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Ring Opening Dynamics of the Cyclopropyl Radical and Cation: The Transition State Nature of the Cyclopropyl Cation

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Abstract

We provide compelling experimental and theoretical evidence for the transition state nature of the cyclopropyl cation. Synchrotron photoionization spectroscopy employing coincidence techniques together with a novel simulation based on high accuracy *ab initio* calculations reveal that the cation is unstable *via* its allowed disrotatory ring opening path. The ring strains of the cation and the radical are similar, but both ring opening paths for the radical are forbidden when the full electronic symmetries are considered. These findings are discussed in light of the early predictions by Longuet-Higgins alongside Woodward and Hoffman; we also propose a simple phase space explanation for the appearance of the cyclopropyl photoionization spectrum. The results of this work allow the refinement of the cyclopropane C–H bond dissociation energy, in addition to the cyclopropyl radical and cation cyclization energies, *via* the Active Thermochemical Tables approach.

Introduction

Cyclic structures have elicited considerable interest since the earliest days of organic chemistry, but open questions remain regarding their properties and dynamics. One of the smallest pericyclic systems, cyclopropyl-allyl (C_3H_5), was the subject of the very first paper by Woodward and Hoffmann on their novel approach to the effects of symmetry in electrocyclic reactions.¹ While the orbital symmetries of the cation and anion are unambiguous, Woodward and Hoffman’s predictions for the radical were disputed by Longuet-Higgins based on the first use of correlation diagrams;² Woodward and Hoffman subsequently agreed that the cyclopropyl radical case required a refinement of their theory because orbital crossings occur for both con- and dis-rotatory ring-opening paths (Fig. 1).³ These predictions based on orbital symmetry theory for the cyclopropyl system have never been adequately tested. We address this archetypal case experimentally and theoretically, utilizing advanced coincidence photoionization spectroscopy techniques along with newly developed computational

methods. The combined results show how the orbital-crossing barriers around the radical lead to its stabilization, while a symmetry-allowed disrotatory ring-opening path makes the cation an unstable transition state instead.

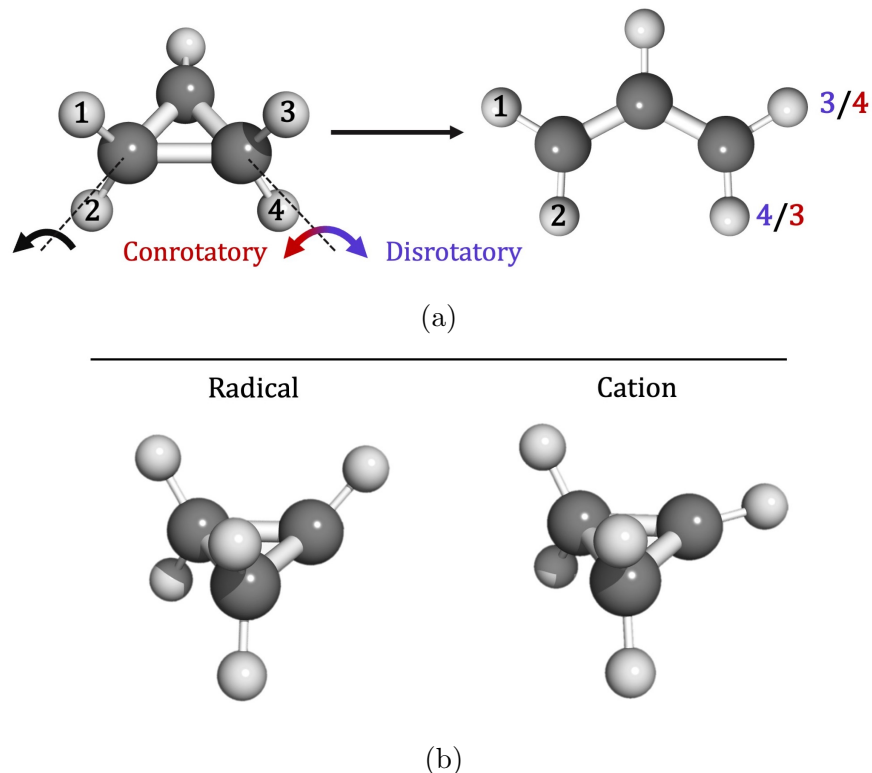


Figure 1: (a) An illustration of the two ring opening paths from the cyclopropyl cation to the allyl cation. (b) Optimized geometries of the cyclopropyl radical and cation. Note the different out of plane angles of the α -C-H bond in the two otherwise similar structures.

The driving force behind the instability of the cyclopropyl species is their unusually distorted geometry, a phenomenon typically termed ring strain. This effect was geometrically rationalized by Baeyer over a century ago when he considered the relative stability of cyclic *vs.* open structures across various chain lengths.⁴ While not universally valid due to the then unknown nature of three dimensional bonding and hybridization, Baeyer's prediction of large ring strain in three membered rings specifically is borne out by the strong destabilization of their cyclic geometries. Aside from their instability, an additional consequence of the highly bent structures of three-membered rings is the high *s* character in the C–H bonds, giving rise to unusually strong, short (close to alkene C–H) bonds,^{5–10} and the high *p* character

in the C–C bonds, forming “quasi π ” bonds.^{11,12} These effects manifest themselves in the chemical properties of different cyclopropyl derivatives, from their relatively slow reaction rates upon nucleophilic attack to their tendency to open upon various activation processes; understanding these effects based on the underlying bond characteristics is important for chemical applications.^{7,11,13–16} Characterizations of the fundamental origins of the unique properties of these small cyclic systems¹⁷ are of value to modern regio- and stereo-selective syntheses utilizing such rings.¹⁸

Despite this longstanding fundamental interest, few direct observations of cyclopropyl exist, no doubt due to the difficulty in forming the bare strained ring while avoiding its opening to allyl. To the best of our knowledge, observations of the radical include a photoelectron study by Dyke *et al.*,¹⁹ a matrix-isolation infrared study by Holtzhauer *et al.*,^{16,20} a high resolution infrared spectrum of the ν_7 vibrational band by Dong *et al.*,²¹ and electron spin resonance studies.^{22–26} For the anion, only indirect measurements of its gas phase proton affinity and the associated radical electron affinity exist, along with an estimation of its high inversion barrier.^{27–31,32} Even less information is available in the literature for the cation, and calculations at different levels of theory disagree regarding its very nature: while some calculations identified a local minimum geometry with C_{2v} symmetry,³³ other calculations found only a cyclic saddle point on the cationic potential energy surface (PES).³⁴ Experimentally, studies of the solvolysis reactions^{35–37} of cyclopropyl derivatives have shown that such processes almost exclusively yield allyl derivatives, indirectly indicating a transition state nature for the cation;^{13,14} however the photoelectron spectrum of the cyclopropyl radical was analyzed assuming that the cation was a local minimum, based on available calculations at that time.^{19,33} The ionization energies obtained by Dyke *et al.* are in fair agreement with various calculations, regardless of their findings concerning the cation stability,^{34,38} but no attempts have been made to simulate the experimental photoelectron spectrum and resolve this question.³⁹

Thus, a controversy regarding the very existence of the cyclopropyl cation as a stable

species still persists. The answer is key to the stability of all three-membered rings: how strong is the driving force for the ring opening? What prevents stable cyclopropyl rings from opening up, despite the extreme bond angles?

In this study, we address these fundamental questions by measuring the cyclopropyl radical photoionization spectrum with modern synchrotron-based mass-selected threshold photoelectron spectroscopy (ms-TPES). Using sophisticated *ab initio* calculations, high accuracy thermochemical protocols, and novel approaches for the Franck-Condon simulation of the photoionization spectrum, we provide compelling evidence that the cation is indeed a transition state, destabilized by the allowed ring-opening disrotatory path. On the other hand, we find that the radical is only kinetically stabilized, due to the electronic symmetry constraints on its ring opening reactions, following the correlation diagram analysis by Longuet-Higgins.² Additionally, we re-evaluate thermochemical quantities relevant to this chemical system, providing the most accurate values to date for the cyclization energy of the radical and the uniquely high C–H bond dissociation energy of cyclopropane leading to the formation of the cyclopropyl radical.

Methods

Experimental

The ms-TPES of the cyclopropyl radical, generated *via* H atom abstraction from cyclopropane by F atoms, was measured using synchrotron vacuum ultraviolet (VUV) radiation and double imaging photoion-photoelectron coincidence spectroscopy (*i*²-PEPICO) at the DESIRS beamline of the SOLEIL synchrotron.^{40–45} Cyclopropane (*c*-C₃H₆ from abcr, 99 % purity, 1.0×10^{14} molecules·cm⁻³) seeded in helium carrier gas (1:100) was introduced into the flow tube reactor (total pressure of 4×10^{-1} mbar) to react with the F atoms (around 4×10^{12} atoms·cm⁻³) produced by a microwave discharge in F₂. The F + *c*-C₃H₆ reaction yielded cyclopropyl radical (*c*-C₃H₅) by H-atom abstraction from the precursor. By

adjusting the experimental conditions (gas flows, F-atom concentration, and injector distance) the production of $c\text{-C}_3\text{H}_5$ radical was optimized while keeping secondary reactions such as multiple H atom abstractions as low as possible. The gas mixture was then skimmed twice before crossing the synchrotron radiation at right angles in the double imaging photoelectron/photoion spectrometer DELICIOUS3.⁴³ The monochromatized photon resolution in the 7.6 – 9.6 eV energy range was about 7 – 11 meV. The photoelectrons and photoions were extracted in opposite directions by a 53 V/cm DC field, and detected by two different velocity-map-imaging detectors. The coincidence scheme allowed ion-mass filtering of the photoelectron images and thus extraction of the mass-selected photoelectron spectra after Abel inversion of the images. The photoelectron signal detected in coincidence with photoions of m/z 41 was recorded as a function of electron kinetic and photon energy, and the signals acquired along the photon-energy scans were corrected for variations in the photon flux. The threshold photoelectron spectrum was then extracted following the method described in Refs. 46-47, with an overall resulting ms-TPES spectral resolution of 50 meV. The calibration of energy scale was achieved with an absolute accuracy of ± 5 meV using the ionization of He by residual third order radiation from the undulator. Note that the 53 V/cm extraction field leads to a field-induced Stark shift of the ionization energies by approximately 5.4 meV.

Theoretical

Thermochemical calculations of the various species studied were performed with CFOUR⁴⁸ following the HEAT-345(Q) protocol,⁴⁹ using frozen-core CCSD(T)/ANO1 for geometry optimization and force field calculations.⁵⁰⁻⁵⁵ Further computational details are given in the Supporting Information (SI). The ionization spectrum was simulated using a novel implementation of propagator-based Franck-Condon simulations. By calculating the time-dependent auto-correlation function generated by propagation of the ground state vibrational wavefunction on the cation PES, the Franck-Condon simulations can be recovered through a Fourier

transform. Here an analytic implementation of the auto-correlation function allowed calculation of the spectrum based on harmonic force fields at the vertical geometry, tolerating positive as well as negative curvature modes.⁵⁶

Results and Discussion

Photoionization Spectrum

Our newly measured ms-TPES of the cyclopropyl radical is shown in Fig. 2. The ms-TPES contains sharp peaks near 8.2 eV, resulting from allyl radicals formed as F-abstraction byproducts, and a broad, unstructured feature associated with the cyclopropyl radical. A comparison of our photoelectron data to that of Dyke *et al.* reveals that the allyl peaks are obscured in the non-threshold photoelectron spectrum and no cyclopropyl vibrational structure is apparent in the ms-TPES (Fig. S1).

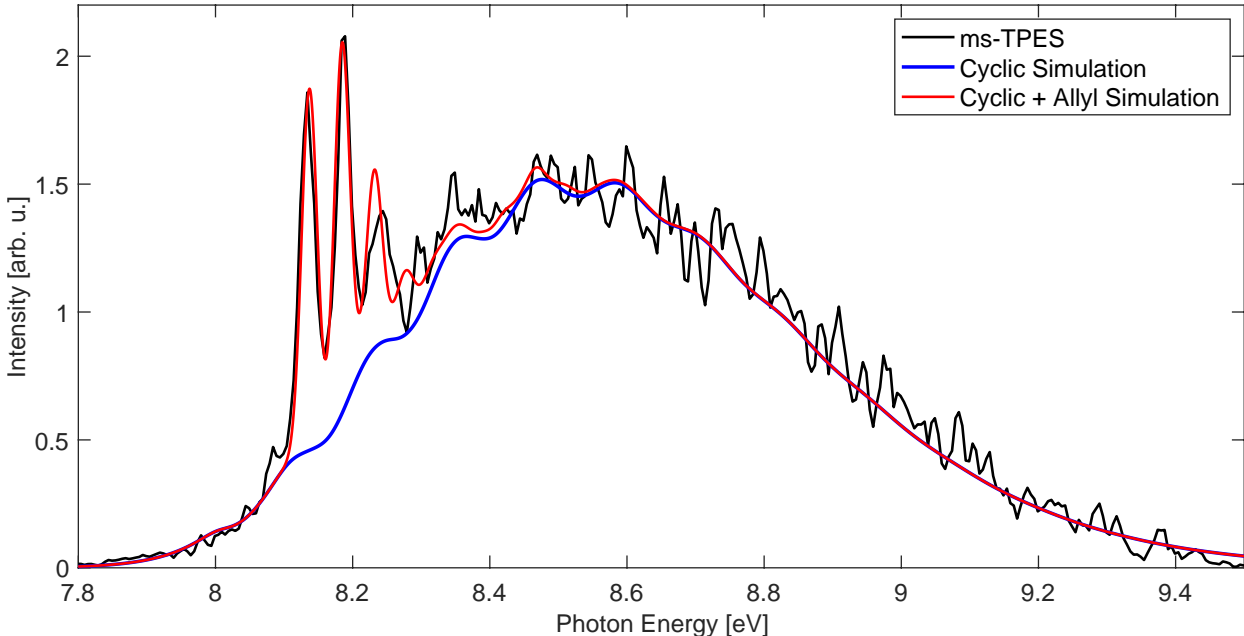


Figure 2: The correlation function-based simulation superimposed on the ms-TPES of the cyclopropyl radical.

Ab initio calculations performed in the present work find a C_s equilibrium geometry for

the radical, in agreement with previous experimental and theoretical studies.^{21,34} The C_{2v} cation, on the other hand, is found to be a transition state (connecting two allyl isomers through rotations of the terminal CH_2 groups, *i.e.* ϕ_{12} and ϕ_{34} , or their con- and dis-rotatory combinations ϕ_{con} and ϕ_{dis} , respectively). The two optimized structures (and their methylene rotations) are shown in Fig. 1. The main difference between the two geometries is the α -C-H bond pointing roughly 40° above the C-C-C plane in the radical case, as opposed to in-plane for the cation. The calculated energies of all species (including allyl and cyclopropane) are in excellent agreement with literature calculations and experimental data, insofar as direct comparisons are possible (Table S1).

A threefold obstacle stands in the way of a satisfactory Franck-Condon simulation of the photoionization spectrum of the cyclopropyl radical: large coordinate displacement in the α -C-H bond out of plane angle; high vibrational energy and state density in the target region of the cation PES; and last but not least the imaginary frequency at the cyclopropyl cation stationary point between the two allyl isomers. In order to overcome these difficulties, we turned to a time-dependent correlation function based method, obtaining the spectrum *via* the Fourier transform of an analytical expression for the time-dependent autocorrelation function, here of the cyclopropyl radical ground state vibrational wavefunction on the cationic PES. The simulated spectrum, including the contribution from allyl impurities, is shown alongside our new ms-TPES of the cyclopropyl radical in Fig. 2. The simulation used fully *ab initio* harmonic force fields (*i.e.* the gradient of the target state and the Hessians of the ground and the target states, all evaluated at the ground state equilibrium geometries of the cyclopropyl and the allyl radicals), and a cubic anharmonic correction to the cyclopropyl radical wavefunction.⁵⁶ Since the wavefunction propagation begins at the vertical geometry, vertical electronic energies align the resulting simulations with the experimental spectrum. The allyl spectrum was thus vertically aligned by 8.139 eV to match the experimental spectrum, in excellent agreement with the theoretical prediction of 8.130 eV (with a deviation well within the experimental resolution, and comparable to the accuracy of the energy cal-

ibration), while the cyclopropyl spectrum was aligned by 8.73 eV, in reasonable agreement with the value of 8.81 eV calculated following the HEAT-345(Q) protocol. Vertical ionization energy estimations unsurprisingly possess higher uncertainties compared to adiabatic ones, due to the existing gradient in the target state and the strong energy sensitivity to geometry; these uncertainties are expected to increase with gradient magnitude, rationalizing the larger discrepancy for the cyclic radical. Furthermore, we expect additional corrections, such as inclusion of the Herzberg-Teller effect, to account for a significant part of this discrepancy.⁵⁶

The striking agreement between simulation and experiment validates the calculated PES and supports our computational conclusion that the cation is a transition state, rather than a stable chemical species.

Phase space influence of transition states

“Transition state spectroscopy” refers to spectroscopic transitions to regions of a PES proximal to transition states.⁵⁷ Several studies have been reported in which a reactive intermediate and/or the vicinity of a saddle point were accessed through anion photodetachment, for example, in a manner not dissimilar from the present work.^{58–62} This body of evidence *prima facie* clashes with the common perception of a transition state as merely an unstable barrier between reactants and products. Here we provide some insight into these seemingly disparate scenarios by a simple phase space explanation that sheds light on the phenomena underlying such transitions and calls into question the conventional sharp distinction between chemical species and transition states.

In a quantum system, the approach to a saddle point is associated with a decrease in the energetic separation between states due to the negative curvature, necessarily increasing the local density of states.⁵² Moreover, following the same trend, the amplitudes of the vibrational wavefunctions approaching the saddle point energy accumulate in the vicinity of the saddle point geometry as the classical turning points merge. Thus, the phase space density, both in terms of state density as a function of energy and probability density as a

function of coordinates, increases around the transition state.

These effects can be straightforwardly illustrated by solving the one-dimensional Schrödinger equation for a single particle in double minimum potentials. Various such cases, including a one-dimensional potential function describing the disrotatory ring opening path of the cyclopropyl cation, were solved using a discrete variable representation (DVR).⁶³ Fig. 3 shows the resulting density of states as a function of energy only $\rho(E)$ or both energy and position $\rho(E, x)$, as calculated by applying a Gaussian smoothing to the probability density function obtained *vs.* both position and energy by plotting the wavefunctions at their corresponding eigenenergies. Interestingly, the global densities of states $\rho(E)$, shown in Fig. 3 (b) and (e), exhibit two similar yet distinct effects: while minima on the PES induce steps in the density of states as a function of energy, a local maximum – or a saddle point – causes a corresponding rise, albeit a peak.⁶⁴ In the two-dimensional density of states plots $\rho(E, x)$, shown in Fig. 3 (c) and (f) for both examined systems, we immediately observe that indeed there is a high state/probability density in the vicinity of the maximum similar to those associated with the minima. In the C_3H_5 cation, the increased phase space density around the cyclic transition state also accumulates overlap of the vibrational wave functions with the ground vibrational wave function of the initial cyclopropyl radical, increasing the probability for the photoionization transition. This spectroscopic perspective directly connects to the concepts of transition state theory, where the transition state is treated as a metastable species in quasi-equilibrium with the reactants.⁶⁵ Accordingly, it seems reasonable that a transition state could generally exert influence on spectra and dynamics not unlike a stable species, and perhaps the distinction between them is more subtle than typically presumed.

Ring Opening Dynamics and Thermochemistry

Examination of the calculated reduced dimension PES for the cation and the radical provides significant insight into the effects governing the stability of the radical in contrast to the instability of the cation. Both cases possess similar allyl-cyclopropyl energy differ-

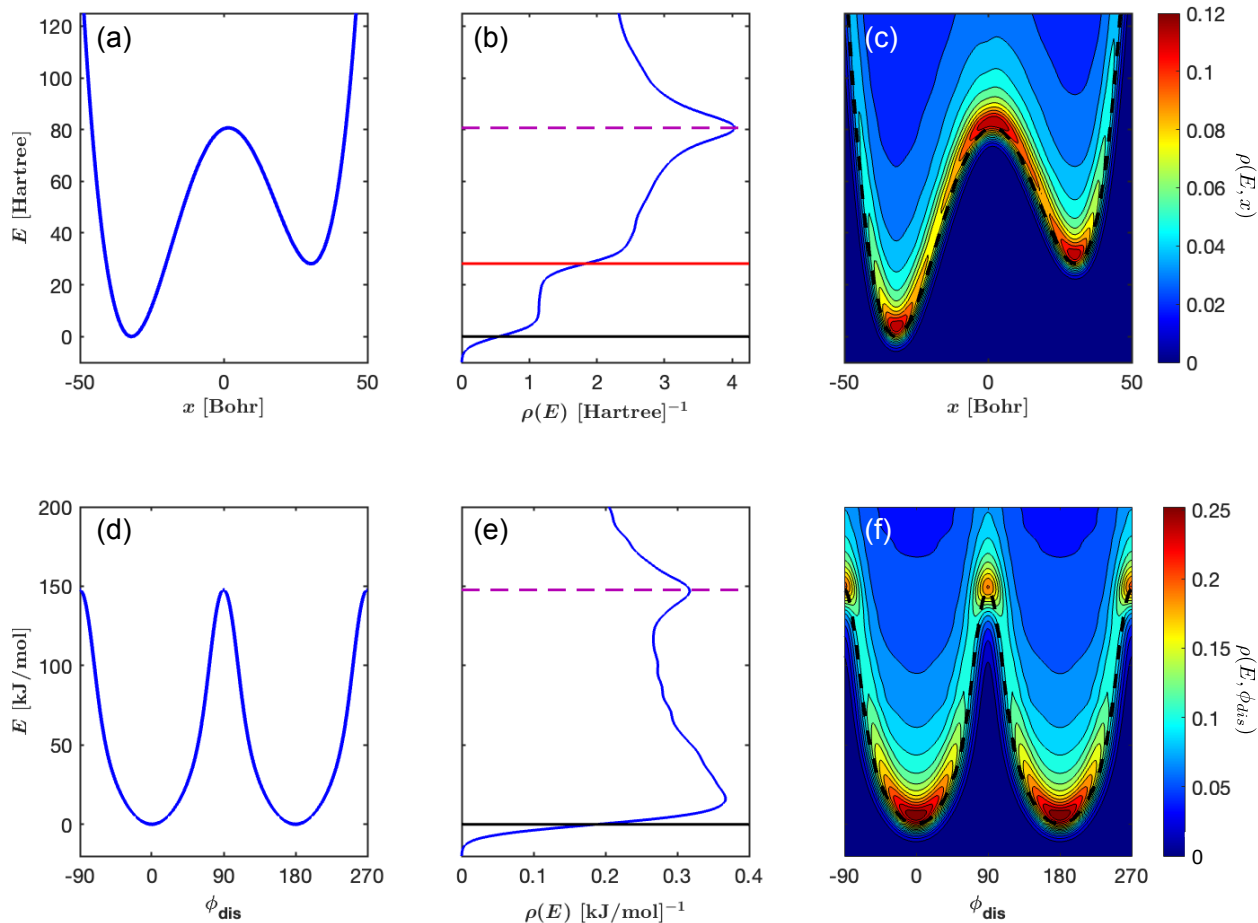


Figure 3: Densities of states as a function of energy $\rho(E)$ and as a function of both position and energy $\rho(E, x)$: (b) and (c) for the model potential shown in (a) respectively, and (e) and (f) for the one dimensional disrotatory potential for the cation shown in (d) respectively. The allylic structures are located at $\phi_{\text{dis}} = \{0, 180^\circ\}$, and the cyclic structures at $\phi_{\text{dis}} = \{90, -90 = 270^\circ\}$. In (b) and (d), solid horizontal lines in are positioned at energies of minima, and dashed horizontal lines are positioned at energies of transition states (local maxima in one dimension).

ences (cyclization energy, often referred to as ring strain) – the cationic value is higher by only 10% based on the calculations. This similarity is also observed experimentally, since the adiabatic ionization energy of allyl and the estimated “adiabatic” value for the cyclic cation are rather similar (*i.e.* the difference in ring strains of the cation and radical states is equal to the difference of the cyclopropyl and allyl “adiabatic” ionization energies), and their spectra partially overlap. However, from the calculations we observe that the cation cyclic geometry has no barrier to opening along a disrotatory path, unlike the radical, which possesses significant barriers along both conrotatory and disrotatory paths (*ca.* 100 kJ/mol for both), as shown in Fig. 4.⁶⁶ As discussed in the Introduction, Woodward and Hoffmann correctly predicted the allowed disrotatory path for the cation, but concluded incorrectly that the radical should behave similarly to the anion, *i.e.* possessing an allowed conrotatory path.¹ On the contrary, the correlation diagrams of Longuet-Higgins correctly predicted the existence of a high barrier for the two radical paths.² These pieces of evidence indicate that the radical stabilization is kinetic, and not thermodynamic. In fact, a correlation diagram analysis for all π conjugated radical ring closure/opening systems can be shown to yield only paths with crossing states, providing kinetic stabilization to the associated rings; while for the closed shell cases, one allowed path will always exist.⁶⁷

The results reported here motivate the re-evaluation of thermochemical quantities, for example of the C-H bond dissociation energy (BDE) of cyclopropane, which is found to be 448.6 kJ/mol at 0 K according to our HEAT-345(Q) calculations. This bond is perhaps the strongest alkane C-H bond, due to the strong *s* character of the carbon orbital participating in the bond.^{5,6,68} Previous reports for the BDE vary between 440-460 kJ/mol,⁷⁻⁹ and we here refine its evaluation using the Active Thermochemical Tables (ATcT) approach^{38,69,70} combining our calculations together with several experimental evaluations and additional theoretical results, yielding a value of 448.87 ± 0.49 kJ/mol at 0 K. Our analysis also provides revised values (at 0 K) of 124.00 ± 0.74 kJ/mol and 137.11 ± 0.74 kJ/mol for the radical and cation cyclization energies, respectively (further details and additional revised

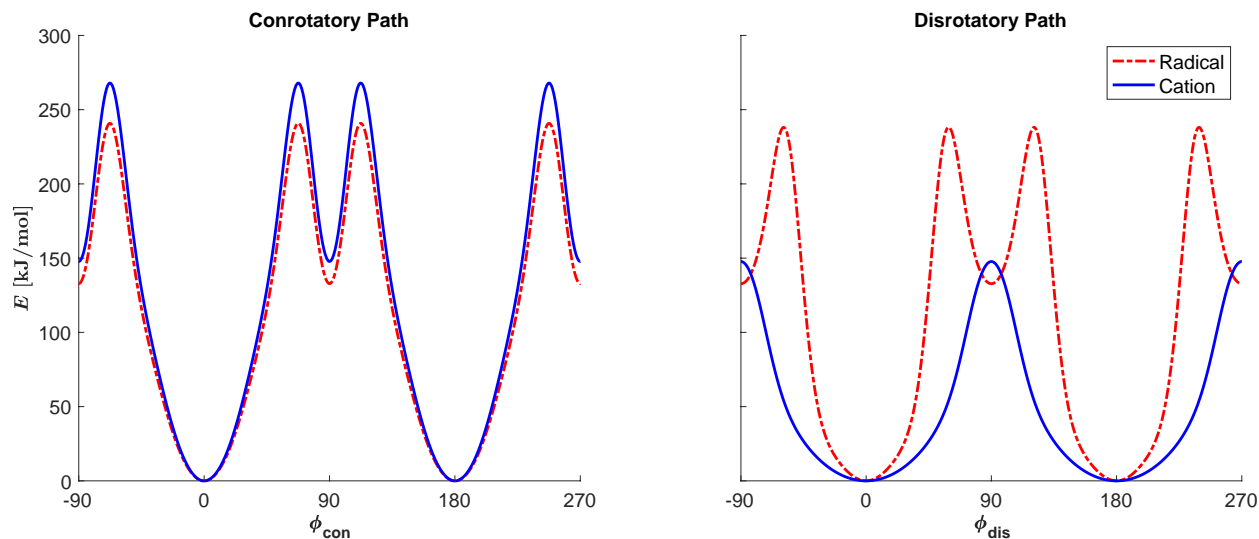


Figure 4: Calculated one dimensional PES for the radical and the cation con- and disrotatory paths. The allylic structures are located at $\phi_{\text{dis}} = \{0, 180^\circ\}$, and the cyclic structures at $\phi_{\text{dis}} = \{90, -90 = 270^\circ\}$.

values are listed in Table S1).

Conclusions

Experimental and theoretical results persuasively demonstrate that the cyclopropyl cation is not a stable species – a transition state rather than a local minimum. Its instability arises from the allowed disrotatory ring-opening path, which does not exist for the cyclopropyl radical, as predicted by Longuet-Higgins,² while their thermochemical instabilities towards the associated allyl species are similar.

Despite the unstable nature of the cation, direct ionization from cyclopropyl radical to the cyclopropyl cation could be observed. This serves as an example of transition state spectroscopy.^{57,59} Using a simple one-dimensional toy model, the underlying dynamics of such a transition were shown to be related to the influence transition states have on the local density of states, which is similar to, yet distinct from, the effects caused by true minima. Using a novel implementation of correlation-function-based Franck-Condon simulations suitable for systems with negative curvature, we are able to faithfully reproduce the newly measured

ms-TPES spectrum, further supporting the computational findings.

Together with the refined estimation for the strong cyclopropane C-H BDE, our findings explain various chemical observations of cyclopropyl derivatives: slow reactivity upon nucleophilic attack and a tendency to open to their allyl counterparts upon solvolysis due to the reluctance of the cyclopropyl ring to accept a positive charge. We encourage the application of these findings toward further understanding of the reaction mechanisms associated with this archetypal ring, important to a wide scope of chemical areas from chiral synthesis to biochemistry.

Supporting Information

Further details regarding the comparison of our spectrum to previous data, calculations of reduced dimensionality PESs, calculated thermochemical values and ATcT values, and construction of the densities of states are given in a supplementary PDF file. Calculated geometries, harmonic frequencies, and relevant force fields for the spectral simulation are supplied in an Excel file.

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