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## Dynamical effects in the vibrationally resolved C 2s<sup>-1</sup> photoionization cross section ratios of Methane

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**Synopsis** The vibrationally resolved C 2s photoionization cross-section of methane was investigated both theoretically and experimentally. When compared to that of C 1s photoionization, a rather different pattern has been observed, suggesting a strong interplay between the electron diffraction and interference effects.

Interference and diffraction effects in molecular photoionization have been recently revealed and subjected to a number of studies [1-5]. The experimental observation of such effects is very difficult when measuring absolute cross sections, but they can be evidenced in a much easier way by monitoring the photon energy dependence of the appropriate ratios of partial cross sections. One such possibility is the study of  $\nu$ -ratios that is cross section ratios of different vibrational levels in the same electronic channel. In absence of any diffraction and interference effects, the  $\nu$ -ratios should be essentially energy-independent, a constant equal to the Franck-Condon ratios. However, the experimentally studied  $\nu$ -ratios of valence [1] and core ionized [4,5] show apparent energy-dependent oscillations, which can be qualitatively predicted from the Cohen-Fano model [1,3] and simple diffraction effects [2,4,5]. The method to study  $\nu$ -ratios has proven to be a very sensitive probe, as it can reveal even the tiny diffraction associated with the light hydrogen atoms, as has been shown in the core ionization of CH<sub>4</sub> [2].

A key feature of the oscillations is their relationship to the molecular geometry, and in particular the bond length between emitting and scattering centers [5]. While the observed patterns are quite accurately reproduced by high quality ab-initio theoretical calculations, a full understanding of all factors involved is still incomplete. To this end we have compared the behavior of  $\nu$ -ratios in the photoionization of the inner-valence 2a<sub>1</sub> orbital of methane which is a linear combination of C 2s and H 1s orbitals, with the completely localized C 1s core orbital. The vibrationally resolved photoionization

cross section ratios of the symmetric stretching mode in the C 1s and C 2s photoionization of CH<sub>4</sub> were measured at PLÉIADES beam-line [6] using a VG-Scienta R4000 spectrometer. Unexpectedly, both experimental and theoretical  $\nu$ -ratios of 2a<sub>1</sub> photoionization exhibit a quite different pattern compared to the C1s photoionization, indicating that in case of the 2a<sub>1</sub> state the relative cross section oscillations are also modulated by other effects in addition to the diffraction of an electron issued from a localized emitter. A possible explanation lays in the more delocalized and spatially extended nature of the initial 2a<sub>1</sub> (C 2s) orbital, although additional complications (e.g. apparent predissociation effects in the experimental spectra) may also come into play. A better understanding of the behavior of the  $\nu$ -ratios of an inner-valence orbital may give us not only structural information (e.g., the C-H distance in this case) but also reveals information of other contributing factors such as the molecular orbital composition (i.e. electron density).

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