

RECOIL EFFECTS IN HIGH-ENERGY MOLECULAR CORE-LEVEL PHOTOEMISSION

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. We have demonstrated experimentally, on the example of methane, that this is not the case and that, in fact, a violation of the Franck-Condon principle takes place due to the photoelectron recoil effect.

Methane (CH_4) is a tetrahedral molecule, which has four normal vibrational modes – symmetric and asymmetric stretch of the C-H bonds and two bending modes. When a carbon $1s$ electron is removed by photoemission, the molecular potential changes and the nuclear geometry will change towards its new equilibrium. As the adjustment – shortening of the C-H bonds – is centrally symmetric, the motion is the same as in the symmetric stretch vibrational mode. The result is the excitation of a symmetric stretch vibrational progression, observed in the C $1s$ photoelectron spectrum of CH_4 (Fig. 1), and theoretically described by the Franck-Condon factors. In our experiment [2], performed at beamline BL27SU, the photoelectron spectra were recorded using a high-resolution Scienta SES-2002 analyzer.

As required by the momentum conservation law, the departing photoelectron with a certain energy and momentum gives the molecule a **recoil momentum** of equal magnitude. The key question is, how is this momentum shared between the nuclei of the molecule? If the molecule would receive the momentum as a rigid body, a *translational* recoil would take place, and we would only observe a small energy loss in the electron spectrum. However, one has to take into account that: (i) core-level photoemission is very well localized to a single atom, the *emitter* and, (ii) the time-scale for ejecting the electron from the molecule is much shorter than the molecular vibrational period. These conditions mean that the recoil momentum is first received solely by the *emitter* atom and is later distributed to the whole molecule

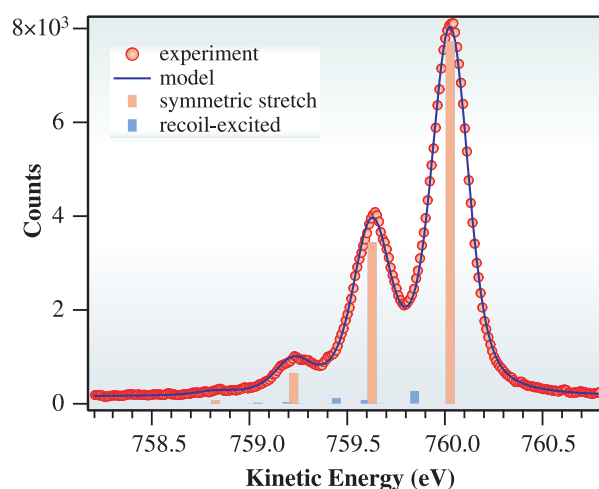


Fig. 1. Carbon $1s$ photoelectron spectrum of methane, excited with 1050 eV photons, and its vibrational structure [2].

through the molecular bonds. The energy and momentum conservation determines the momentum given to each atom (neglecting the quantum effects for now). The end result is that we have both *translational* and *vibrational* recoil, i.e., the recoil momentum can also induce molecular vibrations.

The effects of recoil in C $1s$ photoemission from methane are shown in Fig. 2. Initially, the carbon atom gets a momentum away from the center of the

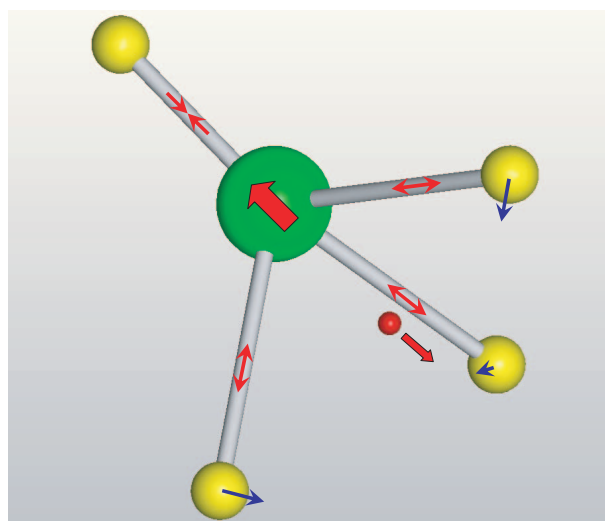


Fig. 2. Recoil excitation of the asymmetric stretch (red arrows) and bending (blue arrows) vibrational modes in a methane molecule, following C $1s$ photoemission.

molecule – a molecular-frame motion that corresponds to a combination of two vibrational modes: the asymmetric stretch and one bending mode. Thus, these two modes can become excited by recoil and the excitation probability increases with the photoelectron (and photon) energy: the higher above the threshold, the stronger the effect becomes. Note that these are *different* modes than the symmetric stretch excited on the basis of the Franck-Condon principle.

Quantum mechanically, the recoil vibrational excitations are quantized, with the average energy given by the classical model. The theory of recoil excitations can be handled conveniently in the momentum space, where one arrives at expressions much akin to the familiar Franck-Condon integrals in the coordinate space. Based on the recoil momentum, molecular symmetry and vibrational wavefunctions in the momentum space, we predicted the recoil-induced

changes in the photoelectron spectrum. A new vibrational structure starts to appear (see Fig. 1), although it is still weak at these electron energies. However, this allowed us to solve the puzzle of apparent long-range photon energy dependency in the vibrational branching ratios of the dominant symmetric stretch progression (Fig. 3). It turned out that the symmetric stretch structure itself does not change, but a new structure, albeit yet unresolved, starts to appear. If the spectrum is still analyzed as if due to a single vibrational mode, then the intensity ratios become distorted by the underlying recoil excitations.

Recent studies [3] have shown that recoil effects play a role also in the core-level photoemission from solids. Future studies using harder X-rays would make the recoil effects much more pronounced, providing access to the vibrational modes that are otherwise hidden, or would even dissociate the molecules.

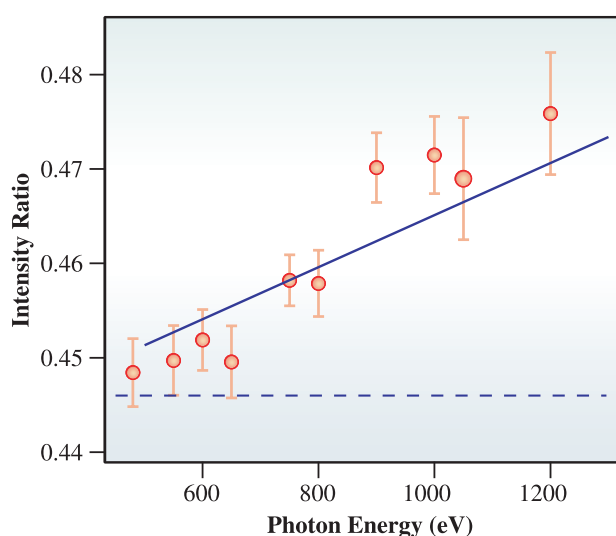


Fig. 3. Conventional analysis of the C 1s photoelectron spectrum using only the symmetric stretch progression. Experimental intensity ratio of the $v = 1$ and $v = 0$ peaks shows a rising trend, which is explained by taking into account the distortion by the underlying recoil excitations (blue line).

Edwin Kukka^{a,*} and Kiyoshi Ueda^b

^a Department of Physics, University of Turku, Finland

^b Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

*E-mail: edwin.kukk@utu.fi

References

- [1] K. Siegbahn: Electron spectroscopy for atoms, molecules and condensed matter: In G. Eksping, editor, Nobel Lectures in Physics 1981-1990, World Scientific, 1993.
- [2] E. Kukka, K. Ueda, U. Hergenhahn, X.-J. Liu, G. Prümper, H. Yoshida, Y. Tamenori, C. Makochekanwa, T. Tanaka, M. Kitajima and H. Tanaka: *Phys. Rev. Lett.* **95** (2005) 133001.
- [3] T. Fujikawa *et al.*: *J. Electron Spectrosc. Relat. Phenom.* **151** (2006) 170; Y. Takata *et al.*: *Phys. Rev. B* **75** (2007) 233404.