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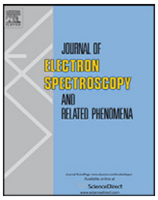

Recoil and related effects in molecular photoemission

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ABSTRACT

Photoemission from free molecules in the gas phase results in a complex spectral structure of electronic, vibrational and rotational transitions. In this review, the effects that can alter this structure and particularly the branching ratios in photoelectron spectra at the kinetic energies well above the ionization thresholds are considered. Simplified models that have nevertheless been found to describe the observations well are presented for photoelectron vibrational and rotational recoil, rotational Doppler broadening, photoelectron scattering and Cohen–Fano type interference phenomena. Experimental examples are shown together with the models. Some future developments and applications of the recoil-related phenomena are briefly considered.

1. Introduction

Since the invention of ESCA in 1960s, photoelectron spectroscopy has been an invaluable tool for physical chemistry and chemical physics for investigating many key properties of single molecules [1]. Charge distribution and the nature of chemical bonding are reflected in the chemical shifts of the photoelectron binding energies; geometry changes upon ionization are revealed by the vibrational structure in the spectrum, *etc.* A major leap in accuracy and flexibility was achieved when X-ray tubes were replaced by synchrotron radiation (SR) sources. High flux and tunable wavelength combined with high-resolution electron energy analyzers has allowed detailed insights into the chemical environment of molecules.

However, there are inherent limitations in photoelectron spectroscopy, *e.g.* energy uncertainty due to the short lifetime of core-hole states, thermal excitations of many rotational states, line broadening due to Doppler shifts in gas-phase molecules. These can be sometimes bypassed by advanced experimental techniques – coincidence measurements and supersonic molecular beam sources (see *e.g.* Refs. [2–5]). These techniques bring also additional complexities and sometimes much reduced detection efficiencies and/or electron energy resolution. Another approach is to take advantage of the very high spectroscopic quality (high count rates, narrow and well-defined instrument functions, accurate calibration, low background) of traditional non-coincidence photoelectron spectroscopy achievable at modern SR sources [6]. This, combined with advanced analysis methods has allowed to investigate the properties of molecular photoemission with unprecedented accuracy.

In this review, we focus on the vibrational and rotational structure in molecular photoemission, as studied by means of high-resolution electron spectroscopy and analyzed by least-squares decomposition methods in combination with theoretical models ranging from simple semi-classical models to advanced scattering theory. It has been a broadly accepted view in the community that, at energies well above the ionization thresholds, one reaches a region where the intensities of the vibrational excitations are determined only by the squares of the overlap integrals of the pre- and post-ionization nuclear wavefunctions, the Franck–Condon factors [7]. Since the beginning of this millennium, however, a number of phenomena were identified that, together, drastically change this view. Recoil, scattering and interference effects have all been shown to influence the structure of the molecular photoelectron spectra at all ionization energies so that there is no pure "Franck–Condon regime". On one hand such effects, if ignored, can cause severe errors in deriving molecular properties from spectroscopic data. On the other hand, all these phenomena carry unique information about the molecule. In the following, we will consider the basis, manifestations and consequences of such phenomena, particularly in respect to the various branching ratios that can be determined from experimental photoelectron spectra. Note that close to the ionization threshold, at low ($\lesssim$100 eV) kinetic energies, the departing photoelectron can be strongly affected by resonance and trapping effects, by effects related to the Cooper minima and numerous others (see, *e.g.* [8,9]). These phenomena will not be covered here.

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2. Vibrational recoil

Photoelectron recoil induced vibrational excitations in free molecules were first observed when following the branching ratios in the symmetric stretching progression in C 1*s* photoemission over a broad kinetic energy range in methane molecules [10]. At that time our expectation was that the ratios approach a constant value at high energies, determined by the Franck–Condon factors. The experimental data showed instead a slight, approximately linear increase. It was finally interpreted not as changes in the symmetric stretching progression itself, but as caused by the appearance of the unresolved vibrational excitations of other modes, caused by the recoil momentum on the carbon atom.

The transition probabilities of the recoil excitations were predicted by a semiclassical model [10]. Later studies [11] confirmed the phenomenon by more direct observations and the model was developed further. As the observations and the model are treated in several reviews [12,13] as well as in the original articles [10,11,14,15], we present here a short summary of the model. The model that was successfully applied to all free molecule recoil data so far is a semiclassical one: the departing photoelectron is treated as a classical particle carrying a momentum $\vec{p}_e$, but nuclear vibrations of the molecule are quantized and described by the nuclear wavefunctions (the wave nature of the photoelectron needs only to be considered insofar as its angular distribution is concerned).

In a photoemission event, the coupling between the bound 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 $p_e = \sqrt{2m_eE_{kin}}$, the nucleus is left with the “recoil” momentum $\vec{p}_N = -\vec{p}_e$. 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. Now an essential assumption is made: the recoil momentum is initially given to a *single atom* in the molecule. In addition, we neglect the momentum carried by the photon, since it is negligible compared to $\vec{p}_e$ in the soft X-ray regime. Following the energy and momentum conservation laws, one arrives at expressions valid classically as well as quantum mechanically. First, the translational recoil energy of the whole molecule with the mass M is

$$E_{trans} = \frac{1}{2M}p_e^2. \tag{1}$$

Secondly, the amount of recoil energy that goes into the internal excitations of the molecule is

$$E_{int} = E_{vib} + E_{rot} = E_{trans}\frac{M - M_A}{M_A}. \tag{2}$$

Here M_A is the mass of the atom receiving the recoil momentum. The energy E_{int} can be partitioned over the internal vibrational and rotational degrees of freedom. Special cases of center-of-mass photoemission [10,11] and emission from diatomic molecules [14] are presented elsewhere. Here we outline the general approach, how to relate the vibrational recoil energy E_{vib} to the excitation probabilities of vibrational levels and to the experimental branching ratios.

There are several vibrational normal modes and rotational axes in polyatomic molecules and the internal recoil momentum $\Delta\vec{p}$ must be distributed among all of them. The procedure to do so is presented in detail in Ref. [11]. It is convenient to work in the momentum space, where each normal mode i of the molecule can be described by a vector $\vec{\eta}_i$ with $3N$ Cartesian components, where N is the number of atoms in the molecule. The $3N$ components of each of the dimensionless vectors $\vec{\eta}_i$ are proportional to the momenta of atoms in that mode. Once the vectors $\vec{\eta}_i$ are known (*e.g.* from quantum chemistry calculations), they are used as a basis in which to represent the recoil momentum $\Delta\vec{p}$:

$$\Delta\vec{p} = \sum_i \delta p_i \vec{\eta}_i \tag{3}$$

where δp_i are the coefficients (with momentum dimension) in the basis of normal mode vectors; these give the change of the internal momentum of every normal mode due to recoil. If a coefficient $\delta p_i = 0$, then the mode i is not excited by recoil. According to our basic assumption, the recoil momentum is initially assigned to a single emitter atom. For example, in C 1*s* photoemission from the CO_2 molecule, the recoil momentum is initially taken up by the carbon atom. The molecule has three vibrational modes: (1) symmetric, (2) asymmetric stretching and (3) bending mode. Of these, only the last two involve the motion of the C atom, *i.e.* only the vectors $\vec{\eta}_2$ and $\vec{\eta}_3$ have components on the C atom. Therefore only $\vec{\eta}_2$ and $\vec{\eta}_3$ are needed to represent the recoil $\Delta\vec{p}$ on the carbon atom; the coefficient $\delta p_1 = 0$, and the symmetric stretching mode is not recoil excited.

Finally, we need to convert the representation (3) into measurable branching ratios. The average kinetic energy into each normal mode i is given by a summation over all components $\eta_{i,j}$ of the corresponding normal mode vector $\vec{\eta}_i$:

$$E_{avg,i} = \sum_j \frac{(\delta p_i \eta_{i,j})^2}{2M_{[j/3]}}, \tag{4}$$

where $M_{[j/3]}$ are the masses of the atoms associated with the component $\eta_{i,j}$. The probabilities for exciting levels of the vibrational mode i are given by the squares of the overlap integrals of the nuclear wavefunctions, also presented in momentum space. It can be shown that in the harmonic oscillator approximation the factors for $0 \rightarrow \nu$ are given by the Poisson distribution:

$$F_{i,\nu} = \frac{S_i^\nu}{\nu!}\exp(-S_i), \quad S_i = \frac{E_{avg,i}}{\hbar\omega_i}, \tag{5}$$

where $\hbar\omega_i$ is the characteristic frequency of mode i. For $\nu = 0$ and $\nu = 1$ this reduces to

$$F_{i,0} = \exp(-S_i), \quad F_{i,1} = S_i\exp(-S_i), \tag{6}$$

and for the branching ratio one simply gets

$$\frac{F_{i,1}}{F_{i,0}} = S_i = \frac{E_{avg,i}}{\hbar\omega_i} \tag{7}$$

As the energy $E_{avg,i}$ is a constant fraction of the total recoil energy when emission takes place from atom A that in turn is proportional to the kinetic energy of the photoelectron, the model predicts a linear increase in the branching ratios $F_{i,1}/F_{i,0}$ of recoil-excited levels. For $F_{i,2}/F_{i,0}$ ratios the predicted increase is quadratic in electron energy scale [11]. It should be kept in mind that the vibrational modes can be excited also by changes in the molecular potential upon ionization, which results in changed equilibrium geometry. These excitations are given by the “traditional” Franck–Condon factors calculated in the coordinate space and are independent of photoelectron energy. Recoil gives an additional excitation probability to be added to these, although it is often the case that a certain mode is excited only by the geometry change, or only by recoil.

The *ab initio* prediction by the model is compared with the experimental values for CF_4 C 1*s* photoemission in Fig. 1. We see an excellent agreement also with the calculated value of the constant slope.

3. Rotational recoil and Doppler broadening

While part of the recoil momentum is distributed over the vibrational degrees of freedom of the residual molecular ion, another