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Analytical and molecular dynamical investigations of the influence of molecular vibrations upon the (e,2e) electron momentum distributions of furan

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Synopsis The role of molecular vibrations has been theoretically investigated in the electronic ground state on the (e, 2e) valence orbital momentum profiles of furan by means of two complementary approaches. The first one relies upon the principles of Born-Oppenheimer Molecular Dynamics (BOMD), whereas the second one, referred as Harmonic Analytical Quantum Mechanical (HAQM) approach, includes on quantum-mechanical grounds the effect of vibrations in the structure factors.

This work [1] analyzes the influence of thermally induced nuclear dynamics (molecular vibrations) on the electron momentum profiles related to the valence orbitals of furan in its initial neutral electronic ground state. To this aim two approaches are used. The first one, referred as the Harmonic Analytical Quantum Mechanical (HAQM) approach [2], implies a decomposition of the structure factor into contributions for each vibrational eigenstates within the frame of the harmonic oscillator - rigid rotor approximation, including on quantum-mechanical grounds the effect of vibrations in the computed (e,2e) momentum distributions. The second one uses the principles of Born-Oppenheimer Molecular Dynamics (BOMD) in order to average (by virtue of the ergodic principle) over a large number of molecular structures the effect of temperature on (e,2e) momentum profiles [3]. In contrast with the HAQM approach, BOMD enables to cope with nonharmonic effects and couplings between vibrations and/or internal rotations as well as the chaotic nature of nuclear motions in polyatomic molecules. The two approaches enable consistent insights into the experimental momentum profiles obtained from newly performed Electron Momentum Spectroscopy measurements with improved energy and momentum resolutions. At 298K both approaches show that nuclear dynamics in the initial neutral electronic ground state has a strong influence on the $9a_1$ orbital momentum profile (Figure 1). The role of specific CH-stretching and bending vibrational modes of A_1 symmetry can be explained according to the symmetry characteristics of orbitals and their energy differences, in line with the Herzberg-Teller principle. This study shows how molecular vibrations and nuclear motions in the initial electronic ground state may affect electron momentum profiles, and gives new guidelines for discriminating these effects from other physical phenomena such as distorted wave effects or nuclear dynamics in the final state (comprising non adiabatic effects).

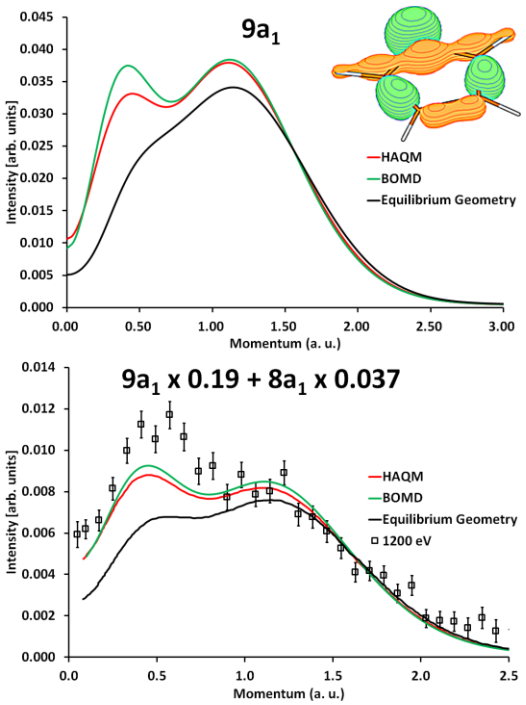

Figure 1. Theoretical momentum profiles for the $9a_1$ orbital (top), and comparison with the experiment (bottom).

References

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[2] N .Watanabe *et al 2012 J. Chem. Phys.* **137** 114301
[3] See e. g. S. H. R. Shojaei *et al 2013 J. Phys. Chem. A* **117** 1918 and references therein

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