

Supporting Information

A Grotthuss-like proton shuttle in the anomalous C_2H_3^+ Carbocation: Energetic and vibrational properties for isotopologues

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SI-1. AB INITIO MOLECULAR DYNAMICS SIMULATION DETAILS

Dynamics is performed using Born-Oppenheimer Molecular Dynamics (BOMD)¹⁻¹⁰, where the electronic energy and gradients are computed “on-the-fly”, and the nuclear degrees of freedoms are propagated using velocity Verlet¹¹. A large number of constant energy (NVE) BOMD simulations were carried out at initial conditions that were carefully chosen to allow the system to equilibrate to different internal temperatures (or average kinetic energy). (See Table SI-I.) This modulates the extent to which the potential surface is sampled. Two different starting geometries, the classical and bridge, were considered at each temperature to achieve better sampling. [As shown in Figure 9 in the paper, four different starting geometries were considered for the singly deuterated isotopologue.] All simulations were performed using a development version of the Gaussian suite of electronic structure programs¹².

TABLE SI-I: Energy conservation properties for dynamics simulations (NVE ensemble). All calculations use M06-2X/6-311+G(3df,2pd) level of theory.

Initial Structure	Duration ^a (ps)	Ave KE ^b (kcal/mol)	Ave Temp ^c (K)	ΔE ^d (kcal/mol)	Hopping
$C_2H_3^+$ bridge	13.3	0.68	57±21	<0.01	no
	13.2	1.27	107±42	<0.01	no
	12.7	1.89	158±57	0.02	no
	13.0	2.44	204±75	0.01	no
	13.2	3.03	254±80	0.02	no
	12.5	3.64	305±102	0.03	no
	23.4	4.70	394±135	0.04	yes
	21.3	5.86	492±181	0.04	yes
	23.1	7.02	588±196	0.04	yes
$C_2H_3^+$ classical	13.1	0.60	50±20	<0.01	no
	13.0	1.19	100±40	<0.01	no
	12.6	1.78	149±57	0.01	no
	12.7	2.38	199±79	<0.01	no
	12.3	2.96	248±98	0.01	no
	12.3	3.56	298±114	0.01	no
	23.3	6.63	556±185	0.10	yes
	22.9	7.88	661±214	0.05	yes
	22.5	8.82	740±242	0.04	yes
$C_2H_2D^+$ bridge-1	40.3	0.70	57±20	<0.01	no
	38.1	1.28	108±38	0.01	no
	38.8	1.86	156±51	0.02	no
	39.8	2.45	206±69	0.02	no
	37.1	3.02	254±79	0.03	no
	38.3	3.62	304±95	0.04	no
	38.7	4.65	391±130	0.09	yes
	39.1	5.85	490±160	0.08	yes
	37.9	6.83	572±196	0.08	yes
$C_2H_2D^+$ classical-1	39.0	1.19	100±32	0.01	no
	36.6	2.00	167±80	0.02	yes
	39.0	4.49	376±121	0.08	yes
	39.0	5.08	426±140	0.08	yes
	37.0	5.70	478±159	0.14	yes
	38.6	6.60	553±184	0.13	yes
	38.8	7.78	652±214	0.05	yes
	36.7	9.00	755±250	0.10	yes

^aTime step 0.25 fs for all simulations.

^bIn units of kcal/mol.

^cIn Kelvin.

^dRoot mean square deviation of the total energy in kcal/mol.

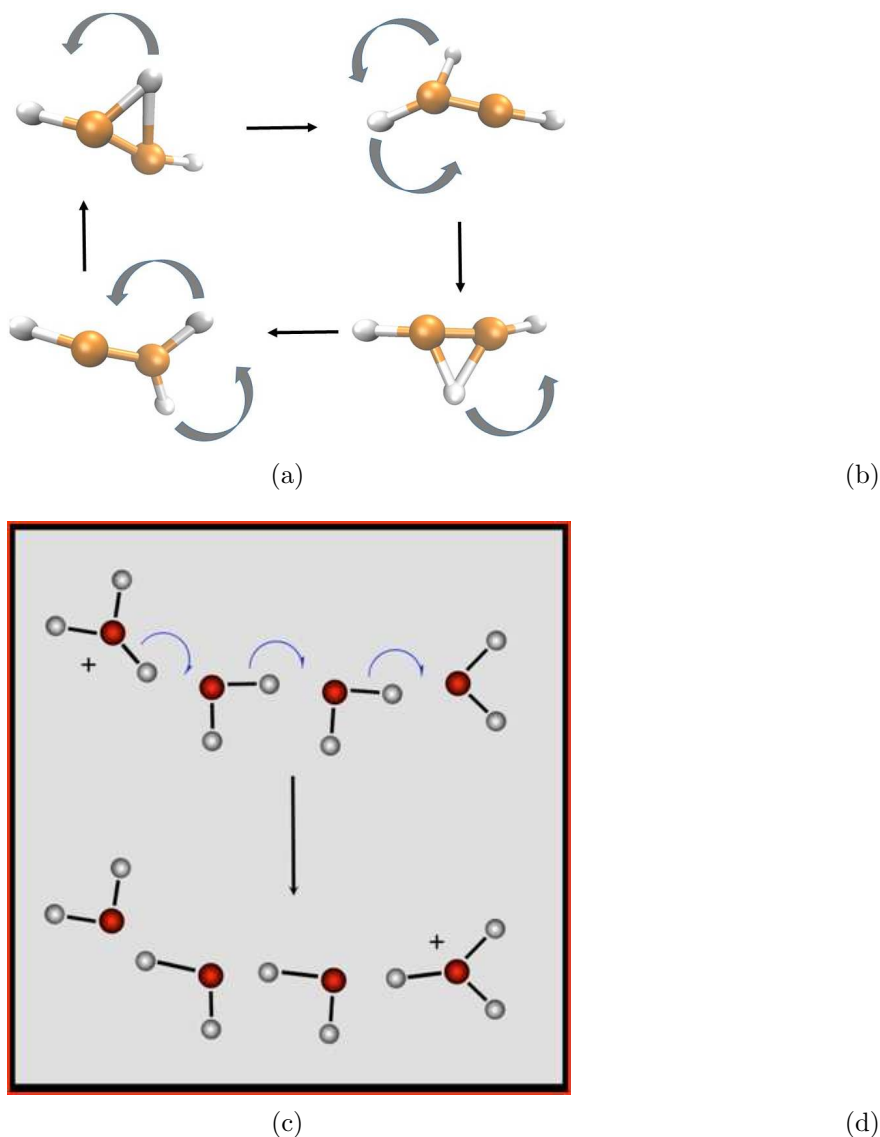


FIG. SI-1: Figure (a) depicts the fluxional nature of $C_2H_3^+$ bridge proton for the high temperature calculations that is also animated in Figure (b). The hopping mechanism here is reminiscent of the “Grotthuss proton shuttle mechanism”¹³ that has been widely invoked for the study of proton transfer in water. This is shown in Figure (c). The animation in Figure (d) reveals the distribution of all three hydrogen nuclei (gray) surrounding the central carbons (shown in orange for all figures). The distribution has not been symmetrized. As can be seen from Table SI-I, all trajectories conserve the total energy of the system to within a few-tenths of a kcal/mol. Figures (b) and (d) are best viewed using Adobe Acrobat. In case this is not an option, an mpeg file can be found here.

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FIG. SI-2: The quantity $\alpha_V(T, \omega; \Delta T)$ (Eq. (B4) in the paper) is plotted in the time-frequency domain for multiple temperatures (animation). This figure is an animation of Figure 8 in the main paper and again an mpeg file can be found here. The critical Bridged (black) and Classical (blue) modes that appear to participate in the Bridged $\leftrightarrow$ Classical transition are noted on the top axis. See Table II in the paper for normal mode descriptions.

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FIG. SI-3: The quantity $\alpha_V(T, \omega; \Delta T)$ (Eq. (B4) in the paper) is plotted in the time-frequency domain for multiple temperatures (animation). This figure is an animation of Figure 12 in the main paper and again an mpeg file can be found here. The critical Bridged-1 (black), Bridged-2 (red), Classical-2 (blue) and Classical-1 (green) modes are marked.

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- ¹¹ Swope, W. C.; Andersen, H. C.; Berens, P. H.; Wilson, K. R. A Computer-Simulation Method for the Calculation of Equilibrium-Constants for the Formation of Physical Clusters of Molecules - Application to Small Water Clusters. *J. Chem. Phys.* **1982**, *76*, 637.
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