Supporting Information for

The Threshold Photoelectron Spectrum of Cyclobutadiene: Comparison with Time-Dependent Wavepacket Simulations

Lea Bosse,[†] Barry P. Mant,[‡] Domenik Schleier,[†] Marius Gerlach,[†] Ingo Fischer,^{*,†} Anke Krueger,[¶] Patrick Hemberger,[§] and Graham Worth^{*,‡}

 †Institute of Physical and Theoretical Chemistry, University of Würzburg, D-97074 Würzburg
 ‡Dept. of Chemistry, University College London, 20, Gordon St., London, WC1H 0AJ
 ¶Institute of Organic Chemistry, University of Würzburg, D-97074 Würzburg
 §Laboratory for Femtochemistry and Synchrotron Radiation, Paul Scherrer Institut (PSI), CH-5232 Villigen

> E-mail: ingo.fischer@uni-wuerzburg.de; g.a.worth@ucl.ac.uk Phone: +49 (0)931 3186360. Fax: +49 (0)931 31863610

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S1 Synthesis of Cyclobutadiene iron tricarbonyl

General Experimental Procedure

Cyclooctatetraene **3**, dimethyl acetylenedicarboxylate and Fe₂(CO)₉ were used as received without further purification. Sulfuryl chloride SO₂Cl₂ was purified by distillation (colorless, bp.: 62 °C) and the solvents were dried and distilled prior to use according to standard protocols. All reactions were performed in dried glassware under an atmosphere of dry nitrogen and the intermediates were stored under nitrogen atmosphere at -26 °C. The reaction steps were monitored by NMR spectroscopy. ¹H- and ¹³C-NMR were recorded on Bruker AVANCE III 400 FT-NMR- (400 MHz) and Bruker AVANCE HD DMX 600 FT-NMR- (600 MHz) spectrometers. Chemical shifts are referenced relative to internal chloroform (CDCl₃: ¹H, δ = 7.26 ppm; ¹³C, δ = 77.16 ppm), except for the ¹H-shifts after step 1, which show the product dissolved in CCl₄. Coupling patterns are assigned as s (singlet), d (doublet), t (triplet) or m (multiplet). Gasphase-infrared (IR) spectra were recorded on a Bruker IFS120HR FT-IR spectrometer. Absorptions are reported in cm⁻¹ and noted as follows: s (strong), w (weak). Time-of-flight mass spectrometry (TOF-MS) was performed on a 10 Hz Nd:YLF based laser system from Ekspla.

Experimental Procedure and Characterization





The synthetic route to obtain the precursor for the pyrolytic formation of cyclobutadiene (1), cyclobutadiene iron tricarbonyl (2), is summarized in Figure S1. The target compound 2 was synthesized by optimising an earlier route reported by Pettit *et al.*^{1,2} The synthesis started from commercially available cyclooctate-traene (3) which was chlorinated by SO₂Cl₂. This chlorinating reagent was proposed in another paper.³ The *cis*-isomer of bicyclic compound 4 was formed as the main product and subsequently reacted in a Diels-Alder reaction with dimethyl acetylenedicarboxylate yielding adduct 5. The isomer ratio could be determined to 53 % *cis*-isomer using CHCl₃ as solvent. The tricyclus 5 was then pyrolytically cleaved by a retro-Diels-Alder reaction. While the resulting *trans*-3,4-dichlorocyclobut-1-ene converted to the openchain 1,4-dichlorobutadiene through a ring opening³, the *cis*-product 6 remained stable and could react with Fe₂(CO)₉ by a ligand exchange to form the final product 2. Details of the preparation and analytical data for the intermediate steps are summarized in the next sections.

Synthesis of *cis*-7,8-dichlorobicyclo[4.2.0]octa-2,4-diene 4:



A solution of 21.5 ml (20.0 g, 190 mmol) cyclooctatetraene (**3**) in 40 ml dry CHCl₃ was stirred in nitrogen atmosphere at room temperature. 18.7 ml (31.2 g, 228 mmol) SO_2Cl_2 were added in portions so that the internal temperature did not exceed 40 °C. Cooling with a water bath allowed faster addition. As soon as gas evolution (HCl and SO_2) was detected and thus the reaction started, the addition could be accelerated. The total addition time was 4 h until no more gas development could be observed. The reaction mixture was stirred at 70 °C for further 30 min. After drying over Na₂CO₃ and subsequent filtering, the yellow product was used for the next step without further purification.

¹**H-NMR** (400 MHz, CCl₄): δ = 5.98 (2H, m, CH_{vinyl.}), 5.85 (2H, m, CH_{vinyl.}), 4.72 (2H, m, CHCl), 3.38 (2H, m, CH) ppm.

Synthesis of dimethyl-cis-3,4-dichlorotricyclo[4.2.2.02,5]deca-7,9-diene-7,8-dicarboxylate 5:



To the solution of **4** in 40 ml CHCl₃ 16.5 ml (19.0 g, 133 mmol) dimethyl acetylenedicarboxylate was added and the mixture stirred in nitrogen atmosphere at 80 °C for 3 h. The reaction mixture turned dark and the solvent was removed under reduced pressure. The brown crude product (36 ml), which solidifies at room temperature, was used directly in the next step without further purification.

¹**H-NMR** (400 MHz, CDCl₃): $\delta = 6.59$ (2H, m, CH_{vinyl}), 4.24 (2H, m, CHCl), 3.86 (2H, m, CH), 3.77 (6H, s, CH₃) 2.80 (2H, m, CH) ppm.

Synthesis of *cis*-3,4-dichlorocyclobut-1-ene 6:



The Diels-Alder adduct **5** was added slowly to an empty flask filled with 25 mbar dry nitrogen and heated to 260 °C. The pyrolytically produced fragments were collected by a distillation bridge in a receiving flask kept at room temperature. The addition lasted 1 h, after which pyrolysis was continued until only little material was left in the flask. The fragments were then fractionated by distillation under reduced pressure. **6** and its isomer were obtained with an overall yield of 6.90 g (56 mmol, 29 % starting from **3**) as a colorless liquid with a *cis:trans* ratio of 52:48. Through ring opening, the *trans* isomer was present as the open-chain 1,4-dichlorobutadiene. It was not necessary to separate the isomers for the next step.

Bp. 80 – 96 °C at 42 mbar; Lit.: 58 – 71 °C at 55 mbar¹.

¹**H-NMR** (400 MHz, CDCl₃): $\delta = 6.39$ (2H, m, CH, *trans*), 6.28 (2H, m, CH, *cis*), 6.25 (2H, m, CHCl, *trans*), 5.15 (2H, m, CHCl, *cis*) ppm.

Synthesis of cyclobutadiene iron tricarbonyl 2:



A solution of 6.90 g (56 mmol) of closed-chain *cis*-6 and open-chain *trans*-6 in 50 ml dry benzene was stirred in nitrogen atmosphere at 50 °C. 30 g (82 mmol) Fe₂(CO)₉ were added in portions. The addition of Fe₂(CO)₉ was adapted to the level of CO formation. As soon as the gas evolution decreases, further Fe₂(CO)₉ could be added. The total addition period was about 5 h. Subsequently, the deep brown reaction mixture was stirred at 50 °C for another hour and filtered over Celite. The residue was washed with pentane. It could be pyrophobic and must be moistened with water immediately after filtration. The solvents were removed under reduced pressure and the filtrate was fractionally destilled to afford 940 mg (4.9 mmol, 53 %) of **2** as a yellow oil.

Bp.: 39 °C at 2 mbar; Lit.: 47 °C at 4 mbar².

¹**H-NMR** (600 MHz, CDCl₃): δ = 3.95 (4H, s, CH) ppm; Lit.: δ = 3.91 ppm.⁴.

¹³C-NMR (600 MHz, CDCl₃): $\delta = 214.9 (C_q)$, 64.12 (C_t) ppm; Lit.: $\delta = 209$, 61 ppm⁴.

FT-IR (gas phase): $\tilde{v} = 2065$ (s, $v_{symm. str.}$ (C-O)), 1995 (s, $v_{asymm. str.}$ (C-O)), 814 (w, v_{Def} (C-H)), 615 (s,

 $v_{\text{symm. def.}}$ (Fe-C-O)), 590 (s, $v_{\text{asymm. def.}}$ (Fe-C-O)) cm⁻¹; Lit.: $\tilde{v} = 2045$, 1965, 822, 610, 585 cm⁻¹⁵.

MS (**TOF**): m/z (%) = 192 ([M⁺], 10), 164 ([M⁺-CO], 3), 136 ([M⁺-2CO], 14), 108 ([M⁺-3CO], 5),

82 ($[M^+ - 3CO, -C_2H_2]$, 37), 56 ($[Fe^+]$, 100); Lit. (MS (CI)): m/z = 193, 165, 137, 109, 83⁶.

S2 Equilibrium and Transition State Vibrational Frequencies

Harmonic vibrational normal mode frequencies were calculated at the D_{2h} equilibrium geometry using Hartree-Fock (HF), MP2, complete active space self-consistent field (CASSCF)⁷ and complete active space perturbation theory (CASPT2) as implemented in Molpro^{8–10}. The 6-311G* basis set¹¹ was used for all methods and the active space was taken to be four electrons in the four frontier π orbitals. The frequencies are shown in Table S1 and compared to experiment.

Table S1 Frequencies of neutral cyclobutadiene (1) calculated at the D_{2h} minimum energy geometry compared to experimental results. All values in cm⁻¹. All calculations use a 6-311G* basis set. *a*) Experimental data taken from ¹², except 1b_{1u}, which was taken from ¹³.

Mode	HF	MP2	CAS(4,4)	CASPT2(4,4)	Experiment ^a)
1a _u	600	467	449	423	-
1b _{2g}	677	527	528	453	531
$1b_{3u}$	704	561	534	535	576
$2a_u$	802	735	725	683	-
$1b_{2u}$	922	753	743	735	721
$1b_{1g}$	1008	820	841	771	-
1b _{3g}	1010	844	961	865	723
1a _g	1025	973	987	914	989
$1b_{1u}$	1142	1055	1113	1048	1028
2ag	1203	1129	1200	1124	1059
$2b_{3g}$	1286	1186	1291	1191	-
$2b_{2u}$	1384	1268	1390	1282	1245
3ag	1756	1569	1508	1427	1678
$2b_{1u}$	1776	1580	1621	1535	1526
$3b_{2g}$	3349	3235	3353	3248	3093
$3b_{2u}$	3365	3249	3368	3263	3107
$3b_{1u}$	3389	3270	3382	3279	3124
$4a_g$	3400	3281	3397	3292	3140

The D_{4h} transition state (TS) structure of neutral cyclobutadiene was optimized using Gaussian16¹⁴ at the CAS(4,4)/6-311G* level of theory. This geometry is used as the Q_0 point around which the vibrational Hamiltonian model is expanded (see below). Harmonic vibrational normal modes and frequencies were calculated at this geometry using the CAS(4,4)/6-311G* method. Their values and symmetry labels are given in Table S2, with the molecule in the *xy*-plane oriented with the axes bisecting the C–C bonds. This is not the conventional orientation, which places the C–H bonds along the axes, but keeps symmetry on deformation to D_{2h} in its standard orientation. As the square planar D_{4h} geometry is a TS between two D_{2h} minima, a single imaginary frequency is obtained for the 2b_{1g} mode. Cartesian coordinates and energies for optimized structures are given in Table S3.

Table S2 Modes and frequencies of neutral cyclobutadiene calculated at D_{4h} TS geometry with symmetry labels and D_{2h} equivalent defined. All values in eV. ^{a)} Transition mode with imaginary frequency.

Mode	Symmetry	ω	D _{2h} equivalent
v_1	1a _{1g}	0.163	2ag
v_2	$2a_{1g}$	0.423	4a _g
<i>V</i> ₃	1a _{2g}	0.162	2b _{3g}
$v_4^{ m a)}$	$2b_{1g}$	0.183i	3ag
v_5	$1b_{1g}$	0.143	1a _g
v_6	1b _{2g}	0.126	1b _{3g}
v_7	$2b_{2g}$	0.418	3b _{3g}
v_{8a}	1eg	0.054	1b _{2g}
v_{8b}	1eg	0.054	$1b_{1g}$
v_9	$1a_{2u}$	0.063	1b _{3u}
v_{10}	$1b_{1u}$	0.061	1a _u
v_{11}	$2b_{1u}$	0.076	$2a_u$
v_{12a}	$1e_u$	0.122	1b _{2u}
<i>v</i> _{12b}	$1e_u$	0.122	1b _{1u}
v_{13a}	$2e_u$	0.178	$2b_{2u}$
<i>v</i> _{13b}	$2e_u$	0.178	2b _{1u}
v_{14a}	$3e_u$	0.420	$3b_{2u}$
v_{14b}	$3e_u$	0.420	$3b_{1u}$

Cyclobu	utadiene neutral D_{4h} (CASPT2(4,4)/6-311G*	** on CAS(4,4) TS E = -154.23698 Hartree
С	0.00000	1.02078	0.00000
С	1.02078	0.00000	0.00000
С	-1.02078	0.00000	0.00000
С	0.00000	-1.02078	0.00000
Н	0.00000	2.09138	0.00000
Н	2.09138	0.00000	0.00000
Н	-2.09138	0.00000	0.00000
Н	0.00000	-2.09138	0.00000
Cyclobi	Itadiene neutral D_{2h} (CASPT2(4,4)//6-311G	** E = -154.24512 Hartree
С	-0.68026	0.77777	0.00000
С	0.68026	0.77777	0.00000
С	-0.68026	-0.77777	0.00000
С	0.68026	-0.77777	0.00000
Н	-1.44686	1.54101	0.00000
Н	1.44686	1.54101	0.00000
Н	-1.44686	-1.54101	0.00000
Н	1.44686	-1.54101	0.00000
Cyclobi	Itadiene cation D_{2h} C	ASPT2(3,4)//6-311G*	** E = -153.96419 Hartree
С	0.75384	0.69352	0.00000
С	-0.75384	0.69352	0.00000
С	-0.75384	-0.69352	0.00000
С	0.75384	-0.69352	0.00000
Н	1.51789	1.46319	0.00000
Н	-1.51789	1.46319	0.00000
Н	-1.51789	-1.46319	0.00000
Н	1.51789	-1.46319	0.00000

Table S3 Optimized Cartesian coordinates (in Å) of cyclobutadiene neutral and cation at the CASPT2 level of theory calculated in Molpro. The CAS space is the four π -orbitals.

S3 Vibronic Coupling Hamiltonian Parameters for Cyclobutadiene

Ab initio energies for neutral cyclobutadiene were calculated along cuts of each normal mode outwards from the D_{4h} TS geometry using three state-averaged CASSCF followed by CASPT2 employing a (4,4) active space using the 6-311G* basis set within Molpro. This method was chosen to balance cost with the need for a multi-configurational method for the cyclobutadiene states. Benchmark calculations using other methods, such as EOM-CCSD, and basis sets was carried out to confirm its reliability. For modes v_1 , v_4 and v_5 which mix together in a Duschinsky rotation on going from D_{4h} to D_{2h} , 2D and 3D cuts along these modes were also calculated.

By making use of the vibronic coupling Hamiltonian¹⁵, the diabatic potentials can be expressed, through a Taylor series in terms of dimensionless, mass-frequency scaled, normal modes Q_{α} around a particular point, \mathbf{Q}_0 , here taken as the D_{4h} TS geometry. The Hamiltonian can therefore be written as

$$\mathbf{H} = \mathbf{H}^{(0)} + \mathbf{W}^{(0)} + \mathbf{W}^{(1)} + \dots$$
(1)

with the zeroth-order diagonal Hamiltonian $\mathbf{H}^{(0)}$ expressed in the harmonic approximation

$$H_{ii}^{(0)} = \sum_{\alpha} \frac{\omega_{\alpha}}{2} \left(\frac{\partial}{\partial Q_{\alpha}^2} + Q_{\alpha}^2 \right)$$
(2)

where the frequencies ω_{α} are those given in Table S2. It should be noted that the frequency for mode Q_4 is taken as the absolute value of the imaginary frequency for this mode. The harmonic oscillator potential for this mode (and some others) was replaced by state-specific Morse potentials for better fitting. This is detailed below.

The subsequent matrices include the effects of electronic excitation and vibronic coupling as a Taylor expansion around a point \mathbf{Q}_0 . The zero order term $\mathbf{W}^{(0)}$ has elements

$$W_{ij}^{(0)} = \left\langle \Phi_i(\mathbf{Q}_0) | H_{el} | \Phi_j(\mathbf{Q}_0) \right\rangle \tag{3}$$

where H_{el} is the standard clamped nuclei electronic Hamiltonian and Φ_i are the diabatic electronic functions. $\mathbf{W}^{(0)}$ is usually a diagonal matrix of excitation energies as it is taken that the diabatic and adiabatic wavefunctions are equal at \mathbf{Q}_0 , but for neutral cyclobutadiene, better fits to the adiabatic energies were obtained using off-diagonal static couplings between Φ_1 and Φ_2

$$\mathbf{W} = \begin{pmatrix} 1.1049 & -0.6971 & 0\\ -0.6971 & 1.1049 & 0\\ 0 & 0 & 2.0276 \end{pmatrix}$$
(4)

where $W_{11}^{(0)} = W_{22}^{(0)} = \frac{1}{2}(E_1 + E_2)$ and $W_{12}^{(0)} = W_{21}^{(0)} = \frac{1}{2}(E_1 - E_2)$ and $E_1 = 0.407$ eV and $E_2 = 1.801$ eV with respect to the D_{2h} equilibrium. This basis is formed from the rotated combinations of the HOMO e_g orbitals as described in the manuscript, i.e. the diabatic states are the kets $|1\rangle$, $|2\rangle$ and $|3\rangle$. We note in passing that E_1 is the barrier height for the transition state from the D_{2h} to D_{4h} geometry and is in good agreement with other calculations¹⁶. E_2 and E_3 are the energy differences from the D_{2h} equilibrium geometry minimum to the first and second excited electronic state energies at D_{4h}.

The linear coupling matrix elements can be written as

$$W_{ij}^{(1)} = \sum_{\alpha} \left\langle \Phi_i(\mathbf{Q}_0) \left| \frac{\partial H_{el}}{\partial Q_{\alpha}} \right| \Phi_j(\mathbf{Q}_0) \right\rangle Q_{\alpha}$$
(5)

where diagonal elements are forces, and the off-diagonal elements the non-adiabatic coupling at Q_0 . For fitting these terms are expressed as

$$W_{ii} = \sum_{\alpha} \kappa^{i}_{\alpha} Q_{\alpha} \tag{6}$$

$$W_{ij} = \sum_{\alpha} \lambda_{\alpha}^{(i,j)} Q_{\alpha}$$
⁽⁷⁾

(8)

where κ_{α}^{i} are on-diagonal linear terms for electronic state *i* and $\lambda_{\alpha}^{(i,j)}$ are off-diagonal linear terms coupling

states *i* and *j*. To obtain good fits, higher order terms are also included for some modes. These are given as

$$W_{ii}^{(2)} = \sum_{\alpha} \frac{1}{2} \gamma_{\alpha} Q_{\alpha}^{2} + \sum_{\alpha < \beta} \gamma_{\alpha\beta}^{(i)} Q_{\alpha} Q_{\beta}$$
⁽⁹⁾

$$W_{ii}^{(3)} = \sum_{\alpha} \frac{1}{3!} \varepsilon_{\alpha} Q_{\alpha}^{3}$$
⁽¹⁰⁾

$$W_{ii}^{(4)} = \sum_{\alpha} \frac{1}{4!} \eta_{\alpha} Q_{\alpha}^{4}$$
(11)

Many of these matrix elements are zero due to symmetry as determined by the product of symmetries of the electronic states and vibrational modes in the integrands. In the diabatic basis, the rules are obtained after rotating from the symmetry adapted functions $|1\rangle = |\tilde{X}({}^{1}B_{1g})\rangle + |\tilde{A}({}^{1}A_{1g})\rangle, |2\rangle = |\tilde{X}({}^{1}B_{1g})\rangle - |\tilde{A}({}^{1}A_{1g})\rangle$ and $|3\rangle = |\tilde{C}({}^{1}B_{2g})\rangle$ to give

$$\kappa_{\alpha}^{(1)}, \kappa_{\alpha}^{(2)} \neq 0 \quad \text{If} \quad \Gamma_{\alpha} \supset \Gamma_{B_{1g}} \quad ; \quad \kappa_{\alpha}^{(3)} \neq 0 \quad \text{If} \quad \Gamma_{\alpha} \supset \Gamma_{A_{1g}}$$
(13)

$$\lambda_{\alpha}^{(1,2)} \neq 0 \qquad \text{If} \quad \Gamma_{\alpha} \otimes \Gamma_{1} \otimes \Gamma_{2} \supset \Gamma_{A_{1g}} \tag{14}$$

$$\lambda_{\alpha}^{(i,3)} \neq 0 \quad \text{If} \quad \Gamma_{\alpha} \otimes \Gamma_{i} \otimes \Gamma_{3} \supset \Gamma_{B_{1g}} \quad \text{For} \quad i = 1,2$$
(15)

$$\gamma_{\alpha,\beta}^{(i)} \neq 0$$
 If $\Gamma_{\alpha} \otimes \Gamma_{\beta} \otimes \Gamma_{i} \supset \Gamma_{B_{1g}}$ For $i = 1,2$ (16)

$$\gamma_{\alpha,\beta}^{(3)} \neq 0 \qquad \text{If} \quad \Gamma_{\alpha} \otimes \Gamma_{\beta} \otimes \Gamma_{i} \supset \Gamma_{A_{1g}} \tag{17}$$

where Γ_{α} denotes a vibrational mode symmetry and Γ_i that of an electronic state.

Parameters for the vibronic coupling Hamiltonian were obtained by least-squares fitting to the *ab initio* energies using the VCHAM package¹⁷, implemented within the Quantics program suite¹⁸. The only non-zero on-diagonal linear coupling constants (κ s) are given in Table S4, the off-diagonal linear coupling constants (κ s) are given in Table S4, the off-diagonal linear coupling constants (λ s) are given in Table S5. Values of $\lambda_i^{(12)} = 0$ due to (14) above, as $\Gamma_{B_{2g}} \otimes \Gamma_{B_{1g}} \otimes \Gamma_{A_{1g}} \not\subset \Gamma_{A_{1g}}$. The on and off-diagonal second order constants are given in Tables S6 and S7 respectively.

Table S4 On-diagonal linear coup	ling constants κ	c parameters for th	e vibronic	coupling model	Hamiltonian of
neutral cyclobutadiene. All values	in eV.				

Mode	$\kappa_i^{(1)}$	$\kappa_i^{(2)}$	$\kappa_i^{(3)}$
v_4	0.4598	-0.4598	-

Table S5 Off-diagonal linear coupling constants λ parameters for the vibronic coupling model Hamiltonian of neutral cyclobutadiene. All values in eV.

Mode	$\lambda_i^{(12)}$	$\lambda_i^{(13)}$	$\lambda_i^{(23)}$
v ₆	-	-0.1189	0.1189
ν_7	-	-0.0172	0.0172

For some modes exhibiting strong anharmonicity cubic and quartic terms were added to the basic harmonic form.

$$V_i = \kappa Q_i + \gamma Q_i^2 + \varepsilon Q_i^3 + \eta Q_i^4.$$
⁽¹⁹⁾

These parameters are in Table S8. Finally, the harmonic diabatic potential for the transition mode v_4 for states 1 and 2 was replaced by Morse potentials, Eq. (20. Parameters for these potentials are given in Table S9.

$$V_i = D_0 \left[\exp(\alpha (Q_i - X_0) - 1) \right]^2$$
(20)

Example plots for cuts along the normal modes v_1 , v_2 , v_4 and v_6 for cyclobutadiene comparing the vibronic coupling Hamiltonian and *ab initio* energies is shown in Figure S2. The adiabatic curves are shown here. For the v_4 mode the ground ${}^{1}B_{1g}$ electronic state has a double minimum around the D_{4h} TS along the $2b_{1g}$ normal mode while for the v_6 $1b_{2g}$ mode, the excited ${}^{1}A_{g}$ electronic state shows a similar structure. Other modes are not shown but display either a harmonic or quartic form without crossings of the electronic states. Further plots of the PES are shown in Figure S3 which show two-dimensional contour plots for the v_4/v_1 , v_4/v_5 , v_4/v_6 normal modes for the lowest adiabatic singlet state, $X^{1}B_{1g}$. The double minimum along the v_4 mode is apparent in all plots, which reflect the symmetries of the couplings.

Mode	$\gamma_i^{(1)}$	$\gamma_i^{(2)}$	$\gamma_i^{(3)}$
<i>v</i> ₁	-0.0149	-0.0149	-0.0045
v_2	-0.0056	-0.0056	-0.0041
<i>v</i> ₃	-0.0154	-0.0154	-0.0196
v_4	-0.0796	-0.0796	-0.0300
v_5	-0.0128	-0.0128	0.0114
v_6	-0.0214	-0.0214	-0.0287
v_7	0.0517	0.0517	0.0621
v_{8a}	0.1251	0.0379	0.1251
v_{8b}	0.1251	0.2403	0.1251
V 9	0.0044	0.0044	0.0126
v_{10}	-0.0077	-0.0077	-0.0019
v_{11}	0.0008	0.0008	-0.0029
<i>v</i> _{12a/b}	0.0011	0.0011	-0.0026
<i>v</i> _{13a/b}	-0.0136	-0.0136	-0.0205
$v_{14a/b}$	0.1224	0.1224	0.1231

Table S6 Quadratic second-order coupling constants γ parameters for the vibronic coupling model Hamiltonian of neutral cyclobutadiene. All values in eV.

Table S7 Bi-linear second-order coupling constants γ parameters for the vibronic coupling model Hamiltonian of neutral cyclobutadiene. All values in eV.

Modes	$\gamma_{i,j}^{(1)}$	$\gamma^{(2)}_{i,j}$	$\gamma^{(3)}_{i,j}$
v_1/v_4	0.0250	-0.0250	-
v_2/v_4	0.0220	-0.0220	-
v_4/v_5	-0.0200	-0.0200	-0.0254
v_1/v_5	-	-0.0011	-



Figure S2 Vibronic coupling Hamiltonian fits (lines) and CASPT2 (4,4)/6-311G* *ab initio* energies for v_1 , v_2 , v_4 and v_6 modes of cyclobutadiene.

Modes	$oldsymbol{arepsilon}_i^{(1)}$	$oldsymbol{arepsilon}_i^{(2)}$	$oldsymbol{arepsilon}_i^{(3)}$
<i>v</i> ₁	-0.0473	-0.0473	-0.0306
v_2	-0.1500	-0.1500	-0.1539
Modes	$\mathbf{v}_i^{(1)}$	$\mathbf{v}_i^{(2)}$	$v_i^{(3)}$
<i>v</i> ₁	0.0098	0.0098	0.0040
v_2	0.0337	0.0337	0.0331
$v_{8a/b}$	0.0466	0.0716	0.0374
<i>V</i> 9	0.0537	0.0537	0.0529
v_{11}	0.0408	0.0408	0.0405

Table S8 Cubic and Quartic Polynomial function parameters used to fit the potential energy curves along modes for ${}^{1}B_{1g}$, ${}^{1}A_{g}$ and ${}^{1}B_{2g}$ electronic states of cyclobutadiene neutral.

Table S9 Morse and Anti-Morse function parameters used to fit the potential energy curves along v_4 mode for ${}^{1}B_{1g}$ and ${}^{1}A_{g}$ electronic states.

Mode	D_0	α	X_0
$v_{4}^{(0)}$	60.737	-0.0280	-3.5241
$v_{4}^{(1)}$	60.737	-0.0280	3.5241



Figure S3 Contour plots of the potential energy surface for the lowest adiabatic singlet state, $X^{1}B_{1g}$, of neutral cyclobutadiene.

The vibronic coupling Hamiltonian model was also used for the cyclobutadiene radical cation. *Ab initio* calculations were carried out similar to those for the neutral using a three state-averaged CASSCF followed by CASPT2 employing a (3,4) active space with the 6-311G* basis set. These calculations were based on an initial restricted HF treatment. Energies for the cyclobutadiene cation were also calculated along cuts of each (neutral) normal mode outwards from the D_{4h} TS geometry. Only energies from the degenerate ${}^{2}E_{g}$ states were used in the vibronic coupling Hamiltonian.

The diabatic states were taken to be the adiabatic states at the D_{4h} geometry (\mathbf{Q}_0) and the $\mathbf{W}^{(0)}$ matrix for the cation is diagonal with energies of 8.0915 eV with respect to the equilibrium D_{2h} geometry of the neutral. Values of the fitting parameters (κ s, λ s and γ s) are given in Tables S10-S13.

As for the neutral molecule, it was necessary to express the diabatic potentials as cubic or quartic polynomials for some modes, with parameters given in Table S14. In addition to this, for modes v_1 and v_4 , mixed polynomials were also required of the form $k_{1,4}^{k,l}v_1^kv_4^l$ with parameters given in Table S15. These mixed polynomials were essential to get the correct shape of the potential for these two modes.

Table S10 On-diagonal linear coupling constants κ parameters for the vibronic coupling model Hamiltonian of cyclobutadiene cation. All values in eV.

Mode	$\kappa_i^{(1)}$	$\kappa_i^{(2)}$
v_1	-0.0041	-0.0041
v_2	-0.0831	-0.0831
v_4	0.2866	-0.2866

Table S11 Off-diagonal linear coupling constants λ parameters for the vibronic coupling model Hamiltonian of cyclobutadiene cation. All values in eV.

Mode	$\lambda_i^{(12)}$
v_6	0.1024
v_7	0.0347

Example plots for cuts along the normal modes v_4 and v_6 for the cyclobutadiene cation comparing the vibronic coupling Hamiltonian and *ab initio* energies is shown in Figure S4. The adiabatic curves are shown here. The v_4 and v_6 Jahn–Teller active modes for the 2E_g states have a double minimum around the

Mode	$\gamma_i^{(1)}$	$\gamma_i^{(2)}$
v_1	-0.0231	-0.0231
v_2	-0.0008	-0.0008
<i>v</i> ₃	-0.0114	-0.0114
v_4	-0.0314	-0.0314
v_5	-0.0299	0.0299
v_6	-0.0214	-0.0214
v_7	0.0517	0.0517
$v_{8a/b}$	0.3368	0.1554
v_9	0.0298	0.0298
v_{10}	-0.0406	-0.0406
v_{11}	0.0595	0.0595
$v_{12a/b}$	-0.0101	0.0132
<i>v</i> _{13a/b}	-0.0149	-0.0149
$v_{14a/b}$	0.1306	0.1264

Table S12 Quadratic second-order coupling constants γ parameters for the vibronic coupling model Hamiltonian of cyclobutadiene cation. All values in eV.

Table S13 Bilinear second-order coupling constants γ parameters for the vibronic coupling model Hamiltonian of cyclobutadiene cation. All values in eV.

Mode	$\gamma_{i,j}^{(1)}$	$\gamma^{(2)}_{i,j}$
v_1/v_4	-0.0180	0.0180
v_4/v_5	-0.0255	-0.0255

 D_{4h} TS where they cross in a conical intersection. Other modes are not shown but display either a harmonic or biquartic form. For normal modes which preserve the degeneracy of the ${}^{2}E_{g}$ states, the potential curves overlap.

Figure S5 shows two-dimensional contour plots for the v_4/v_1 , v_4/v_5 , v_4/v_6 normal modes for the lowest adiabatic singlet state, X^2E_g . The contraction of the cation compared to the neutral is clear, with the minima lying closer to the conical intersection at \mathbf{Q}_0 . The v_4/v_6 cut shows the strong $E \otimes \beta$ Jahn-Teller coupling involving these 2 modes. The strong coupling between the v_4 and v_1 modes is also evident.

Mode	$arepsilon_i^{(1)}$	$arepsilon_i^{(2)}$
v_1	-0.0287	-0.0287
v_2	-0.1348	-0.1348
<i>v</i> ₅	-0.0337	-0.0337
Mode	$\eta_i^{(1)}$	$\eta_i^{(2)}$
v_1	0.0123	0.0123
v_2	0.0338	0.0338
v_5	0.0176	0.0176
$v_{8a/b}$	0.0091	0.0505
<i>V</i> 9	0.0515	0.0515
v_{10}	0.0074	0.0074
v_{11}	0.0367	0.0367

Table S14 Polynomial function parameters used to fit the potential energy curves along modes for ${}^{2}E_{g}$ degenerate electronic states of cyclobutadiene cation.

Table S15 Mixed	polynomial	terms for cyclobutadiene cation
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Mode ^k	Mode ^l	$k_{1,4}^{k,l}$
$(v_4^{(1/2)})^2$	$v_1^{(1/2)}$	-0.0126
$v_4^{(1/2)}$	$(v_1^{(1/2)})^2$	0.0014
$(v_4^{(1/2)})^2$	$(v_1^{(1/2)})^2$	0.0010



Figure S4 Vibronic coupling Hamiltonian fits (lines) and CASPT2 (3,4)/6-311G* *ab initio* energies for v_4 and v_6 modes of cyclobutadiene cation.



Figure S5 Contour plots of the potential energy surface for the lowest adiabatic singlet state, $X^2 E_g$, of cyclobutadiene cation.

S4 MCTDH Calculations and Photoelectron Spectra

The photoelectron spectrum was calculated in a similar manner to that described previously, e.g. for cyclobutadiene¹⁹ and phenol²⁰ from wavepacket dynamics simulations using the MCTDH method²¹ implemented in Quantics¹⁸. The ground state nuclear wavefunction of neutral cyclobutadiene was obtained using energy relaxation (propagation of wavepacket in imaginary time²¹) using the vibronic coupling model Hamiltonian for the neutral molecule. The initial guess was taken as the ground-state harmonic oscillator eigenfunction of the zero-order Hamiltonian.

Next a vertical excitation is performed, which corresponds to the instantaneous removal of an electron with no relaxation of the nuclear framework, by placing one component of the ground state neutral wavefunction on one of the cation ${}^{2}E_{g}$ electronic states. The wavepacket is then propagated on this state using the MCTDH method for 150 fs. The photoelectron spectrum was then obtained from the Fourier transform of the autocorrelation function as

$$I(\boldsymbol{\omega}) \propto \boldsymbol{\omega} \int_{-\infty}^{\infty} \mathrm{d}t \, C(t) e^{i\boldsymbol{\omega} t} e^{(-t/\tau)},\tag{21}$$

where the last factor is an exponential dampening term to simulate experimental broadening in the photoelectron spectra and

$$C(t) = \langle \Psi(0) | \Psi(t) \rangle = \left\langle \Psi\left(\frac{t}{2}\right)^* \middle| \Psi\left(\frac{t}{2}\right) \right\rangle.$$
(22)

Details of the MCTDH calculations are given in Table S16. Eight modes were included in the calculation which is effectively reduced to five as some modes were combined to form particles. For all modes the primitive basis functions are harmonic oscillator DVRs.

Table S16 Number of basis functions used in the MCTDH wavepacket propagation calculations used to simulate the photoelectron spectrum of cyclobutadiene. $n_{i/j}$ are the number of primitive basis functions used to describe each mode. N_i are the number of single-particle functions used for the wavepacket on each state. Column 3 refers to the neutral molecule, column 4 the cation.

Mode(s)	(n_i, n_j)	N_0, N_1, N_2	N_1, N_2
V4	61	4,4,2	12,12
<i>V</i> ₅	31	4,4,2	8,8
v_{8a}, v_{8b}	21,21	3,3,2	6,6
v_6, v_7	21,11	4,4,2	6,6
v_1, v_2	31,31	4,4,4	8,8

S5 Composition of main peaks in photoelectron spectrum

The photoelectron spectrum of CBD, shown in Figure 2 of the manuscript, has 3 main peaks assigned to the 3 vibrations $v_1(1a_{1g})$, $v_4(2b_{1g})$ and $v_5(1b_{1g})$. These are, however, coupled in a triple Fermi resonance. To get an estimation of the strength of the coupling and the composition of the resulting peaks, the vibronic coupling Hamiltonian including only these 3 modes was diagonalised to get the eigenvalues, which approximate to the frequencies of the lines in the spectrum. The Hamiltonian was then diagonalised for each vibration in turn to get zero-order frequencies, and then in the pairs v_4/v_1 and v_4/v_5 to get the shifts of these zero-order frequencies due to the pair-wise coupling (modes v_1 and v_5 have insignificant coupling). The zero-order frequencies, couplings, final frequencies are given in Table S17, along with the composition of the final eigenvectors. The stick spectrum from the diagonalisation of the 3-mode Hamiltonian is given in Figure S6 with the peaks of interest numbered.

Table S17 Estimation of Frequencies and Composition of the 3 main peaks in the Photoelectron Spectrum of CBD. The numbers with the Final Frequencies relate to the peak numbers on Figure S6

Vibration	Zero-order	Coupling	Final	Composition
	Frequency (eV)	to v_4 (eV)	Frequency (eV)	$% v_1/v_4/v_5$
$v_1(1a_{1g})$	0.1512	0.0156	(2) 0.1444	75 / 15 / 10
$v_4(2b_{1g})$	0.1670	_	(3) 0.1795	22 / 72 / 6
$v_5(1b_{1g})$	0.1276	0.0143	(1) 0.1220	3 / 13 / 84



Figure S6 Stick spectrum from diagonalising a 3-mode Hamiltonian for the CBD cation. Marked peaks are the combination peaks analysed in Table S17



Figure S7 Comparison of the experimental TPES of C_4H_4 and the simulations presented in the main paper (magenta line) with a simple adiabatic Franck-Condon simulation using ezSpectrum²² (grey line, shifted by +10 meV) based on CBS-QB3 computations. In particular, the intensity distribution in the band around 8.2 eV is not well represented without taking vibronic coupling into account.

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