

# Electron momentum spectroscopy investigation of flexible molecules considering vibrational effects

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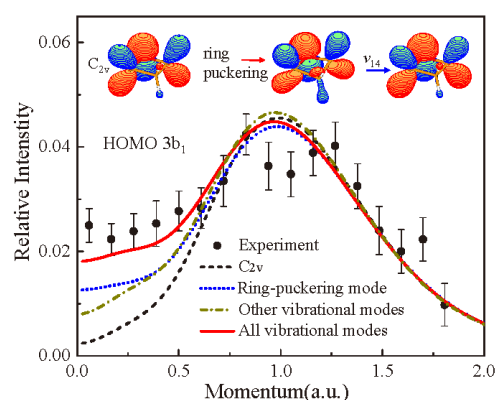
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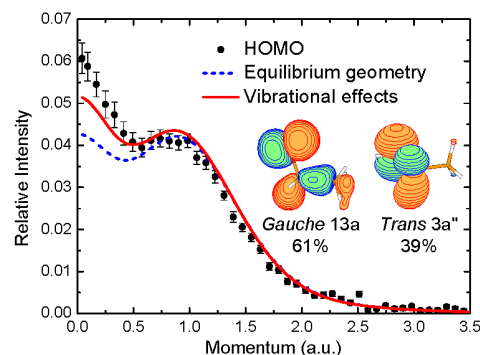
**Synopsis** We report the recent electron momentum spectroscopy study of the oxetane and ethanol molecules. The agreement between theoretical and experimental momentum profiles of outer-valence orbitals is greatly improved when considering vibrational effects in the calculation, indicating the significant influence of molecular vibrations on electronic wavefunctions.

Electron momentum spectroscopy (EMS) [1] is a robust technique for exploring the electronic structures of atoms and molecules. The technique bases on high-energy electron impact (e, 2e) reaction under the Bethe ridge conditions. Within a series of approximations including Born-Oppenheimer, binary encounter, weak coupling, and plane wave impulse approximations, the triple differential cross section (TDCS) of the (e, 2e) reaction is proportional to the modulus square of the wave function of the ionized orbital in momentum space, that is, electron momentum profile. However, careful treatments should be carried out when interpreting EMS experimental results due to the possible invalidity of these approximations and the complexity of polyatomic molecules.

Recently EMS studies [2] showed that vibrational effects or nuclear dynamics in the electronic ground state are important when interpreting the experimental electron momentum distributions (EMDs) of some molecular orbitals. For molecules with flexible structures, attentions are often paid to the low frequency, large-amplitude vibrational modes. In this talk, we will report our recent EMS study on oxetane having a large-amplitude ring-puckering motion [3] and ethanol having two conformers [4]. The EMDs of outer-valence orbitals of oxetane and ethanol have now been interpreted quantitatively when considering vibrational effects comprehensively. It exhibits that vibrational motions influences the EMDs of outer-valence orbitals of oxetane and ethanol remarkably not only through the low-frequency vibrational modes but also through high-frequency modes (Fig.1 and 2). The case of oxetane and ethanol exhibits the significance of checking all vibrational effects when investigating flexible molecules.



**Figure 1.** Electron momentum profiles of the HOMO of oxetane with theoretical ones considering vibrational effects.



**Figure 2.** Electron momentum profiles of the HOMO of ethanol with theoretical ones considering conformational and vibrational effects.

## References

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