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To cite this article: Edwin Kukk et al 2009 J. Phys.: Conf. Ser. 194 012007

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Photoelectron recoil effects in free molecules

Edwin Kukk$^{1,2}$, T. Darrah Thomas$^3$ and Kiyoshi Ueda$^4$

$^1$Dept. of Physics and Astronomy, University of Turku, FIN-20014 Turku, Finland
$^2$Turku University Centre of Materials and Surfaces (MatSurf)
$^3$Department of Chemistry, Oregon State University, Corvallis, OR 97331, USA
$^4$Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

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, a model to treat the recoil effects in free molecules is presented and its applicability to core-level as well as valence photoionization is illustrated by experimental examples.

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, 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 C.P. Flynn [5]. Notably, effects very similar to the photoemission recoil are present in nuclear $\beta$-decay taking place in molecules. The quantum mechanical formulation including the vibrational and rotational recoil in $\beta$-decay is presented in Ref. [6].

The first observation of the effect was made in the C 1s photoelectron spectra of methane, which showed slight but consistently more severe distortions to the symmetric stretching progression as the ionizing photon energy increased [7]. These were assigned to the recoil-induced excitation of other vibrational modes. Later, the experiment was repeated on the CF$_4$ molecule, where the conditions to observe the recoil effect are much more favourable [8]. These were followed by experimental studies of diatomic molecules showing also rotational recoil effects [9]. Independently, photoelectron recoil effects have been recently observed in solids [10, 11].

In this review, we present the current status of our understanding of this effect on the basis of recent gas-phase experiments on several molecules: CH$_4$ [7], CF$_4$ [8], N$_2$ [9], as well as on unpublished results on these and the CO molecule. First, the principles and the application of our model for different cases is laid out. In the second part, experimental examples are given on core-level vibrational recoil excitations in CF$_4$ and on valence-level rotational recoil excitations in N$_2$.

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.

In a photoemission event, the coupling between the core electron and the nucleus is broken. It is illustrative to construct a simple Bohr-orbital-type analogy, where the orbiting electron and the 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 $p_e = \sqrt{2m_eE_{\text{kin}}}$, 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. 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 $E_{\text{kin}}$ 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 $E_{\text{trans}} = \frac{1}{2M}p_e^2$, where $M$ is the molecular mass. On the other hand, the recoil energy that is initially contained only in the emitter atom is larger, $E_A = \frac{1}{2M_A}p_e^2$. The energy difference that goes into internal excitation of the molecule is therefore

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

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 that 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 $\mu$ 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

$$\Delta p = -\frac{M_B}{M} p_e. \quad (2)$$

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 $\Delta p$ 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]:

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

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

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

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 probabilities 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 this case 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 in 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.

2.4. Recoil in multi-atom molecules

There are several vibrational normal modes and rotational axes in multiatomic molecules and the internal recoil momentum $\Delta \mathbf{p}$ must be distributed among all of them. The procedure to do so is presented in detail in Ref. [8]. Just as for diatomic molecules, it is convenient to work in the momentum space.

One begins with the momentum vectors $\mathbf{p}_n$ of all the constituent atoms. Each normal mode $i$ of the molecule can be described by a vector $\mathbf{n}_i$ with $3N$ Cartesian components, where $N$ is the number of atoms in the molecule. The $3N$ components of each of the dimensionless vectors $\mathbf{n}_i$ are proportional to the momenta of atoms in that mode. Also the three translational modes are described in this representation. The normal mode vectors can be obtained by using standard quantum chemistry computational packages such as GAUSSIAN [13], which provide the normal mode vectors in coordinate space that can be converted into $\mathbf{n}_i$ [8].

Once the normal mode vectors $\mathbf{n}_i$ are known, they are used as a basis in which to represent the recoil momentum $\Delta \mathbf{p}$:

$$\Delta \mathbf{p} = \sum_i \delta p_i \mathbf{n}_i$$

where $\delta p_i$ are the coefficients 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 1s photoemission from the $\text{CO}_2$ 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 $\mathbf{n}_{2,3}$ have components on the C atom. Therefore only $\mathbf{n}_{2,3}$ are needed to represent the recoil $\Delta \mathbf{p}$ on the carbon atom, the coefficient $\delta p_1=0$ and the symmetric stretching mode is not recoil excited.
So far, the quantization of the vibrational motion has not been taken into account. All the changes $\delta p_i$ lead to certain excitation probabilities of the vibrational levels of different normal modes. These probabilities can be calculated using Eq. (4), where $p$ and $\Delta p$ are replaced by $p_i$ and $\delta p_i$, respectively and $\mu$ is replaced by the reduced mass corresponding to the normal mode $i$.

2.5. Recoil in valence photoemission
The assumption that a bound electron is localized to a single atom in a molecule is natural for core levels, but is not valid for valence electrons. As discussed, the momentum of the photon is negligible and according the our simple model, the departing photoelectron carries away a momentum it already possesses as a bound electron. Because of the very short time-scale of photoemission, one should consider an electron wavepacket moving in the molecular field rather than the complete time-independent wavefunction. The electron can be emitted only, if during its brief interaction with the radiation the electron wavepacket is found in a region of the molecular field where its momentum is suitable, $p_e = \sqrt{2m_eE_{\text{kin}}}$, $E_{\text{kin}}$ being its eventual kinetic energy as a free electron. For high-energy photoemission it is therefore required that the wavepacket be localized in the regions of the molecule where it has high momentum – the regions in close proximity of the nuclei. The wavefunctions of the valence electrons penetrate close to the nuclei, albeit with small probability (hence low cross-sections of high-energy photoionization). Therefore, also the valence electrons must be localized to individual atoms in case of high-energy photoemission and can be treated essentially with the same approximations and model as for the core electrons, except that for any specific required momentum of the valence electron’s wavepacket, the localization probabilities in the proximity of all atoms in the molecule must be calculated. In the semi-classical treatment the recoil excitation energies are then calculated as an average. In the case of diatomics:

$$E_{\text{exc}} = n_A \frac{M_B}{2(M_A \times M)} p_e^2 + n_B \frac{M_A}{2(M_B \times M)} p_e^2, \quad (6)$$

where $n_A$ and $n_B$ are the probabilities that the photoelectron originates from either atom A or B, respectively.

2.6. Comparison of models
In the first theoretical treatment of the recoil effects [3], Domcke and Cederbaum used the secondary quantization formalism together with a simplified LCAO molecular orbital description to derive the vibrational excitation matrix elements that include the recoil corrections to the Franck-Condon principle. In order to formulate the theory, a set of approximations such as continuum electrons as plane waves and the exclusion of the $s-p$ hybridization was made. The theory demonstrates that there are interference effects causing, for example, oscillatory behaviour in the recoil shifts as a function of the kinetic energy of the electron. However, at high photoelectron kinetic energies the interference effects become small, and in this case the formalism of Domcke and Cederbaum gives identical results with the present model.

The formulation of the generalized Franck-Condon factors [4] introduces a phase factor $e^{i\phi}$ to the matrix element of vibrational excitation, initially just nuclear overlap integrals. The recoil effects are introduced through $\phi \sim \vec{p}_e \cdot \vec{R}$, where $\vec{R}$ is the internuclear radius vector of a diatomic molecule.

3. Experimental examples
3.1. CF$_4$
Fluoromethane is a tetrahedral molecule with the carbon atom at its centre of mass. It has nine vibrational normal modes: one symmetric stretching mode, three degenerate asymmetric
stretches, two degenerate symmetric bending modes, and three degenerate asymmetric bending modes. Carbon 1s ionization leads to a shortening of the C-F bond length by about 0.6 pm [14], which leads to a weak excitation of only one vibrational mode, the symmetric stretching mode.

We investigated the C 1s photoemission over a broad photon energy range. The measurements were performed at the SPring-8 synchrotron using a Scienta SES-2000 analyzer. Full details are given in Ref. [8]. Figure 1 shows the C 1s photoelectron spectra taken close to the ionization threshold and at high photon energy. The least-squares curve fitting result is shown together with the experimental data points. The fitting was performed using constraints for vibrational spacings [8] and a common value for the core-hole lifetime broadening. The spectrum taken at 330 eV is quite well reproduced by taking account only the weak symmetric stretch progression. The peak shape is influenced by the post-collision interaction (PCI), which is also included in the fit. In the spectrum taken at 1500 eV photon energy, a new structure appears.

We applied the above-presented recoil model to describe this excitation. The normal mode analysis shows that the recoil momentum is divided between the asymmetric bending mode and the asymmetric stretching mode, with the latter being more strongly excited. The symmetric modes cannot be excited by C 1s recoil, since in these modes the C atom is at rest. The model therefore gives the assignment of the new structure as the $v=1$ peak of the asymmetric stretching progression and the $v=1$ peak of the asymmetric bending progression, excited by recoil. In the least-squares fit of the spectrum at 1500 eV the position of the new peak (dotted blue line in Fig. 1) is fixed according to the known vibrational spacing of the asymmetric stretching mode [8].

In Fig. 2 the intensity ratio $v=1/v=0$ for the asymmetric stretching progression is followed over a range of the photoelectron kinetic energy. The model, using the harmonic oscillator wavefunctions in momentum space, predicts a linear increase in the $v=1$ to $v=0$ ratio, shown by the solid line. Experimental data obtained by curve fitting are compared with the prediction of the recoil model and are seen to be in a good agreement. Note that the prediction contains no adjustable parameters; it is based on the recoil model presented here and GAUSSIAN normal mode analysis.
Figure 2. Ratio of $\nu=1$ to $\nu=0$ intensities for the asymmetric stretching mode in the carbon 1s photoelectron spectrum of CF$_4$.

3.2. $N_2$

The second example illustrates the photoelectron recoil effect in molecular valence ionization and also the rotational excitations due to recoil. The B state in the valence photoelectron spectrum of the $N_2$ molecule is suitable for this study, since it is dominated by a single sharp $\nu = 0$ vibrational peak. The centroid position of this peak was followed at different photon energies. The measurement was performed at the SPring-8 synchrotron radiation facility and at the MAX II synchrotron, with full experimental details given in Ref. [9]. The shifts of the peak centroids in the binding energy scale were obtained by curve fitting the $\nu=0$ peaks and the Ar 2p peaks in the photoelectron spectra of a mixture of $N_2$ and Ar gases. Figure 3 displays the centroid binding energy of the $\nu=0$ peak of the B state as a function of the photoelectron energy. A linear interpolation through the data points gives the slope of the binding energy increase as $1.4(0.1) \times 10^{-5}$, which is compared with the theoretically predicted value of $1.30 \times 10^{-5}$. The theoretical prediction assumes that the photoemission from the B state is isotropic and that the electron is localized near a single nucleus when the photoionization occurs. The prediction is thus in excellent agreement with the experiment and the model is able to represent also the rotational recoil from delocalized valence orbitals.

A more accurate quantum mechanical description of the recoil excitations in the photoemission from homonuclear diatomic molecules includes interference terms [9]. The interference introduces a weak oscillation to the theoretical prediction for the centroid shift that, according to the model used here, is a linear function of the photoelectron energy. So far, however, such oscillations have not been experimentally verified.

4. Summary

Photoelectron recoil effects are an integral part of molecular photoemission, causing excitations of vibrational and rotational energy levels. These effects become increasingly prominent as the kinetic energy of the departing electron increases and they are observed both in core- and valence-level photoemission. All results obtained in the gas phase so far could be explained by a model which assumes a localization of the photoelectron to a single atom prior to its emission, both for core and valence levels.
Figure 3. Binding energy of the $\nu=0$ peak of the B state of N$_2$ plotted against the photoelectron kinetic energy. Experimental data points are fitted with a straight line and compared to the theoretical prediction of the recoil model.

Acknowledgments

Financial contributions from the following sources is acknowledged: the Academy of Finland; Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy; grants in aid for scientific research provided by the Japan Society for Promotion of Science (JSPS). The authors are thankful to all collaborators – coauthors in Refs. [7, 8, 9] – in the photoelectron recoil experiments and theory development and for the help provided by the SPring-8 and MAX-lab staff during the measurements.

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