This distinction becomes important when dealing with valence photoemission later on.

As a consequence of the assumption (i), the recoil momentum of a core photoelectron is initially given to a single atom in the molecule—this is the basis of our entire approach to the photoelectron recoil effects. Consider a diatomic molecule AB initially at rest, where the photoelectron with kinetic energy E_{kin} and linear momentum p_e leaves the atom A (the *emitter*) along the molecular (z-) axis and both atoms are initially at rest. Momentum conservation requires the whole molecule to have a momentum $p_M = -p_e$ associated with the translational motion of its center-of-mass. This corresponds to the energy $E_{trans} = 1/2Mp_e^2$, where M is the molecular mass. On the other hand, the recoil energy that is initially contained only in the emitter atom is larger, $E_A = 1/2M_A p_e^2$. The energy difference that goes into internal excitation of the molecule is therefore

$$E_{exc} = E_A - E_{trans} = \frac{M_B}{2(M_A \times M)} p_e^2. \tag{1}$$

This difference and the possibility of internal excitation arises because in the photoemission event the molecule does not act as a rigid structure.

Let us consider this process also in terms of internal momentum, which will be the key quantity in calculating quantum mechanical excitation probabilities. Instead of the momenta of the individual atoms, we use the internal coordinate $z = z_A - z_B$ and the internal momentum $p = \mu\dot{z}$, where μ is the reduced mass of the molecule. The photoelectron removes the momentum p_e from atom A but the *spectator* atom B is initially unaffected. The internal coordinate starts changing with the speed $\Delta\dot{z} = \Delta\dot{z}_A = -p_e/M_A$, in other words, the molecule starts to vibrate. From the momentum conservation, the change in the internal momentum can be easily calculated as

$$\Delta p = -\frac{M_B}{M} p_e. \tag{2}$$

Eqs. (1) and (2) show that the lighter the electron emitter A compared to the spectator atom B, the stronger is the internal excitation due to recoil.

2.2. Quantum mechanical model

The classical vibrational recoil energy (1) must be translated into excitation probabilities of quantum mechanical vibrational energy levels. Similar problems are well known in massive particle–molecule collision experiments. Whiteley et al. [12] studied ion–molecule collisions and obtained quantum mechanical formulae for the vibrational excitation probabilities. They used harmonic oscillator wavefunctions *in momentum space*, which is a natural environment for studying fast, impulsive collisions. One can regard molecular inner-shell photoemission on the same formal basis. In the molecular ion, the momentum-space wavefunction is shifted by Δp along the internal momentum axis with respect of the initial-state wavefunction of the neutral molecule. The eigenfunctions of the harmonic oscillator in the momentum space are given as [12]:

$$\psi_v(p) = N_v \ \exp\left(\frac{-p^2}{2\mu\omega}\right) H_v\left(\frac{p}{\sqrt{\mu\omega}}\right), \tag{3}$$

where v is the vibrational quantum number, N_v the normalization constant, ω the vibrational frequency, and H_v the Hermite polynomial. The displaced wavefunction $\psi_0(p + \Delta p)$ is not an eigenfuction of the oscillator, but can be represented as a linear combination of oscillator functions as follows:

$$\psi_0(p + \Delta p) = \sum_v c_v \psi_v(p), \, c_v = \langle \psi_v(p + \Delta p) | \psi_v(p) \rangle. \tag{4}$$

One notices an analogy between Eq. (4) and the Franck–Condon principle formulated in coordinate space. In the latter, vibrational excitations are induced by a shift of the molecular potential along the internuclear axis, so that the vibrational wavefunction of the initial state must be presented as an expansion in the new eigenfunctions of the final state. The transition probabilities are given as squares of the expansion coefficients. In the present case, the potential does not change, but the wavefunction itself is shifted due to recoil momentum. However, the transition probabilities to the final vibrational levels v are still given by c_v^2, the squares of the overlap integrals.

2.3. Rotational recoil

In a typical gas-phase nonresonant photoemission measurement, the orientation of the molecular axis is random. Above we considered the case of axial photoemission from diatomics. On the other hand, a core-level photoelectron emitted perpendicular to the molecular axis cannot directly excite molecular vibrations, although the recoil energy available for internal excitations is still given by Eq. (1) due to assumption (i). The energy is now used to excite the rotational levels of the molecule. Here, a full quantum mechanical treatment is somewhat superfluous since the individual rotational states cannot be resolved in typical photoelectron spectra. Instead, each vibrational peak consists of an envelope of a number of excited rotational states and, although one can calculate the up- and down-excitation probabilitities due to recoil for each state, the final observable effect is an overall shift of the rotational envelope (the vibrational peak) to the higher binding energies in the photoelectron spectrum, by the energy given by Eq. (1).

In order to interpret real experimental data, averaging over all possible electron emission directions with respect to the molecular axis must be made. The simplest approximation is that the electron emission probability distribution in the molecular frame of reference is isotropic. In the case of a linear molecule, averaging over all emission angles gives that 2/3 of the available excitation energy E_{exc} goes into rotational excitation and 1/3 into vibrational recoil excitation [3]. Photoemission anisotropy in the molecular frame changes this partition and expressions for calculating the vibrational excitation probabilities and the recoil-induced shifts of the rotational envelopes are given by Domcke and Cederbaum [3] for several different cases. In a typical photoelectron spectroscopy measurement the electrons are detected in a narrow solid angle of emission in the laboratory frame, defined by the experimental geometry. In this case the orientation of the axes of the emitting molecules with respect to the electron detection direction is also important—any anisotropy in the orientation of the emitting molecules modifies the partition of the rotovibrational recoil. As an example, we note that an oriented ensemble can be created by resonant excitations to an intermediate core-excited state.