



Theoretical study of the photoelectron spectra of ketene using a hybrid model for computing Franck–Condon factors



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Abstract

Method: The equilibrium structures, harmonic and anharmonic vibrational frequencies of ketene and three of its lowest-lying cationic states were calculated using the (time-dependent) B3LYP (red, Figs. 2-4), PBE1PBE (green), M06-2X (orange) and ω B97XD (blue) density functionals of the density functional theory. The aug-cc-pVTZ basis set was utilized. The Franck–Condon factors were calculated using a hybrid model of harmonic^[1] and anharmonic oscillators, from which the photoelectron spectra of ketene were simulated.

Conclusion: The errors of the excitation energies of the hybrid model are less than those of the harmonic model. The simulated photoelectron spectra of ketene are in harmony with the experiment.

Results and Discussion

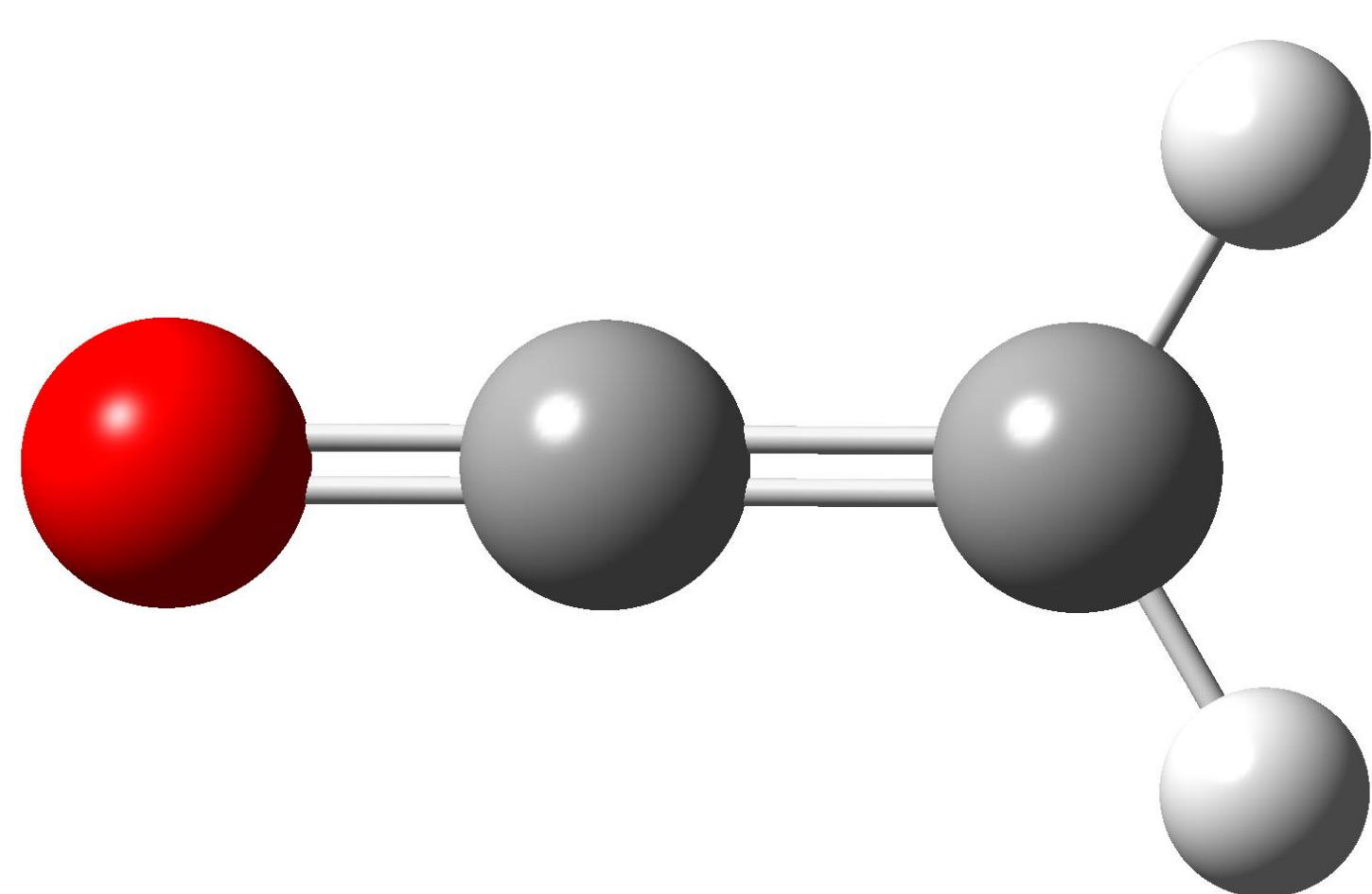


Fig. 1. The equilibrium structures of ketene

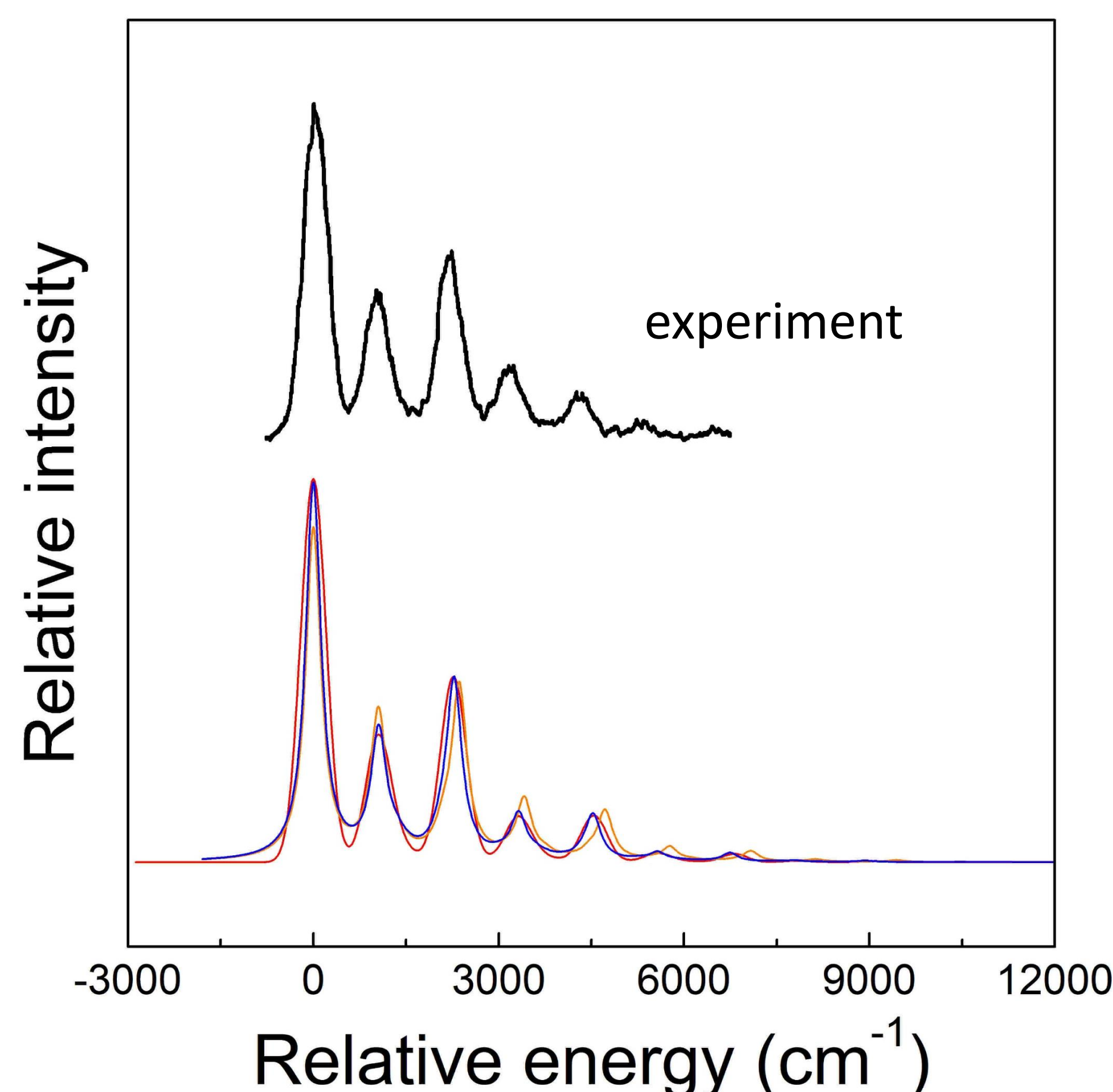


Fig. 2. The simulated photoelectron spectra of the cationic ground state of ketene compared with the experiment^[2].

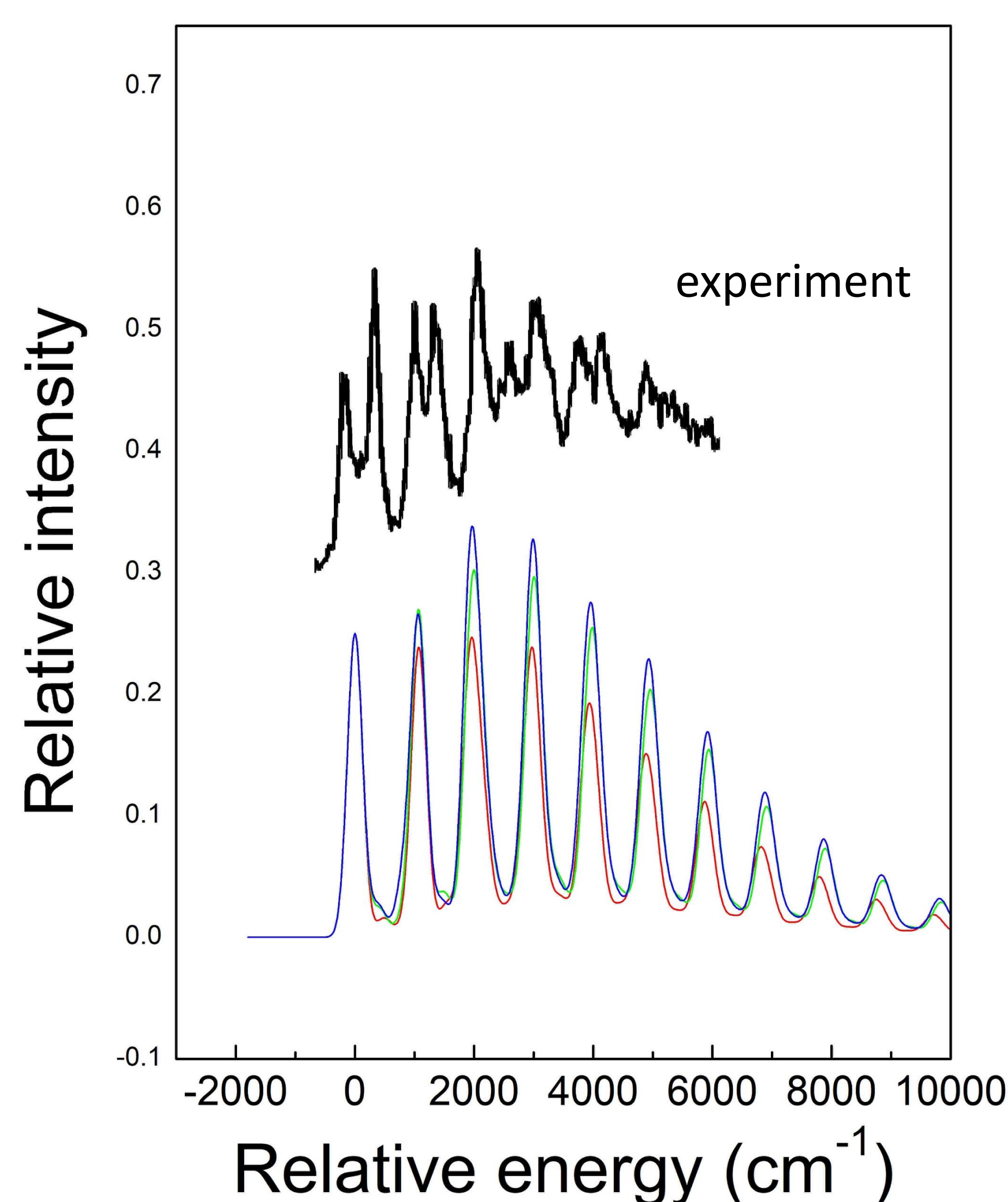


Fig. 3. The simulated photoelectron spectra of the first excited state of ketene compared with the experiment^[3].

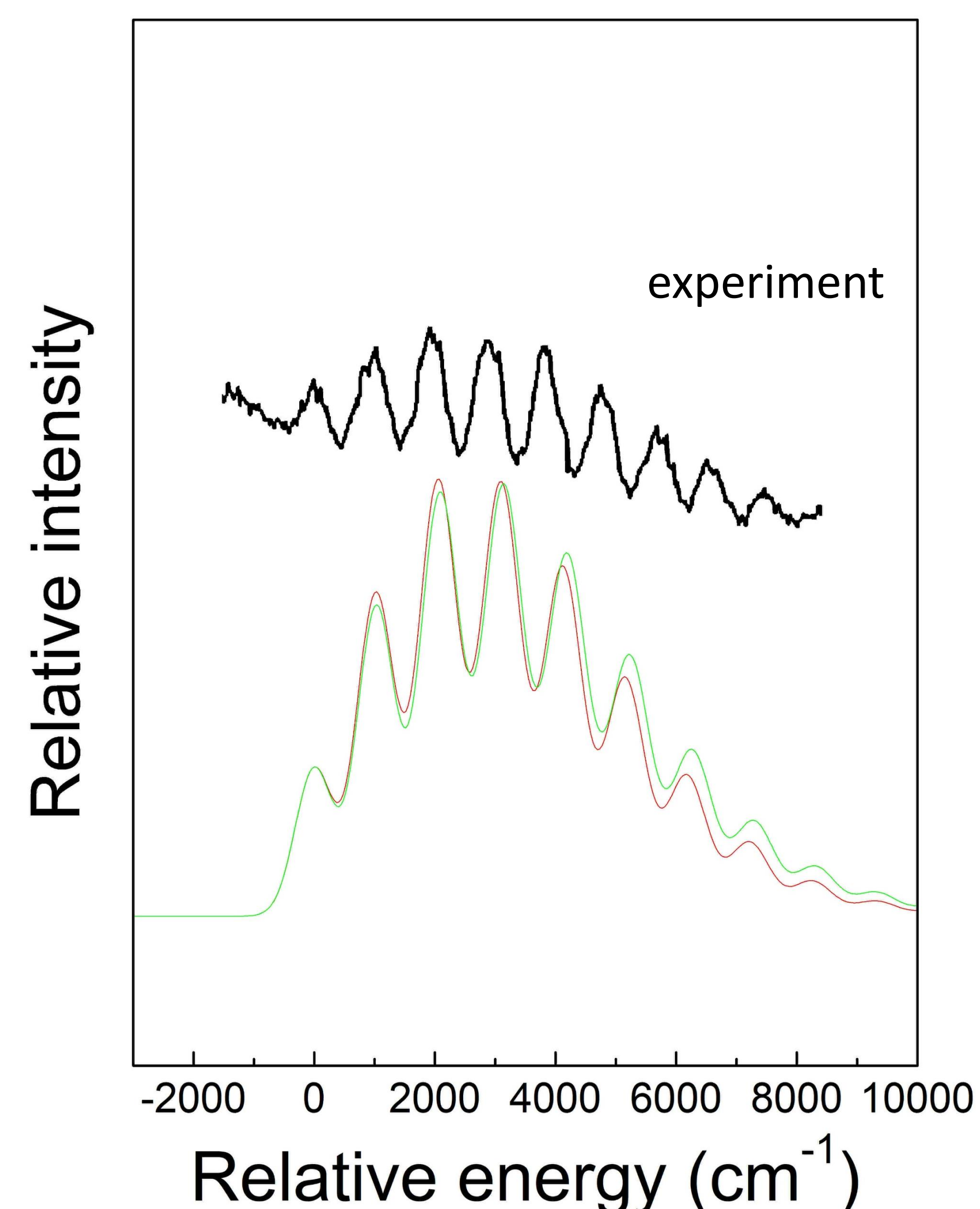


Fig. 4. The simulated photoelectron spectra of the second excited state of ketene compared with the experiment^[3].

References

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- [3] *J. Chem. Phys.* 99, 2520 (1993); doi: 10.1063/1.465215

