

## High-energy non-Franck-Condon vibrational excitation of CH<sub>4</sub> by intramolecular photoelectron diffraction

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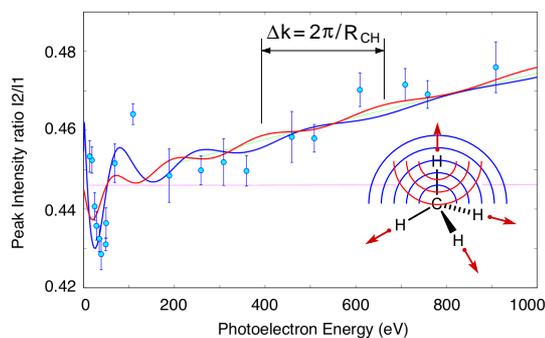
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**Synopsis** Distinct oscillations in vibrationally resolved cross section ratios for the photoionization of CH<sub>4</sub> from the C 1s orbital at photon energies as high as 1keV are predicted. The oscillations are attributed to the different relative vibrational excitation due to the scattering of the photoelectron by the peripheral hydrogen atoms. The latter effect is also responsible for the well known EXAFS oscillations in the integrated photoelectron spectrum. The calculations are performed with an *ab-initio* DFT method [1], as well as with a single-particle semi-analytical model, which incorporate both the effect of the nuclear recoil and of the Coulomb corrections.

We investigated theoretically the vibrationally resolved photoionization (PI) cross section of methane from the C 1s orbital at photon energies up to 1200 eV with two complementary approaches. Alongside an elaborated DFT method, tailored to the molecular ionization continuum and capable of accurate quantitative predictions [1], we utilized a simple one-particle model which incorporates both the effect of the recoil and of the Coulomb corrections to the photoelectron wave function at the level of the first-order Born approximation to interpret the results obtained with the *ab-initio* method. We found that the EXAFS oscillations in the total PI cross section, which are expected as a result of the scattering of the photoelectron by the peripheral hydrogen atoms, are virtually invisible in this case, due the rapid decrease of the total cross section. However, when the ratio between the yields of different  $a_1$  vibrational states of the parent ion is plotted, clear oscillations attributable to the same mechanism appear. On the one hand, this result unambiguously reveals, for the first time, intramolecular photoelectron scattering in an isolated polyatomic molecule in the gas phase. On the other hand, the change in the relative yield of different vibrational states points to a novel mechanism for the break-up of the Franck-Condon approximation (FC). Deviations from the Franck-Condon approximation in the PI of methane from the C 1s orbital at high photon energies ( $h\nu \sim 1\text{keV}$ ), due to the nuclear recoil associated to the photoelectron ejection, were recently reported [2]. While the lat-

ter is an essentially classical effect, though, the phenomenon we are highlighting is purely quantum in nature. Indeed, the photoelectron scattering amplitude is much smaller than the direct one, therefore it mostly manifest itself in the *interference* term between the two amplitudes. Very good agreement between the DFT prediction and the available experimental data is observed. Even if present experimental data do not allow to draw definitive conclusions on the existence of the oscillations, the measurement of this effect is within the capabilities of today's experimental apparatuses.



**Figure 1.** Intramolecular photoelectron scattering excites CH<sub>4</sub> breathing. Exp. data from [2]; Red line: model's prediction; Blue line: DFT result.

### References

- [1] Canton, S. E. *et al.* 2011 *Proc. Nat. Acad. Sci. in press*
- [2] Kukk, E. *et al.* 2005 *Phys. Rev. Lett.* **95** 133001

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