



Research paper

Matrix-isolated infrared absorption spectrum of CH₂BrOO radicalXu Zhang^{a,*}, Stanley P. Sander^{a,*}, Lan Cheng^b, Venkatesan S. Thimmakonda^b, John F. Stanton^{b,*}^aJet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109-8099, United States^bInstitute for Theoretical Chemistry, Department of Chemistry, University of Texas, Austin, TX 78712, United States

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ABSTRACT

The bromomethylperoxy radical, CH₂BrOO, has been generated in cryogenic matrices. Six fundamental bands for CH₂BrOO have been observed in an argon matrix at 5 K. The experimental frequencies (cm⁻¹) are: $\nu_4 = 1274.3$, $\nu_5 = 1229.4$, $\nu_6 = 1086.7$, $\nu_7 = 961.8$, $\nu_8 = 879.9$, and $\nu_{10} = 515.4$, two of which are detected for the first time. Ab initio calculations have been performed employing coupled-cluster methods. The experimental frequencies are shown to be in good agreement with the computation as well as the four bands (ν_4 , ν_6 , ν_7 and ν_8) observed by Huang and Lee in the gas phase.

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1. Introduction

Alkylperoxy radicals, ROO, are important intermediates in the oxidation of alkanes in the atmosphere [1]. Halogenated alkyl peroxy radicals have received attention due to the importance of chlorine (Cl) and bromine (Br) atoms in the degradation of stratospheric ozone [2–5]. For instance, bromomethylperoxy radical (CH₂BrOO) can be generated *via* reaction CH₂Br + O₂ in the atmosphere (especially in the marine boundary layer), while the CH₂Br radicals are formed *via* abstraction of a hydrogen atom from CH₃Br by OH or Cl [6,7]. The UV absorption spectrum of gaseous CH₂BrOO has been studied, revealing a broad and structureless feature at 240 nm [2,4,8]. The rate coefficient [4] of its self-reaction has been determined to be $(1.1 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Recently, the IR spectrum of CH₂BrOO has been studied by Huang and Lee [9]. CH₂BrOO radicals were produced by 248 nm photolysis of a flowing mixture of CH₂Br₂ and O₂. A step-scan Fourier-transform spectrometer coupled to a multipass absorption cell was employed to record temporally resolved infrared (IR) absorption spectra of reaction intermediates. In the IR spectrum, four vibrational bands were observed and assigned to *syn*-CH₂BrOO; they are $\nu_4 = 1276.1$, $\nu_6 = 1088.3$, $\nu_7 = 961.0$, $\nu_8 = 884.9 \text{ cm}^{-1}$. The assignment was made to *syn*-CH₂BrOO as a carrier according to the comparison of observed vibrational wavenumbers, relative IR intensities, and rotational contours with those predicted using the B3LYP/aug-cc-pVTZ method.

In this paper, we have used a different method to generate CH₂BrOO radicals, specifically *via* the reaction CH₂Br + O₂ when the reactants in tandem supersonic nozzles are deposited in a 10 K Ar matrix. Here we report the infrared absorption spectrum

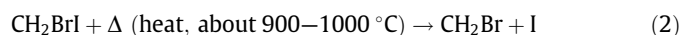
of the CH₂BrOO radical in an Ar matrix. Fundamental vibrational frequencies and infrared intensities were calculated using scalar-relativistic coupled-cluster methods. The experimental frequencies and intensities are compared to computational results as well as the results obtained by Huang and Lee in the gas phase.

2. Experimental section

Analogous to earlier studies [10,25] of matrix-isolated CH₃OO and CH₂IOO radicals, CH₂BrOO can be generated in the Ar matrix *via* reaction (1):



In this work CH₂Br radicals were generated *via* thermal decomposition of CH₂BrI (reaction (2)).



Tandem nozzles were used. The dosing nozzle for CH₂Br production is the hyperthermal nozzle described elsewhere [11]. Briefly, this consists of a resistively heated 1 mm diameter SiC tube at the output of a Parker General Valve Series 9 pulsed solenoid valve (100 Hz frequency and about 1 ms pulse width). The hyperthermal nozzle can be heated to *ca.* 1800 K to thermally dissociate a radical precursor; residence time for the radicals in the hyperthermal nozzle is approximately 100 μs. The CH₂BrI precursor (97% purity) was purchased from Aldrich. The dosing nozzle for O₂ was a continuous stainless steel tube at room temperature; a needle valve was used to adjust the dosing rate. The hyperthermal nozzle was mounted to the vacuum shroud of an Advanced Research System cryostat inside a water-cooled mini-chamber. The second valve was attached to the vacuum shroud by attaching the stainless steel tube *via* an O-ring-sealed compression fitting on the side of the shroud. These valves were positioned at a 45° angle

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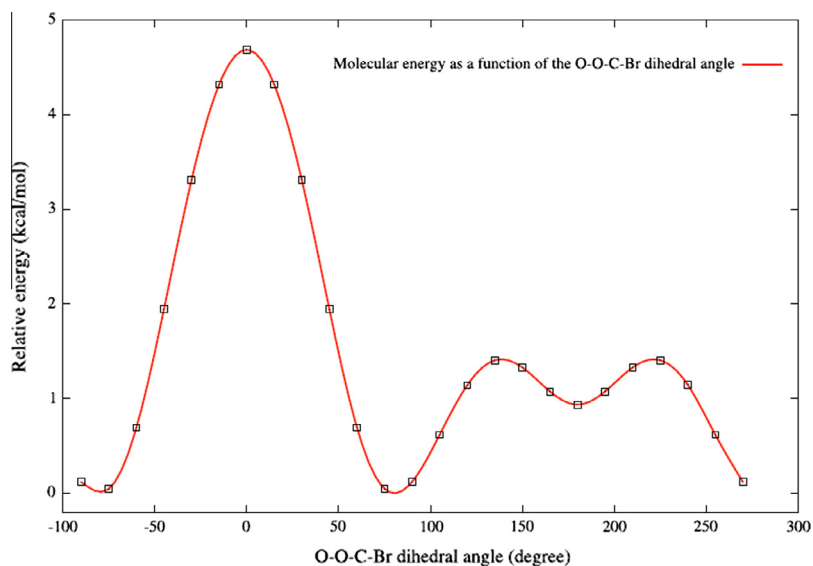


Fig. 1. Energy as a function of the torsional angle computed at SFX2C-1e-CCSD(T)/ANO0 level. Other geometrical parameters have been optimized for each torsional angle.

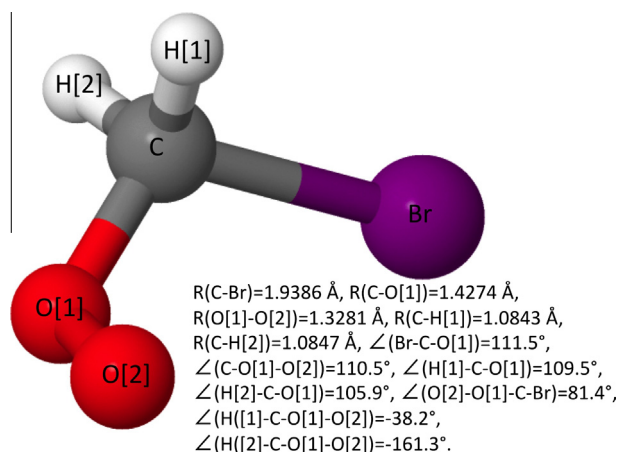


Fig. 2. The equilibrium structure of CH_2BrOO (*syn*- CH_2BrOO conformer) with C_1 symmetry computed at the SFX2C-1e-CCSD(T)/ANO1 level.

with respect to each other and were approximately 2.5 cm away from the cryogenic CsI sample window. Behind the pulsed valve for the hyperthermal nozzle was the gas mixture of CH_2BrI and Ar ($\text{CH}_2\text{BrI}:\text{Ar} \approx 1:200$) in a 1.2 L stagnation reservoir with 1.1 atm stagnation pressure. The gas mixture for the O_2 nozzle was made at approximately 0.8 atm stagnation pressure in a 4 L flask with the $\text{O}_2:\text{Ar}$ ratio at about 1:4. The pressure drop in each reservoir was measured using a capacitance manometer to determine the gas flow rate. The dosing rate for each nozzle was about 0.4 mmol per minute. The O_2 (Research grade: 99.999%) and Ar (Ultra High Purity: 99.999%) gases were purchased from Airgas. The CsI sample window was kept at 10 K during dosing (dosing time is usually a couple of hours); once the radicals were trapped in the matrix, the temperature was lowered to about 5 K and the IR spectrum of the sample was measured. Matrix spectra were recorded using a Nicolet 6700 Fourier transform infrared spectrometer equipped with a mercury/cadmium/telluride (MCT-A) detector and a Deuterated Triglycine Sulfate (DTGS) detector. The spectral resolutions of the two detectors are 0.5 and 1 cm^{-1} . The cryostat is equipped with a pair of CsI side windows to accommodate the FTIR beam.

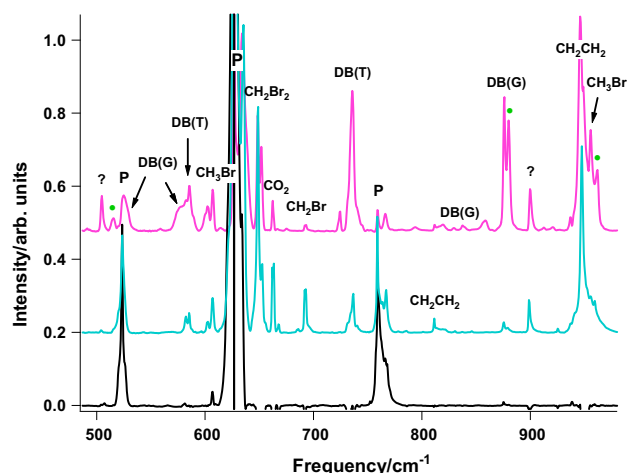


Fig. 3. IR spectra of CH_2BrOO in the $490\text{--}990 \text{ cm}^{-1}$ region. The black trace (bottom) is the spectrum of CH_2BrI at room temperature. The blue trace (middle) is the spectrum of CH_2BrI pyrolysis only at around 900°C with no added O_2 . The pink (top) trace is the spectrum of CH_2BrI pyrolysis at around 1000°C with O_2 added. As described in the text, CH_2Br and O_2 react in the 10 K Ar matrix producing CH_2BrOO . The peaks marked by a green bullet (\bullet) are assigned to CH_2BrOO . The peaks marked by **DB(T)** are assigned to $\text{BrCH}_2\text{CH}_2\text{Br}$ (1,2-dibromoethane) with *trans* conformation. The peaks marked by **DB(G)** are assigned to $\text{BrCH}_2\text{CH}_2\text{Br}$ (1,2-dibromoethane) with *gauche* conformation. And the peaks marked by **P** are assigned to the precursor CH_2BrI . The peaks marked by (?) are unknown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Ab initio calculations

Employing the CFOUR program package [12], the fundamental frequencies and infrared intensities of CH_2BrOO have been computed at the coupled-cluster singles and doubles (CCSD) augmented [13] with a perturbative treatment of triple excitations (CCSD(T)) level [14]. The spin-free exact two-component theory in its one-electron variant (SFX2C-1e) has been used [15,16] to provide a cost-effective treatment of scalar-relativistic effects. Harmonic frequencies and intensities have been calculated using atomic-natural-orbital (ANO) basis sets of triple-zeta quality (ANO1) specifically contracted for the SFX2C-1e scheme [17–19].

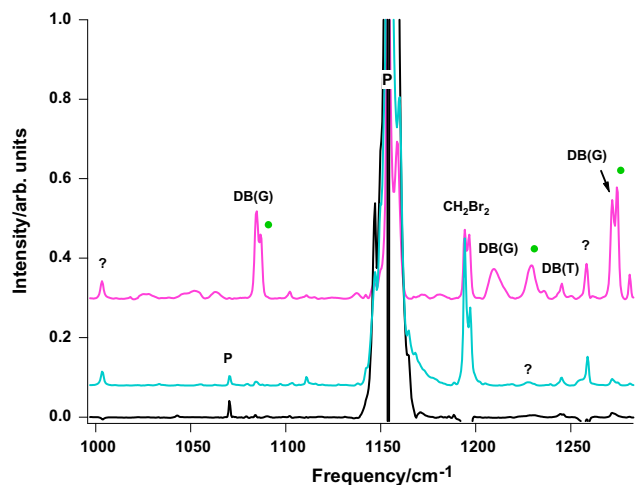


Fig. 4. IR spectra of CH_2BrOO in the $990\text{--}1290\text{ cm}^{-1}$ region. The black trace (bottom) is the spectrum of CH_2BrI at room temperature. The blue trace (middle) is the spectrum of CH_2BrI pyrolysis only at around $900\text{ }^\circ\text{C}$ with no added O_2 . The pink (top) trace is the spectrum of CH_2BrI pyrolysis at around $1000\text{ }^\circ\text{C}$ with O_2 added. As described in the text, CH_2Br and O_2 react in the 10 K Ar matrix producing CH_2BrOO . The peaks marked by a green bullet (\bullet) are assigned to CH_2BrOO . The peaks marked by **DB(T)** are assigned to $\text{BrCH}_2\text{CH}_2\text{Br}$ (1,2-dibromoethane) with trans conformation. The peaks marked by **DB(G)** are assigned to $\text{BrCH}_2\text{CH}_2\text{Br}$ (1,2-dibromoethane) with gauche conformation. And the peaks marked by **P** are assigned to the precursor CH_2BrI . The peaks marked by (?) are unknown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The anharmonic corrections to frequencies and intensities have been obtained from second-order perturbation theory [20] using linear, quadratic, and cubic force fields as well as the semi-diagonal elements of the quartic force fields computed with the corresponding double-zeta ANO (ANO0) basis sets. Thirty-four core electrons (the 1s electrons of C and O, as well as the 1s, 2s, 2p, 3s, 3p, 3d electrons of Br) have been kept frozen in all the CC calculations presented here. The geometry optimization and the computations of force fields have been greatly facilitated by the availability of the analytic gradients for the SFX2C-1e scheme [21,22] and for the CCSD(T) method [23,24] in the CFOUR program package.

4. Results

Our computational results have confirmed that the equilibrium structure of CH_2BrOO is the *syn*- CH_2BrOO conformer and has C_1

symmetry with 12 vibrational modes, all of which are infrared active. The anti- CH_2BrOO conformer (with the BrCOO dihedral angle equal to 180°) lies around 0.8 kcal/mol higher in energy, as shown in Fig. 1. Consequently, in an Ar matrix at 5 K , only the *syn*- CH_2BrOO conformer can be observed. Fig. 2 shows the equilibrium structure of CH_2BrOO (*syn*- CH_2BrOO conformer) obtained at the SFX2C-1e-CCSD(T)/ANO1 level. Two of the twelve modes are high frequency C–H vibrations with vibrational frequencies of about 3000 cm^{-1} . The difference between the vibrational frequencies of the two isotopologues $\text{CH}_2^{79}\text{BrOO}$ and $\text{CH}_2^{81}\text{BrOO}$ is less than 1 cm^{-1} for all the modes (for example, the frequency for the Br–C stretching mode in $\text{CH}_2^{81}\text{BrOO}$ is 0.8 cm^{-1} smaller than that in $\text{CH}_2^{79}\text{BrOO}$) and thus is insignificant for the present study. This is in line with the finding by Huang and Lee. Intuitively this can be attributed to the fact that the substitution of ^{79}Br with ^{81}Br does not significantly change the reduced mass of the Br–C diatomic fragment and thus does not affect the Br–C stretching frequency much. In the following we focus our discussion on $\text{CH}_2^{79}\text{BrOO}$.

The IR spectra of CH_2BrOO in the $490\text{--}990\text{ cm}^{-1}$ region are shown in Fig. 3. The black trace (bottom) is the spectrum resulting from precursor CH_2BrI only at room temperature. The blue trace (middle) shows peaks from the pyrolysis product CH_2Br as well as the precursor. Some secondary pyrolysis products are also observed including $\text{CH}_2\text{Br}\text{--}\text{CH}_2\text{Br}$ (marked as DB), CH_3Br , CH_2CH_2 and CH_2Br_2 . For 1,2-dibromoethane (or DB), there are two conformers, trans (T) and gauche (G). The assignment for the gauche conformer is tentative due to some intensity discrepancies between the literature [26] and our experiment. For example, in the literature [26] a strong band was observed at 836 cm^{-1} for the gauche conformer, but in our spectrum, the band near 836 cm^{-1} is relatively weak. Possible explanation is that in the literature the spectrum was collected at room temperature liquid phase, while our spectrum is measured in 5 K Ar matrix. The differences in the experimental conditions may cause changes in band intensities. However, more studies are needed to better understand this issue. The pink (top) trace in Fig. 3 is the spectrum of CH_2BrI pyrolysis with O_2 added. As described earlier, CH_2Br and O_2 react in the 10 K Ar matrix to produce CH_2BrOO . The peaks marked by a green bullet (\bullet) are assigned to the title peroxy radical (CH_2BrOO). Again $\text{CH}_2\text{Br}\text{--}\text{CH}_2\text{Br}$ (marked as DB), CH_3Br , CH_2CH_2 and CH_2Br_2 are observed as secondary pyrolysis products.

The IR spectra of CH_2BrOO in the $990\text{--}1290\text{ cm}^{-1}$ region are shown in Fig. 4. The black trace (bottom) is the spectrum resulting from precursor CH_2BrI only at room temperature. The blue trace (middle) shows peaks from the pyrolysis product CH_2Br as well as the precursor. Also shown are secondary pyrolysis products

Table 1
 CH_2BrOO fundamental vibrational modes from this work and earlier study by Huang and Lee.

| This work | | Ar matrix IR/10 K | | | | CCSD(T) | | | Huang and Lee [9] ^a | |
|-----------|-------------------------------------|----------------------------|-------------|----------------------------|----------------------------|-------------|----------------------------|----------------------------|--------------------------------|-------|
| Mode | Description | ν (cm^{-1}) | A ratio (%) | ν (cm^{-1}) | A (km mol^{-1}) | A ratio (%) | ν (cm^{-1}) | ν (cm^{-1}) | Calc. | |
| 1 | C–H asym stretch | na | | 3058 | 0 | 0 | na | 3054.1 | (3) | |
| 2 | C–H sym stretch | na | | 2989 | 7 | 22 | na | 2985.8 | (11) | |
| 3 | C–H scissor/umbrella | na | | 1424 | 2 | 7 | na | 1413.5 | (8) | |
| 4 | C–H umbrella/scissor | 1274.3 ± 1.5 | 68 ± 13 | 1278 | 34 | 98 | 1276.1 | (109) | 1265.8 | (84) |
| 5 | C–H rocking | 1229.4 ± 2.6 (T) | 28 ± 10 | 1229 | 8 | 23 | 1243 | (?) | 1233.5 | (26) |
| 6 | O–O stretch | 1086.7 ± 1.5 | 35 ± 7 | 1086 | 20 | 56 | 1088.3 | (51) | 1103.3 | (42) |
| 7 | C–O stretch | 961.8 ± 2.2 | 75 ± 20 | 957 | 26 | 75 | 961.0 | (66) | 943.6 | (61) |
| 8 | C–H, C–Br scissor | 879.9 ± 1.7 | 100 | 882 | 35 | 100 | 884.9 | (100) | 858.1 | (100) |
| 9 | C–Br stretch | na | | 637 | 38 | 109 | na | | 609.9 | (150) |
| 10 | O–O–C bend/torsion and C–Br stretch | 515.4 ± 2.0 (T) | 14 ± 3 | 504 | 10 | 28 | na | | 500.3 | (26) |
| 11 | Torsion/Br–C–O bend/C–Br stretch | na | | 286 | 1 | 2 | na | | 279.2 | (3) |
| 12 | Torsion | na | | 89 | 1 | 3 | na | | 82.6 | (3) |

T: Tentative assignment. A: Integrated IR intensities (in km mol^{-1}); A ratio: Ratio of integrated IR intensities relative to ν_8 mode (in%).

^a A ratio values (in%) are listed in parentheses. And (?) means tentative assignment because of small intensity.

including CH₂Br–CH₂Br (marked as DB), CH₃Br, CH₂CH₂ and CH₂Br₂. The pink (top) trace in Fig. 4 is the spectrum of CH₂BrI pyrolysis with O₂ added. The peaks marked by a green bullet (●) are assigned to the title peroxy radical (CH₂BrOO). Again CH₂Br–CH₂Br (or DB), CH₃Br, CH₂CH₂ and CH₂Br₂ are observed as secondary pyrolysis products.

Table 1 lists the matrix IR bands of CH₂BrOO along with our calculated band positions and intensities. Six fundamental vibrational modes (ν_4 , ν_5 , ν_6 , ν_7 , ν_8 and ν_{10}) are observed. All experimental frequencies are in reasonable agreement with our calculations. For the four bands (ν_4 , ν_6 , ν_7 and ν_8) previously observed by Huang and Lee, our experimental results compare favorably with the previous report as well as our computational results (all within 5 cm⁻¹). The two new bands that we observed, ν_5 and ν_{10} , are in good agreement with our calculations. Since the band intensity for ν_{10} is small, it is marked as tentative (or T). ν_5 is also marked as tentative due to some interference by a peak from an unknown species. The band intensities are in reasonable agreement among our experimental results, our calculations and the results by Huang and Lee.

To conclude, the matrix-isolated IR absorption spectrum of the bromomethylperoxy radical CH₂BrOO has been detected in an Ar matrix. Six vibrational bands of the CH₂BrOO radical in a 5 K Ar matrix have been observed: $\nu_4 = 1274.3$, $\nu_5 = 1229.4$, $\nu_6 = 1086.7$, $\nu_7 = 961.8$, $\nu_8 = 879.9$, and $\nu_{10} = 515.4$. Two of them, ν_5 and ν_{10} , are observed for the first time.

Acknowledgements

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