

The Synthesis of ^{15}N - and ^{18}O -Isotopically-Enriched Nitryl Bromide, IR Matrix Spectra, and Force Fields of BrNO_2 , *cis*- BrONO , and *trans*- BrONO

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Received March 17, 1998

The gas phase reaction between BrNO and O_3 at low pressure (<10 mbar) results in the formation of BrNO_2 in about 60% yield. In this manner ^{15}N - and ^{18}O -labeled BrNO_2 are prepared. In addition, it is shown that BrNO_2 also forms by the heterogeneous low-temperature reaction between gaseous BrNO and solid sulfuric acid, doped with H_2O_2 . It can be assumed that BrNO_2 may be formed in a similar way under stratospheric conditions. The isotope scrambling in the reaction between BrNO and $^{18}\text{O}_3$ as well as in the gas phase equilibrium $\text{BrNO} + \text{NO}_2 \rightleftharpoons \text{BrNO}_2 + \text{NO}$ are investigated. For the equilibrium constant a lower limit of $K_{298} \geq 1 \times 10^{-3}$ is deduced from infrared measurements. A detailed IR and Raman study on BrNO_2 is performed. Photolysis of matrix-isolated BrNO_2 at different wavelengths leads to a mixture of *cis*- and *trans*- BrONO . The vibrational data of BrNO_2 (6 fundamentals, 7 combinations), *cis*- BrONO (5 fundamentals, 1 overtone), and *trans*- BrONO (4 fundamentals, 8 combinations) as well as the calculated force fields are in excellent agreement with the ab initio values, predicted by T. J. Lee (*J. Phys. Chem.* **1996**, *100*, 19847).

Introduction

The first attempts to synthesize nitryl bromide were reported in the early 1960s.^{1,2} Kuhn and Olah tried to use nitryl bromide in Friedel–Crafts type nitration reactions of aromatics. They explored a number of possible formation reactions: the halogen exchange of nitryl chloride with KBr in liquid SO_2 , the reaction of BBr_3 with either anhydrous nitric acid or N_2O_5 , the reaction of bromosulfonic acid with nitric acid, and the ozonolysis of nitrosyl bromide. But in all cases the isolation of BrNO_2 was not accomplished.¹ Martin et al. conducted gas phase studies of the system BrNO/ClO_2 and, under photolytic conditions, the system Br_2/NO_2 . They concluded that, while BrNO_2 cannot be formed at room temperature, there is evidence for its formation in the phase diagram of $\text{Br}_2/\text{N}_2\text{O}_4$ at low temperature.² IR spectra of the reaction products of bromine atoms with NO_2 isolated in an argon matrix, have been assigned to BrNO_2 and BrONO .^{3,4} No reference was made to the *cis* or *trans* isomer. Due to increasing interest in bromine compounds and their possible importance in atmospheric chemistry, recently several experimental and theoretical studies of the title compounds were undertaken. Gaseous BrNO_2 was detected for the first time⁵ in a long-path gas cell and identified by the strongest IR bands at 787, 1292, and 1660 cm^{-1} following the reaction of N_2O_5 with BrNO or solid NaBr . Subsequently it was shown that BrNO_2 can be formed in the troposphere, by the reaction of N_2O_5 with sea salt aerosol.^{6,7} After formation, photolysis of BrNO_2 into

Br and NO_2 was assumed. The impact of bromine atoms on the Arctic tropospheric ozone concentration has been confirmed by field measurements.^{8,9} Under stratospheric conditions BrNO_2 is possibly formed via the reaction of N_2O_5 with HBr on nitric acid trihydrate particles.¹⁰ In recent laboratory experiments it was found that BrNO_2 was formed in a continuous-flow system by the reaction of either diluted gaseous ClNO_2 or Br_2 with aqueous solutions of NaBr or NaNO_2 , respectively.^{11,12} This synthetic approach¹¹ has enabled us to isolate pure BrNO_2 for the first time and to study its properties in detail.¹³ It was possible to record 5 fundamental and 4 combination bands in the infrared region and to study the UV/vis spectrum between 180 and 600 nm. Photolysis of matrix-isolated BrNO_2 resulted in *trans*- BrONO , and some infrared bands of this isomer were assigned. BrNO_2 was found to be surprisingly stable in the gas phase at room temperature, where it exhibits a lifetime of about 1 h in our vacuum system. It was hence possible for us to record a high-resolution (<0.003 cm^{-1}) infrared spectrum and to determine rotational and centrifugal distortion constants for the ground and $\nu_4 = 1$ states of $^{79}\text{BrNO}_2$ and $^{81}\text{BrNO}_2$.¹⁴

The lifetime of BrNO_2 appears to be limited by heterogeneous decomposition on the walls of our vacuum system. Using the fitted parameters for unimolecular decay, a gas phase lifetime of about 7 h at 298 K was found.¹² This is clearly inconsistent

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with an earlier value of 2.3 s reported by Kreuter and Wine.^{15,16} They observed the decay of Br atoms in the reaction with NO₂, and it may be assumed that BrONO was formed in their experiments, in analogy to the reaction of Cl atoms with NO₂, where ClONO is formed.^{17,18} ClONO isomerizes heterogeneously to ClNO₂.¹⁹ Hence BrONO seemed to be less stable than BrNO₂, in agreement with a recent ab initio study.²⁰

This study suggests a Br–N bond energy of 94 kJ mol⁻¹, which is comparable to the experimental activation energy of 89 ± 9 kJ mol⁻¹ for unimolecular decay.¹² In addition, molecular structures, relative enthalpies ($\Delta H(\text{cis-BrONO-BrNO}_2) = 26.8$, $\Delta H(\text{trans-BrONO-BrNO}_2) = 43.1$ kJ mol⁻¹) and complete vibrational spectra for the title compounds were predicted.²⁰ This prompted us to complete the experimental spectrum of BrNO₂ by Raman measurements and to reinvestigate the photoisomerization of matrix-isolated BrNO₂ in order to detect both *cis*- and *trans*-BrONO. Additional vibrational data were needed for the calculation of reliable force fields. For this purpose a convenient synthesis of isotopically-enriched BrNO₂ was needed.

In this paper a new synthesis and a possible further route to BrNO₂ in the stratosphere are communicated.

Experimental Section

CAUTION! Ozone and hydrogen peroxide are potentially explosive, especially in the presence of organic materials or of catalytic traces of transition metal ions adsorbed on glass walls. It is important to take safety precautions when these compounds are handled in the pure liquid state. Reactions involving either one of them should be carried out only with millimolar quantities.

General Procedures and Reagents. Volatile materials were manipulated in a glass vacuum line equipped with a capacitance pressure gauge (221 AHS-1000 MKS Baratron, Burlington, MA), three U-traps, and valves with PTFE stems (Young, London, U.K.). The vacuum line was connected to an IR cell (optical path length 200 mm, Si windows 0.5 mm thick) contained in the sample compartment of the FTIR instrument. This allows one to observe the purification processes and to follow the course of reactions. Glass reactors (250 mL bulbs) fitted with 10 mm valves with PTFE stems were carefully cleaned with hot concentrated sulfuric acid and distilled water prior to use. The following chemicals were obtained from commercial sources: bromine (p.a. quality, Merck), nitric oxide (99.8% Messer Griesheim, Düsseldorf, Germany), and nitrogen dioxide (99% Baker, Philipsburg, NY). They were purified by trap-to-trap condensation prior to use. Sulfuric acid (96%, p.a. quality, Merck), hydrogen peroxide (80%, Solvay, Interlox GmbH, Hannover, Germany), and mercury (Riedel de Haen AG, Seelze, Germany) were used without further purification.

Thermally-labile products were vacuum transferred in glass ampules, flame-sealed, and stored under liquid nitrogen in a long-term Dewar vessel. The ampules were opened and resealed using an ampule key.²¹

Synthesis of O₃. Ozone was made in an ozonizer (model 301, Sander, Eltze, Germany) and trapped using liquid oxygen as coolant in order to prevent the condensation of oxygen. Oxygen dissolved in ozone was removed in a vacuum at -196 °C.

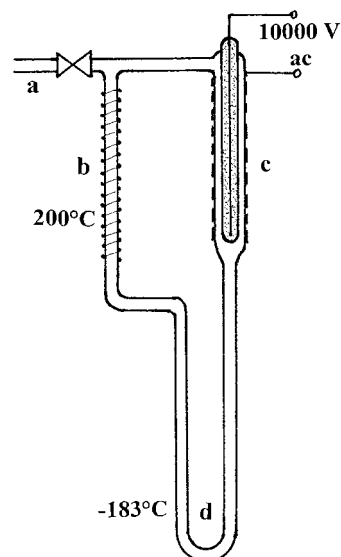


Figure 1. Glass ozonizer for the synthesis of isotopically-enriched ¹⁸O₃: (a) electrical connection to the vacuum line; (b) electrical heater; (c) electrical field between concentric tubes; (d) U-trap.

Isotopically-enriched ¹⁸O₃ was synthesized from ¹⁸O₂ (99.5 atom % ¹⁸O, Chemotrade, Düsseldorf, Germany) in a small homemade ozonizer with an internal volume of 60 mL (see Figure 1), attached to the vacuum line (internal volume ca. 100 mL). In the ozonizer, ¹⁸O₂ at a pressure of about 500 mbar was circulated by an electrical heater. After oxygen was passed through the electrical field of 20 kV cm⁻¹ in the concentric glass tubes, the produced ¹⁸O₃ was trapped at -183 °C. The conversion of ¹⁸O₂ into ¹⁸O₃ was followed by monitoring the pressure. After about 3 h, 2 mmol of ¹⁸O₃ was formed. The excess ¹⁸O₂ was recovered by cryopumping the oxygen into a vessel containing molecular sieves (5 Å) held at -196 °C.

Synthesis of BrNO. For the synthesis of BrNO and Br¹⁵NO a dry, evacuated reaction vessel with an internal volume of 250 mL was filled with a mixture of 150 mbar of Br₂ (1.5 mmol) and 320 mbar of NO (3.2 mmol). After a reaction time of 30 min at 20 °C, the products were passed in a vacuum through three U-traps held at -65, -120, and -196 °C. The trap held at -120 °C contained about 2.4 mmol of pure BrNO (≈80% yield).

¹⁵NO was made by the reaction of sulfuric acid, mercury, and Na¹⁵NO₃ (>99 atom % ¹⁵N, Isotec Inc., Miamisburg). A 250 mL bulb equipped with a 10 mm Young valve was charged with 688 mg of Na¹⁵NO₃ (8 mmol) and 15 g of mercury (75 mmol) and then evacuated. About 10 g of H₂SO₄ (containing 20 wt % H₂O) was slowly introduced through the valve into the evacuated reaction vessel. The contents were shaken for 1 h at room temperature, and the gaseous reaction products were passed in a vacuum through U-traps held at -100 and -196 °C. The trap at -196 °C contained ¹⁵NO with a few percent ¹⁵N₂O as impurity.

Synthesis of BrNO₂. In the course of this study, it was found that BrNO can be oxidized to BrNO₂ by O₃ or H₂SO₄/H₂O₂ under appropriate conditions.

The dry evacuated 250 mL reaction vessel was charged with 10 mbar of ozone at 20 °C (0.1 mmol). Into this vessel containing the ozone was slowly introduced 0.07 mmol of BrNO within a few minutes. **CAUTION!** This slow filling process was very important, because otherwise the contents did explode. After a reaction time of about 5 min the products were slowly passed in a vacuum through three U-traps held at -90, -125, and -196 °C. In the trap at -125 °C, yellow solid nitryl bromide was collected (yield ca. 60%). An excess of ozone during the synthesis was necessary in order to remove NO_x as the less volatile side product N₂O₅. Br¹⁵NO₂ was formed in the same manner from Br¹⁵NO and O₃. Treatment of BrNO with ¹⁸O₃ resulted in an equimolar mixture of BrN¹⁶O₂, BrN¹⁶O¹⁸O, and BrN¹⁸O₂ as well as N₂O₅ containing ¹⁸O.

Another route to BrNO₂ was the heterogeneous reaction of BrNO on a cold H₂SO₄/H₂O₂ surface. First, 3.5 g of a solution of hydrogen

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peroxide (80%) in concentrated sulfuric acid (96%) at a mass ratio of 1:20 was distributed as a thin film over the inner surface of the 250 mL reaction vessel. Then, after being cooled to -20 or -80 °C, the vessel was evacuated and charged with 0.25 mmol of BrNO. The course of the reaction was followed by removal of small samples (0.05 mmol) for infrared analysis. At -20 °C the BrNO was converted into BrNO₂, some Br₂, N₂O₅, and HNO₃ within 1 min. At -80 °C the same reaction required several hours.

Determination of the Equilibrium $\text{BrNO} + \text{NO}_2 \rightleftharpoons \text{BrNO}_2 + \text{NO}$. Into the IR cell, containing NO₂ with a pressure of about 3 mbar, was introduced BrNO within a few seconds to achieve a total pressure of about 6 mbar. Simultaneously the IR measurement was started and repeated every 10 s. The maximal partial pressure of BrNO₂ was calculated from the observed absorbance at 1301 cm⁻¹ with the help of the known absorption cross section.¹³ For the calculation of the equilibrium constant, the partial pressure of NO was set equal to the partial pressure of BrNO₂, because NO is formed together with BrNO₂ simultaneously. The molar ratio NO:BrNO₂ is slightly affected by the decomposition of BrNO₂, which is slow in comparison to the BrNO + NO₂ reaction.

Preparation of the Matrices. Small amounts of pure BrNO₂ samples (ca. 0.1 mmol) were transferred in a vacuum into a small U-trap kept in liquid nitrogen. This U-trap was mounted in front of the matrix support and allowed to reach a temperature of -125 °C. A gas stream (3 mmol h⁻¹) of argon was directed over the solid BrNO₂, and the resulting gas mixture was immediately quenched on the matrix support at 12 K. For each BrNO₂ sample two different amounts of matrix material (1 and 4 mmol, respectively) were deposited. Photolysis experiments were undertaken in the visible (>350 , >450 nm) and UV regions (254 nm) by using a 250 W tungsten halogen lamp (Osram) and a high-pressure mercury lamp (TQ 150, Heraeus), respectively, in combination with cutoff and interference filters (Schott). Details of the matrix apparatus have been described elsewhere.²²

Instruments. Matrix infrared spectra were recorded on a Bruker IFS 66v FT spectrometer in the reflectance mode using a transfer optic. A DTGS detector together with a KBr/Ge beam splitter operated in the region 5000–400 cm⁻¹. In this region 64 scans were co-added for each spectrum using apodized resolutions of 1.2 or 0.3 cm⁻¹. A far-IR DTGS detector together with a 6 μm Mylar beam splitter was used in the region 440–80 cm⁻¹. In this region 128 or 64 scans were co-added for each spectrum using apodized resolutions of 1.2 or 0.3 cm⁻¹, respectively.

Gas phase infrared spectra were recorded on a Nicolet Impact 400 D FTIR spectrometer operating between 5000 and 400 cm⁻¹ at a resolution of 2 cm⁻¹.

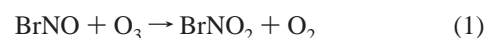
Raman spectra of solid BrNO₂ at -196 °C were recorded with a resolution of 2 cm⁻¹ on a Bruker FRA 106 FT Raman spectrometer using the 1064 nm exciting line of a narrow-band Nd:YAG laser (DPY 301, ADLAS, Lübeck, Germany).

Results and Discussion

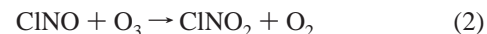
Syntheses. All syntheses of BrNO₂ described previous^{5,11,12} are inefficient, have low product yields, and are inappropriate for the preparation of isotopically-enriched Br¹⁵NO₂ and BrN¹⁸O₂. In a previous study on the properties of BrNO₂ we were able to demonstrate that its decomposition into Br₂ and NO₂ is strongly affected by heterogeneous wall reactions.¹³ In dry glass vacuum systems, pretreated with NO₂ and O₃, the lifetime of BrNO₂ at partial pressures of a few millibars at room temperature is about 1 h, which is sufficient for all manipulations.

The formation of BrNO₂ in equilibrium with Br₂ and N₂O₄ in the liquid or solid state, as assumed earlier,² must be ruled out, because by Raman measurements we are unable to see the bands of BrNO₂ although the detection limit is as low as 0.1%.

In reference to the reaction



which results in the formation of BrNO₂ in about 60% yield, we note that the analogous reaction



was reported in 1929 by Schumacher and Sprenger.²³ This reaction is kinetically hindered and is catalyzed by traces of NO_x, presumably NO₃.²⁴ Reaction 1 goes to completion in a few minutes at room temperature, and this indicates the participation of the same catalysis. In contrast to ClNO, BrNO easily decomposes according to



and NO as a catalyst is always present in situ.

The large heat of reaction 1 needs to be dissipated in the reaction mixture. It is therefore important to introduce BrNO slowly into the reaction vessel containing ozone. In addition, it is observed that BrNO catalyzes the decomposition of BrNO₂. In order for this to be prevented, BrNO must be introduced into the excess of ozone and not in the opposite way, ozone into an excess of BrNO.

As described in the experimental part, BrNO reacts with ¹⁸O₃ in an equilibrium mixture of BrNO₂, BrNO¹⁸O, and BrN¹⁸O₂. This result may be rationalized by a fast Br atom exchange between BrNO₂ and the decomposition products of the byproduct N₂O₅ according to



followed by



By introducing ¹⁵NO₂ into an IR cell containing BrNO₂ we have been able to demonstrate that the exchange in reaction 5 is fast compared to the formation rate of BrNO₂ according to reaction 1. Very fast isotope scrambling reactions between nitrogen oxides as formulated in reactions 4 and 6 are well-known.^{25,26}

The investigation of the reaction



shows that an equilibrium can be achieved very fast from either side at 3 mbar partial pressure of each component at 25 °C (<5 s, the time-resolving limit of our spectrometer). It is possible by IR spectroscopy to determine the equilibrium pressure of BrNO₂ by mixing NO₂ with BrNO in the IR cell. This approach is preferred over the reverse reaction between BrNO₂ and NO, because BrNO is more easily prepared and purified than BrNO₂. After introducing BrNO into the NO₂-containing gas cell, BrNO₂ appears in the IR spectrum in less than 5 s, but it decays subsequently into Br₂ and NO₂, because BrNO catalyzes the decomposition of BrNO₂. Hence the highest BrNO₂ concentration, observed in several experiments, determines the lower limit of the equilibrium constant $K(7) \geq 1 \times 10^{-3}$.

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Table 1. Vibrational Band Positions (cm⁻¹) of Natural and Isotopically-Enriched BrNO₂

ab initio ^a		IR (Ar matrix)					Raman ^c BrNO ₂	assign. according C _{2v} sym
CCSD(T)/TZ2P	I ^b	BrNO ₂	I ^b	Br ¹⁵ NNO ₂	BrN ¹⁸ O	BrN ¹⁸ O ₂		
		3294.61	2	3224.45	3265.71	3233.04		2ν ₄
		2931.01	6	2881.35	2893.55	2856.41		ν ₁ + ν ₄
		2840.39	0.3	2776.08	2816.70	2790.50		ν ₄ + 2ν ₆
		2574.45	2	2537.41	2528.46	2492.55		2ν ₁
		2498.34	0.5	2453.97	2464.13	2428.75		ν ₁ + 2ν ₆
1663	86	1659.62	92	1623.84	1645.15	1628.77	1584, m	ν ₄ (b ₁)
		1564.87	0.2	1543.59	1538.17	1510.44		2ν ₂
1288	100	1290.98	100	1277.16	1266.65	1245.03	1273, m	ν ₁ (a ₁)
		1195.88	16	1167.11	1186.60	1176.54	1210, w	2ν ₆
799	58	782.68	54	772.59	769.47	755.43	785, s	ν ₂ (a ₁)
613	1	605.72	2	590.05	602.14	598.56	612, w	ν ₆ (b ₂)
349	0.03						366, s	ν ₅ (b ₁)
281	8	281.83	8	279.85	278.05	272.69	314, vs	ν ₃ (a ₁), ⁷⁹ Br
		280.67		278.56	276.65	271.43		ν ₃ (a ₁), ⁸¹ Br

^a Reference 20, harmonic wavenumbers, no scaling factor used. ^b Relative integrated absorbance. ^c Solid sample at -196 °C.

For the analogous reaction



the equilibrium constant is determined from kinetic²⁷ and IR²⁸ measurements to be 1.01×10^{-4} and 1.23×10^{-4} , respectively. For this reaction a chlorine atom transfer mechanism is established.²⁷

It is now well documented, on the basis of several laboratory experiments, that BrNO₂ can be formed in the troposphere by heterogeneous reactions between N₂O₅ or ClNO₂ with sea salt aerosol.^{6,7} However, possible routes to BrNO₂ in the stratosphere, suggested by laboratory experiments, are yet unknown. The stratospheric background aerosol, called the Junge layer, consists mainly in 40–80 wt % sulfuric acid doped with different compounds.²⁹ If NO₃ enters the aerosol and H₂O₂ is formed,³⁰ the aerosol particles should exhibit strong oxidizing power. This oxidizing power is demonstrated by heating sulfuric acid containing H₂O₂, which results in ozone in up to a 30% yield.^{31,32} In order to check for the possible formation of BrNO₂ in the stratosphere, we have studied the heterogeneous reaction between BrNO and sulfuric acid, doped with H₂O₂.

BrNO at a pressure of ca. 1 mbar over thin layers of H₂SO₄/H₂O₂ at -20 °C is converted within seconds into BrNO₂, Br₂, N₂O₅, and HNO₃. At -80 °C this reaction requires several hours for completion. This heterogeneous reaction has to be studied in detail, to establish its impact on the stratospheric chemistry.

Vibrational Spectra. The molecules BrNO₂, *cis*-BrONO, and *trans*-BrONO have been studied recently at the CCSD(T)/TZ2P level of theory.²⁰ Reliable energies, molecular geometry, dipole moments, harmonic vibrational wavenumbers, and IR intensities were predicted at a time when our experimental study on the properties of BrNO₂ and its photoisomerization into *trans*-BrONO was in press.¹³ With all predicted vibrational data now at hand, some of our previously communicated band positions of *trans*-BrONO¹³ must be assigned to *cis*-BrONO. In order to complete our previous experimental study on the vibrational spectra of BrNO₂ and *trans*-BrONO,¹³ we have recorded a

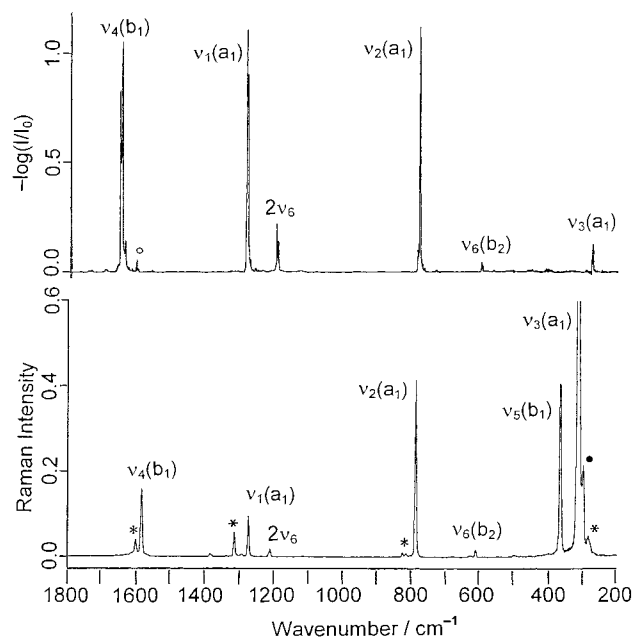


Figure 2. Vibrational spectra of BrNO₂. Upper trace: IR spectrum, argon matrix at 15 K. Lower trace: Raman spectrum, solid at 77 K. Impurities: (O) NO₂, (*) N₂O₄, (●) Br₂.

Raman spectrum of BrNO₂ and have reinvestigated the photoisomerization of matrix-isolated BrNO₂ and its isotopomers into *cis*- and *trans*-BrONO.

In Figure 2 are shown IR and Raman spectra of BrNO₂, and in Table 1, all experimental data of BrNO₂ are compared with the calculated wavenumbers and relative IR intensities of the 6 fundamentals. The fundamental ν₅, which is not detectable by IR, due to its low absorption cross section, is observed for the first time in the Raman spectrum of solid BrNO₂. Considering that all calculated band positions are based on harmonic vibrations (without use of a scaling factor) while all observed band positions are affected by anharmonicity as well as by matrix and solid state effects, the agreement between calculated and observed band positions and intensities of IR bands is excellent. The proposed assignment of the observed combinations and overtones is strongly supported by the vibrational data of ¹⁵N- and ¹⁸O-labeled BrNO₂ molecules. The isotopic shifts of the fundamentals are also used for force field calculations (vide infra).

The UV absorption spectrum of BrNO₂ suggests that, at λ_{max} = 199, 247, and 372 nm, at least three electronically excited

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Table 2. IR Band Positions (cm^{-1}) of Natural and Isotopically-Enriched *cis*-BrONO Isolated in an Argon Matrix

ab initio ^a		IR (Ar matrix)						assign.
CCSD(T)/TZ2P	I ^b	BrONO	I ^b	BrO ¹⁵ NO	Br ¹⁸ ONO	BrON ¹⁸ O	Br ¹⁸ ON ¹⁸ O	according C _s sym
		3262.4	3	3204.49				2ν ₁
1664	100	1650.70	100	1623.88	1650.7	1608.63	1606.13	ν ₁ (a')
845	3	862.6	2					ν ₂ (a')
558	27	573.47	48	565.54	558.43	573.47	558.43	ν ₃ (a')
429	38	420.15	30	418.93	402.31	419.05	401.34	ν ₄ (a')
210	0.03							ν ₅ (a')
357	0.6	368.25	2	361.71	362.06	365.14	358.98	ν ₆ (a'')

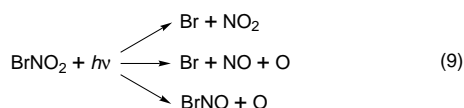
^a Reference 20, harmonic wavenumbers, no scaling factor used. ^b Relative integrated absorbance.

Table 3. IR Band Positions (cm^{-1}) of Natural and Isotopically-Enriched *trans*-BrONO Isolated in an Argon Matrix

ab initio ^a		IR (Ar matrix)						assign.
CCSD(T)/TZ2P	I ^b	BrONO	I ^b	BrO ¹⁵ NO	Br ¹⁸ ONO	BrON ¹⁸ O	Br ¹⁸ ON ¹⁸ O	according C _s sym
		3413.0	7	3354.27	3409.7	3330.1	3325.3	2ν ₁
		2895.2	2	2848.2				ν ₁ + 2ν ₃
		2560.7	1	2520.1				ν ₁ + ν ₂
		2315.69	6	2280.06	2293.25	2271.69	2249.17	ν ₁ + ν ₃
		2119.78	3	2087.06	2110.34	2067.66	2059.39	ν ₁ + ν ₄
1740	100	1723.38	100	1693.25	1721.95	1680.34	1678.98	ν ₁ (a')
		1414.3	4	1399.10	1376.5	1404.0	1365.6	ν ₂ + ν ₃
		1222.5	1	1210.2				ν ₂ + ν ₄
835	44	835.89	48	825.78	817.89	826.16	807.55	ν ₂ (a')
601	82	586.88	93	582.60	565.77	585.22	564.23	ν ₃ (a')
385	20	391.21	13	389.25	382.95	382.95	375.12	ν ₄ (a')
226	0.01							ν ₅ (a')
		299.3	2	294.6				2ν ₆
158	0.001							ν ₆ (a'')

^a Reference 20, harmonic wavenumbers, no scaling factor used. ^b Relative integrated absorbance.

states are accessible,¹³ so that irradiation of matrix-isolated BrNO₂ with UV light of different energy should cause bond rupture into various products with a variable amount of excess energy:



Recombination of the fragments in the matrix cage can lead in principle to *trans*-BrONO and *cis*-BrONO. If the O atom escapes the matrix cage, BrNO and BrON may form as well. During irradiation, the products can be photolyzed, too, so that finally a photostationary product mixture is formed. Figure 3 presents typical IR spectra of the photolysis products, which are assigned by comparison with predicted IR spectra of *cis*- and *trans*-BrONO based on ab initio calculations²⁰ and reference spectra. The molar *cis*:*trans* ratios were deduced from the observed integrated intensity ratios between ν₃(*cis*-BrONO) near 573 cm⁻¹ and ν₃(*trans*-BrONO) near 587 cm⁻¹ and the respective calculated integrated band strength of 1:3.7 obtained by ab initio calculations. By use of visible light of λ > 450 nm, the yield of *cis*-BrONO is the highest (the molar *cis*:*trans* ratio is 3.1:1), and unfiltered light of a tungsten halogen lamp forms a mixture of BrONO isomers with an increased *trans*-BrONO content (the molar *cis*:*trans* ratio is 2.5:1). A similar result is observed with the strong 254 nm emission of a high-pressure mercury lamp (the molar *cis*:*trans* ratio is 1.2:1), but in these experiments weak additional bands at 1799.1 cm⁻¹ (BrNO), 1820.1 cm⁻¹ (BrON),³³ and 1858.2 cm⁻¹(NO)³⁴ are observed. The assignment of the *trans*- and *cis*-BrONO bands is based on the observed relative band intensities in different

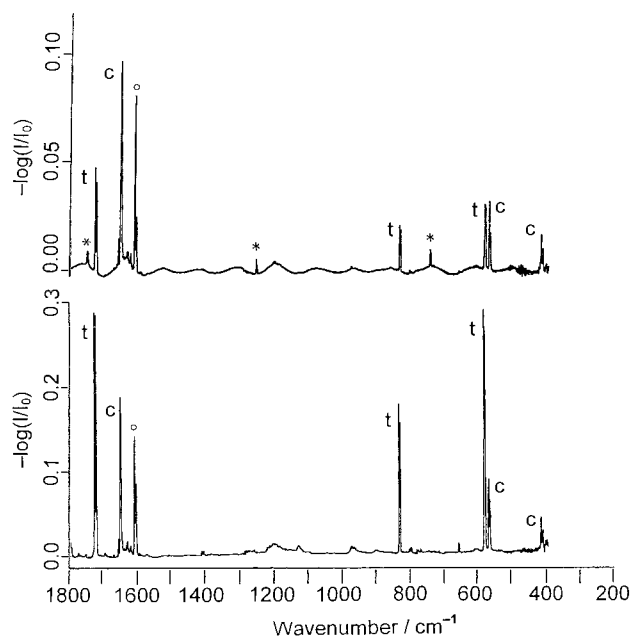


Figure 3. Photolysis products of BrNO₂ isolated in an argon matrix. Residual bands of BrNO₂ are subtracted electronically; c, *cis*-BrONO; t, *trans*-BrONO. Upper trace: after irradiation with light λ > 450 nm. Lower trace: after irradiation with light λ = 254 nm. Impurities: (O) NO₂, (*) N₂O₄.

photolysis experiments and supported by comparison with the band positions obtained in the ab initio study.²⁰ In Tables 2 and 3 the wavenumbers and relative IR intensities of the fundamentals, obtained by ab initio calculations, are presented together with experimental data for the *cis*- and *trans*-BrONO isomers. With the exception of the very weak IR bands ν₅ for *cis*- and *trans*-BrONO and ν₆ for *trans*-BrONO, experimental

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Table 4. Input Data^a (cm⁻¹) for the Force Field Calculation of BrNO₂^b

<i>i</i>	ν_i^c	$\Delta\nu_i^d$		
		Br ¹⁵ NO ₂	BrN ¹⁸ O ₂	⁸¹ BrNO ₂
1	1277 ^e (1277)	11 (15)	52 (46)	0.0 (0.0)
2	782.68 (782.66)	10.2 (10.9)	27.5 (27.5)	0.00 (0.05)
3	281.83 (281.89)	2.00 (2.31)	9.14 (8.29)	1.16 (1.27)
4	1659.62 (1659.59)	36.1 (36.9)	31.2 (31.5)	0.00 (0.00)
5	366 (366)	(1.7)	(17)	(0.3)
6	605.72 (605.71)	15.7 (15.8)	7.16 (7.46)	0.00 (0.04)

^a Uncertainties of values without a decimal point and with one digit and two digits behind the decimal point are ± 2 , ± 0.2 , and ± 0.05 cm⁻¹, respectively. ^b Values in parentheses are calculated data with the final force field. ^c Fundamentals according to Table 1. ^d $\Delta\nu = \nu(\text{BrNO}_2) - \nu(\text{isotopomer})$. ^e Fermi-resonance corrected, see text.

Table 5. Input Data^a (cm⁻¹) for the Force Field Calculation of *cis*-BrONO^b

<i>i</i>	ν_i^c	$\Delta\nu_i^d$			
		BrO ¹⁵ NO	Br ¹⁸ ONO	BrON ¹⁸ O	Br ¹⁸ ON ¹⁸ O
1	1650.70 (1650.66)	27.1 (28.3)	0.0 (2.6)	42.5 (42.4)	45.0 (45.1)
2	862.6 (862.6)	(12.3)	(11.5)	(15.9)	(27.6)
3	573.47 (573.47)	8.0 (8.1)	15.2 (17.0)	0.0 (0.2)	15.2 (17.4)
4	420.15 (420.15)	1.2 (1.4)	18.0 (18.0)	1.1 (1.0)	19.0 (19.0)
5	(210)	(0.5)	(1.3)	(7.1)	(8.3)
6	368.25 (368.25)	6.5 (6.7)	6.2 (5.9)	3.1 (3.3)	9.3 (9.3)

^a Uncertainties of values without a decimal point and with one digit and two digits behind the decimal point are ± 2 , ± 0.2 , and ± 0.05 cm⁻¹, respectively. ^b Values in parentheses are calculated data with the final force field. ^c Fundamentals according to Table 2. ^d $\Delta\nu = \nu(\text{BrONO}) - \nu(\text{isotopomer})$.

values for all fundamentals are known. Again, the agreement between calculated²⁰ and observed values for both wavenumbers and relative intensities of the fundamentals is excellent. In addition the wavenumber of the band assigned to $2\nu_6$ fits with the wavenumber for ν_6 , predicted from ab initio calculation.²⁰ With the exception of ν_1 , the assignment of the fundamentals for the two BrONO isotopomers containing one ¹⁸O atom is not straightforward. The fundamentals are assigned by calculated band position using the respective force fields (vide infra).

With the help of the available matrix data in Tables 1–3, which are unambiguous, the results of early matrix experiments^{3,4} on the cocondensation of NO₂ with Br atoms can now be reinterpreted. In the carefully conducted experiments by Tevault,³ 11 of the observed IR band positions coincide with our data. These bands are attributed to a mixture of mainly BrNO₂ and *cis*-BrONO as well a small amount of *trans*-BrONO. The spectral data obtained from similar experiments by Feuerhahn et al.⁴ are not in good agreement, because only two bands coincide with our data. In conclusion, it is interesting to note that by cocondensation of Br atoms with NO₂ the more stable *cis*-BrONO is formed in a thermodynamically-controlled manner and the photoisomerization of BrNO₂ in a matrix leads mainly to the less stable *trans*-BrONO with increasing energy of the light radiation.

Table 6. Input Data^a (cm⁻¹) for the Force Field Calculation of *trans*-BrONO^b

<i>i</i>	ν_i^c	$\Delta\nu_i^d$			
		BrO ¹⁵ NO	Br ¹⁸ ONO	BrON ¹⁸ O	Br ¹⁸ ON ¹⁸ O
1	1723.38 (1723.36)	30.4 (31.0)	1.44 (1.05)	43.5 (43.8)	44.8 (44.9)
2	835.89 (835.91)	10.2 (10.7)	18.2 (16.9)	9.82 (10.84)	28.6 (28.2)
3	586.88 (586.30)	4.32 (5.61)	21.3 (21.1)	1.68 (0.29)	22.9 (22.3)
4	391.21 (391.22)	1.98 (1.89)	8.34 (7.71)	8.34 (8.69)	16.3 (16.2)
5	(221)	(2.1)	(4.2)	(2.7)	(6.9)
6	(158)	(2.3)	(1.4)	(3.4)	(4.8)

^a Uncertainties of values without a decimal point and with one digit and two digits behind the decimal point are ± 2 , ± 0.2 , ± 0.05 cm⁻¹, respectively. ^b Values in parentheses are calculated data with the final force field. ^c Fundamentals according to Table 3. ^d $\Delta\nu = \nu(\text{BrONO}) - \nu(\text{isotopomer})$.

Table 7. Quadratic Force Fields^a for BrNO₂, *cis*-BrONO, and *trans*-BrONO

	BrNO ₂		<i>cis</i> -BrONO		<i>trans</i> -BrONO		
	ASYM20	ab initio ^b	ASYM20	ab initio ^b	ASYM20	ab initio ^b	
	1.481	1.371	2.445	2.475	2.682	2.996	<i>F</i> ₁₁
	0.500	0.761	0.868	0.768	0.422	0.244	<i>F</i> ₂₁
	11.424	12.091	2.323	1.760	1.694	1.608	<i>F</i> ₂₂
	-0.132	-0.499	-0.559	0.004	0.751	-0.070	<i>F</i> ₃₁
	0.724	0.798	2.934	2.021	1.889	1.926	<i>F</i> ₃₂
	1.655	2.022	12.573	12.830	13.364	13.641	<i>F</i> ₃₃
			0.451	0.258	0.070	0.277	<i>F</i> ₄₁
			0.502	0.391	0.313	0.172	<i>F</i> ₄₂
			0.228	-0.025	0.264	0.172	<i>F</i> ₄₃
	9.113	9.181	1.239	1.373	0.944	0.937	<i>F</i> ₄₄
			-0.086	-0.299	0.232	0.230	<i>F</i> ₅₁
			0.571	0.614	0.208	0.210	<i>F</i> ₅₂
			0.798	0.674	0.436	0.500	<i>F</i> ₅₃
	0.414	0.411	0.071	-0.018	0.324	0.327	<i>F</i> ₅₄
	0.947	0.857	2.436	2.230	1.962	1.922	<i>F</i> ₅₅
	0.371	0.380	0.224	0.211	0.109	0.109	<i>F</i> ₆₆

^a Force constants in 10² N m⁻¹, normalized on 100 pm bond length. For BrNO₂, symmetry internal coordinates (including order) are defined as follows: r_{BrN} , $2^{-0.5}(r_{\text{NO}_1} + r_{\text{NO}_2})$, $\angle\text{ONO}$, $2^{-0.5}(r_{\text{NO}_1} - r_{\text{NO}_2})$, $2^{-0.5}(\angle\text{BrNO}_1 - \angle\text{BrNO}_2)$, δ oop. For the BrONO isomers, the following internal coordinates have been used: r_{BrO} , r_{ON} , r_{NO} , $\angle\text{BrON}$, ONO , τ (torsional coordinate). ^b Reference 20.

General Valence Force Fields. The structural parameters for BrNO₂, *cis*-BrONO, and *trans*-BrONO from ab initio calculations²⁰ together with the wavenumbers of the fundamentals and their isotopic shifts (Tables 4, 5, and 6, respectively) are taken as input data for the calculation of the general valence force fields with the program ASYM20.³⁴ Strong Fermi resonance between ν_1 and $2\nu_6$ is observed in the IR spectra of BrNO₂. Therefore the band position of ν_1 for BrNO₂ in Table 4 was corrected using the equation

$$\nu_{\text{corr}} = (\nu_a + \nu_b)/2 \pm (\nu_a - \nu_b)(s - 1)/[2(s + 1)], \quad s = I_a/I_b$$

(ref 35). Also the isotopic shifts $\Delta\nu_1$ of BrNO₂ are affected by

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Table 8. Valence Force Constants of XNO and XNO₂ Molecules, X = F, Cl, Br

	FNO FNO ₂	CINO CINO ₂	BrNO BrNO ₂
$f(\text{NO})$	15.912 ^a	15.282 ^a	15.254 ^a
$f(\text{XN})$	2.133 ^a	1.257 ^a	1.101 ^a
$f(\text{NO})$	11.5 ^b	10.61 ^c	10.27
$f(\text{XN})$	2.7 ^b	2.20 ^c	1.48

^a Reference 36. ^b Reference 37. ^c Reference 38.

Fermi resonance. They are corrected by the difference between calculated $2\Delta\nu_6$ and observed $2\Delta\nu_6$ (-3.3 and $+5$ cm^{-1} for the ¹⁵N and ¹⁸O species, respectively). All isotopic shifts are multiplied by 1.01 to correct for anharmonicity. The resulting shifts for $\Delta\nu_1$ ^{14/15}N and ^{16/18}O are 11 and 52 cm^{-1} , respectively. All other isotopic shifts are reliable, because no combination bands are in the vicinity of these fundamentals and uncertainties arise solely from the precision of the measurements. As mentioned above, all measured isotope shifts were increased by 1%. In the cases where fundamentals are not observed experimentally, the respective wavenumbers from ab initio calculation²⁰ are used. In the iteration procedure, the ab initio force constants from Table 7 are used as preliminary force fields and the input

data from Tables 4–6 are weighted by their uncertainties. With preliminary force fields for the *cis*- and *trans*-BrONO isomers, the wavenumbers of the ¹⁸O-monosubstituted species are calculated, allowing a correct assignment of the observed bands (Tables 2 and 3). The iteration procedure is ended, after all vibrational data are reproduced within their experimental uncertainties as presented in Tables 4–6. The agreement between the ab initio and the final experimental force fields of the three BrNO₂ isomers is excellent (see Table 7). This demonstrates that high-level ab initio calculations are very valuable for detailed analysis of experimental vibrational spectra. In Table 8, the inner force constants $f(\text{NO}) = (F_{11} + F_{44})/2$ and $f(\text{BrN}) = F_{22}$ of BrNO₂ are compared with the respective force constants of similar molecules. In both series the trends in $f(\text{NO})$ and $f(\text{XN})$ as well $f(\text{NO})$ for CINO₂ and BrNO₂ are very similar. The weak BrN bonds are responsible for the thermal instability of these molecules.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft (DFG), the European Union (EU Contract LAMOCs ENV-CT95-0046), and the Fonds der Chemischen Industrie is gratefully acknowledged.

IC9803006