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Properties of Pure Nitryl Bromide. Thermal Behavior, UV/Vis and FTIR Spectra, and Photoisomerization to *trans*-BrONO in an Argon Matrix[‡]

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$BrNO_2$ is produced by the heterogeneous reaction of $ClNO_2$, highly diluted in He, with an aqueous bromide solution and subsequent trapping at −155 °C. The crude product is purified by trap to trap condensation and fractional sublimation in vacuo. At 300 K and a pressure of 1 mbar, a half-life of about 1 h is observed. The decomposition produces Br_2 and NO_2. The UV/vis and IR absorption cross sections of gaseous $BrNO_2$ are determined in the ranges 185−600 nm and 2000−400 cm^{-1}, respectively. Irradiation of matrix-isolated $BrNO_2$ with visible light causes nearly quantitative isomerization to *trans*-BrONO, while $ClNO_2$ is converted by UV light into a mixture of *cis*- and *trans*-ClONO. It is possible to assign all fundamentals of $BrNO_2$ and *trans*-BrONO by comparison to the respective band position of the analogous molecules XNO_2 and XONO (X = Cl, F).

Introduction

The isomeric molecules of the type XNO_2 and XONO (X = halogen) have been studied by experimental and computational methods. While the properties of the fluorides[1,2] and chlorides[2,3] have been thoroughly investigated, little is known about the bromides. In the troposphere, $BrNO_2$ can be formed by the reaction of N_2O_5 with sea salt aerosol.[4,5] Subsequent photolysis into Br and NO_2 is assumed. The Br atom reacts with O_3 to BrO and contributes to the artic ozone depletion[6,7] and to the oxidation of dimethyl sulfide.[8] Under stratospheric conditions, $BrNO_2$ is possibly formed via the reaction of N_2O_5 with HBr on nitric acid trihydrate surface.[9]

The UV/vis spectrum of $BrNO_2$ has so far not been measured, and the reports of the IR absorptions are contradictory.[10−12] IR bands of the reaction products of atomic bromine with NO_2, isolated in an argon matrix, have been assigned to $BrNO_2$ and BrONO. The gas phase absorption bands of $BrNO_2$ were observed in a long-path cell after the reaction of N_2O_5 with BrNO or solid NaBr.[12] They are centered at 787, 1292, and 1660 cm^{-1}, consistent with one of the matrix studies.[10] From measurements of the association reaction Br + NO_2, thermochemical parameters for $BrNO_2$ (possibly BrONO, see below) were obtained[13] using the available spectroscopic data for third-law analysis. On the basis of these measurements an upper limit of 2.3 s was estimated for the lifetime at 300 K toward unimolecular decomposition.[14]

Very recently, it has been found that $BrNO_2$ is formed in good yield in a continuous flow by $ClNO_2$ with a dilute aqueous solution of NaBr.[15] This synthesis with high yield enabled us to isolate pure $BrNO_2$ and to study its properties in detail. In this paper we present the complete IR and UV/vis spectra and the macroscopic properties of $BrNO_2$. The obtained absorption cross sections now allow quantitative analysis and calculation of photolysis lifetimes in the atmosphere.

Experimental Section

Synthesis and Purification of $BrNO_2$. A continuous gas flow of highly diluted $BrNO_2$ in He was produced by passing $ClNO_2$ over an aqueous solution of NaBr (8×10^{-4} mol L^{-1}) at 2 °C, as described previously.[15] The gas flow was directed through a trap cooled to −60 °C to remove water and then through a U-trap kept at −155 °C (methylbutane slush). Within 3.5 h about 0.03 mmol of product was collected. The crude product was passed in vacuo through a series of traps kept at −80, −125, and −196 °C. $BrNO_2$ was collected in the −125 °C trap.

Small batches (2×10^{-3} mmol) of the most volatile fractions were slowly sublimed into the evacuated infrared or UV cell, which were directly attached to the vacuum line.

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[‡] Dedicated to Prof. Dr. mult. Dr. h.c. Alois Haas on the occasion of his 65th birthday.

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(1) Smardzewski, R. R.; Fox, W. B. *J. Chem. Phys.* **1974**, *60*, 2980.
(2) Bernitt, D. L.; Miller, R. H.; Hisatsune, I. C. *Spectrochim. Acta, Part A* **1967**, *23*, 237.
(3) Tevault, D. E.; Smardzewski, R. R. *J. Chem. Phys.* **1977**, *67*, 3777.
(4) Finlayson-Pitts, B.; Livingston, F.; Berko, H. *Nature* **1990**, *343*, 622.
(5) Behnke, W.; Scheer, V.; Zetzsch, C. *J. Aerosol Sci.* **1994**, *25 Suppl. 1*, 277.
(6) Le Bras, G.; Platt, U. *Geophys. Res. Lett.* **1995**, *22*, 599.
(7) Barrie, L. A.; Bottenheim, J. W.; Hart, W. R. *J. Geophys. Res.* **1994**, *99*, 25313.
(8) Toumi, R. *Geophys. Res. Lett.* **1994**, *21*, 117.
(9) Hanson, D. R.; Ravishankara, A. R. *J. Phys. Chem.* **1992**, *96*, 9441.
(10) Tevault, D. E. *J. Phys. Chem.* **1979**, *83*, 2217.
(11) Feuerhahn, M.; Minkwitz, R.; Engelhardt, U. *J. Mol. Spectrosc.* **1979**, *77*, 429.
(12) Finlayson-Pitts, B. J.; Livingston, F. E.; Berko, H. N. *J. Phys. Chem.* **1989**, *93*, 4397.
(13) Kreutter, K. D.; Nicovich, J. M.; Wine, P. H. *J. Phys. Chem.* **1991**, *95*, 4020.
(14) Wine, P. H.; Nicovich, J. M.; Stickel, R. E.; Zhao, Z.; Shackelford, C. J.; Kreutter, K. D.; Daykin, E. P.; Wang, S.; In *Halogen and sulfur reactions relevant to polar chemistry. The Tropospyheric Chemistry of Ozone in the Polar Regions*; Niki, H., Becker, K. H., Eds.; Springer-Verlag: Berlin, 1993.
(15) Frenzel, A.; Scheer, V.; Behnke, W.; Zetzsch, C. *J. Phys. Chem.* **1996**, *100*, 16447.

S0020-1669(96)00694-5 CCC: $14.00

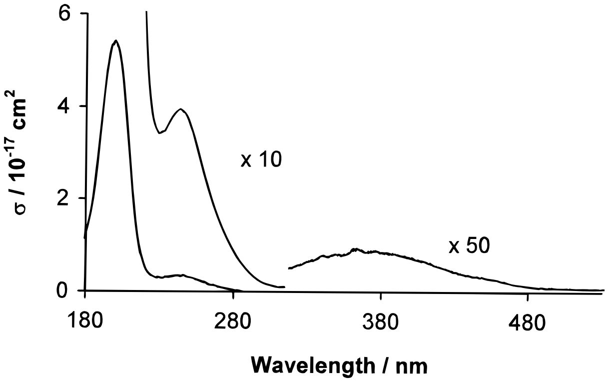

Figure 1. UV/vis spectrum of $BrNO_2$ in the gas phase.

Table 1. UV/Vis Absorption Cross Sections of Gaseous $BrNO_2$ at 25 °C

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
185	2048	305	15	420	11
190	3601	310	11	425	10
195	5013	315	11	430	9
200	5386	320	10	435	8
205	4499	325	12	440	7
210	2521	330	13	445	7
215	1170	335	14	450	6
220	554	340	16	455	5
225	373	345	15	460	5
230	343	350	16	465	4
235	362	355	16	470	3
240	387	360	18	475	3
245	390	365	19	480	3
250	363	370	17	485	2
255	310	375	18	490	2
260	251	380	17	495	2
265	197	385	17	500	2
270	154	390	16	505	2
275	116	395	15	510	2
280	88	400	14	515	2
285	63	405	14	520	2
290	44	410	13	525	1
295	30	415	12	530	1
300	20				

Small amounts of the samples were removed in vacuo until no further impurities were detectable by IR or UV/vis spectroscopy. $ClNO_2$ is more volatile and N_2O_4 or Br_2 are less volatile than $BrNO_2$. It can be estimated that the purity of the final product was about 95%. For matrix investigations a small quantity (10^{-2} mmol) of pure $BrNO_2$ was transferred into a small U-trap, which was placed in front of the matrix support. $ClNO_2$ was obtained according to a literature procedure.[16]

Preparation of the Matrices. During this study six different argon matrices were prepared by directing a gas stream (3 mmol h^{-1}) of argon over solid $BrNO_2$ cooled to −120 °C. The resulting gas mixture was immediately quenched on the matrix support at 11 K. In addition, four matrix samples were prepared from gaseous mixtures of $ClNO_2$ and Ar (1:500). Photolysis experiments were performed with visible or UV light, using a 250 W tungsten halogen lamp (Osram) in combination with a 395 nm long-pass filter (Schott) or a Hg high-pressure lamp TO150 (Heraeus), respectively.

Instrumentation. Matrix IR spectra were recorded on an IFS 66v FT spectrometer (Bruker) equipped with a reflectance device in the sample compartment. The IR beam was directed through a CsI window to the cold remote mirror covered with the matrix, from where it was reflected to re-enter the standard optical path. Further details on the matrix apparatus are reported elsewhere.[17] A DTGS detector, together with a Ge/KBr beam splitter, operated in the region 5000−400 cm^{-1} (128 scans), employing an apodized resolution of the spectrometer of 1.3 cm^{-1}. A 6 μm Mylar beam splitter was used in the 500−200 cm^{-1} region (DTGS detector with CsI window). Thirty-two scans were coadded for each spectrum, using an apodized resolution of ca. 0.3 cm^{-1}.

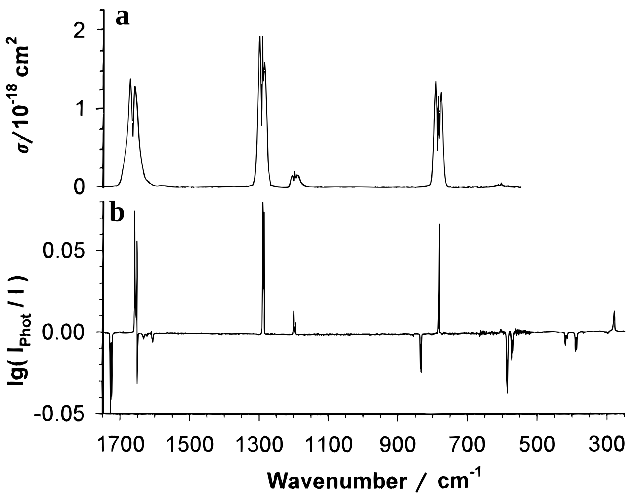

Figure 2. (a) IR spectrum of $BrNO_2$ in the gas phase. (b) Difference IR spectrum of $BrNO_2$ isolated in an Ar matrix before and after photolysis. Bands due to $BrNO_2$ are pointing upward, and bands of *trans*-BrONO are pointing downward.

Gas phase FTIR spectra were recorded on a Nicolet Impact 400D instrument in the spectral range 4200−400 cm^{-1} at a nominal resolution of 4 cm^{-1} by coadding 16 scans for each spectrum. The IR gas cell (optical path length 20 cm, Si windows 0.5 mm thick), placed in the sample compartment of the infrared spectrometer, was connected to the vacuum line. This instrument was used for monitoring the purification process of $BrNO_2$.

UV/vis spectra were recorded with a 1024 diode array spectrometer system (Spectroscopy International) using a CLD 30 W deuterium (Zeiss) or a tungsten halogen lamp as the light source. Hg emission lines were used for wavelength calibration. The Duran glass cell (optical path length 10 cm), equipped with quartz lenses (Suprasil, Heraeus), a pressure sensor (MKS Baratron 122A, 10 mbar absolute), and PTFE valves (Young), was connected via the vacuum line to the sample reservoir. The 0.25 m monochromator with a holographic grating (300 grooves mm^{-1}, resolution 1 nm) and the housing of the absorption cell were flushed with N_2 to eliminate absorption of atmospheric O_2. Spectra in the UV and visible regions were recorded within 100 and 33 ms, respectively.

Results and Discussion

Behavior of BrNO$_2$. Both gaseous and solid pure $BrNO_2$ (>−120 °C) were observed to decompose according to

$$2BrNO_2 \rightarrow Br_2 + 2NO_2 \qquad (1)$$

The decomposition in the gas phase was monitored in four different gas cells equipped with AgCl, Si, or SiO_2 windows by IR and UV spectroscopy and by the pressure increase. No simple rate law was observed. In some cases the rate increased and in other cases it decreased with time. Half-lives between 15 min and 1 h were observed for $BrNO_2$ pressures of a few millibar at room temperature. This indicates surface catalysis. Wine et al.[14] determined thermochemical parameters for the product of the gas phase reaction of Br atoms with NO_2. This product was assumed to be $BrNO_2$, not BrONO, referring to the experiments of Tevault.[10] Since the half-lives extrapolated from their data are 3 orders of magnitude lower than those observed in this work, we assume that the gas phase reaction Br + NO_2 yields BrONO, not $BrNO_2$. For the reaction of Cl

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(16) *Handbuch der Präparativen Anorganischen Chemie*; Brauer, G., Ed.; Enke-Verlag: Stuttgart, 1975; p 476.

(17) Argüello, G. A.; Grothe, H.; Kronberg, M.; Mack, H. G.; Willner, H. *J. Phys. Chem.* **1995**, *99*, 17525.

Table 2. Vibrational Wavenumbers (cm^{-1}) for IR-Band Positions of $BrNO_2$ and Their Assignments in Comparison to $ClNO_2$ and FNO_2

$BrNO_2$ gas[a]	σ[b]	$BrNO_2$ in Ar matrix[c]	I[d]	$ClNO_2$[e] gas	FNO_2[e] gas	approx descrip of modes	assign acc C_{2v} sym
		3294.1	1				$2\nu_4$
		2930.6	4				$\nu_1 + \nu_2$
		2574.1	2				$2\nu_1$
R 1674	1.4						
1667, b		1659.2	89	1685 vs	1792 vs	$\nu_{as}(NO_2)$	ν_4 (b_1)
R 1301	1.9						
Q 1292, a		1290.7	100	1267 s	1310 s	ν_s (NO_2)	ν_1 (a_1)
Q 1200, a		1200.8	13	1319 m			$2\nu_6$
R 794	1.3						
Q 787, a		782.9	61	793 s	822 s	δ (NO_2)	ν_2 (a_1)
Q 605, c		605.6	2	652 w	742 m	δ (oop)	ν_6 (b_2)
		(290 sh	0.5)[f]	408 vw	560 w	ρ (NO_2)	ν_5 (b_1)
		281.75, ^{79}Br 280.45, ^{81}Br	8	370 s	568 m	ν (X−N)	ν_3 (a_1)

[a] Type of band contour, a, b, c. [b] Absorption cross section in 10^{-18} cm^2 $molecule^{-1}$. [c] Most intense matrix site. [d] Integrated relative intensities $I(\nu_1) = 100$. [e] Reference 2. [f] Tentative, see text.

Table 3. Vibrational Wavenumbers (cm^{-1}) for IR-Band Positions of BrONO and Their Assignments in Comparison to ClONO and FONO

t-BrONO Ar matrix[a]	I[b]	ab initio *t*-ClONO[e]	ab initio *c*-ClONO[e]	ab initio *t*-FONO[f]	ab initio *c*-FONO[f]	approx descrip of modes	assign acc C_s sym
1727.9	100	1754 (297)	1715 (252)	1758 (212)	1753 (212)	ν (N=O)	$\nu_1(a')$
833.2	48	855 (102)	850 (17)	783 (115)	771 (47)	δ (ONO)	$\nu_2(a')$
584.8	93	662 (182)	638 (21)	954 (59)	927 (5)	ν (X−O)	$\nu_3(a')$
573.8	45						$\nu_4 + \nu_5$
420.3	8						$2\nu_5$
391.1	13	407 (98)	416 (167)	411 (114)	399 (157)	ν (O−N)	$\nu_4(a')$
(299.3 $2\nu_6$	2)[d]	170 (0.01)	341 (1.3)	205 (0.3)	355 (0.3)	tors	$\nu_6(a'')$
197[c]		262 (0.2)	249 (0.1)	305 (1.7)	271 (0.6)	δ (XON)	$\nu_5(a')$

[a] Most intense matrix site. [b] Integrated relative intensities $I(\nu_1) \equiv 100$. [c] Calculated from $\nu_1 + \nu_5$ and $2\nu_5$. [d] Tentative, see text. [e] Reference 19, CCSD(T)/TZ2P, values in parentheses are IR intensities in km mol^{-1}. [f] Reference 20, CCSD(T)/TZ2P.

with NO_2, Niki et al.[22] showed that ClONO is the main product, though it is thermodynamically less favorable. Janowski et al.[21] observed that the half-life of ClONO toward isomerization is heterogeneously influenced and is on the order of 4−20 h at $T = 230-221$ K. Further measurements of the unimolecular decomposition rate into Br + NO_2 are required.

In the solid state at −120 °C, $BrNO_2$ was observed to decompose into Br_2 and N_2O_4 quite slowly within 2 h. Therefore, small quantities of $BrNO_2$ could be purified by sublimation at low temperatures and subsequent quenching of the vapor at −196 °C. $ClNO_2$ (bp −14 °C) is more and N_2O_4 (bp 21 °C) less volatile than $BrNO_2$.

UV/Vis Spectrum of Gaseous $BrNO_2$. The absorption cross sections for nitryl bromide were obtained from five spectra with sample pressures between 0.2 and 4 mbar. The absorption spectra obeyed Beer's law, and each cross section (reported in Table 1) below 280 nm has a relative standard deviation of ±5% due to the estimated impurities of the samples. The smaller cross sections above 280 nm are more uncertain, because $BrNO_2$ could not be handled at sample pressures above 4 mbar without significant decomposition. The absorption spectrum (Figure 1) suggests that at least three electronically excited states at λ_{max} = 199, 247, and 372 nm are accessible. The respective transitions in $ClNO_2$ are similar but blue shifted to λ_{max} = <185, 215, and 320 nm.[18] The three absorptions of $BrNO_2$ can be approximated by the sum of three Gaussian functions between 200 and 500 nm:

$$\sigma \approx \sum_{i=1}^{3} I_i e^{-(\nu-\nu_i)^2/\delta_i^2} \tag{2}$$

where ν is the wavenumber in cm^{-1}. The parameters from a fit to ln(σ) at 199 nm are $I_1 = 5.4 \times 10^{-17}$ cm^2 $\nu_1 = 50\,100$ cm^{-1}, and $\delta_1 = 2792$ cm^{-1}; at 247 nm are $I_2 = 0.36 \times 10^{-17}$ cm^2, $\nu_2 = 41\,500$ cm^{-1}, and $\delta_2 = 4700$ cm^{-1}; and at 372 nm are $I_3 = 0.019 \times 10^{-17}$ cm^2, ν_3 and 27 500 cm^{-1}, and $\delta_3 = 4760$ cm^{-1}.

IR Spectra and Assignment of the Bands. The infrared spectra of $BrNO_2$, obtained in the gas phase and in an argon matrix, are presented in Figure 2. The IR absorption cross sections given in Figure 2 and listed in Table 2 were determined from the mass balance of the $BrNO_2$ decomposition according to eq 1 and reference spectra of pure NO_2, recorded under the same conditions. The three σ values (10^{-18} cm^2 $molecule^{-1}$) listed in Table 2 (1.4, 1.9, 1.3) agree within ±20% with those obtained by comparison of UV and IR spectra of $BrNO_2$ in a gas flow through coupled UV and IR cells (1.2, 1.6, 1.2) and with σ values (1.5, 2.2, 1.4) reported earlier.[15]

Irradiation of the matrix-isolated $BrNO_2$ with visible light λ > 395 nm caused a decrease in intensities for all bands belonging to $BrNO_2$, while the bands from small amounts of impurities like NO_2/N_2O_4 were not affected and new bands appeared. Figure 2b shows the difference spectrum before and after photolysis. Bands due to $BrNO_2$ are pointing upward and bands of the photolysis products (shown later to belong to *trans*-BrONO) downward. All observed band positions, together with their relative integrated intensities and the proposed assignments, are collected in Tables 2 and 3. In earlier experiments, $BrNO_2$ and BrONO have been produced in a complex mixture by

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(18) Illies, A. J.; Takacs, G. A. *J. Photochem.* **1976**, *6*, 35.
(19) Lee, T. J. *J. Phys. Chem.* **1994**, *98*, 111 and references therein.
(20) Lee, T. J.; Rice, J. E. *J. Chem. Phys.* **1992**, *97*, 4223 and references therein.
(21) Janowski, B.; Knauth, H.-D.; Martin, H. *Ber. Bunsen-Ges. Phys. Chem.* **1977**, *81*, 1262.
(22) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *Chem. Phys. Lett.* **1978**, *59*, 78.

codeposition of bromine atoms and NO_2 in an excess of argon at 10 K.[10,11] Of 13 bands in the fundamental region of $BrNO_2$ and BrONO observed by us, only nine or two, respectively, are in agreement with the results of Tevault[10] or Feuerhahn et al.[11] Corresponding to the selection rule for the point group C_{2v} for $BrNO_2$

$$\Gamma_{\text{vib}} = 3a_1\ (\text{IR, Ra p}) + 2b_1\ (\text{IR, Ra dp}) + b_2\ (\text{IR, Ra dp}) \tag{3}$$

all six fundamentals will be IR and Raman active and should appear in the presented spectral range (Figure 2).

$BrNO_2$ is an asymmetric top with the principal inertia axis *A* parallel to C_2, *B* perpendicular to C_2 and in the molecular plane, and *C* perpendicular to the molecular plane. Therefore a_1, b_1, and b_2 vibrations should exhibit a-, b-, and c-type band contours, respectively. All bands of the gas phase spectrum (Figure 2a) show clearly the expected band contours and were assigned by comparison with the fundamentals of $ClNO_2$[2] and FNO_2[2]. Most striking is the high intensity of $2\nu_6$, because ν_1 is perturbed by Fermi resonance with $2\nu_6$ just as in $ClNO_2$[2]. Below 600 cm^{-1}, the fundamentals ν_5 and ν_3 are expected, but only one band around 280 cm^{-1} with a $^{79/81}Br$ isotopic splitting of 1.30 cm^{-1} was observed. Because this isotopic shift is exactly the same as expected for the simple two-mass model $NO_2(46){-}Br(79/81)$ (calcd 1.28 cm^{-1}), this band was assigned to ν_3 (ν(Br−N)). The absorption due to ν_5 should be weaker and higher in wavenumbers than ν_3 in comparison to the spectra of $ClNO_2$ and FNO_2. Therefore, the shoulder near ν_3 at 290 cm^{-1} was tentatively assigned to ν_5.

Photolysis of $BrNO_2$ isolated in an argon matrix can lead to different fragments or to BrONO. Therefore, new bands appear in the matrix spectrum, which are shown in Figure 2b, and the band positions are listed in Table 3. Of all possible fragments only minor amounts of NO ($\nu = 1858$ cm^{-1}) are detected, and therefore, all new bands must belong to BrONO. For bromine nitrite, BrONO, two isomers are possible with the BrO bond orientated either cis or trans to N═O. But, according to bands observed in the N═O stretching region, where both isomers should be easily distinguishable (see FNO_2 and $ClNO_2$ isomers, Table 3), only one isomer is formed.

Additional experiments on UV irradiation of $ClNO_2$ isolated in an Ar matrix resulted in six new bands in the infrared spectrum at 1755 (vs), 1711 (m), 855 (w), 852 (m), 658 (w), and 649 (m) cm^{-1}, which were assigned to ClONO isomers by comparison with ab initio data gathered in Table 3. While the band at 1755 cm^{-1} belongs to the trans isomer and the band at 1711 cm^{-1} to the cis isomer, all other bands cannot be assigned unambiguously. A detailed IR matrix study on both ClONO isomers is intended by us. Nevertheless, on the basis of the relative band intensities observed in this experiment, it can be concluded that mainly *trans*-ClONO is formed. Also, *trans*-BrONO is formed by photolysis of matrix-isolated $BrNO_2$ because of the following: (i) The mechanism for photoisomerization of both XNO_2 species X = Cl; Br should be similar. Rearrangement of excited XNO_2 in the matrix cage by the smallest geometric deformation leads to *trans*-XONO. It is interesting to note that *cis*-ClONO is the main product in the gas phase reaction between Cl_2O and ClNO[21] or between Cl atoms and NO_2,[22] respectively. (ii) The N═O stretching wavenumber or BrONO (1727.9 cm^{-1}) should be lower than the vibration of the corresponding ClONO isomer. This is true only for the trans form. Support for this assumption comes from the trend in $\nu(N{=}O)_{\text{avg}} = 1531, 1514, 1501$ cm^{-1} observed in the series of halogen nitrates O_2NOX, X = [23]F, [24]Cl, [24]Br, respectively.

Because no further photolysis products are detectable in the matrix spectrum of $BrNO_2$ and BrONO, other than small amounts of NO, the relative band intensities for I($BrNO_2$, ν_1): I(BrONO, ν_1) are 1:2.0.

All six fundamentals of *trans*-BrONO (C_s symmetry) are infrared active.

$$\Gamma_{\text{vib}} = 5a'\ (\text{IR, Ra p}) + a''\ (\text{IR, Ra dp}) \tag{4}$$

Because the experimental vibrational data of *trans*-FONO[1] and *trans*-ClONO[2] are incomplete, the observed vibrations of BrONO were compared with the respective calculated fundamentals in Table 3. In this manner the bands at 1727.9, 833.2, 584.8, and 391.1 cm^{-1} were assigned to ν_1, ν_2, ν_3, and ν_4, respectively. The additional bands at 573.8 and 420.3 cm^{-1} were assigned to $\nu_4 + \nu_5$ and $2\nu_5$, which gain intensity by anharmonic resonance with ν_3 and ν_4, respectively. These combinations allowed us to calculate the missing fundamental $\nu_5 = 197$ cm^{-1}. Below ν_4, the fundamental $a''(\nu_6)$ is expected as a weak band. The only weak band which appeared in this region can be seen at 299.3 cm^{-1}. Because this frequency is unexpectedly high, it is assigned tentatively to $2\nu_6$.

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(23) Casper, B.; Dixon, D. A.; Mack, H.-G.; Ulic, S. E.; Willner, H.; Oberhammer, H. *J. Am. Chem. Soc.* **1994**, *116*, 8317.

(24) Wilson, W. W.; Christe, K. O. *Inorg. Chem.* **1987**, *26*, 1573.