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High resolution Fourier transform infrared spectrum of $^{79}Br^{14}N^{18}O$: analysis of the ν_1 band

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Paper in the honour of Dr Walter Lafferty for his many contributions to science

Abstract

The first high-resolution Fourier transform infrared spectrum of the ν_1 fundamental band of the $^{79}Br^{14}N^{18}O$ isotopic species of nitrosyl bromide located at 1751.29495(2) cm^{-1} has been analyzed. Using the Watson-type A-reduced Hamiltonian, the study of the rovibrational transitions has been performed. Rotational constants, quartic and sextic centrifugal distortion terms for the $v_1=1$ and for the vibrational ground state have been derived. The ground state parameters obtained in this work have been compared to the corresponding constants determined by an empirically refined MRCI (MultiReference Configuration Interaction) force field available in the literature.

Keywords: Nitrosyl bromide; High resolution; Rotational constants; ν_1 band; Anharmonic force field

1. Introduction

The nitrosyl bromide molecule (BrNO) is a highly unstable bromine reservoir species of potential interest for stratospheric chemistry [1]. It is produced in the atmosphere by recombination of NO with Br atoms or by reaction of sea aerosols with HNO_2. In recent years the bromine chemistry has received growing attention for its key role in ozone depletion and for this reason BrNO has been the subject of various experimental and theoretical investigations [2–13] with the goal of improving the knowledge of the force field and structure of this molecule. This bent triatomic molecule has three vibrational modes ν_1 (N–O stretch), located at 1798.7513 and 1798.7427 cm^{-1} for the $^{79}Br^{14}N^{16}O$ and $^{81}Br^{14}N^{16}O$ isotopomers, respectively [6], and ν_2 (BrNO bent) and ν_3 (Br–N stretch) located near 542.0 and 266.4 cm^{-1} respectively [2]. For the $^{79}Br^{14}N^{16}O$, $^{81}Br^{14}N^{16}O$, $^{79}Br^{15}N^{16}O$, and $^{81}Br^{15}N^{16}O$ isotopic species the rotational spectra were investigated in the ground vibrational state ([3,4,7] and references there in) leading to the determination of various rotational and quadrupole hyperfine parameters. For the $^{81}Br^{14}N^{16}O$ and $^{79}Br^{14}N^{16}O$ this rotational study was somehow extended to the 2^1, 2^2, 3^1, 3^2 and 3^3 low lying excited states [4,10,13] and in this case it was necessary to account explicitly for the C-type Coriolis resonance which couples the 2^1 and 3^2 rotational energy levels. In the infrared region, only the ν_1 band for the $^{79}Br^{14}N^{16}O$, and $^{81}Br^{14}N^{16}O$ isotopomers was analyzed at high resolution using Fourier transform technique [6], and this band appears as unperturbed. The analysis was completed by the identification of the $\nu_1+\nu_3-\nu_3$ hot band at 1768.622 cm^{-1} [8]. The aim of some of these studies [2–4,6,7,10], which were completed by ab initio calculations [5,9,12], was to determine—or to validate—the structure of the BrNO molecule and to get accurate information that would improve the determination of the potential energy function (up to the cubic terms). Recently, the geometry and anharmonic force field of BrNO

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were investigated using the multireference configuration interaction (MRCI) method and, for comparison, the multireference perturbation theory to second and third order (CASPT2, CASPT3) [12]. In addition, the MRCI force field and geometry were empirically refined by least squares adjustments of the force constants against all available experimental spectroscopic parameters. Since the refined force field was found to well reproduce all the data and parameters for the isotopic species considered to a good accuracy [12], they are expected to predict with a reasonable accuracy the spectroscopic constants for the other isotopic species not considered at that time both in the ground and in the three fundamental vibrational states.

Up to now, no detailed high-resolution studies have been performed for the $^{79}Br^{14}N^{18}O$ isotopic species. In the present work we report the first high-resolution infrared analysis of the ν_1 band of $^{79}Br^{14}N^{18}O$ by Fourier transform spectroscopy. The purpose of this study is to validate the quality of the BrNO structure and force field parameters achieved in Ref. [12] by testing the quality of the predicted rotational constants calculated for the ground and 1^1 excited vibrational state. This work involves the recording of the absorption spectrum of $^{79}Br^{14}N^{18}O$ in the 1000–2000 cm^{-1} spectral region on the FTIR spectrometer Bruker 120HR at the University of Wuppertal and an extended analysis of the ν_1 band of $^{79}Br^{14}N^{18}O$ leading to the 1^1 vibrational energy and to a set of rotational and centrifugal distortion constants for the 1^1 and ground vibrational states. Finally the parameters achieved from this study were compared to the corresponding constants by a empirically determined refined MRCI force field available in the literature.

2. Experimental details

The synthesis of $^{79}Br^{14}N^{18}O$ was performed in a similar way as described previously (see Ref. [14]). In the three step procedure the following isotopic enriched starting materials have been used: Na^{79}Br (98.6% ^{79}Br, 1.4% ^{81}Br, Oak Ridge, Tennessee), $D_2^{18}O$ (98.5% ^{18}O, 0.7% ^{17}O; Alfa Products) and $^{18}O_2$ (99.5% ^{18}O, 0.2% ^{17}O, Alfa Products).

(i) In the first step 195 mg of Na^{79}Br (1.5 mmol) and 160 mg of $KMnO_4$ (1 mmol) were mixed and placed in a glass reactor ($V\sim 10$ mL) equipped with a glass valve with PTFE piston (Young, London). After evacuation about 1 mL conc. H_2SO_4 was slowly introduced through the valve into the reactor held at −196 °C. The reaction proceeded at room temperature and after separation of the volatile products in a series of traps held at −40, −80, −196 °C the trap at −80 °C contained 0.75 mmol of pure $^{79}Br_2$.

(ii) For the synthesis of $N^{18}O$ a dry 250 mL round bottom glass flask equipped with a glass valve with PTFE piston (Young, London) was charged with 5 g $D_2^{18}O$. After cooling with liquid nitrogen the reactor was evacuated and filled with 5 mmol NO and 2.5 mmol $^{18}O_2$. The reactor was kept at room temperature for 18 h and shaken occasionally. An IR check at the most volatile products indicated the formation of about 60% $N^{18}O$ (1873.6/1824.2 cm^{-1}). Subsequently the oxygen was removed in vacuo at −196 °C and 7 mmol of chlorine were added into the reactor. At room temperature formation of $DN^{18}O_3$ occurred within 16 h according to

$$2N^{18}O + 3Cl_2 + 4D_2^{18}O_2 \rightarrow DN^{18}O_3 + 6HCl.$$

About 10 g of mercury was slowly introduced through the valve into the reaction vessel. After shaking the content for 1 h at room temperature the gaseous reaction products were passed in vacuo through U-traps held at −100 and −196 °C. The trap at −196 °C contained ca. 4 mmol $N^{18}O$ (>98% enrichment, ~80% yield) with a few percent of $N_2^{18}O$ as an impurity.

(iii) For the synthesis of $^{79}BrN^{18}O$ a dry evacuated reaction vessel ($V\approx 10$ mL) was filled with a mixture of 0.75 mmol $^{79}Br_2$ and 1.5 mmol $N^{18}O$. After a reaction time of 30 min. at room temperature in the dark, the product was directly used for recording its high resolution IR spectrum in a cooled cell at −50 °C.

For recording the high-resolution spectra, the broad-band light source employed was a Globar, and the detector an MCT diode cooled with liquid nitrogen. The bandwidth of the spectra (1100–2100 cm^{-1}) was limited by the CaF_2 beamsplitter on the low wavenumber side and by an optical low-pass filter on the high wavenumber side. The spectral resolution was limited to 0.0022 cm^{-1} (Bruker definition). The absorption cell, made of stainless steel, was equipped with KBr windows fixed to the cell with Viton O-ring seals. Note that after a few days, the transmittance of the windows was affected by a solid deposit due to surface reactions with the gaseous samples.

During the first day, three high-resolution spectra with different concentrations of $^{79}Br^{14}N^{18}O$ (all at a total pressure of about 0.3 mbar) were recorded using the Bruker IFS 120 HR interferometer at University of Wuppertal (averaging respectively 60, 248 and 60 high-resolution scans). Although no ^{16}O-containing species were introduced into the cell, slow isotopic conversion into $^{79}Br^{14}N^{16}O$ was observed, as well as traces of $^{14}N^{18}O_2$, $^{14}N^{16}O^{18}O$, $^{14}N^{16}O_2$, and $N^{18}O$.

Line centers were determined from the absorption spectra using the peakfinder routine in the Bruker OPUS software. The absolute wavenumber calibration was performed using residual H_2O lines together with the IUPAP recommended line positions of Ref. [15]. The accuracy of the wavenumber calibration is about 0.0003 cm^{-1} (RMS).

3. Band analysis and discussion

The ν_1 fundamental band (N–O stretching mode) of BrNO corresponds to the strongest infrared band of this