# Supporting Information

# Proton relays in anomalous carbocations dictate spectroscopy, stability and mechanisms: Case studies on $C_2H_5^+$ and $C_3H_3^+$

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#### SI-1. AB INITIO MOLECULAR DYNAMICS SIMULATION DETAILS

Dynamics simulations were performed using Born-Oppenheimer Molecular Dynamics  $(BOMD)^{1-10}$ , where the electronic energy and gradients were computed "on-the-fly" and the nuclear degrees of freedom were propagated using velocity Verlet<sup>11</sup>. Multiple constant energy (NVE) BOMD simulations were completed with variable input kinetic energies thoughtfully chosen to allow the system to equilibrate to different average total energies, modulating the extent of sampling of the potential surface. All simulations were performed using a developmental version of the Gaussian suite of electronic structure programs<sup>12</sup>. The 6-311++G<sup>\*\*</sup> functional was used in all simulations in this work. Additional simulation details can be found in the subsequent tables. Note that the average total energy was calculated for each system with reference to the lowest-energy structure/isomer for that system.

For  $C_2H_5^+$ , because the "classical" structure is a transition state and not a true minimum, the "bridged" structure was the only initial geometry employed. Due to the experimental use of a "straight" propargyl bromide compound, only the "straight" simulations were used for analysis.

$Duration^{a}$	AVE KE	AVE PE	AVE TE	$\operatorname{Drift}^{b}$	$\Delta E^c$	Bridge : Classical $d$
(ps)	(kcal/mol)	$(\rm kcal/mol)$	$(\rm kcal/mol)$	$(\rm kcal/mol)$	$(\rm kcal/mol)$	
10.0	$2.68 {\pm} 0.64$	$2.70 {\pm} 0.65$	$5.37{\pm}0.01$	-0.010	0.008	1.00:0.00
10.0	$4.44{\pm}1.12$	$4.48{\pm}1.12$	$8.92{\pm}0.02$	-0.022	0.018	1.00:0.00
10.0	$5.36 {\pm} 1.36$	$5.44{\pm}1.36$	$10.79 {\pm} 0.04$	0.089	0.041	1.00:0.00
10.0	$6.87 {\pm} 1.84$	$7.43 \pm 1.84$	$14.31 {\pm} 0.02$	0.004	0.015	0.96:0.04
10.0	$8.74{\pm}2.14$	$9.16 {\pm} 2.14$	$17.90{\pm}0.01$	0.026	0.015	0.96:0.04
10.0	$10.16 {\pm} 2.69$	$11.34{\pm}2.69$	$21.50{\pm}0.07$	0.129	0.068	0.85:0.15

TABLE SI-I: AIMD simulations for  $C_2H_5^+$ . M062X functional with "bridged" initial structure (Vibr. ZPE = 38.4 kcal/mol)

<sup>*a*</sup>Time step 0.1 fs for all simulations

<sup>b</sup>Difference between the average total energy of the last 1000 time steps and the average total energy of the first 1000 time steps.

 $^{c}$ Root mean square deviation of the total energy

<sup>d</sup>The unsymmetrized classical distribution constructed along the reduced dimensional coordinate defined in Figure 5 of the main paper ranged from approximately 36 degrees to 90 degrees. Through inspection, geometries with a reduced dimensional coordinate below 70 degrees were attributed to the "classical" configuration, and geometries with a reduced dimensional coordinate above 70 degrees were attributed to the "bridged" configuration.

$Duration^a$	AVE KE	AVE PE	AVE TE	$\mathrm{Drift}^b$	$\Delta E^c$	Cyclic : $Straight^d$
(ps)	$(\rm kcal/mol)$	$(\rm kcal/mol)$	$(\rm kcal/mol)$	$(\rm kcal/mol)$	$(\rm kcal/mol)$	
6.50	$1.51 {\pm} 0.39$	$35.76 {\pm} 0.39$	$37.27 {\pm} 0.01$	0.024	0.009	0.00:1.00
7.18	$3.02 {\pm} 0.84$	$37.25 {\pm} 0.84$	$40.27 {\pm} 0.04$	0.075	0.038	0.00:1.00
5.85	$4.53 {\pm} 1.19$	$38.71 \pm 1.19$	$43.24 {\pm} 0.03$	0.020	0.027	0.00:1.00
4.93	$6.04{\pm}1.63$	$40.17 {\pm} 1.63$	$46.21 {\pm} 0.03$	0.062	0.031	0.00:1.00
3.78	$7.59{\pm}1.88$	$41.51 \pm 1.88$	$49.10 {\pm} 0.05$	-0.097	0.050	0.00:1.00
7.24	$9.00{\pm}2.47$	$43.15 \pm 2.47$	$52.14 \pm 0.03$	0.027	0.032	0.00:1.00
10.0	$15.11 \pm 3.96$	$48.97 {\pm} 3.96$	$64.08 {\pm} 0.06$	-0.128	0.061	0.00:1.00
2.92	$22.28 \pm 5.77$	$56.83 {\pm} 5.78$	$79.11 {\pm} 0.08$	0.258	0.078	0.00:1.00
10.0	$29.49 {\pm} 8.70$	$64.52 {\pm} 8.71$	$94.01 {\pm} 0.14$	0.344	0.138	0.00:1.00
10.0	$44.16{\pm}12.57$	$79.62{\pm}12.57$	$123.78 {\pm} 0.05$	0.120	0.052	0.00:1.00
5.15	$58.22{\pm}16.48$	$95.18{\pm}16.49$	$153.39 {\pm} 0.06$	-0.186	0.064	0.11:0.89
10.0	$77.14 \pm 23.42$	$106.14 \pm 23.44$	$183.28 {\pm} 0.10$	-0.175	0.100	0.80:0.20
10.0	$95.31 {\pm} 31.78$	$153.36 \pm 31.80$	$248.67 {\pm} 0.27$	-0.629	0.271	0.72: 0.28

TABLE SI-II: AIMD simulations for  $C_3H_3^+$ . M062X functional "straight" initial structure (Vibr. ZPE = 27.0 kcal/mol)

<sup>a</sup>Time step 0.1 fs for all simulations

 $^{b}$ Difference between the average total energy of the last 1000 time steps and the average total energy of the first 1000 time steps.

 $^c\mathrm{Root}$  mean square deviation of the total energy

<sup>d</sup>The unsymmetrized classical distribution constructed along the reduced dimensional coordinate defined in Figure 7 of the main paper ranged from approximately 90 degrees to 180 degrees. Through inspection, geometries with a reduced dimensional coordinate below 120 degrees were attributed to the "cyclic" configuration, and geometries with a reduced dimensional coordinate above 120 degrees were attributed to the "straight" configuration.

$Duration^a$	AVE KE	AVE PE	AVE TE	$\mathrm{Drift}^b$	$\Delta E^c$	Cyclic : $Straight^d$
(ps)	$(\rm kcal/mol)$	$(\rm kcal/mol)$	$(\rm kcal/mol)$	(kcal/mol)	$(\rm kcal/mol)$	
2.69	$1.51 {\pm} 0.39$	$26.80{\pm}0.39$	$28.31 {\pm} 0.00$	-0.001	0.000	0.00:1.00
1.78	$3.01 {\pm} 0.79$	$28.28 {\pm} 0.79$	$31.29 {\pm} 0.00$	0.000	0.000	0.00:1.00
3.16	$4.52 \pm 1.21$	$29.75 \pm 1.21$	$34.27 {\pm} 0.00$	-0.008	0.003	0.00:1.00
5.23	$6.04{\pm}1.74$	$31.21 \pm 1.74$	$37.25 {\pm} 0.00$	-0.008	0.004	0.00:1.00
6.21	$7.54{\pm}2.16$	$32.69 {\pm} 2.16$	$40.23 {\pm} 0.00$	-0.000	0.003	0.00:1.00
4.05	$9.02 \pm 2.54$	$34.19 {\pm} 2.54$	$43.21 {\pm} 0.01$	-0.011	0.005	0.00:1.00
3.38	$15.09 {\pm} 4.18$	$40.05 {\pm} 4.18$	$55.14 {\pm} 0.00$	0.003	0.004	0.00:1.00
4.07	$22.35 \pm 5.90$	$47.68 {\pm} 5.90$	$70.03 {\pm} 0.01$	-0.003	0.005	0.00:1.00
2.91	$30.26 \pm 8.29$	$54.70 {\pm} 8.30$	$84.96 {\pm} 0.01$	0.013	0.006	0.00:1.00
7.80	$44.39 {\pm} 12.07$	$70.36{\pm}12.07$	$114.75 {\pm} 0.01$	0.026	0.006	0.00:1.00
2.10	$58.40 \pm 16.69$	$86.14{\pm}16.69$	$144.54{\pm}0.01$	0.043	0.014	0.02: 0.98
8.77	$71.23 \pm 20.66$	$103.12{\pm}20.66$	$174.35 \pm 0.02$	0.043	0.017	0.02: 0.98
9.04	$80.32 \pm 27.17$	$123.84{\pm}27.18$	$204.16 {\pm} 0.02$	0.020	0.017	0.14:0.86

TABLE SI-III: AIMD simulations for  $C_3H_3^+$ . B3LYP functional with "straight" initial Structure (Vibr. ZPE = 26.8 kcal/mol)

<sup>a</sup>Time step 0.1 fs for all simulations

 $^{b}$ Difference between the average total energy of the last 1000 time steps and the average total energy of the first 1000 time steps.

 $^{c}$ Root mean square deviation of the total energy

<sup>d</sup>The unsymmetrized classical distribution constructed along the reduced dimensional coordinate defined in Figure 7 of the main paper ranged from approximately 90 degrees to 180 degrees. Through inspection, geometries with a reduced dimensional coordinate below 120 degrees were attributed to the "cyclic" configuration, and geometries with a reduced dimensional coordinate above 120 degrees were attributed to the "straight" configuration.

(101.2112 = 10.0  kour more)							
$Duration^a$	AVE KE	AVE PE	AVE TE	$\mathrm{Drift}^b$	$\Delta E^c$		
(ps)	$(\rm kcal/mol)$	$(\rm kcal/mol)$	$(\rm kcal/mol)$	$(\rm kcal/mol)$	$(\rm kcal/mol)$		
5.14	$3.08 {\pm} 0.60$	$2.90 {\pm} 0.60$	$5.98 {\pm} 0.02$	-0.005	0.019		
2.82	$5.27 {\pm} 0.87$	$3.65 {\pm} 0.87$	$8.92 {\pm} 0.01$	-0.017	0.009		
5.44	$7.47{\pm}1.07$	$4.46{\pm}1.07$	$11.93 {\pm} 0.01$	0.032	0.009		
5.06	$9.46{\pm}1.44$	$5.45 \pm 1.44$	$14.90 {\pm} 0.03$	-0.040	0.031		

TABLE SI-IV: AIMD simulations for  $H^+N_2Ar_2$  (proposed impurity in Ref. 13: M062X functional.) (Vibr. ZPE = 10.6 kcal/mol)

<sup>*a*</sup>Time step 0.1 fs for all simulations

 $^{b}$ Difference between the average total energy of the last 1000 time steps and the average total energy of the first 1000 time steps.

<sup>c</sup>Root mean square deviation of the total energy

#### SI-2. HARMONIC MODES OF $C_2H_5^+$

To study the conformational transitions, we chose to follow a few critical modes. Here we explain the harmonic fundamentals for the "bridged" case and note how these fundamentals may be perturbed as the "bridge" proton walks towards the "classical" structure. The C-H stretch frequency for the "bridged" structure under the harmonic approximation may be understood as follows: The  $C_{3v}$  symmetry of the "bridged" structure allows symmetric and antisymmetric linear combinations of individual CH<sub>2</sub> symmetric and antisymmetric stretches, and these are the four frequencies above  $3000 \text{ cm}^{-1}$ , two of which are IR active in Figure 9(a) of the main paper. The fifth "bridge" proton stretch is axial to the system. These modes are pictorially represented in Figure SI-1. As the "bridge" proton migrates towards one of the carbons to eventually yield the "classical" configuration, the aforementioned  $C_{3v}$  symmetry is broken, and the two individual triatomic CH<sub>2</sub> symmetric stretch and antisymmetric stretches are not allowed to combine as they did before in the "bridged" case. In fact, the CH<sub>2</sub> group that embraces the "bridge" proton allows its symmetric and antisymmetric stretches to symmetrically and anti-symmetrically combine with the "bridge" proton stretch, and the other  $CH_2$  vibration remains inert. As a result of combination of these three modes (a) the "bridge" proton stretch and (b) the symmetric and antisymmetric triatomic  $CH_2$  stretches combine to give three new peaks, two of which fall in the 2800 cm<sup>-1</sup> region. These three modes are displayed in Figure SI-2.



FIG. SI-1: Harmonic modes for the "bridged" structure.



FIG. SI-2: Harmonic modes for the "classical" structure.

## SI-3. VIBRATIONAL SPECTRAL PROPERTIES COMPUTED FROM AIMD TRAJECTORIES OVER A RANGE OF ENERGIES

Simulated vibrational properties computed using the one-dimensional Fourier Transform of the Dipole-Dipole Auto-correlation Function (Eq. (B1) in the paper) of our AIMD simulations are shown here. The kinetic energy of the classical AIMD treatment gradually tunes anharmonicity by varying the range of the potential surface sampled. To correct for AIMD simulations not containing nuclear quantization, the calculated frequencies for all computed spectra are scaled by 0.972 and 0.975 for M062X and B3LYP simulations respectively. Figures SI-3, SI-4, and SI-5 show the energy evolution of the vibrational spectra for  $C_2H_5^+$  and  $C_3H_3^+$  (using M062X and B3LYP respectively).

In the case of  $C_2H_5^+$ , our low-energy computed spectra (shown in red) parallel the harmonic spectra of the "bridged" isomer. These spectral signatures are shown in red in Figure SI-3. At high energies (blue in Figure SI-3), contributions from the "classical" configuration appear in the range of approximately 2800 cm<sup>-1</sup>. To identify "bridged" and "classical" signatures in the computed spectra, the characteristic ( $\approx 2142 \text{ cm}^{-1}$  for the "bridged" and  $\approx 2837 \text{ cm}^{-1}$  for the "classical") used to track the interconversion of geometries in the twodimensional time-frequency spectra presented in Section IV B 1 are highlighted in grey in Figure SI-3.

In the case of  $C_3H_3^+$ , low-energy computed spectra (shown in red in Figures SI-4 and SI-5) demonstrate contribution from both "cyclic" and "straight" structures with the "straight" configuration dominating the spectra. As energy is increased, the system is likely excited to a higher eigenstate. The excited reduced dimensional quantum nuclear eigenstates (Eq. (1) in the paper) show increasing population of the "cyclic" configuration. The spectroscopic contributions from the "cyclic" isomer hence increase, facilitating combinations of modes from both isomers. The simulations in which the aforementioned mixing is apparent are shown in blue in Figures SI-4 and SI-5, and sections of the spectra where such mixing is most apparent are highlighted in grey.



FIG. SI-3: IR spectra for  $C_2H_5^+$  computed using  $\alpha_{\mu}^{QC}(\omega)$  (Eq. (B1) in the paper). In all cases the average total energy relative to the "bridged" structure is noted. The bottom two panels are harmonic spectra for the "bridged" and "classical" structures, and the top panel is the experimental Infrared Photodissociation Spectrum from Ref. 13. The calculated frequencies are scaled by a factor of 0.972.



FIG. SI-4: Selected IR spectra for  $C_3H_3^+$  computed using  $\alpha_{\mu}^{QC}(\omega)$  (Eq. (B1) in the paper) for the M062X simulations. In all cases the average total energy relative to the "cyclic" structure is noted. The bottom two panels are harmonic spectra for the "cyclic" and "straight" structures, and the top panel is the experimental Infrared Photodissociation Spectrum from Ref. 14. The calculated frequencies are scaled by a factor of 0.972.



FIG. SI-5: Selected IR spectra for  $C_3H_3^+$  computed using  $\alpha_{\mu}^{QC}(\omega)$  (Eq. (B1) in the paper) for the B3LYP simulations. In all cases the average total energy relative to the "cyclic" structure is noted. The bottom two panels are harmonic spectra for the "cyclic" and "straight" structures, and the top panel is the experimental Infrared Photodissociation Spectrum from Ref. 14. The calculated frequencies are scaled by a factor of 0.975.

# SI-4. ANALYSIS OF POSSIBLE IMPURITY $H^+N_2Ar_2$ IN THE EXPERIMENTAL $C_2H_5^+$ SPECTRUM DISCUSSED IN REF. 13

As previously mentioned in Section IV B 1 of the main paper, Ref. 13 attributes the peaks (marked as blue asterisks in Figure SI-6) to an  $H^+N_2Ar_2$  impurity. As can be seen in Figure SI-6, this impurity has characteristic Harmonic peaks in the regions of 2100 cm<sup>-1</sup> and 2650 cm<sup>-1</sup> (frequencies scaled by 0.972). Hence, two so-called impurity peaks in the regions of 2800 cm<sup>-1</sup> and 3000 cm<sup>-1</sup> are not likely to be from this substance but rather from the "classical" isomer which does possess spectral features in this region. However, as can be seen from Figure SI-6, the spectrum computed from AIMD simulations of H<sup>+</sup>N<sub>2</sub>Ar<sub>2</sub> demonstrates substantial peak broadening created by Argon "chatter" into the aforementioned region. It is thus feasible that the H<sup>+</sup>N<sub>2</sub>Ar<sub>2</sub> impurity may contribute to the experimental spectra; however, the small peaks between 2800 cm<sup>-1</sup> and 3000 cm<sup>-1</sup> as well as the shoulder on the peak at approximately 3150 cm<sup>-1</sup> exactly reproduced in our spectra computed from AIMD simulations in which no impurity was present indicates that the "classical" structure may have pronounced appearance in the experimental result.



FIG. SI-6: IR spectra for  $H^+N_2Ar_2$  computed using  $\alpha_{\mu}^{QC}(\omega)$ . In all cases the average total energy relative to the optimized structure is noted. The bottom three panels are harmonic spectra for the "bridged," "classical," and "impurity" structures, and the top panel is the Infrared Photodissociation Spectrum from Ref. 13. The calculated frequencies are scaled by 0.972 to account for AIMD simulations not containing nuclear quantization.



FIG. SI-7: Harmonic spectra for the "bridged," "classical," and "impurity" structures are shown in the bottom three panels. The top panel presents the experimental Infrared Photodissociation Spectrum from Ref. 13. The calculated frequencies are scaled by a factor of 0.972.

### SI-5. REDUCED DIMENSIONAL NUCLEAR QUANTUM EFFECTS USING "DISTRIBUTED APPROXIMATING FUNCTIONALS" (DAFS)

Quantum nuclear effects were computed by constructing the nuclear Hamiltonian in the one dimensional reduced dimensional coordinate system, in the dimensionality of  $\theta$  (see Eq. (1) in the main paper). Specifically,

$$H(\theta, \theta') = -\sum_{I=1}^{2} \frac{\hbar^2}{2m} \tilde{K}(\theta^I, \theta'^I) + \tilde{V}_{\beta} \left(\theta^I, \theta'^I\right) \delta_{\theta^I, \theta'^I}, \qquad (SI-1)$$

for the potential  $\tilde{V}_{\beta}$  in Eq. (1). The kinetic energy operator is represented using "Distributed Approximating Functionals" (DAFs)<sup>9,15–18</sup>:

$$\tilde{K}(x_i, x_j) = \frac{1}{\sigma\sqrt{2\pi}} \left(\frac{-1}{\sqrt{2\sigma}}\right)^2 \exp\left(-\frac{(x_i - x_j)^2}{2\sigma^2}\right) \sum_{n=0}^{M/2} \left(\frac{-1}{4}\right)^n \frac{1}{n!} H_{2n+k}\left(\frac{x_i - x_j}{\sqrt{2\sigma}}\right) (SI-2)$$

where  $H_{2n+k}$  are Hermite polynomials. A major advantage of the representation in Eq. (SI-2) is that it provides a banded-Toeplitz representation for the discretized free-propagator and the derivative operator. A Toeplitz matrix is one where  $A_{i,j} \equiv A(|i-j|)$ . Furthermore, the representation in Eq. (SI-2) is banded due to appearance of the Gaussian function. These properties lead to an  $\mathcal{O}(N)$  algorithm for eigenstate calculation and wavepacket propagation as described in the appendix in Ref. 19.

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