

# THRESHOLD PHOTOELECTRON SPECTRUM OF CYCLOBUTADIENE: COMPARISON WITH TIME-DEPENDENT WAVE PACKET SIMULATIONS

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## INTRODUCTION

Antiaromaticity is a chemical property of a cyclic molecule with a  $\pi$  electron system that has higher energy, i.e., it is less stable due to the presence of  $4n$  delocalised ( $\pi$  or lone pair) electrons in it, as opposed to aromaticity. Unlike aromatic compounds, which follow Hückel's rule ( $[4n+2]$   $\pi$  electrons)<sup>[1]</sup>. Antiaromaticity leads to low stability, thus antiaromatic compounds are highly reactive. Cyclobutadiene (CBD),  $C_4H_4$ , is the prime model for antiaromaticity and thus a molecule of considerable interest in chemistry<sup>[2]</sup>.

## METHODOLOGY

CBD was reinvestigated by photoelectron-photoion coincidence spectroscopy (PEPI-CO), a technique that allows to record ion mass-selected (threshold) photoelectron spectra (ms-TPES) for each composition by correlating ions<sup>[3]</sup> and electrons. This avoided a possible issue in traditional photoelectron spectroscopy of reactive compounds, which is the potential for signal disturbance from contaminations.

A simulation model of the photoelectron spectrum was retreated by utilizing wavepacket dynamics simulations and a new vibronic coupling model Hamiltonian<sup>[4][5]</sup>, carefully reparametrized by using calculations based on complete active space with second-order perturbation theory (CASPT2).

Cyclobutadiene (1) is generated by pyrolysis from the Pettit Complex (2)

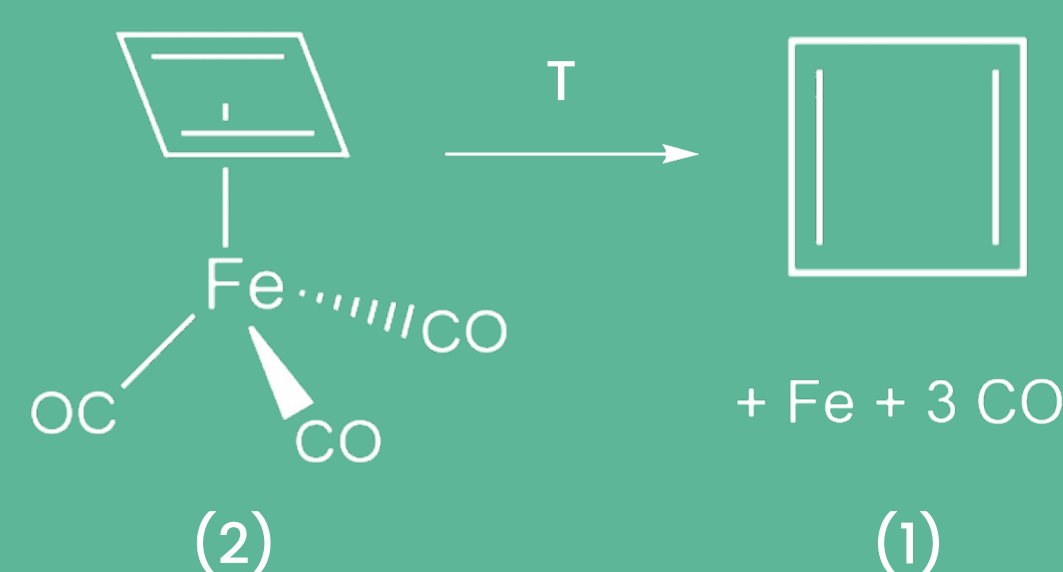


Figure.1

## RESULTS

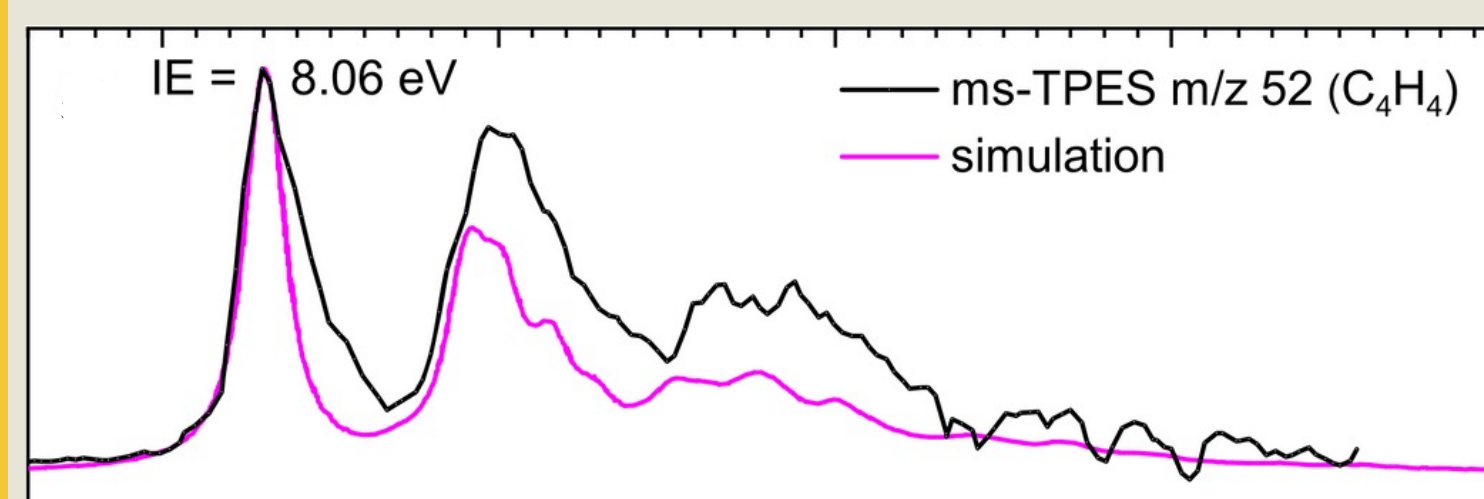


Figure 2. Ms-TPES (black) generates an IE of 8.06 eV in a very good match with the simulation (magenta).

The mass-selected photoelectron spectrum shows a signal of IE=8.06eV at  $m/z$  52. This reflects the adiabatic ionization energy of CBD with an accuracy within  $\pm 0.02$  eV. The obtained IE highly matches the time-dependent wavepacket dynamics simulation calculated by CASPT2. It is, however, 0.1 eV less than the value that Kohn and Chen<sup>[6]</sup> previously published.

## Reference

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## ANALYSIS

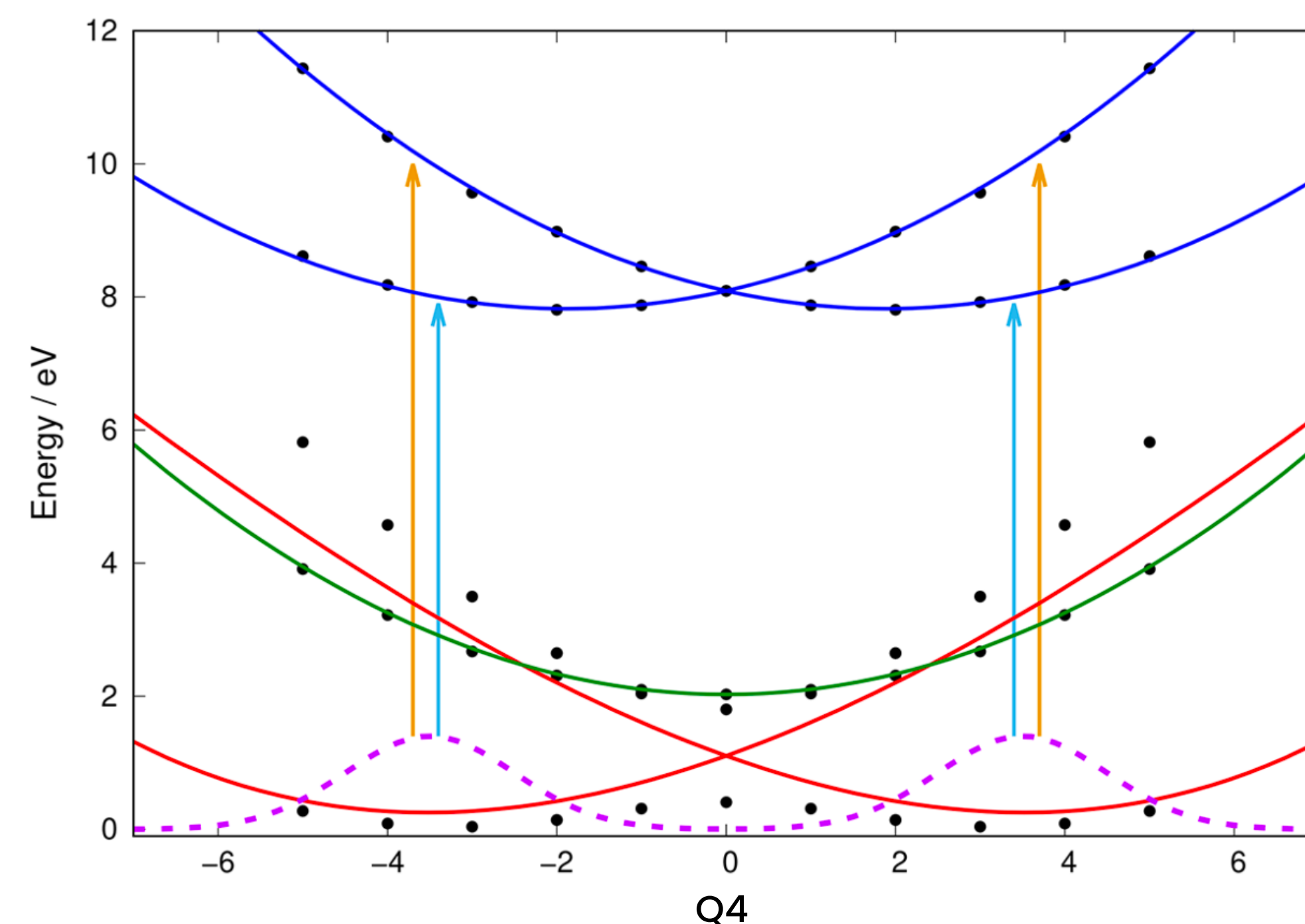
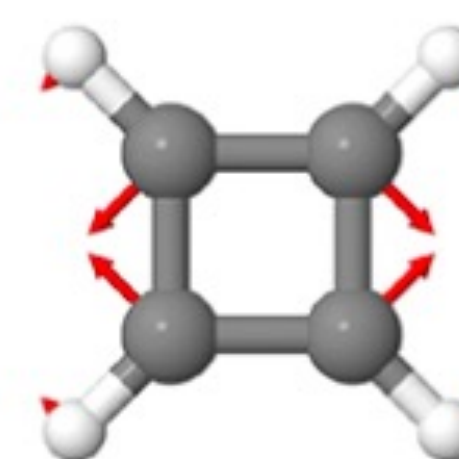


Fig 3. Relaxed wavepacket (purple dashed line), diabatic representation of neutral CBD ground states  $|1\rangle$  and  $|2\rangle$  from mixing  $|\tilde{X}(1B1g)\rangle$  and  $|\tilde{A}(1A1g)\rangle$  adiabatic states (red lines), excited neutral state  $|3\rangle = |\tilde{B}(1B2g)\rangle$  (green line), degenerate  $2E_g$  cation states (blue lines), and adiabatic CASPT2 energies (black dots).  $Q_4 = 0$  is the  $D_{4h}$  point.

Figure 3. portrays the slices through the CBD potential energy surface along the  $v_4$  vibrational coordinate and wavepacket excitation from neutral to cation along the  $v_4$  vibrational coordinate. The  $v_4$  vibration is strongly coupled to the  $v_1$  and  $v_5$  vibrations, as the addition of the  $v_4$  vibration leads to the peaks of  $v_1$  and  $v_5$  observed in the spectrum. This vibration transfers the structure between two rectangular minima with  $D_{2h}$  symmetry through a square transition state with  $D_{4h}$  symmetry.



$v_4$

The peaks in ms-TPES (Fig.1) indicate different vibrations of CBD due to the Jahn-Teller effect. The photoelectron spectra of CBD are explained in terms of both a Jahn-Teller effect in the cation and a pseudo-Jahn-Teller effect in the neutral. The consistency of the experimental and simulated spectra demonstrates that the  $v_4$  vibration dominates the dynamic behaviour of both neutral and cationic CBD.

## CONCLUSION

The adiabatic ionization energy of cyclobutadiene (CBD) is revised to  $8.06 \pm 0.02$  eV. The mass-selected (threshold) photoelectron spectrum of CBD agrees well with the time-dependent wavepacket dynamics simulation calculated by CASPT2. The photoelectron spectrum of CBD is interpreted by several vibration modes that originate from the Jahn-Teller distortion observed in CBD. The research also concludes that the dynamic behaviour of the neutral and cationic CBD is dominated by the vibration  $v_4$ .