EMS study of vibrational effects on electron momentum distributions of C_2H_4 and CH_2F_2

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Synopsis We report an electron momentum spectroscopy study of vibrational effects on the electron momentum distributions for the outer valence orbitals of C_2H_4 and CH_2F_2. The symmetric noncoplanar (e,2e) experiment has been conducted at impact energy of 1.2 keV. Furthermore, a theoretical method of calculating electron momentum distributions has been developed with vibrational effects being involved. The experimental and theoretical results for these molecules strongly suggest that vibrational effects on electron momentum distributions tend to be appreciable for non-total symmetry molecular orbitals delocalized over some equivalent CH-bond sites.

The influence of molecular vibration on electronic wavefunction is of great importance for many physical and chemical processes. For instance, the appearance of dipole-forbidden lines in optical spectra has generally been explained by such influence; deformation of electronic wavefunctions owing to molecular vibration changes the dipole selection rule. Electron momentum spectroscopy (EMS), also known as binary (e,2e) spectroscopy, is a method that enables one to look at individual electron orbitals in momentum space, and thus may provide a powerful tool to investigate how molecular vibration affects molecular orbital patterns. In spite of their importance in EMS studies, however, investigations of vibrational effects on electron momentum profiles are scarce. In this contribution, we report our recent experimental and theoretical study of vibrational effects on electron momentum profiles for the outer-valence orbitals of C_2H_4 [1] and CH_2F_2 [2].

The symmetric noncoplanar (e,2e) experiment was carried out for the molecules at impact energy of $E_0 = 1.2$ keV. In the experiment, two fast outgoing electrons having equal energies ($E_1=E_2$) and making equal polar angles ($\theta_1=\theta_2= 45°$) with respect to the incident electron beam axis were detected in coincidence. In this way, (e,2e) data were obtained as a function of binding energy and the ion recoil momentum. We also performed plane-wave impulse approximation (PWIA) calculations with vibrational effects being involved.

Fig. 1 shows the experimental momentum profile for the $2b_1$ orbital of CH_2F_2. Also depicted in the figures are two kinds of theoretical calculations. One is theoretical momentum profile that has been calculated at the equilibrium geometry and the other is that involving vibrational effects. It can be seen from the figure that

the equilibrium geometry calculation predicts typical 'p-type' momentum profile having a node at the momentum origin ($p = 0$). On the other hand the experiment clearly exhibits noticeable intensity near $p = 0$ and understanding of the observation thus requires consideration of additional effects that the equilibrium geometry calculation does not take into account. It is evident from the figure that the vibrational effects calculation gives substantial intensity near the momentum origin and reproduces the experimental result satisfactorily. The findings clearly indicate that molecular vibration plays an important role in the (e,2e) ionization process of the $2b_1$ orbital. By assessing contributions from individual normal modes, it has been revealed that the CH_2 asymmetric stretching and CH_2 rocking vibrational modes significantly affect the momentum distribution of the $2b_1$ orbital.
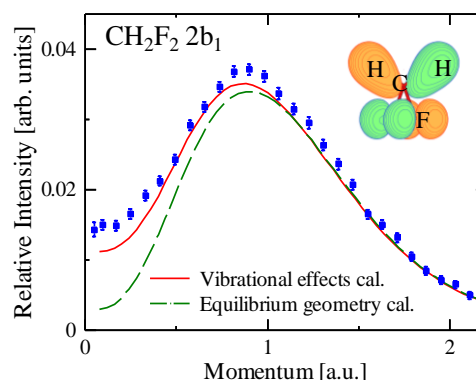

Figure 1. Momentum profiles for the $2b_1$ orbital of CH_2F_2.

References

[1] N. Watanabe, M. Yamazaki, and M. Takahashi, 2011 *J. Chem. Phys.* **137** 114301

[2] N. Watanabe, M. Yamazaki, and M. Takahashi, 2014 *J. Chem. Phys.* **141** 244314

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