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Vibrationally resolved molecular frame photoelectron angular distributions of diatomic and polyatomic molecules

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Synopsis Vibrationally resolved molecular frame photoelectron angular distributions (MFPADs) of fixed-in-space molecules have been evaluated for diatomic and polyatomic molecules. Calculations have been performed by using an extension of the static-exchange density functional theory formerly developed by P. Decleva [1] and coworkers and extended in order to include the nuclear motion in the Born-Oppenheimer approximation. The method proved to be very accurate for diatomic molecules [2, 3, 5], particularly at high energy of the photoelectron. In this work, we present the results obtained for the inner shell photoionization of C_2H_2, NH_3, CH_4, CF_4, BF_3 and SF_6.

Our predictions for the MFPADs of C_2H_2 show the signature of electron confinement and coherent two-centre interferences as those previously found in H_2 [4] and N_2 [5].
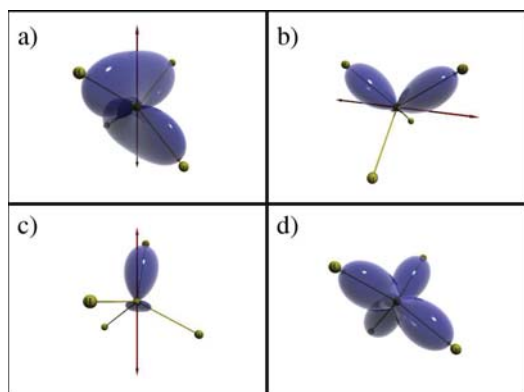

Figure 1. MFPADs for the C1s photoionization of CH_4 at a photoelectron energy of 4.35 eV. The MFPADs have been calculated with the present DFT method using a LDA(VWN) functional for different orientations of the polarization vector (indicated by a double arrow) - a) polarization vector aligned to a C_2 symmetry axis, b) polarization vector perpendicular to a C_2 axis and in the plane of two hydrogen bonds, c) polarization vector perpendicular to a C_3 axis along one bond and in a plane with another bond, d) averaged MFPADs.

C1s MFPADs of methane calculated by using the present DFT method (Figure 1) are in good agreement with the theoretical and experimental ones published in [6]. Analysis of the MFPADs for different orientation of the polarization vec-

tors shows that, as described in [6], for molecules containing a heavy central atom surrounded by hydrogen atoms, the resulting distribution is due to the propensity of the photoelectron to follow preferentially the direction of the bonds and the direction of the polarization vector. Hence, the MFPADs obtained after averaging over all the orientations of the polarization vector gives a totally symmetric distribution, which directly images the molecular geometry at low energy. We have found that this geometry imaging is lost only a few eV above threshold.

For molecules in which the central atom is surrounded by heavy atoms, the averaged MFPAD never reflects the molecular geometry at low photoelectron energy. Interestingly, at higher energies, the signature of molecular structure shows up but in a quite different way. A systematic study of these MFPADs for all the molecules mentioned above will be presented at the conference.

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