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The role of intramolecular scattering in K-shell photoionization

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Synopsis We report evidence of intramolecular scattering occurring in inner shell photoionization of small molecules. Pronounced oscillations of the ratios between vibrationally resolved cross sections (ν -ratios) as a function of photon energy have been observed theoretically and experimentally. Qualitative agreement with a 1st Born model confirms that they are due to intramolecular scattering: when an electron is ejected from a very localized region in the center of a polyatomic molecule, such as the $C(1s)$ orbital in a CF_4 molecule, it is diffracted by the surrounding atomic centers, encoding the geometry of the molecule [1,2].

The advent of third generation synchrotron radiation sources, in combination with high energy-resolution detection techniques, opened the way to the investigation of vibrationally-resolved inner-shell photoionization in small molecules, such as CO , BF_3 or CF_4 , in which an electron can be ejected from a $1s$ orbital of a first-row atom. We explore these problems with full first-principle calculations, comparing with experimental data and we show that most of the relevant features can be understood by means of simple models.

Vibrationally resolved cross sections have been calculated employing the B-spline static-exchange Many-Body Density Functional Theory method [3–5], which makes use of the Kohn-Sham DFT to describe the molecular ionic states and of the Galerkin approach to evaluate continuum electron wave functions in the field of the corresponding Kohn-Sham density. A more sophisticated time-dependent version of the DFT method [3–5], that takes into account the coupling between continuum channels, also has been employed. In K-shell photoionization, both methods converge at high photoelectron energies, the latter being more accurate near threshold, where sharp structures due to shape resonances might appear in the spectra [2].

Nuclear motion is taken into account at the Born–Oppenheimer level by including in the wave function the eigenstates of the totally symmetric stretching mode [1,2,6], i.e., the most affected by the structural rearrangement that accompanies core ionization, as the experimental data clearly indicates.

We have found that the ν -ratios exhibit pronounced oscillations at high energies that are due to intramolecular scattering. Experiments carried out for photon energies from 70 to 1000 eV are in excellent agreement with our first-principles calculations and qualitatively agree with a first-Born approximation model [1,2], in which intramolecular scattering is the only mechanism responsible for the change with energy of the relative intensity of symmetric-stretching vibrational photoelectron peaks. Furthermore, the model indicates and the ab-initio calculation confirms that the results of all individual ν -ratios can be gathered in a generalized ν -ratio which contains structural information of the molecule and improves the statistical significance of the experimental data [2].

This study also demonstrates that the information carried by the ν -ratios is a fingerprint of the molecular geometry and can thus be used to determine structural parameters, such as bond lengths, before and immediately after ionization, i.e., for both the neutral molecule and the core-hole species, which can live for a few femtoseconds before the Auger decay occurs [2].

References

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