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Citation: The Journal of Chemical Physics 141, 164302 (2014); doi: 10.1063/1.4897982
View online: http://dx.doi.org/10.1063/1.4897982
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/141/16?ver=pdfcov
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Infrared absorption of gaseous CH₂BrOO detected with a step-scan Fourier-transform absorption spectrometer

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(Received 21 August 2014; accepted 1 October 2014; published online 22 October 2014)

CH₂BrOO radicals were produced upon irradiation, with an excimer laser at 248 nm, of a flowing mixture of CH₂Br₂ and O₂. A step-scan Fourier-transform spectrometer coupled with a multipass absorption cell was employed to record temporally resolved infrared (IR) absorption spectra of reaction intermediates. Transient absorption with origins at 1276.1, 1088.3, 961.0, and 884.9 cm⁻¹ are assigned to ν₄ (CH₂-wagging), ν₅ (O–O stretching), ν₇ (CH₂-rocking mixed with C–O stretching), and ν₈ (C–O stretching mixed with CH₂-rocking) modes of CH₂BrOO, respectively. The assignments were made according to the expected photochemistry and a comparison of observed vibrational wavenumbers, relative IR intensities, and rotational contours with those predicted with the B3LYP/aug-cc-pVTZ method. The rotational contours of ν₇ and ν₈ indicate that hot bands involving the torsional (ν₄) mode are also present, with transitions 7ν₁2e and 8ν₁2e, ν = 1–10. The most intense band (ν₂₂) of anti-CH₂BrOO near 1277 cm⁻¹ might have a small contribution to the observed spectra. Our work provides information for directly probing gaseous CH₂BrOO with IR spectroscopy, either in the atmosphere or laboratory experiments. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4897982]

I. INTRODUCTION

Bromomethylperoxy radical (CH₂BrOO) is an important intermediate in the oxidation of brominated methanes in the atmosphere, especially in marine regions.¹⁻⁵ Initiation of the oxidation proceeds via abstraction of a hydrogen atom of CH₃Br, which is the main source of stratospheric bromine,⁶ by OH or Cl to form the CH₂Br radical.⁷,⁸ The CH₂Br radical reacts readily with ambient O₂ to form the CH₂BrOO radical.⁹,¹⁰ The main decay processes of CH₂BrOO radical would be either its self-reaction¹¹,¹² or reaction with other atmospheric constituents such as NO¹³ and HO₂.¹¹ These reactions might lead to the production of free bromine atoms that are engaged in the depletion of stratospheric ozone with high efficiency.¹⁴⁻¹⁶

Nielsen et al. reported UV absorption spectrum of the B2A′′ ← X 2A′ transition of the gaseous CH₂BrOO radical, produced from the reaction of F + CH₃Br in O₂ using pulse radiolysis.¹² The spectrum was later revised because of partial interference by the absorption of the CH₃Br-F adduct.¹⁷ The revised spectrum agrees satisfactorily with that reported by Villenave and Lesclaux,¹¹ who employed the reaction Cl + CH₂Br in O₂ to produce gaseous CH₂BrOO radicals. The spectrum resembles those of most alkyl and halogen-substituted alkylperoxy radicals, showing a broad feature without structure with a maximal cross section of σ = (3.59 ± 0.11) × 10⁻¹⁸ cm² molecule⁻¹ at 240 nm. This reported cross section was used to monitor the concentration of CH₂BrOO in the study of its self-reaction,

CH₂BrOO + CH₂BrOO → 2CH₂BrO + O₂ and other products, (1)

to determine a rate coefficient of k₁ = (1.1 ± 0.4) × 10⁻¹² cm³ molecule⁻¹s⁻¹ at 298 K.¹¹ The CH₂BrO thus formed is reported to undergo subsequent unimolecular decomposition,¹⁸,¹⁹

CH₂BrO → H₂CO + Br. (2)

The end products observed for the self-reaction of CH₂BrOO are H₂CO, CO, and H(Br)CO.¹²,¹⁸

As the intense UV absorption of the B ← X transition employed in kinetic investigations has no distinct structure, selective detection among various alkylperoxy radicals is precluded. Even though the A ← X transition of CH₂BrOO is expected to have some vibronic progressions, similar to those reported for CH₃OO and CD₃OO,²⁰ this transition is expected to be weak; no observation of the A ← X transition of CH₂BrOO has been reported. There is no report of the infrared (IR) or microwave spectrum of CH₂BrOO.

We have demonstrated that time-resolved Fourier-transform infrared (FTIR) absorption spectra of transient intermediates in gaseous reactions can be detected with a step-scan Fourier-transform infrared spectrometer coupled with a multipass absorption cell.²¹,²² The IR absorption spectra of several alkylperoxy radicals, such as CH₃OO,²³ cis-CH₃C(O)OO and trans-CH₃C(O)OO,²⁴ and cis-C₆H₅C(O)OO,²⁵ have been identified with this method. Here, we report an application of this technique to record the IR absorption spectra of gaseous CH₂BrOO radical.

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II. EXPERIMENTS

Detailed description of our experimental setup has been published previously.\textsuperscript{21} Briefly, a White cell with a base path of length 15 cm and an effective path of length 3.6 m was placed in the external port of a step-scan Fourier-transform spectrometer (Bruker, Vertex 80v). The White cell, of volume $\sim 1.4 \text{ L}$, accommodates two rectangular quartz windows ($3 \times 12 \text{ cm}^2$) to pass photolysis beams that propagate perpendicularly to multi-passing IR beams. A KrF excimer laser (Lambda Physik, CompexPro 102F, 11 Hz, $\sim 176 \text{ mJ pulse}^{-1}$, beam size $1.3 \times 0.9 \text{ cm}^2$) emitting at 248 nm passed through these quartz windows and was reflected six times with two external laser mirrors to photodissociate a flowing mixture of $\text{CH}_2\text{Br}_2$ and $\text{O}_2$.

We obtained temporally resolved difference absorption spectra from interferograms recorded consecutively with ac- and dc-coupled signals. The preamplified ac- and dc-coupled signals from the MCT detector were sent directly to the internal 24-bit analogue-to-digital converter (ADC) of the spectrometer. Typically, 100 data points were acquired at 12.5-\(\mu\text{s}\) integrated intervals for a period 1250 \(\mu\text{s}\) after photolysis; the signal was typically averaged over 15 laser shots at each scan step. With appropriate optical filters to define a narrow spectral region, we performed undersampling to decrease the number of points in the interferogram, hence the duration of data acquisition. For spectra in the range 800–3949 cm\(^{-1}\) at resolution 4.0 cm\(^{-1}\), 1999 scan steps were completed within $\sim 1 \text{ h}$. For spectra in the range 800–1500 cm\(^{-1}\) at resolution 0.5 cm\(^{-1}\), 3046 scan steps were completed within $\sim 1.5 \text{ h}$. To improve further the ratio of signal to noise, we recorded and averaged nine sets of data under similar experimental conditions. The instrumental resolution is listed in the text unless otherwise noted; the effective full-width at half-maximum (FWHM) after apodization with the Blackman-Harris 3-Term function is $\sim 128\%$ of the listed instrumental resolution.

$\text{O}_2$ was employed as both a reactant and an efficient quencher. A stream of $\text{N}_2$ was bubbled through liquid $\text{CH}_2\text{Br}_2$ before entering the reactor. Experimental conditions were as follows: flow rates $F_{\text{CH}_2\text{Br}_2} \equiv 0.07$, $F_{\text{N}_2} \equiv 0.2$ and $F_{\text{O}_2} \equiv 23.7 \text{ STP cm}^3 \text{ s}^{-1}$ (STP denotes standard temperature 273.15 K and pressure 1 atm); total pressure $\sim 86 \text{ Torr}$; $T = 298 \text{ K}$. The efficiencies of photolysis of $\text{CH}_2\text{Br}_2$ are estimated to be $\sim 5\%$ based on the absorption cross section of $\sim 2.7 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ at 248 nm\textsuperscript{26} and the laser fluence $\sim 1.9 \times 10^{17} \text{ photons cm}^{-2}$. $\text{CH}_2\text{Br}_2$ (99%, Alfa Aesar) and $\text{O}_2$ (99.999%) were used without further purification.

III. COMPUTATIONS

The equilibrium geometry, vibrational wavenumbers, IR intensities, and rotational parameters of $\text{CH}_2\text{Br}_2$ and $\text{CH}_2\text{Br}_2$ were calculated with the B3LYP density-functional theory using the Gaussian 09 program.\textsuperscript{27} The B3LYP method uses Becke’s three-parameter hybrid exchange functional with a correlation functional of Lee, Yang, and Parr.\textsuperscript{28, 29} Dunning’s correlation-consistent polarization-valence triple-zeta basis set, augmented with s, p, d, and f functions (aug-cc-pVTZ)\textsuperscript{30, 31} was applied in these calculations. Analytic first derivatives were utilized in geometry optimization and vibrational wavenumbers were calculated analytically at each stationary point. The predictions of the corresponding anharmonic wavenumbers are also carried out by calculating the analytical second derivatives. Rotational parameters for each vibrational state ($v_1 = 1$) were also calculated.

Geometries of $\text{CH}_2\text{Br}_2$ and $\text{CH}_2\text{Br}_2$ were calculated with the B3LYP/aug-cc-pVDZ and MP2/6-31G(d) methods have been reported;\textsuperscript{32–35} they are compared with those calculated with the B3LYP/aug-cc-pVTZ method in Fig. 1. These predicted values deviate within $1\%$ with previous results except the C–H bond length of $\text{anti-CH}_2\text{Br}_2$, which might be due to a typing error in previous reports.\textsuperscript{33, 34} Two stable conformers of $\text{CH}_2\text{Br}_2$ exist. The $\text{anti-CH}_2\text{Br}_2$ conformer was optimized with the $C_i$ symmetry, but geometry optimization without symmetry restriction converged to the $\text{syn-CH}_2\text{Br}_2$ conformer, which is 3.1 kJ mol\(^{-1}\) more stable than $\text{anti-CH}_2\text{Br}_2$. The Br–C–O–O dihedral angle of $\text{syn-CH}_2\text{Br}_2$ is 86.9°, whereas the Br–C–O–O skeleton of $\text{anti-CH}_2\text{Br}_2$ is planar. Compared with the corresponding bonds of $\text{anti-CH}_2\text{Br}_2$, $\text{syn-CH}_2\text{Br}_2$ has a shorter C–O bond and a longer C–Br bond.\textsuperscript{53} Rotational parameters for the equilibrium geometry, the vibrational ground state, and excited states ($v_1 = 1$) of each vibrational mode of the two conformers of $\text{CH}_2\text{Br}_2$ were calculated with the B3LYP/aug-cc-pVZ method; the ratios of $A'/A''$, $B'/B''$, and $C'/C''$, in which the prime and double primes indicate the vibrationally excited and ground states, respectively, are listed in Table I. The corresponding values of $\text{CH}_2\text{Br}_2$ are listed in Table SI of the supplementary material;\textsuperscript{36} they are nearly the same as those of $\text{CH}_2\text{Br}_2$.

Harmonic and anharmonic vibrational wavenumbers, IR intensities, and approximate mode descriptions of $\text{CH}_2\text{Br}_2$ predicted with the B3LYP/aug-cc-pVTZ method are listed in Table II; those of $\text{anti-CH}_2\text{Br}_2$ are listed in Table III. Corresponding values of $\text{CH}_2\text{Br}_2$ deviate from...
those of CH$_2$BrOO within 1 cm$^{-1}$ so they are not listed. Bands of CH$_2$BrOO with anharmonic vibrational wavenumbers greater than 750 cm$^{-1}$, the lower limit of our spectral detection, are predicted at 3054 ($\nu_1$), 1277 ($\nu_2$), 1157 ($\nu_3$), 1143 ($\nu_4$), 887 ($\nu_5$), and 883 ($\nu_6$) cm$^{-1}$ for syn-CH$_2$BrOO and 3034 ($\nu_1$), 2995 ($\nu_2$), 1442 ($\nu_3$), 1277 ($\nu_4$), 1157 ($\nu_5$), 1143 ($\nu_6$), 887 ($\nu_7$), and 883 ($\nu_8$) cm$^{-1}$ for anti-CH$_2$BrOO.

Predicted displacement vectors (thin arrows), the associated dipole derivatives (thick arrows), and the three rotational axes $a$, $b$, and $c$ (arrows with dashed lines) for each vibrational mode of syn-CH$_2$BrOO are available in Fig. S1 of the supplementary material. The squares of the projections of dipole derivative onto the three rotational axis for each vibrational mode of CH$_2$BrOO determine the mixing ratios of bands of types $a$, $b$, and $c$ in each transition.

### IV. RESULTS AND DISCUSSION

Although previous researchers on UV absorption experiments used the reaction of F or Cl with CH$_3$Br to generate CH$_2$Br for its reaction with O$_2$, we employed photolysis of CH$_2$Br$_2$ as the source of CH$_2$Br because of its ease of operation and less interference. As a test, conventional FTIR measurements were performed with a static cell containing CH$_2$Br$_2$ (1.2 Torr) and O$_2$ (87 Torr). The end products were identified as H$_2$CO (at 1500, 1746, and 2782 cm$^{-1}$), HBr/CO (at 1271 and 1798 cm$^{-1}$), CH$_2$BrOO (at 1214 cm$^{-1}$), and CO$_2$ (at 2349 cm$^{-1}$). These end products except CO$_2$ agree with those obtained by UV photolysis of a mixture of CH$_3$Br (1 Torr) and Cl$_2$ (0.5 Torr) in 700 Torr of air.

### A. Photolysis of CH$_2$Br$_2$ in O$_2$

To avoid the interference from internally excited reactants and products, we employed excessive O$_2$ in the reactor to serve as both a reactant and a quencher to thermalize CH$_2$Br$_2$, CH$_2$BrOO, and other products upon UV irradiation. Representative survey spectra (resolution 4 cm$^{-1}$) recorded before and after irradiation, with an excimer laser at 248 nm, of a flowing mixture of CH$_2$Br$_2$ (0.25 Torr), N$_2$ (0.60 Torr), and O$_2$ (85.1 Torr) at 298 K are shown in Figs. 2(a)–2(e), respectively. Difference spectra were recorded after irradiation; traces (b)–(d) were recorded at 25–$\mu$s intervals, whereas trace (e) was recorded during 250–275 $\mu$s after irradiation. In these difference spectra, features pointing upward indicate production, whereas those pointing downward indicate destruction. The downward features of the parent compound, near 1195 cm$^{-1}$, are due to destruction of CH$_2$Br$_2$ upon irradiation. New features in a group near 885, 960, 1090, and 1275 cm$^{-1}$,
designated group A, appeared immediately upon irradiation and decayed rapidly with a decay time constant $\sim 130 \mu$s. The feature near 1015 cm$^{-1}$, designated as B, showed temporal behavior distinct from features in group A; it increased in intensity to reach its maximum near 90 $\mu$s after irradiation. Weak absorption of internally excited CO$_2$ and CO appeared immediately upon UV irradiation and became thermalized near 150 $\mu$s.

**B. Assignments of bands A1–A4 to CH$_2$BrOO**

The major product on photolysis of CH$_2$Br$_2$ was reported to be CH$_2$Br; CH$_2$Br subsequently reacts with O$_2$ to form CH$_2$BrOO,$^9,10$

$$\text{CH}_2\text{Br} + \text{O}_2 + \text{M} \rightarrow \text{CH}_2\text{BrOO} + \text{M},$$  

with a rate coefficient of $k_1(T) = 1.2 \times 10^{-30} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$ for the termolecular reaction with M = He in the temperature range of 241–363 K.$^9$ At 298 K and 86 Torr, this reaction is expected to be completed within 1 $\mu$s. Although the reaction of CH$_2$I with O$_2$ produces the important Criegee intermediate CH$_2$OO, the corresponding reaction,

$$\text{CH}_2\text{Br} + \text{O}_2 \rightarrow \text{CH}_2\text{OO} + \text{Br},$$  

is endothermic by 51 kJ mol$^{-1}$.$^{10,32}$ the reaction might proceed only when CH$_2$Br has enough applicable energy to overcome the barrier of height $\sim 51$ kJ mol$^{-1}$. The observed bands in group A disagree with those observed for CH$_2$OO because the IR spectrum of gaseous CH$_2$OO has been well characterized,$^{22}$ with vibrational wavenumbers $\nu_3 = 1435$, $\nu_4 = 1286$, $\nu_5 = 1241$, $\nu_6 = 908$, and $\nu_8 = 848$ cm$^{-1}$.

Possible secondary reactions in this system are

$$\text{CH}_2\text{BrOO} + \text{CH}_2\text{BrOO} \rightarrow 2\text{CH}_2\text{BrO} + \text{O}_2 \text{ and other products},$$  

$^{1'}$

**FIG. 2.** Survey spectra of transient differential absorption spectra recorded upon 248-nm photolysis of a flowing mixture of CH$_2$Br$_2$/O$_2$/N$_2$ ($\sim$1/24/340, 86 Torr, 298 K). Path length is 3.6 m; resolution is 4.0 cm$^{-1}$. (a) Spectrum of CH$_2$Br before irradiation. (b)–(e) Spectra recorded 0–25, 25–50, 50–75, and 250–275 $\mu$s after irradiation; bands in group A and B are indicated.

**FIG. 3.** Comparison of the observed spectrum with simulated spectra of possible candidates. (a) Difference absorption spectrum recorded 0–25 $\mu$s after 248-nm photolysis of a flowing mixture of CH$_2$Br$_2$/O$_2$/N$_2$ ($\sim$1/24/340, 86 Torr, 298 K); IR spectra of syn-CH$_2$BrOO (b), anti-CH$_2$BrOO (c), CH$_2$BrO (d), and CH$_2$BrOOBr (e) simulated with rotational parameters, vibrational wavenumbers, and IR intensities predicted with the B3LYP/aug-cc-pVTZ method. The integrated absorbance of predicted bands represents the predicted IR intensities.

$$\text{CH}_2\text{BrO} \rightarrow \text{H}_2\text{CO} + \text{Br},$$  

(2')

$$\text{CH}_2\text{BrOO} + \text{CH}_2\text{Br} \rightarrow \text{CH}_2\text{BrO} + \text{CH}_2\text{BrO},$$  

(5)

$$\text{CH}_2\text{BrOO} + \text{Br} \rightarrow \text{CH}_2\text{BrOOBr},$$  

(6)

The rate coefficient of reaction (1') is reported to be $k_1 = 1.1 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ at 298 K (Ref. 11) and reaction (2') is reported to occur rapidly.$^{18,19}$ We thus expect that, in addition to CH$_2$BrOO, other possible species responsible for the observed new features might be CH$_2$BrO and CH$_2$BrOOBr. IR spectra of syn-CH$_2$BrOO and anti-CH$_2$BrOO in the region 800–1400 cm$^{-1}$ simulated with anharmonic vibrational wavenumbers, IR intensities, and rotational parameters predicted with the B3LYP/aug-cc-pVTZ method are shown in Figs. 3(b) and 3(c), respectively; simulation of rotational contours is discussed later. IR spectra of CH$_2$BrO and CH$_2$BrOOBr simulated with the same method are shown in Figs. 3(d) and 3(e), respectively; the parameters used are listed in Table SII of the supplementary material.$^{36}$

Bands observed near 885, 960, 1090, and 1275 cm$^{-1}$ clearly agree satisfactorily with those predicted at 858, 944, 1103, and 1266 cm$^{-1}$ for syn-CH$_2$BrOO, with deviations less than 3%. The $\nu_3$ band predicted at 1234 cm$^{-1}$ might correspond to a weak band near 1243 cm$^{-1}$, but its identification is uncertain because of its small intensity. The contribution of anti-CH$_2$BrOO is expected to be small because of its higher energy, but its presence cannot be positively excluded because its $\nu_3$ and $\nu_4$ bands are predicted to be weak, and the intense $\nu_4$ band might be overlapped with that of syn-CH$_2$BrOO. Predicted bands of CH$_2$BrO and CH$_2$BrOOBr disagree with our observations for neither band position nor rotational contour.
To support further the assignments of bands in group A to syn-CH2BrOO, we recorded the spectra under similar experimental condition at instrument resolution 0.5 cm\(^{-1}\) (effective FWHM 0.64 cm\(^{-1}\)) and simulated the band contour using the molecular parameters predicted with the B3LYP/aug-cc-pVTZ method for comparison. No experiment with higher resolution was attempted because the rotational parameters of CH2BrOO are small and partial resolution of the rotational structures with our current setup is unlikely. Figs. 4(a) and 4(b) show the spectra recorded 0–25 and 1000–1125 \(\mu\)s after laser irradiation, respectively. As the observed bands \(A_3\) and \(A_4\) in Fig. 4(a) near 1090 and 1275 cm\(^{-1}\) are overlapping with the absorption of \(\text{H}_2\text{CO}\) and \(\text{H(Br)CO}\), respectively, the contributions from these two species were separately subtracted by spectral stripping of the corresponding bands of \(\text{H}_2\text{CO}\) and \(\text{H(Br)CO}\) shown in Fig. 4(b) to yield the corrected spectrum shown in Fig. 4(c).

With the PGopher program,\(^{36}\) we simulated the spectrum of each band using predicted ratios of rotational parameters \(A', A'', B', B'', C',\) and \(C''\) (listed in Table I), \(J_{\text{max}} = 140, T = 298\) K, and a Gaussian width 0.64 cm\(^{-1}\). Simulated \(a-, b-,\) and \(c\)-type spectra for \(v_g\) \(v_{6g}-v_8\) of syn-CH2BrOO are shown in Fig. S2 of the supplementary material.\(^{36}\) The projections of the dipole derivatives for each vibrational mode of syn-CH2BrOO, shown in Fig. S1 of the supplementary material.\(^{36}\) onto rotational axes \(a, b,\) and \(c\) determine the weighting of bands of types \(a, b,\) and \(c\) in each vibrational absorption band. The resultant rotational contours according to these weighting factors are shown also as the bottom trace for each vibrational band in Fig. S2 of the supplementary material.\(^{36}\)

The corrected \(A_3\) band near 1090 cm\(^{-1}\) recorded 0–25 \(\mu\)s upon irradiation at resolution 0.5 cm\(^{-1}\) is shown in Fig. 5(a) with open circles and compared with the O–O stretching \((v_{6g})\) band, simulated for syn-CH\(_2\)\(^79\)BrOO and syn-CH\(_2\)\(^81\)BrOO with predicted spectral parameters, as shown in Fig. 5(b). This band is mostly \(a\)-type with a significant Q branch; the weighting of types \(a, b, c = 0.75:0.11:0.14\). The difference between the simulated bands of syn-CH\(_2\)\(^79\)BrOO and syn-CH\(_2\)\(^81\)BrOO is negligibly small. Using a population ratio of syn-CH\(_2\)\(^79\)BrOO: syn-CH\(_2\)\(^81\)BrOO = 50.7:49.3, the resultant simulated spectrum is shown as a solid curve in Fig. 5(a); it agrees satisfactorily with experiments. The fitted vibrational wavenumber is \(v_{6g} = 1088.3\) cm\(^{-1}\).

The observed \(A_3\) band near 885 cm\(^{-1}\) recorded, at resolution 0.5 cm\(^{-1}\), 0–25 \(\mu\)s upon irradiation (open circles, Fig. 6(a)) is compared with the \(v_g\) band simulated for syn-CH\(_2\)\(^79\)BrOO and syn-CH\(_2\)\(^81\)BrOO with predicted spectral parameters (Fig. 6(b)); this mode is approximately described as the C–O stretching mode coupled with the CH2-rocking mode. This band is mostly \(a\)-type with a weighting factor of types \(a:b:c = 0.92:0.02:0.06\). Similarly to \(v_{6g}\), the simulated bands of syn-CH\(_2\)\(^79\)BrOO and syn-CH\(_2\)\(^81\)BrOO are nearly identical. Using a population ratio of syn-CH\(_2\)\(^79\)BrOO: syn-CH\(_2\)\(^81\)BrOO = 50.7:49.3, the resultant simulated spectrum is shown as a solid curve in Fig. 6(a), which differs significantly from our experimental observation. We noticed a series of Q-bands in the structure of the observed spectrum and suggest that this series might be contributed by hot bands from levels of the low-energy vibrational mode. The smallest vibrational wavenumber of syn-CH\(_2\)BrOO is predicted to be 83 cm\(^{-1}\) for the torsional \((v_{12})\) mode. We located the positions of the first four Q-bands in the observed spectrum, and consequently assumed that the shifts for additional bands from absorption initiated from vibrationally excited levels of \(v_{12}\) due to anharmonicity are regular, the contours of the hot bands are similar to that of the fundamental, and the population distributions of these excited levels of \(v_{12}\) are Boltzmann. We obtained a satisfactory fit of our observed spectrum to a simulated spectrum comprising the fundamental and ten additional hot bands, \(^{81}12^{,12}\) with \(v = 0–10\). The contribution of each component is shown in Fig. 6(d) and the resultant spectrum (solid line) is compared with experimental observation in Fig. 6(c). The fitted fundamental vibrational wavenumber of \(v_{6g}\) is 884.9 cm\(^{-1}\); the peak positions and relative populations of other components are presented in Table IV.
The observed $A_2$ band near 960 cm$^{-1}$ recorded 0–25 $\mu$s upon irradiation at resolution 0.5 cm$^{-1}$ (open circles, Fig. 7(a)) is compared with the $v_7$ band simulated for syn-CH$_2$BrOO and syn-CH$_2$BrOO with predicted spectral parameters (Fig. 7(b)); this mode is approximately described as the CH$_2$-rocking mode coupled with C–O stretching mode. This band is mostly type $a$ with a significant Q branch; the weighting of types $a$: $b$ is 0.98:0.02. Similarly to $v_6$, no difference between the simulated bands of syn-CH$_2$BrOO and syn-CH$_2$BrOO is discernible; the simulation of these two bands with origins both at 960.3 cm$^{-1}$ and a population ratio of CH$_2$BrOO:CH$_2$BrOO = 50.7:49.3 yielded a spectrum shown as a solid curve in Fig. 7(a), which shows some small deviations from the experimental results. The Q-branch in the experimental spectrum is smaller and broader than the simulated one. We consider that this effect might be due to (1) a slightly greater width needed for the simulated spectrum or (2) contributions of hot bands from $v_{12}$. The simulated

\begin{table}
\centering
\begin{tabular}{lcccc}
\hline
\textbf{Band origin (cm$^{-1}$)} & \textbf{$v_7^{12}$} & \textbf{$v_7^{12}$} & \textbf{Relative population} \\
\hline
0 & 961.0 & 884.9 & 1.00 \\
1 & 960.1 & 883.0 & 0.67 \\
2 & 959.3 & 881.4 & 0.46 \\
3 & 958.5 & 879.9 & 0.33 \\
4 & 957.8 & 878.4 & 0.24 \\
5 & 957.1 & 877.1 & 0.18 \\
6 & 956.5 & 875.9 & 0.14 \\
7 & 956.0 & 874.9 & 0.11 \\
8 & 955.5 & 874.0 & 0.10 \\
9 & 955.2 & 873.2 & 0.08 \\
10 & 954.8 & 872.6 & 0.07 \\
\hline
\end{tabular}
\caption{Band origins and relative populations of the fundamental and hot bands of $7^{12}$ and $8^{12}$.}
\end{table}
spectrum with additional Lorentzian width of 0.5 cm\(^{-1}\) (solid line) is compared with experimental results (open circle); the agreement became improved, as illustrated in Fig. 7(c). We tried also to simulate the spectrum by considering hot bands of \(7_1^1\) and \(7_1^1\) with a smaller anharmonic shift (50\% of the spacing of \(8_1^1\); hot bands) and a similar Boltzmann distribution as \(8_1^1\). The resultant simulation with a fitted fundamental vibrational wavenumber 961.0 cm\(^{-1}\) of \(ν_7\) is shown as a solid curve in Fig. 7(d), which also agrees with the experimental spectrum. The contribution of each component is shown in Fig. 7(e); the fitted peak positions of individual bands are presented in Table IV.

The observed \(A_2\) band near 1275 cm\(^{-1}\) recorded at 0.5 cm\(^{-1}\) resolution and 0–25 μs (open circles, Fig. 8(a)) is compared with the \(ν_4\) band simulated for \(syn\text{-}CH_2\text{BrOO}\) and \(syn\text{-}CH_2\text{BrOO}\) with predicted spectral parameters. This band, approximately described as the CH\(_2\) wagging mode, is mostly \(a\)-type with a significant Q branch and a weighting factor types \(a\): \(b\): \(c\) = 0.78:0.20:0.02. Similarly to other modes, no difference between the simulated bands of \(syn\text{-}CH_2\text{BrOO}\) and \(syn\text{-}CH_2\text{BrOO}\) (thin lines in Fig. 8(a)) is discernible. The resultant simulated spectrum from these two isotopologues is shown as a thick solid line in Fig. 8(a), which shows some deviations from our experimental result. The most intense band (\(ν_4\)) of \(anti\text{-}CH_2\text{BrOO}\) (1277 cm\(^{-1}\)) was predicted to have anharmonic vibrational wavenumber 11 cm\(^{-1}\) greater and intensity twice more than that of \(syn\text{-}CH_2\text{BrOO}\) (1266 cm\(^{-1}\)). If the predicted energy difference of 3.1 kJ mol\(^{-1}\) is correct, we expect the population ratio of \(anti\text{-}CH_2\text{BrOO}: syn\text{-}CH_2\text{BrOO}\) to be 0.14:1.00 at 298 K, assuming a Boltzmann distribution. We simulated the spectra on adding the \(ν_4\) bands of both \(syn\text{-}\) and \(anti\text{-}CH_2\text{BrOO}\) with the band origin of \(anti\text{-}CH_2\text{BrOO}\) varied from 1273 to 1280 cm\(^{-1}\) to search for the best fit. The best simulated spectrum (thick line in Fig. 8(b)) with the \(ν_4\) modes of \(syn\text{-}CH_2\text{BrOO}\) at 1276.1 cm\(^{-1}\) and that of \(anti\text{-}CH_2\text{BrOO}\) at 1277.0 cm\(^{-1}\) (thin line in Fig. 8(b)) is shown as thick line in Fig. 8(b); the agreement is improved. We simulated also the spectrum on considering slightly Lorentzian-broadened (\(L = 0.2\) cm\(^{-1}\)) \(anti\text{-}CH_2\text{BrOO}\) with the \(ν_4\) mode of \(syn\text{-}CH_2\text{BrOO}\) at 1276.1 cm\(^{-1}\) and that of \(anti\text{-}CH_2\text{BrOO}\) at 1277.0 cm\(^{-1}\) having a ratio of \(anti\text{-}CH_2\text{BrOO}: syn\text{-}CH_2\text{BrOO}\) = 0.13:1.00. The resultant simulation is shown as a solid curve in Fig. 8(c), which agrees best with the experimental spectrum. Hence we assign the observed \(A_2\) band to the CH\(_2\) wagging mode of \(syn\text{-}CH_2\text{BrOO}\), with a possibility of a small contribution of \(anti\text{-}CH_2\text{BrOO}\). As the intensities of other bands of \(anti\text{-}CH_2\text{BrOO}\) (\(ν_6\) and \(ν_7\)) are much smaller, they could not be observed with the current ratio of signal to noise.

For all 12 vibrational modes of \(syn\text{-}CH_2\text{BrOO}\), eight modes are within our detection range (>750 cm\(^{-1}\)); we detected the four most intense modes; the fifth mode predicted near 1234 cm\(^{-1}\) (\(ν_5\)) might have been observed near 1243 cm\(^{-1}\) (Fig. 3(a)), but the intensity was too small for a positive identification. The other three unobserved modes have predicted IR intensities less than 4 km mol\(^{-1}\). The observed vibrational wavenumbers and relative IR intensities are compared with theoretical computations in Table II; the deviations between observed wavenumbers and predicted anharmonic vibrational wavenumbers are less than 27 cm\(^{-1}\) (3\%); the agreements in relative IR intensities are satisfactory.

The peroxy radicals that we observed all have similar O–O stretching wavenumbers; \(CH_3OO\),\(^{23}\) \(cis\text{-}CH_3C(O)OO\),\(^{24}\) \(trans\text{-}CH_2C(O)OO\),\(^{24}\) \(C_6H_5C(O)OO\),\(^{25}\) and \(CH_3SOO\)\(^{40}\) absorb at 1117 ± 2, 1078 ± 6, 1102 ± 3, 1108 ± 4, and 1110 ± 3 cm\(^{-1}\), respectively, even though some modes are mixed with other vibrations. The IR spectra of other methyl halogenated peroxy radicals have also been observed. The reported O–O stretching and C–O stretching wavenumbers for \(CH_2CIOO\) in Ar matrix are 1088.2 and 884.6 cm\(^{-1}\).\(^{41}\) The corresponding wavenumbers for \(CH_3IOO\) in \(p\text{-}H_2\) matrix are 1085.6 and 917.7 cm\(^{-1}\).\(^{42}\) These results agree with the corresponding values of 1088.3 cm\(^{-1}\) and 884.9/961.0 cm\(^{-1}\) that we observed.

C. Possible assignment of band B to \(CH_2BrOOBr\)

As discussed previously, the intensity of band B increased to a maximum near 90 μs, followed by a decay with a decay constant ∼180 μs. When the concentration of \(CH_2Br_2\) was increased, the period for band B to reach its maximum decreased, indicating that the carrier was formed from secondary reactions involving \(CH_3Br\) or \(Br\).

As discussed in Sec. IV B, \(CH_2Br\) and \(Br\) were the main products upon irradiation of \(CH_2Br_2\); \(CH_2Br\) reacted readily.
with excessive O₂ in the flow system to produce CH₂BrOO. The most likely products of secondary reactions are CH₂BrO, H₂CO, and CH₂BrOOBr. The simulated spectra of CH₂BrO and CH₂BrOOBr appear in Figs. 3(d) and 3(e), respectively. The most intense band of CH₂BrOOBr in Fig. 3(e) agrees satisfactorily with the experimental observation; the intensities of the other three bands of CH₂BrOOBr predicted near 1261, 1229, and 904 cm⁻¹ are too small to be observed. As the small intensity precludes reliable comparison of rotational contours, the assignment is tentative.

Similarly, we observed also three absorption bands of C₆H₅C(O)Br near 1793, 1176, and 1195 cm⁻¹ when we photolyzed a mixture of C₆H₅Br and CO; C₆H₅C(O)Br was produced from a secondary reaction of C₆H₅CO with Br, which was produced also upon photolysis of precursor C₆H₅Br₂.⁴³

V. CONCLUSION

We observed four transient IR bands of the bromomethyl peroxy radical CH₂BrOO upon photolysis of gaseous CH₂Br₂ in O₂ using a step-scan Fourier-transform infrared absorption spectrometer; the IR spectrum of CH₂BrOO is previously unreported. Bands with origins at 1276.1, 1088.3, 961.0, and 884.9 cm⁻¹, assigned to ν₂ (CH₂-wagging), ν₆ (O–O stretching), ν₅ (CH₂-rocking mixed with C–O stretching), and ν₈ (C–O stretching mixed with CH₂-rocking) modes of syn-CH₂BrOO, respectively, and their relative IR intensities agree with those predicted with the B3LYP/aug-cc-pVTZ method. A weak band near 1243 cm⁻¹ might be assigned to the CH₂ twisting (v₅g) mode. Observed rotational contours of these bands also conform satisfactorily to those simulated according to rotational parameters derived from quantum-chemical calculations. The rotational contours of v₂ and v₅ indicate that hot bands involving ν₁ and ν₂ are also present, with transitions 7₀⁵₁₂₄₂ and 8₀⁵₁₂₄ν, v = 1–10. The possibility that the most intense band of anti-CH₂BrOO near 1277 cm⁻¹ might have a small contribution cannot be excluded. An additional weak band near 1015 cm⁻¹, observed at a later period after laser irradiation, is assigned to CH₂BrOOBr that was produced from a secondary reaction of CH₂BrOO with Br. Our work provides information for directly probing gaseous CH₂BrOO with IR spectroscopy, in either the atmosphere or laboratory experiments.

ACKNOWLEDGMENTS

Ministry of Science and Technology (Grant No. MOST103-2745-M-009-001-ASP) and Ministry of Education, Taiwan (“Aim for the Top University Plan” of National Chiao Tung University) supported this work. The National Center for High-Performance Computation provided computer time.

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36See supplementary material at http://dx.doi.org/10.1063/1.4899782 for comparison of rotational parameters of syn-CH₂BrOO, anti-CH₂BrOO, CH₂BrO, and CH₂BrOOBr in their ground and vibrationally excited states, the predicted displacement vectors and directions of dipole derivatives for all vibrational modes of syn-CH₂BrOO, and the simulated rotational contours for v₂ and v₅ for syn-CH₂BrOO.