

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

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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 and coworkers [1] and extended in order to include the nuclear motion in the Born-Oppenheimer approximation. The method proved to be very accurate for diatomic molecules [2,3,4], particularly at high energy of the photoelectron. In this work, we present the results obtained for the inner shell photoionization of C₂H₂, NH₃, CH₄, CF₄, BF₃ and SF₆.

Our predictions for the MFPADs of C₂H₂ show the signature of electron confinement and coherent two-centre interferences as those previously found in and N₂ [4].

C1s MFPADs of methane calculated by using the present DFT method are in good agreement with the theoretical and experimental ones published in [5]. Analysis of the MFPADs for different orientation of the polarization vectors shows that, as described in [5], 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.

References:

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