

Supplementary information

Strong field ionization and dissociation dynamics of vinyl bromide (C_2H_3Br) initiated by few-cycle pulses

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1. Computed relative energies of vinyl bromide cationic states

Tables S1–S3 summarize the relative energies of the monocation, singlet dication, and triplet dication computed at the B3LYP/6-311++G(3d,2p), CCSD/cc-pVTZ, and CBS-QB3 levels of theory.

Table S1. Monocation fragment system enthalpies at 0 K (in eV)

System 0K Enthalpy (eV)	B3LYP/6-311++g(3d,2p)	CCSD/cc-pVTZ	CBS-QB3
$C_2H_3Br^+$ D0 Vertical (S0 Neutral Geom)	0.00	0.00	0.00
Br^+ S0, C_2H_3 D0	7.50	6.75	6.78
Br^+ T0, C_2H_3 D0	5.66	5.13	5.46
Br D0, $C_2H_3^+$ S0	2.38	2.10	2.25
HBr S0, $C_2H_2^+$ D0	2.80	2.43	2.59
HBr T0, $C_2H_2^+$ D0	6.62	6.22	6.48
$C_2H_2Br^+$ S0, H radical	3.11	2.78	2.74
$C_2H_2Br^+$ T0, H radical	4.70	4.47	4.57
CBr D0, CH_3^+ S0	5.88	5.48	5.65
CBr D0, CH_3^+ T0	9.29	9.00	9.47
CBr ⁺ S0, CH_3 D0	4.91	4.45	4.53
CBr ⁺ T0, CH_3 D0	7.59	7.10	7.38
CH_2 S0, CHBr ⁺ D0	9.11	8.59	8.91
CH_2 T0, CHBr ⁺ D0	8.64	8.12	8.57
CH_2^+ D0, CHBr T0	10.48	9.88	10.57

Table S2. Singlet dication fragment system enthalpies at 0 K. Intermediates are labeled as “int” and the transition states between systems A and B are denoted as “TS: A→B”.

System 0K Enthalpy (eV)	B3LYP/6-311++g(3d,2p)	CCSD/cc-pVTZ	CBS-QB3
C ₂ H ₃ Br ⁺² S0 Vertical (S0 Neutral Geom)	0.00	0.00	0.00
TS: C ₂ H ₃ Br ⁺² S0 → C ₂ H ₃ ⁺ S0, Br ⁺ S0	1.66	1.74	1.57
Br ⁺ S0, C ₂ H ₃ ⁺ S0	-1.48	-1.90	-1.81
TS: C ₂ H ₃ Br ⁺² S0 → Int CH ₃ -CBr ⁺² S0	-0.92	-0.76	-0.77
Int CH ₃ -CBr ⁺² S0	1.38	1.68	1.88
TS: Int CH ₃ -CBr ⁺² S0 → CBr ⁺ S0, CH ₃ ⁺ S0	0.31	0.18	0.24
CBr ⁺ S0, CH ₃ ⁺ S0	-2.81	-3.07	-2.94
C ₂ H ₂ Br ⁺ S0, H ⁺	-0.95	-0.83	-0.92

Table S3. Triplet dication fragment system enthalpies at 0 K. Intermediates are labeled as “int” and the transition states between systems A and B are denoted as “TS: A→B”.

System	B3LYP/6-311++g(3d,2p)	CCSD/cc-pVTZ	CBS-QB3
C ₂ H ₃ Br ⁺² T0 Vertical (S0 Neutral Geom)	0.00	0.00	0.00
TS: C ₂ H ₃ Br ⁺² T0 → Br ⁺ T0, C ₂ H ₃ ⁺ S0	0.58	0.75	0.61
Br ⁺ T0, C ₂ H ₃ ⁺ S0	-3.26	-3.59	-3.48
TS: C ₂ H ₃ Br ⁺² T0 → Int CH ₃ -CBr ⁺² T0	1.51	1.60	1.51
Int CH ₃ -CBr ⁺² T0	-1.65	-1.49	-1.84
TS: Int CH ₃ -CBr ⁺² T0 → CBr ⁺ T0, CH ₃ ⁺ S0	1.51	1.60	1.51
CBr ⁺ S0, CH ₃ ⁺ T0	0.66	0.39	0.54
CH ₂ ⁺ D0, CHBr ⁺ D0	1.44	1.09	1.29
HBr ⁺ D0, C ₂ H ₂ ⁺ D0	-3.01	-3.27	-3.16
CHBr ⁺ D0, CH ₂ ⁺ D0	1.44	1.09	1.29
CBr ⁺ S0, H, CH ₂ ⁺ D0	2.47	2.04	2.01

The relative energies (eV) of the low-lying electronic states of the vinyl bromide dication, calculated at the ground-state geometry of neutral vinyl bromide, are summarized in Tables S4–S5. Ionization potentials from the neutral species are also included. The dominant configuration of each state is represented using the following notation: ‘**2**’ denotes a doubly occupied orbital, ‘**u**’ and ‘**d**’ indicate singly occupied orbitals with up- or down-spin electrons, respectively, and ‘**0**’ denotes an unoccupied orbital.

Table S4. The relative energies (eV) at the single state of vinyl bromide dication.

State	Dominant Configuration	CASSCF	CASPT2	EOMCC
S ₀	222200	0.96	0.96	0.96
S ₁	222ud0	1.55	1.40	1.50
S ₂	2u22d0	4.63	3.83	2.27
S ₃	2u2d20	5.19	4.38	4.66
S ₄	222020	5.42	4.71	6.36
S ₅	22ud20	5.84	4.95	7.71

Table S5. The relative energies (eV) at the triplet state of vinyl bromide dication.

State	Dominant Configuration	CASSCF	CASPT2	EOMCC
T ₀	22u2u0	1.29	1.29	1.29
T ₁	2u22u0	2.08	2.18	1.91
T ₂	222uu0	4.03	3.53	2.78
T ₃	22uu20	4.68	4.17	4.95
T ₄	2uu220	4.78	4.23	5.01
T ₅	2u2u20	6.11	5.37	5.33

2. Vibrational frequencies of Key Intermediates and Transition States in the Reaction Pathway

The vibrational frequencies (cm⁻¹) of Int₁ and TS₆, computed at the B3LYP/6-311++G(3d,2p), CBS-QB3, and CCSD/cc-pVTZ levels of theory, are presented in Tables S6 and S7.

Table S6. Vibrational frequencies of Int₁

Vibrational Frequency (cm ⁻¹)	B3LYP/6-311++G(3d,2p)	CBS-QB3	CCSD/cc-pVTZ
V1	328.8	326.7	332.4
V2	329.1	326.7	332.4
V3	660.5	662.6	670.3
V4	813.5	808.7	827.7
V5	814.4	809.0	827.7
V6	1185.3	1174.2	1235.7

V7	1185.3	1174.3	1235.7
V8	1241.6	1234.1	1267.5
V9	1529.9	1540.2	1497.3
V10	2762.4	2759.4	2830.1
V11	2788.6	2790.6	2893.0
V12	2791.2	2791.4	2893.0

Table S7. Vibrational frequencies of TS₆

Vibrational Frequency (cm ⁻¹)	B3LYP/6-311++G(3d,2p)	CBS-QB3	CCSD/cc-pVTZ
V1	-145.7	-139.1	-168.0
V2	155.9	152.2	169.7
V3	156.0	152.3	169.7
V4	470.4	440.1	573.0
V5	470.7	440.4	573.4
V6	1046.5	1047.8	1105.3
V7	1377.1	1366.5	1388.9
V8	1407.3	1396.8	1434.0
V9	1407.9	1397.4	1434.0
V10	3019.7	3041.4	3049.8
V11	3215.1	3242.7	3249.9
V12	3215.4	3243.0	3249.9