Chemical Physics Letters 458 (2008) 44–47

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Infrared band intensities of bromine nitrate, $BrONO_2$

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ARTICLE INFO

Article history:
Received 19 March 2008
In final form 21 April 2008
Available online 26 April 2008

ABSTRACT

The integrated band intensities at 296 K of gaseous bromine nitrate ($BrONO_2$) in the spectral range 500–2000 cm^{-1} have been measured using Fourier-transform absorption spectroscopy. The absorption spectra were calibrated to absolute absorption cross-sections using the integrated band strength of the ν_3 band around 803 cm^{-1} ($2.70 \pm 0.50 \times 10^{-17}$ cm $molecule^{-1}$) published previously. In this way, integrated band intensities were determined for the first time for the ν_1 band around 1709 cm^{-1} ($2.43 \pm 0.48 \times 10^{-17}$ cm $molecule^{-1}$), the ν_2 band around 1286 cm^{-1} ($2.99 \pm 0.60 \times 10^{-17}$ cm $molecule^{-1}$), the weak ν_4/ν_8 bands between 720 and 760 cm^{-1} ($0.16 \pm 0.04 \times 10^{-17}$ cm $molecule^{-1}$) and the ν_5 band around 559 cm^{-1} ($1.02 \pm 0.20 \times 10^{-17}$ cm $molecule^{-1}$). The results are compared with the infrared band strengths of chlorine nitrate and with *ab initio* calculations.

1. Introduction

Bromine nitrate ($BrONO_2$) is an important bromine and NO_x reservoir in the Earth's atmosphere; it represents a large fraction of the total bromine in the stratosphere and is also involved in tropospheric chemistry [1–3]. It was first investigated in the 1960s [4] but its atmospheric relevance was only discovered in the early 1970s [5].

Pure samples of bromine nitrate are rather difficult to synthesize and to handle, and decompose rapidly at ambient conditions. Therefore, only very few spectroscopic studies of $BrONO_2$ have been reported in the past [5–9]. However, its structural parameters have been obtained from electron diffraction [10], and several theoretical calculations of its structure, vibrational and electronic energy levels, dipole moment and dipole moment derivates have been published [11–13]. Although the most important chemical reactions of $BrONO_2$ have been investigated, too (see [14,15] and references therein), the infrared band intensities of $BrONO_2$ have not been measured, except for the ν_3 band around 803 cm^{-1} [7].

On the other hand, infrared band intensities are important reference data for studying chemical kinetics, for example using tropospheric reaction chambers (see e.g. [16–18]). Furthermore, in a recent study of the European Space Agency (ESA), $BrONO_2$ was included in the list of target species for future satellite missions focusing on atmospheric chemistry [19]. However, the only infrared band for which the absolute intensity is known [7] is located below 1000 cm^{-1}, where windows made of CaF_2 that are typically used in such experiments are no longer transparent, which might be a problem for future laboratory and field studies. Therefore, to determine the integrated band intensities of the ν_1 and ν_2 fundamental bands that are located above 1000 cm^{-1} [6,8] and to provide experimental data for comparisons with the recent *ab initio* calculations, unpublished spectra of $BrONO_2$ that were originally measured in 1993 in the spectral region 500–2000 cm^{-1} [8] were calibrated to absolute absorption cross-sections using the integrated band strength of the ν_3 band around 803 cm^{-1} [7]. In this way, integrated band intensities of the ν_1, ν_2, ν_4/ν_8 and ν_5 fundamentals were obtained.

2. Experimental

Pure samples of bromine nitrate were synthesized using the reaction between pure $ClONO_2$ and Br_2 with $ClONO_2$ in excess. The $ClONO_2$ was obtained using the method of *Schmeisser* [20], i.e. the reaction between pure Cl_2O and N_2O_5. Cl_2O was synthesized using the reaction of gaseous Cl_2 with dry yellow HgO, and N_2O_5 was obtained by reaction of freshly synthesized HNO_3 with P_2O_5. All reactions were carried out under vacuum (10^{-2} mbar) avoiding organic materials and metallic surfaces that could induce chemical decomposition. Several low-temperature distillations were carried out in order to separate reactants and products. Pure $BrONO_2$ at low temperatures forms yellow crystals and sublimates into the gas phase when warming it up slowly to about −30 °C.

Absorption spectra of $BrONO_2$ at different partial pressures were recorded using the step-scan high-resolution Fourier-transform spectrometer at LPPM. For the experiments described here, a maximum spectral resolution of 0.03 cm^{-1} was used. The absorption cell was made of Pyrex glass and equipped with AgCl windows and a Teflon (Young type) valve. Other window materials than AgCl (NaCl, KBr) were observed to react with $ClONO_2$ and $BrONO_2$ forming solid deposits ($NaNO_3$, KNO_3) on the windows' surfaces. The only impurity observed in the $BrONO_2$ spectra was HNO_3, either

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doi:10.1016/j.cplett.2008.04.089

from the hydrolysis of $BrONO_2$ with residual H_2O in the gas transfer line (although no HOBr was observed in the absorption spectra) or as residual impurity from the synthesis. Typically, the recording time of one spectrum was about 30 min. All experiments were carried out at room temperature (296 K). More details of the experimental setup and procedure are given in Ref. [8]. The spectra were corrected for the HNO_3 absorption using a reference spectrum of pure HNO_3 vapour recorded under the same conditions as the $BrONO_2$ spectra. Note that the overlap of the bands of HNO_3 and of $BrONO_2$ can be a source of systematic errors both in this work and future quantitative studies using the infrared spectrum of $BrONO_2$.

The uncertainty of the absolute values for the integrated band intensities of this study (20%) is mainly due to the uncertainty of the measurement employed as Ref. [7], with an estimated uncertainty of 0.50×10^{-17} cm molecule^{-1} at 296 K, corresponding to 18.5% of the integrated band intensity of the ν_3 band around 803 cm^{-1} (2.70×10^{-17} cm molecule^{-1}). The relative band intensities of this study are more accurate, with an estimated uncertainty of 5–10% except for the weak ν_4/ν_8 bands between 720 and 760 cm^{-1}.

3. Results

An overview spectrum of the infrared bands of $BrONO_2$ observed in this study is presented in Fig. 1. The strong ν_3 band around 803 cm^{-1} that has been measured previously by *Burkholder et al.* [7] is shown in Fig. 2. The band contour is different from the corresponding band in $ClONO_2$ [8,21], and the integrated cross-section at 296 K of the ν_3/ν_4 bands of $ClONO_2$ (interacting by a strong Fermi resonance [22]) is 3.16×10^{-17} cm molecule^{-1} [8,23,24], i.e. about 17% larger. The principal rotational constants of bromine nitrate are relatively small [10,11]; this and the nearly equal natural abundances of the two main bromine isotopomers, together with the existence of several low-lying vibrational states that are significantly populated at room temperature, lead to a highly congested spectrum that is too dense to show rotationally resolved structure.

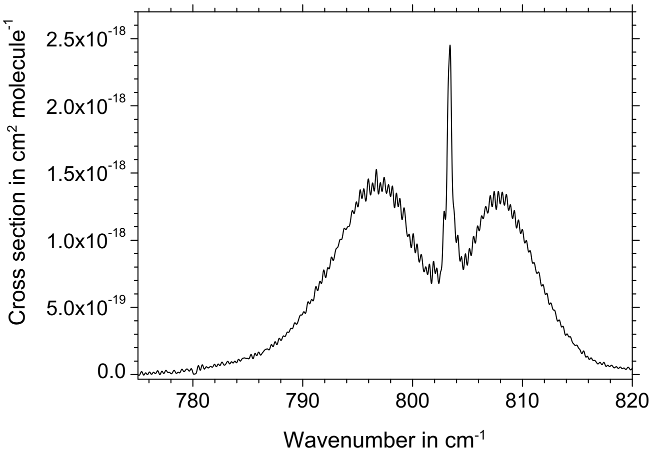

Fig. 2. The ν_3 band of $BrONO_2$ corresponding to the Br–O stretching vibration. This band has been previously observed by Burkholder et al. [7] and was used to determine the absolute amount of $BrONO_2$ in the absorption cell (containing a mixture of $BrONO_2$ and Br_2).

Table 1
Integrated band intensities of $BrONO_2$ compared to *ab initio* calculations

Band	Band center, cm^{-1}	This work, km mol^{-1}	Ref. [11], km mol^{-1}	Ref. [12], km mol^{-1}	Ref. [13], km mol^{-1}
ν_1	1709	146 ± 29	325	353	352
ν_2	1286	180 ± 36	272	297	284
ν_3	803	162 ± 32	204	204	196
ν_4/ν_8	722	9.6 ± 2.5	11	16	16
ν_5	559	61 ± 12	85	93	101

In Table 1, the integrated band intensities of this study are compared to the results of several recent *ab initio* calculations. One can state that the agreement of the relative intensities (taking e.g. the ν_2 band as reference) is relatively good for the ν_2, ν_4/ν_8 and ν_5 fundamentals, but that there are significant differences between the experiment and the theoretical predictions for the ν_1 (antisymmetric N–O stretching vibration) and ν_3 (NO_2 angle bending vibration) bands. Furthermore, the theoretical band intensities of the strongest bands are too high compared to the experimental values, possibly due to the depletion of the population of the vibrational ground state at room temperature, that needs to be taken into account in the theoretical calculations, or because of anharmonic effects. Also in contrast to the calculations, the ν_2 band of $BrONO_2$ around 1286 cm^{-1} (see Fig. 3) is observed to be the strongest band (having a similar shape as the corresponding band of chlorine nitrate [25]) with an integrated absorption cross-section of

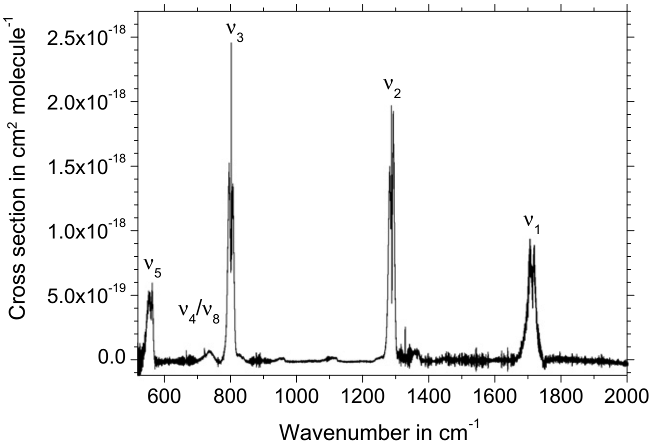

Fig. 1. Absorption cross-sections of the infrared bands of $BrONO_2$. The spectral resolution is 0.075 cm^{-1}. The high-frequency structure at the baseline is from the correction for residual H_2O and HNO_3 absorption, and due to noise.

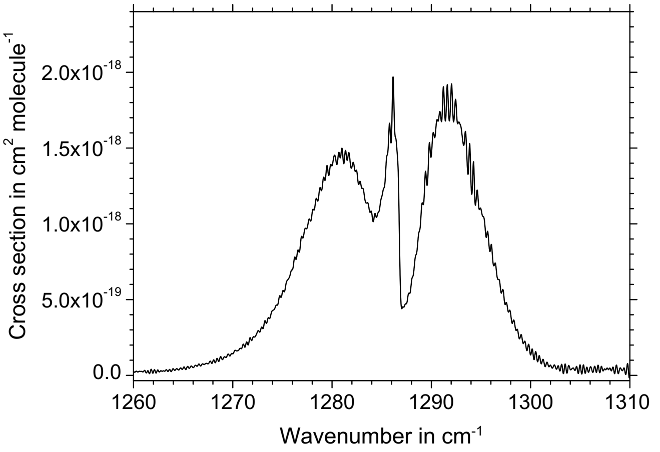

Fig. 3. The ν_2 band of $BrONO_2$ corresponding to the symmetric N–O stretching vibration. This is the strongest infrared band of bromine nitrate, its shape and intensity are similar to the corresponding band of chlorine nitrate [25].

2.99×10^{-17} cm molecule^{-1}. This value is about 27% lower than the integrated band intensity at 296 K of the ν_2 band of $ClONO_2$ centered around 1292 cm^{-1} (3.80×10^{-17} cm molecule^{-1}) [23–26].

The ν_5 band of $BrONO_2$ centered around 559 cm^{-1} (see Fig. 4) has an integrated cross-section of 1.02×10^{-17} cm molecule^{-1} and has a band contour that is very similar to the ν_5 band of chlorine nitrate (centered at 563 cm^{-1} [27] with an integrated cross-section of 1.16×10^{-17} cm molecule^{-1} at 296 K [28]). The ν_1 band of $BrONO_2$ around 1709 cm^{-1} (see Fig. 5) with an integrated band intensity of 2.43×10^{-17} cm molecule^{-1} carries less than 50% of the intensity of the ν_1 band in $ClONO_2$ [23–26], 5.68×10^{-17} cm molecule^{-1}, in disagreement with the *ab initio* calculations, however the origin of this discrepancy remains unresolved. Further experimental and theoretical work is required to investigate this issue. The ν_8 and ν_4 bands of $BrONO_2$ are very weak, with a progression of Q-branches around 722–725 cm^{-1} that is possibly due to coupling of the ν_8 and ν_9 (torsional) modes. As already observed for $ClONO_2$ [29], the P-branch of the ν_8 band is extremely weak due to a rather large Herman-Wallis effect. Note that the weakness of the ν_4 band of $BrONO_2$ illustrates the strong coupling between the ν_3 (809 cm^{-1}) and ν_4 (780 cm^{-1}) bands of $ClONO_2$ [22] where the ν_4 band is much stronger due to anharmonic interactions.

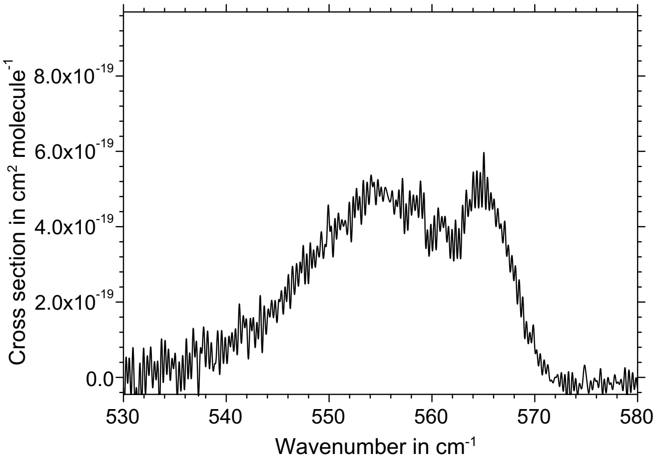

Fig. 4. The ν_5 band of $BrONO_2$ showing noise due to the limited sensitivity of the infrared detector in this region. The position and overall contour of this band are very similar to the corresponding fundamental band in chlorine nitrate [27].

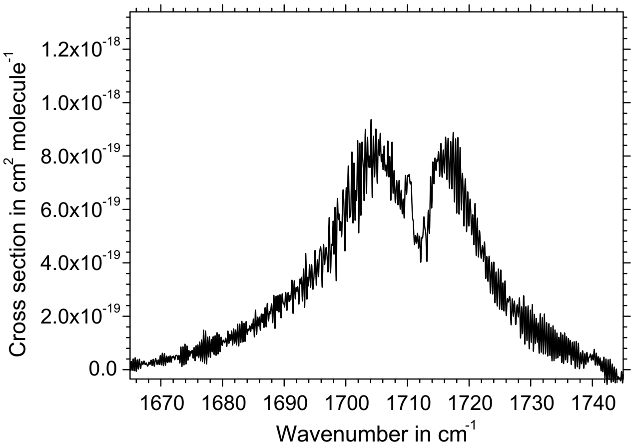

Fig. 5. The ν_1 band of $BrONO_2$ corresponding to the antisymmetric N–O stretching vibration with dominant *b*-type structure, and a less pronounced Q-branch from weak a-type transitions. Part of the high-frequency structure is from the correction for residual HNO_3 absorption which is rather strong in this region. The overlap of the bands of $BrONO_2$ and HNO_3 in this region is a potential source for systematic errors, both for this work and for future quantitative studies.

Concerning the atmospheric detection of $BrONO_2$, Burkholder et al. [7] have estimated that the ν_3 band of bromine nitrate around 803 cm^{-1} would have a peak absorbance of 0.04% at an air mass factor of 10, assuming a column abundance of 2×10^{13} cm^{-2} at night. Since the present study shows that the ν_3 band has the strongest peak cross-section (see Fig. 1) and since it is the only band that falls into an atmospheric absorption window, it will indeed be very difficult to detect $BrONO_2$ in the atmosphere by infrared spectroscopy, even using instruments with high sensitivity, but it might neverthelesss be useful to look for $BrONO_2$ in atmospheric spectra with very high signal-to-noise ratio.

No evidence for the existence of the bromine nitrate isomer BrOONO (bromine peroxynitrite) [30] was found, in agreement with previous studies. BrOONO is predicted to have strong characteristic absorption bands in the mid-infrared, with the strongest band in the region 1800–1900 cm^{-1} [31]. However, no absorption was observed in this range (see Fig. 1), so that the relative amount of BrOONO in the spectra of the present study must have been less than 2% of $BrONO_2$.

4. Conclusions

In this Letter, the integrated band intensities at 296 K of the ν_1, ν_2, ν_4/ν_8 and ν_5 fundamental bands of bromine nitrate have been determined for the first time. The results have been compared with recent *ab initio* calculations and with the band intensities of chlorine nitrate, $ClONO_2$. No absorptions that would indicate the presence of the isomer BrOONO (bromine peroxynitrite) were observed. In conclusion, the data of this work are useful for future laboratory studies of atmospheric chemistry and may be interesting for the detection of atmospheric $BrONO_2$ using infrared spectroscopy.

References

[1] D.J. Lary, J. Geophys. Res. D 101 (1996) 1505.
[2] D.J. Lary, M.P. Chipperfield, R. Toumi, T. Lenton, J. Geophys. Res. D 101 (1996) 1489.
[3] D.J. Lary, J. Geophys. Res. D 102 (1997) 21515.
[4] M. Schmeisser, L. Taglinger, Chem. Ber. 94 (1961) 1533.
[5] J.E. Spencer, F.S. Rowland, J. Phys. Chem. 82 (1978) 7.
[6] W.W. Wilson, K.O. Christe, Inorg. Chem. 26 (1987) 1573.
[7] J.B. Burkholder, A.R. Ravishankara, S. Solomon, J. Geophys. Res. D 100 (1995) 16793.
[8] J. Orphal, Ph.D. Thesis, Université de Paris-Sud (Orsay), 1995.
[9] B. Deters, J.P. Burrows, J. Orphal, J. Geophys. Res. D 103 (1998) 3563.
[10] B. Casper, P. Lambotte, R. Minkwitz, H. Oberhammer, J. Phys. Chem. 97 (1993) 9992.
[11] S. Parthiban, T.J. Lee, J. Chem. Phys. 109 (1998) 525.
[12] S. Parthiban, T.J. Lee, J. Chem. Phys. 113 (2000) 145.
[13] P. Zou, A. Derecskei-Kovacs, S.W. North, J. Phys. Chem. A 107 (2003) 888.
[14] R. Soller, J.M. Nicovich, P.H. Wine, J. Phys. Chem. A 105 (2001) 1416.
[15] R. Soller, J.M. Nicovich, P.H. Wine, J. Phys. Chem. A 106 (2002) 8378.
[16] R. Bröske, Ph.D. Thesis, Fachbereich Chemie, Bergische Universität – Gesamthochschule (Wuppertal), 2000.
[17] B.J. Finlayson-Pitts, L.M. Wingen, A.L. Sumner, D. Syomin, K.A. Ramazan, Phys. Chem. Chem. Phys. 5 (2003) 223.
[18] J.-F. Doussin, B. Picquet-Varrault, R. Durand-Jolibois, H. Loirat, P. Carlier, J. Photochem. Photobiol. A 157 (2003) 283.
[19] H. Kelder et al. (Ed.), Operational Atmospheric Chemistry Missions, Final Report for ESA Project 17237/03/NL/GS (CAPACITY), ESA-ESTEC, 2005.
[20] M. Schmeisser, W. Fink, K. Brändle, Angew. Chem. 69 (1957) 780.
[21] J. Orphal, M. Morillon-Chapey, A. Diallo, G. Guelachvili, J. Phys. Chem. A 101 (1997) 1062.
[22] J.-M. Flaud, J. Orphal, W.J. Lafferty, M. Birk, G. Wagner, J. Geophys. Res. D 107 (2002), doi:10.1029/2002JD002628.
[23] A. Goldman, C.P. Rinsland, J.-M. Flaud, J. Orphal, J. Quant. Spectrosc. Rad. Transf. 60 (1998) 875.
[24] G. Wagner, M. Birk, J. Quant. Spectrosc. Rad. Transf. 82 (2003) 443.
[25] J. Orphal, M. Morillon-Chapey, G. Guelachvili, J. Geophys. Res. D 99 (1994) 14549.

[26] J. Ballard, A.B. Johnston, M.R. Gunson, P.T. Wassell, J. Geophys. Res. D 93 (1988) 1659.
[27] D.G. Johnson, et al., Geophys. Res. Lett. 23 (1996) 1745.
[28] J.A. Davidson, C.A. Cantrell, R.E. Shetter, A.H. McDaniel, J.G. Calvert, J. Geophys. Res. 92 (1987) 10921.
[29] J.-M. Flaud, W.J. Lafferty, J. Orphal, M. Birk, G. Wagner, Mol. Phys. 101 (2003) 1527.
[30] S. Kovacic, A. Lesar, M. Hodoscek, J. Koller, Chem. Phys. 323 (2006) 369.
[31] A. Lesar, S. Prebil, M. Mühlhäuser, M. Hodoscek, Chem. Phys. Lett. 368 (2003) 399.