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Spectroscopic and Computational Studies of the Laser Photolysis of Matrix Isolated 1,2-Dibromoethanes: Formation and Fate of the Bromoethyl Radicals[†]

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We report experimental and computational studies of the photolysis of atmospherically important 1,2-dibromoethanes (1,2-C₂X₄Br₂; X = H, F) in Ar matrixes at 5 K. Using the pulsed deposition method, we find that significant conformational relaxation occurs for 1,2-C₂H₄Br₂ (EDB; observed anti/gauche ratio = 30:1) but not for 1,2-C₂F₄Br₂ (TFEDB; anti/gauche = 3:1), which is traced to a larger barrier to rotation about the C–C bond in the latter. Laser photolysis of matrix-isolated EDB at 220 nm reveals the growth of infrared bands assigned to the gauche conformer and C₂H₄–Br₂ charge transfer complex (both as major products), and the C₂H₄Br radical and C₂H₃Br–HBr complex as minor (trace) products. The presence of the C₂H₄–Br₂ complex is confirmed in the UV/visible spectrum, which shows an intense charge transfer band at 237 nm that grows in intensity upon annealing. In contrast to previous reports, our experimental and computational results do not support a bridged structure for the C₂H₄Br radical in either the gas phase or matrix environments. We also report on the laser photolysis of matrix-isolated TFEDB at 220 nm. Here, the dominant photoproducts are the anti and gauche conformers of the C₂F₄Br radical, the vibrational and electronic spectra of which are characterized here for the first time. The increase in yield of radical for TFEDB vs EDB is consistent with the stronger C–Br bond in the fluoro-substituted radical species. The photochemistry of the C₂F₄Br radical following excitation at 266 nm was investigated and found to lead C–Br bond cleavage and formation of C₂F₄. The implications of this work for the atmospheric and condensed phase photochemistry of the alkyl halides is emphasized.

I. Introduction

Polyhalomethanes (halons) such as the chlorofluorocarbons (CFC's) represent a fascinating class of compounds that have received much attention due to their role in atmospheric chemistry and ozone depletion. It is well appreciated, for example, that the photolytic release of halogen atoms from CFCs represents an important contribution to catalytic cycles for ozone depletion.^{1–6} Of the bromine-containing halons, 1,2-dibromoethane (denoted EDB following literature precedent) has been widely used as an additive in gasolines and oils and as a pesticide, and the tetrafluoro analogue of EDB (1,2-C₂F₄Br₂, hereafter referred to as TFEDB) was widely used as a flame retardant and fumigating agent. Due to this array of anthropogenic sources,^{7–9} EDB has been found in a recent study of the tropical troposphere and lower stratosphere to be the most abundant bromine-containing halon,¹⁰ although it is expected to have a relatively short tropospheric lifetime, on the order of several hundred days.¹¹ The photochemistry and ultimate atmospheric fate of EDB and related compounds is a topic of current interest.¹¹

The ultraviolet (UV) photodissociation dynamics of EDB has been investigated by several groups over the past decade.^{12–14} Like other alkyl halides, UV excitation induces an *n*– σ^* transition that leads to carbon–halogen bond cleavage. The consensus of the photodissociation experiments was, until

recently, that *n*– σ^* excitation leads to a concerted three-body decay to C₂H₄ + Br + Br, as the initially formed haloethyl radical undergoes spontaneous secondary decomposition due to the very weak C–Br bond in the radical (dissociation energy ~33 kJ/mol).¹² However, very recent experiments using cavity ring down detection of molecular bromine have suggested the existence of a molecular channel forming C₂H₄ + Br₂ products, which is presumed to arise through a four-center elimination. The quantum yield for Br₂ formation in the photolysis of EDB was determined to be 0.36 ± 0.18.¹⁴

TFEDB, or Halon-2402, is another important atmospheric species with an estimated atmospheric lifetime of some 20 years,¹⁴ long enough to afford ready transport to the stratosphere. The gas-phase photodissociation of TFEDB at wavelengths of 193, 233, and 266 nm was studied by North and co-workers using photofragment translational energy spectroscopy.¹⁵ At wavelengths of 193 and 233 nm, the quantum yield of Br formation was 1.9 ± 0.1; this dropped to 1.4 ± 0.1 at 266 nm. The increased yield at shorter wavelengths was attributed to secondary dissociation of the C₂F₄Br radical prior to collisional stabilization, and a C–Br bond dissociation energy of 67 ± 8 kJ/mol was determined for the radical, which is around twice that of bromoethyl. To date, there is little spectroscopic information available for this radical, although it was the focus of a recent theoretical study using gradient-corrected density functional theory (DFT) methods.¹⁶

The condensed phase photochemistry of these and related halons has also received significant attention, owing in part to the importance of the radicals in stereospecific control of halogenation reactions in solution.¹⁷ Thus, there has been

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significant interest in the structure of the haloethyl radicals as to whether a bridged or nonbridged (classical) structure is the global minimum,^{16,18} and this is still an open question. It has been suggested on the basis of a computational study utilizing Hartree–Fock (HF), DFT, and second-order Moller–Plesset perturbation (MP2) methods in combination with a 6-31G** basis set for C, H and an effective core potential for the halogen atom that the global minimum for the C_2H_4Br radical is the bridged structure.¹⁸ However, a later computational study using DFT methods considered only the classical (nonbridged) structure.¹⁹

In this work, we examine the photolysis of EDB and TFEDB isolated in an Ar matrix at 5 K. The goal of our experiments was to trap and spectroscopically interrogate the C_2X_4Br ($X = H, F$) radicals, and we have carried our extensive ab initio calculations in support of this effort. The outline of the paper is as follows. Section II describes the experimental and computational methodologies used in this work. Section III provides our results and discussion, focusing initially on the conformational distribution of the parent molecules, and moving to the photochemistry and spectroscopic and computational interrogation of the photoproducts. We close this section by discussing the implications of our results for the atmospheric and condensed phase photochemistry of these alkyl halides. Finally, section IV summarizes the main conclusions of this study.

II. Experimental and Computational Methods

Experimental Section. The matrix isolation apparatus and the experimental design are identical to those described in our earlier studies,^{20–22} and therefore, only details pertinent to these studies will be described. The EDB sample (Sigma-Aldrich, 98% stated purity) or TFEDB sample (SynQuest Laboratories, >99% stated purity) was placed into a stainless steel bubbler, which in turn was placed into a cold bath to regulate the sample vapor pressure. In both cases, the sample was purified by several freeze–pump–thaw cycles to remove any volatile impurities, and high purity Ar gas was bubbled through the sample at a typical pressure of ~ 3 bar, producing a mixture of typically 1:560 $C_2H_4Br_2/Ar$ (bath temperature = 267 K) and 1:2000 $C_2F_4Br_2/Ar$ (bath temperature = 195 K). The mixtures were deposited onto the cold KBr window held at ~ 5 K using the pulsed deposition technique;^{23–26} typical conditions were 1 ms pulse duration, 5 Hz repetition rate, and 1 h deposition time.

Following deposition, the samples were irradiated with 220 nm radiation generated from the frequency-doubled output of a dye laser system (Lambda-Physik Scanmate 2E) operating on Coumarin 440 dye, pumped by the third harmonic (355 nm) of a Nd:YAG laser (Continuum NY-61). This laser produced 10 ns pulses of 1 mJ energy at a repetition rate of 10 Hz. The photolysis beam was expanded using a 4:1 beam expander to fill the cold window and avoid damage to the cryostat optical (KBr) windows. Typically, the irradiation time was 1.5 h. Subsequently, the irradiated sample was annealed by heating the cold window to 33 K and recooling. Following each cycle of deposition, irradiation, and annealing, infrared and UV/visible spectra were taken, with the reference being the cold sample window prior to deposition. Typically, for the IR spectra 128 scans were recorded at an instrumental resolution of 2 cm^{-1} , and for the UV/visible spectrum, an integration time of 1 s was used. All spectra were transferred to a spreadsheet and analysis program (Origin 8.0) for subsequent workup.

Computational. All calculations on the parent molecules and photolysis products were performed using the Gaussian 03,

Figure 1. (a) Infrared spectrum of EDB in an Ar matrix at 5 K, with the calculated [unscaled B3LYP/6-311++G(2df,2p)] spectra for the anti and gauche conformers. The calculated spectrum indicates a 30:1 anti/gauche ratio. (b) Experimental and calculated spectra of matrix isolated TFEDB, which indicate a 3:1 anti/gauche ratio.

Gaussian 09, or GAMESS suites of electronic structure programs.^{27–29} Unconstrained geometry optimizations and frequency calculations were performed using various DFT functionals (B3LYP, CAM-B3LYP, M06, and M06-2x) and post-Hartree–Fock (MP2, CCSD) methods in combination with Pople [typically 6-311++G(2df,2p)] or Dunning’s series of correlation consistent (aug-)cc-pVnZ ($n = D, T$, and Q) basis sets. Vertical excitation energies and oscillator strengths of the electronic transitions were computed using time-dependent density functional theory. For the parent compounds, barriers to internal rotation were investigated by performing relaxed redundant coordinate scans on the ground state potential energy surface at the B3LYP/aug-cc-pVnZ ($n = D, T$) levels.

III. Results and Discussion

A. Conformational Distribution in the Matrix. Figure 1 displays IR spectra of matrix isolated EDB (a) and TFEDB (b) together with spectra of the respective anti and gauche conformers calculated at the B3LYP/6-311++G(2df,2p) level. The experimental and calculated spectra are in excellent agreement. Using the calculated intensities, we determine a conformational ratio (anti/gauche) of 30:1 for EDB and 3:1 for TFEDB. The former may be compared with a previous Ar matrix study utilizing continuous deposition that reported an anti/gauche ratio of $\sim 8:1$.³⁰ In comparison with conventional continuous deposition methods, pulsed deposition produces a transient heat load at the cold surface that leads to a transient temperature rise in the matrix surface layers and self-annealing. For systems with

Figure 2. Calculated (B3LYP/aug-cc-pVDZ) relaxed energy profiles for C–C bond rotation in TDB and TFEDB. Energies in kJ/mol.

Figure 3. IR difference spectrum following 220 nm laser photolysis of an EDB/Ar (1:560) sample at 5 K. The calculated spectrum of the gauche conformer of EDB [B3LYP/6-311++G(2df,2p)] and $C_2H_4-Br_2$ complex [MP2/aug-cc-pVTZ] are shown.

low barriers to rotation, annealing can result in substantial conformational cooling, and we believe that this is the origin of the enhanced anti/gauche ratio relative to continuous deposition; that is, $\sim 30:1$ vs $\sim 8:1$. In contrast, the higher barrier to rotation in 1,2- $C_2F_4Br_2$ results in less efficient cooling and, therefore, a smaller anti/gauche ratio ($\sim 3:1$). To characterize these barriers, we performed relaxed potential energy scans at the B3LYP/aug-cc-pVDZ level along the Br–C–C–Br dihedral for both EDB and TFEDB, as shown in Figure 2. The barriers to conformational interconversion and the relative energies of the conformers are in good agreement with previous theoretical and experimental studies.^{31–36} At this level of theory, the calculated barriers to gauche $\rightarrow$ anti interconversion are 9.8 kJ/mol for EDB and 19.6 kJ/mol for TFEDB. These increase to 11.5 and 22.6 kJ/mol, respectively, at the B3LYP/aug-cc-pVTZ level.

B. Photolysis of Matrix-Isolated EDB. The photochemistry of matrix-isolated EDB was investigated by 220 nm laser irradiation of a 1:500 EDB/Ar sample held at ~ 5 K. Figure 3 shows a difference IR spectrum following photolysis, where bands of the anti conformer decrease in intensity and the growth of bands corresponding to several distinct photoproducts are observed, including the gauche conformer and $C_2H_4-Br_2$ charge transfer complex as major products, and the C_2H_4Br radical and $C_2H_3Br-HBr$ complex as minor (trace) products. The latter was confirmed by the observation of a similar (but much more

intense) spectrum following photolysis of the 1,1-isomer, which will be reported in a future publication. Shown also in Figure 3 are calculated spectra for the gauche conformer at the B3LYP/6-311++G(2df,2p) level and the $C_2H_4-Br_2$ complex at the MP2/aug-cc-pVTZ level. Bands of the latter grow in intensity upon annealing the matrix to 33 K and recooling to 5 K. All of the primary photoproduct peaks have been assigned according to the computational predictions. In particular, the structure and spectra of the $C_2H_4-Br_2$ complex was extensively investigated using post-HF methods in combination with large basis sets, and the results are given in Tables 1 and 2. This complex has previously been studied in an Ar matrix using IR spectroscopy,³⁰ following the seminal work by Belander and co-workers on related complexes^{37–39} and in the gas-phase using microwave spectroscopy.⁴⁰ Our observed IR absorptions (960, 1338, 1441, 1612 cm^{-1}) are in excellent agreement with the previous matrix study.

Figure 4 displays UV–visible spectra for (a) the as-deposited EDB/Ar matrix, (b) the matrix following 220 nm laser irradiation, and (c) the matrix following photolysis and subsequent annealing. Upon photolysis at 220 nm, the parent band decreased and new peaks were observed: an intense band with $\lambda_{max} = 237$ nm, assigned to the $C_2H_4-Br_2$ charge transfer complex based upon ab initio predictions (Table 2), and two weaker bands ($\lambda_{max} = 260, 363$ nm) assigned to molecular bromine. Upon annealing to 33 K, the bands assigned to Br_2 decrease in intensity, and the 237 nm feature significantly increases. This is consistent with trends observed in the IR spectrum and confirms the formation and stabilization of the $C_2H_4-Br_2$ charge transfer complex in the solid Ar matrix following photolysis of EDB. This represents, to our knowledge, the first report of the UV–visible spectrum of this complex. Our reported position of the charge-transfer band is in excellent agreement with TDDFT predictions (Table 2) using the B3LYP, CAM-B3LYP, and M06 family of gradient-corrected functionals with augmented double- and triple- ζ quality basis sets.

Assuming that the IR and UV spectra sample the same region in the matrix, the integrated IR and UV absorbance can be combined with calculated IR intensities to estimate the oscillator strength of the charge transfer band. Thus, the integrated IR absorbance of the 960 cm^{-1} feature was divided by the calculated intensity (in km/mol , Table 1) to derive a column density in the matrix. The oscillator strength of a given electronic (UV/visible) band was then obtained according to the following formula:⁴¹

$$f = \frac{\int A_{UV}(\tilde{\nu}) d\tilde{\nu}}{N_{IR}} \times (1.87 \times 10^{-7} \text{ mol/km}) \quad (1)$$

where N_{IR} is the column density derived from the IR measurements. Using this approach, the derived oscillator strength of the charge transfer band is 0.51, which is very close to the TDDFT predictions (Table 2). Given the assumptions in this procedure, the level of agreement may be fortuitous; however, we have observed a similar level of agreement in other systems.²²

In the previous matrix study of the $C_2H_4-Br_2$ complex, the photochemistry of the complex was investigated by excitation at $\lambda > 300$ nm, which was presumed to access the charge-transfer band.³⁰ The observed photoproducts were the gauche and anti conformers of EDB, produced in a nearly 1:1 ratio. This was rationalized in terms of initial Br_2 bond cleavage to form a caged C_2H_4Br-Br radical pair, with subsequent cis or trans attack of

TABLE 1: Calculated Harmonic Vibrational Frequencies in cm^{-1} (intensities in km/mol) of the $\text{C}_2\text{H}_4\text{--Br}_2$ Complex

mode	B3LYP/ aug-cc-pVDZ aug-cc-pVTZ	CAM-B3LYP/ aug-cc-pVDZ aug-cc-pVTZ	M06/ aug-cc-pVDZ aug-cc-pVTZ	M062x/ aug-cc-pVDZ aug-cc-pVTZ	MP2/ aug-cc-pVDZ aug-cc-pVTZ	CCSD/ aug-cc-pVDZ
ν_1	63 (0.4) 58 (0.2)	53 (0.1) 49 (0.1)	67 (0.4) 61 (0.3)	60 (0.2) 59 (0)	70 (0.3) 70 (0.2)	50 (0.1)
ν_2	65 (0.4) 59 (0.3)	55 (0.2) 51 (0.1)	70 (0.3) 83 (0.5)	66 (0.1) 60 (0.2)	71 (0.4) 71 (0.3)	51 (0.1)
ν_3	100 (20) 86 (15)	85 (11) 76 (7)	124 (13) 135 (9)	112 (10) 111 (7)	110 (25) 107 (19)	87 (7)
ν_4	132 (0.5) 119 (0.4)	113 (0.3) 102 (0.3)	140 (0.5) 149 (0.4)	127 (0.3) 129 (0.2)	142 (0.3) 140 (0.3)	105 (0.2)
ν_5	241 (0.3) 209 (0.4)	187 (0.3) 161 (0.3)	239 (0.4) 245 (0.2)	219 (0.3) 190 (0.3)	242 (0.4) 222 (0.5)	164 (0.3)
ν_6	266 (35) 281 (28)	302 (18) 313 (13)	288 (28) 303 (20)	314 (18) 323 (13)	276 (28) 304 (24)	291 (8)
ν_7	830 (0.2) 837 (0.1)	834 (0.1) 842 (0.1)	801 (0) 803 (0)	823 (0) 835 (0)	823 (0) 823 (0)	826 (0)
ν_8	988 (0) 998 (158)	1011 (170) 1005 (163)	983 (0) 972 (146)	1019 (166) 1013 (158)	951 (0) 936 (0)	958 (0)
ν_9	1004 (159) 1000 (0.1)	1019 (0) 1021 (0)	988 (148) 976 (0)	1023 (0) 1021 (0)	991 (159) 983 (152)	988 (147)
ν_{10}	1024 (0) 1046 (0)	1048 (0) 1066 (0)	1023 (0) 1022 (0)	1048 (0) 1069 (0)	1035 (0) 1049 (0)	1032 (0)
ν_{11}	1230 (0) 1247 (0)	1237 (0) 1254 (0)	1191 (0) 1205 (0)	1223 (0) 1244 (0)	1226 (0) 1242 (0)	1234 (0)
ν_{12}	1364 (13) 1375 (11)	1377 (5) 1388 (4)	1341 (5) 1349 (4)	1371 (5) 1384 (4)	1363 (9) 1370 (7)	1370 (2)
ν_{13}	1463 (11) 1482 (10)	1467 (12) 1487 (12)	1413 (14) 1429 (13)	1452 (12) 1477 (11)	1466 (8) 1475 (9)	1473 (7)
ν_{14}	1654 (49) 1667 (39)	1696 (25) 1705 (17)	1663 (31) 1673 (26)	1687 (24) 1695 (16)	1642 (25) 1653 (18)	1674 (9)
ν_{15}	3146 (4) 3136 (5)	3163 (4) 3152 (5)	3130 (5) 3148 (4)	3159 (3) 3150 (3)	3177 (2) 3174 (2)	3152 (7)
ν_{16}	3156 (5) 3146 (4)	3178 (2) 3166 (1)	3144 (4) 3159 (2)	3174 (1) 3164 (1)	3192 (1) 3189 (0.5)	3170 (0)
ν_{17}	3231 (0) 3209 (0)	3251 (0) 3227 (0)	3217 (0) 3223 (0)	3246 (0) 3229 (0)	3277 (0) 3266 (0)	3241 (0)
ν_{18}	3258 (4) 3236 (6)	3275 (5) 3253 (6)	3245 (6) 3248 (5)	3273 (4) 3255 (4)	3304 (3) 3292 (2)	3268 (10)

TABLE 2: Calculated Wavelengths (oscillator strengths) of the Vertical Electronic Transitions of the $\text{C}_2\text{H}_4\text{--Br}_2$ Complex^a

state	B3LYP/ aug-cc-pVDZ aug-cc-pVTZ aug-cc-pVQZ	CAM-B3LYP/ aug-cc-pVDZ aug-cc-pVTZ aug-cc-pVQZ	M06/ aug-cc-pVDZ aug-cc-pVTZ aug-cc-pVQZ	M062x/ aug-cc-pVDZ aug-cc-pVTZ aug-cc-pVQZ
S_1	456.0 (0.0006) 434.3 (0.0006) 431.5 (0.0007)	426.8 (0.0005) 406.2 (0.0006) 403.6 (0.0006)	414.6 (0.0006) 395.0 (0.0006) 393.0 (0.0006)	436.9 (0.0004) 406.1 (0.0005) 404.1 (0.0005)
S_2	452.0 (0.0003) 431.7 (0.0004)	424.8 (0.0003) 404.8 (0.0004)	412.2 (0.0002) 393.3 (0.0003)	434.8 (0.0002) 404.4 (0.0003)
S_3	429.0 (0.0004) 274.4 (0.0002) 270.0 (0.5220) 269.7 (0.5138)	402.3 (0.0004) 248.5 (0.0002) 235.7 (0.0002)	391.4 (0.0003) 255.6 (0.0002) 247.1 (0.5031)	402.5 (0.0003) 245.3 (0.0002) 230.6 (0.0002)
S_4	269.7 (0.5138) 273.3 (0.0010) 259.2 (0.0001) 257.5 (0.0001)	234.3 (0.0002) 248.1 (0.0005) 235.4 (0.0006) 234.1 (0.0006)	246.7 (0.4966) 255.0 (0.0006) 241.6 (0.0001) 240.4 (0.0001)	229.6 (0.0002) 244.9 (0.0004) 230.3 (0.0008) 229.3 (0.0008)
S_5	269.7 (0.5819) 258.7 (0.0004) 257.0 (0.0004)	238.1 (0.5988) 231.3 (0.5293) 230.2 (0.5222)	252.7 (0.5903) 241.3 (0.0005) 240.1 (0.0005)	235.8 (0.5725) 224.5 (0.5533) 223.4 (0.5471)

^a The orbital configurations associated with the reported transitions are given in Table 1S of the Supporting Information.

the Br atom on the radical center leading to, respectively, gauche or anti products. Our analysis shows that excitation of the matrix-isolated complex at $\lambda > 300$ nm does not access the charge-transfer band but, rather, transitions localized on the Br_2

chromophore. In future work, we plan to selectively form this complex in the matrix by codeposition of ethylene and Br_2 using a late-mixing nozzle and investigate the photochemistry associated with charge-transfer excitation.

C. Photolysis of Matrix-Isolated TFEDB. The photochemistry of matrix-isolated TFEDB was also investigated by 220 nm laser irradiation of a 1:2000 TFEDB/Ar sample held at ~ 5 K. Figure 5 displays a difference IR spectrum following photolysis, where the parent bands decrease in intensity and

Figure 4. UV/visible spectrum of (a) an EDB/Ar (1:560) sample at 5 K, (b) the same sample following laser photolysis at 220 nm, and (c) the irradiated sample following annealing. The growth of a band at 237 nm, assigned to the $\text{C}_2\text{H}_4\text{--Br}_2$ complex, is observed.

Figure 5. IR difference spectrum following 220 nm laser photolysis of a TFEDB/Ar (1:2000) sample at 5 K. The calculated spectrum of the gauche and anti conformers of the C_2F_4Br radical at the B3LYP/aug-cc-pVTZ level are shown.

TABLE 3: Calculated Harmonic Vibrational Frequencies, in cm^{-1} (intensities in km/mol), of the Anti and Gauche Conformers of the C_2F_4Br Radical

Mode	anti		gauche	
	B3LYP/ aug-cc-pVTZ	Observed	B3LYP/ aug-cc-pVTZ	Observed
ν_1	72 (0)		59 (0.1)	
ν_2	132 (0.3)		150 (0.5)	
ν_3	211 (2)		218 (2)	
ν_4	293 (0)		297 (1)	
ν_5	295 (7)		302 (3)	
ν_6	365 (0.3)		321 (0.1)	
ν_7	513 (0)		438 (2)	
ν_8	556 (22)	564	573 (14)	574
ν_9	588 (31)	605	615 (6)	
ν_{10}	664 (36)	672	757 (23)	766
ν_{11}	838 (252)	874	923 (275)	944
ν_{12}	1130 (246)	1132	1051 (177)	1071
ν_{13}	1170 (164)		1139 (175)	1147
ν_{14}	1286 (240)	1281	1256 (240)	1263
ν_{15}	1368 (31)	1366	1332 (76)	1337

TABLE 4: Calculated Wavelengths, in nm (oscillator strengths), of the Vertical Electronic Transitions of the C_2F_4Br Radicals at the B3LYP/aug-cc-pVTZ Level

state	anti	gauche
D ₁	320.2 (0.0000)	267.6 (0.0020)
D ₂	315.2 (0.0026)	264.9 (0.0024)
D ₃	258.5 (0.0513)	253.5 (0.0050)
D ₄	221.9 (0.0001)	235.4 (0.0000)
D ₅	221.5 (0.0416)	233.8 (0.0001)

the growth of bands corresponding to the anti and gauche conformers of the one major photoproduct, the C_2F_4Br radical, are observed. The vibrational spectrum of this radical is reported here for the first time. To confirm our results, we carried out calculations of the structure and spectra of this radical at the B3LYP/aug-cc-pVTZ level. The predicted spectra are shown in the upper panel of Figure 5, and the calculated results are summarized in Tables 3 and 4. Upon annealing to 33 K, the bands attributed to the radical disappear, as expected, and bands of the anti and gauche conformers of the TFEDB parent grow in intensity.

Figure 6 displays the corresponding UV/visible spectrum of the matrix following 220 nm laser irradiation, where a new feature ($\lambda_{max} = 306$ nm) is observed that disappears upon annealing and is assigned to the C_2F_4Br radical. Using the

Figure 6. UV/visible spectrum following laser photolysis (220 nm) of a TFEDB/Ar (1:2000) sample at 5 K. Shown as a stick spectrum are the predicted transitions at the TDB3LYP/aug-cc-pVTZ level.

Figure 7. IR difference spectrum following sequential 220 and 266 nm photolysis of a TFEDB/Ar (1:2000) sample at 5 K. The disappearance of bands assigned to the gauche and anti conformers of the C_2F_4Br radical and growth of bands assigned to C_2F_4 is observed.

approach described above, the derived oscillator strength of the UV band at 306 nm is 0.05, which is very close to the TDDFT predictions for the strongest band in this region (0.052). Table 4 lists predicted vertical excitation energies and oscillator strengths of the lowest excited electronic states of the C_2F_4Br conformers.

The photochemistry of the C_2F_4Br radical was investigated by a second irradiation at 266 nm, a wavelength that does not overlap with the matrix spectrum of the TFEDB parent but strongly overlaps with the C_2F_4Br absorption feature (Figure 6). As shown in Figure 7, photolysis led to the depletion of IR absorptions assigned to the C_2F_4Br radical and the growth of bands assigned to C_2F_4 .

D. Photolysis Mechanism(s): Comparison with the Gas Phase. The observed photoproducts in the photolysis of EDB indicate a mechanism that is summarized in Figure 8. Previous gas-phase studies of the photodissociation at 248 nm show a dominant three body decay to $C_2H_4 + 2Br$,¹² or an elimination yielding $C_2H_4 + Br_2$,¹⁴ and indeed, photolysis in the matrix produces free C_2H_4 , and only a trace amount of the C_2H_4Br radical. Our results indicate that the majority of caged photoproducts recombine to yield the four observed sets of products: (1) gauche 1,2- $C_2H_4Br_2$, resulting from trans addition of Br to C_2H_4Br ; (2) anti 1,2- $C_2H_4Br_2$, resulting from cis addition; (3) the $C_2H_4-Br_2$ complex, resulting from Br abstraction or recombination following secondary decomposition; and (4) the vinyl bromide-HBr complex, resulting from H abstraction.

The structure of C_2H_4Br and related haloethyl radicals has been extensively debated in the literature. Several structures are possible: (i) a classical (nonbridged) structure, (ii) a symmetrical bridged structure, and (iii) an asymmetrical bridged structure. In 1999, Goddard and co-workers examined this question

Figure 8. Schematic mechanism for the photolysis of matrix isolated EDB.

Figure 9. A color map surface representing the (a) UB3LYP/aug-cc-pVDZ and (b) UMP2/aug-cc-pVDZ relaxed redundant coordinate scans along the C–C–Br angle and H–C–C–Br dihedral for the C_2H_4Br radical. Energies are given in kcal/mol.

theoretically using various methodologies (HF, MP2, and different DFT functionals) in combination with a 6-31G** basis set for C, H and an effective core potential for the halogen atom.¹⁸ The bridged structure was found to be the lowest energy structure for the gas-phase radical. Later, Phillips and co-workers also examined the C_2H_4Br radical using DFT methods, but considered only the classical nonbridged structure.¹⁹ We have reexamined this radical theoretically using various methods (gradient-corrected DFT, MP2, CCSD) in combination with correlation-consistent basis sets.

Figure 9 shows relaxed scans along the Br–C–C–H dihedral and the C–C–Br angle in the classical (nonbridged) C_2H_4Br radical at the (a) UB3LYP/aug-cc-pVDZ and (b) UMP2/aug-cc-pVDZ levels of theory. The classical (nonbridged) radical is the global minimum in both cases. However, whereas the

Figure 10. Relaxed redundant coordinate scans along the C–C–Br angle using different DFT and ab initio methods and the aug-cc-pVDZ basis set. The critical points extracted from this figure were used as guess structures for full geometry optimization.

symmetrically bridged radical structure is a local minimum at the UMP2 level, it is a first-order saddle point at the UB3LYP level of theory. To reduce the dimensionality of the problem and hence obtain a more accurate description, relaxed redundant coordinate scans were performed along the C–Br–Br angle in the classical (nonbridged) C_2H_4Br radical using different DFT functionals and ab initio methods (Figure 10).

The upper panel of Figure 10 shows the similar UB3LYP and UCAM-B3LYP energy profiles, which are qualitatively different from the UM06-2X, UMP2, and UCCSD results shown in the lower panel. The primary findings here are (i) the asymmetrically bridged structure is a local minimum on the UB3LYP and UCAM-B3LYP PES, but a transition state on the UM06-2x, UMP2, and UCCSD PES; (ii) the symmetrically bridged structure is a local minimum on the UM06-2x, UMP2, and UCCSD PES, but a transition state on the UB3LYP and UCAM-B3LYP PES. The relative energy of the

TABLE 5: Energies (in kcal mol⁻¹) of the Fully Optimized Transition State (TS) and Bridged Structures of C₂H₄Br Relative to the Energies of the Classical Radical

	M06-2X/ aug-cc-pVDZ aug-cc-pVTZ	MP2/ aug-cc-pVDZ aug-cc-pVTZ
TS	14.9 13.7	30.7 37.1
bridged	12.6 10.9	10.8 19.4

transition state (TS in Figure 10) seems to be overestimated at the UMP2 level. This was not corrected for by a further increase in basis set description because poor convergence with respect to further basis set increase was manifested (Table 5). On the basis of the UCCSD results, it seems that (i) the UB3LYP and UCAM-B3LYP results are in error; (ii) the UM06-2X high nonlocality functional provides a very good description of the open shell system under the scope; and (iii) although the MP2 method captures general topological features, it seems to provide a relatively poor description of the system under the scope. It is important to note that the surface topology does not depend on the choice of basis set because similar results were obtained when a triple- ζ quality basis set was used in these calculations.

The critical points extracted from Figure 10 were used as guess structures for full (unconstrained) geometry optimization, and selected results from these calculations are given in Table 5. At all levels of theory used, the bridged structure lies >10 kJ/mol above the classical, nonbridged structure, indicating that in the gas phase, the classical structure is the global minimum. Focusing on the present experimental results, these too are consistent with the predominance of the classical structure in the matrix environment for the following reasons. First, our IR spectra show no evidence of absorptions consistent with the bridged radical, although the yield of the radical is small enough that these could easily be missed. Second, and more important, if the bridged radical were formed, subsequent recombination (Figure 8) would favor the anti conformer of the parent.

In addition to the mechanisms shown in Figure 8, the C₂H₄-Br₂ complex could also be produced directly via a four-center molecular elimination, as indicated by the recent gas-phase study of Lin and co-workers,¹⁴ who reported a quantum yield of 0.36 ± 0.18 for Br₂ elimination at $\lambda = 248$ nm. Of course, it is impossible for us to distinguish between the various possible mechanisms for the formation of this complex. Following photolysis, we do observe infrared absorptions of similar intensity for “free” C₂H₄ (944 cm⁻¹) and the C₂H₄-Br₂ complex (960 cm⁻¹). Upon annealing, the latter increases in intensity at the expense of the former. Using the column densities derived above and assuming that upon recombination, the anti and gauche conformers of 1,2-C₂H₄Br₂ are produced in a 1:1 ratio,³⁰ the yield of the C₂H₄-Br₂ complex following annealing is determined to be ~ 0.13 .

Turning now to TFEDB, photolysis at 220 nm also leads initially to C-Br bond cleavage and formation of a caged •C₂F₄Br-•Br radical pair, yet the level of secondary decomposition is reduced in this case due to the stronger C-Br bond in the radical. The C₂F₄Br radical clearly has a classical nonbridged structure, in agreement with a previous theoretical study,¹⁶ and the gauche and anti conformers of the radical are produced in a nearly equal ratio (Figure 5). The recombination of the radical pairs, as observed in annealing experiments, occurs via either cis addition of the Br atom to radical center, producing the gauche conformer of TFEDB, or trans addition, producing the anti conformer. The larger yield of the radical as compared with

EDB can be attributed to the different C-Br bond strengths in the corresponding radicals.

Photolysis of TFEDB under atmospheric conditions will result in formation of the C₂F₄Br radical and a Br atom. Whether the radical undergoes secondary decomposition depends upon the photolysis wavelength. As discussed by North and co-workers,¹⁵ in the upper troposphere, the solar flux is largely concentrated at wavelengths longer than 290 nm, and for TFEDB photolysis at this wavelength, the resulting radical is stable with respect to secondary decomposition. It was therefore suggested that in the upper troposphere, this radical would rapidly react with O₂ to form a peroxy radical (C₂F₄BrO₂). However, our results show that the radical itself absorbs at these wavelengths ($\lambda_{\text{max}} = 306$ nm), and its photolysis yields C₂F₄ and Br. Using estimates for the clear sky terrestrial solar flux and our measured absorption profile and assuming a unit quantum yield for photolysis, we estimate a tropospheric photolysis rate (J) of ~ 0.2 s⁻¹ for the radical.⁴²

IV. Conclusions

We find significantly different behavior in the photolysis of two atmospherically important 1,2-dibromoethanes, EDB and TFEDB, in Ar matrixes at 5 K. Photolysis of EDB using laser irradiation at 220 nm reveals the growth of infrared bands assigned to the gauche conformer and C₂H₄-Br₂ charge transfer complex (both major products), and the C₂H₄Br radical and C₂H₃Br-HBr complex as minor (trace) products. The corresponding UV/visible spectrum shows an intense charge transfer band at 237 nm of the C₂H₄-Br₂ complex that grows in intensity upon annealing. In contrast, the photolysis of matrix-isolated TFEDB at 220 nm yields as the dominant photoproducts the anti and gauche conformers of the C₂F₄Br radical, and the vibrational and electronic spectra and photochemistry of this radical were characterized here for the first time, supported by an *ab initio* calculations. The increase in yield of radical for TFEDB vs EDB is consistent with the stronger C-Br bond in the fluoro-substituted radical species.

We find significant differences in the conformational relaxation of EDB and TFEDB, due to the different barriers to C-C bond rotation. We demonstrate that the pulsed deposition method, as compared with conventional continuous deposition methods, can lead to significant conformational relaxation for systems with low barriers to internal rotation.

Finally, we have conducted extensive *ab initio* calculations on the C₂H₄Br radical to assess whether a bridged or classical (nonbridged) structure is the global minimum. Our experimental and computational results suggest that in both the gas-phase and matrix environments the classical structure is the global minimum energy structure.

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Supporting Information Available: A table of the orbital configurations associated with the transitions reported in Table 2 and a figure of the calculated molecular orbitals for the

C₂H₄–Br₂ complex. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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