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Gas phase detection of the unstable halofulminate BrCNO by millimeter wave spectroscopy

C.W. Gillies [1], J.Z. Gillies [2], H. Lichau, B.P. Winnewisser, M. Winnewisser

Physikalisch-Chemisches Institut, Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-35392 Gießen, Germany

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Abstract

The millimeter wave spectrum of the unstable halofulminate BrCNO was observed in a low-pressure pyrolysis of Br_2CNOH. Ground-state rotational constants of ^{79}BrCNO and ^{81}BrCNO were determined to be 1739.930 07(10) and 1726.961 86(11) MHz, respectively. Least-squares fits of the bromine quadrupole hyperfine splittings gave χ values of 656.8(88) and 551(10) MHz for the ground states of ^{79}BrCNO and ^{81}BrCNO, respectively. The observed vibrational satellite pattern arising from the BrCN bending mode indicates that the molecule exhibits extremely quasilinear behavior, roughly analogous to that of OCCCO. © 1998 Elsevier Science B.V.

1. Introduction

Fulminic acid, HCNO, is the simplest member of the nitrile oxides, a versatile class of compounds noted for their synthetic utility particularly in cycloaddition reactions [1]. Gas phase investigations of its rotational and vibrational spectra have provided a basis for a fuller understanding of quasilinearity in linear polyatomic molecules [2]. A pronounced anharmonicity in the two-dimensional HCN bending potential causes a large amplitude HCN bending motion and an irregularity of the vibrational energy levels. Analysing the rotational and vibrational data using a semirigid bender model, Bunker et al. determined the effective HCN bending potential of HCNO in the vibrational ground state to be rather flat with a barrier to linearity of 11.49(19) cm^{-1} [3]. They derived an equilibrium HCN bending potential from the excited vibrational state data which has a barrier to linearity of 0.2 cm^{-1}, with an estimated uncertainty of 2 cm^{-1}. It is not easy to determine the equilibrium structure and HCN bending potential from ab initio calculations. In a recent study using the CCSD(T) method and Dunning's cc-pVQZ basis set, HCNO was found to have a planar trans equilibrium structure with $\angle(HCN) = 165.13°$ and $\angle(CNO) = 176.58°$ [4]. The calculated HCN potential function is quite anharmonic with a barrier to linearity of the HCNO chain of 7.6 cm^{-1}. Upon extrapolation to an infinite basis set, a barrier of ≈ 3 cm^{-1} was obtained, which is in good agreement with the experimental equilibrium potential function described above.

Gas phase spectroscopic studies of simple substituted fulminates include a microwave investigation

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[1] Permanent address: Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180, USA.

[2] Permanent address: Department of Chemistry, Siena College, Loudonville, NY 12211, USA.

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[5] and a millimeter wave study [6] of acetonitrile oxide (methylfulminate), CH_3CNO, which provide evidence for large amplitude bending [2]. The halofulminates ClCNO and BrCNO were first detected by Maier and Teles in an argon matrix at 10 K by infrared spectroscopy [7]. Recently, BrCNO has been identified in the gas phase by photoelectron and photoionization mass spectroscopy and by low-resolution infrared spectroscopy [8]. Two intense infrared bands observed at 2211 and 1321 cm^{-1} have been assigned to the antisymmetric (ν_1) and symmetric (ν_2) CNO stretches, respectively. The overtone of ν_2 is assigned to a weak band observed at 2632 cm^{-1}. These gas phase measurements correlate well with the argon matrix infrared work [7]. None of the remaining normal modes have been observed including the BrCN bend ν_5, which is important to the question of quasilinearity. Ab initio calculations of the equilibrium BrCN bending potential result in a zero to moderate barrier to linearity, depending on the extent to which triple excitations are included in the calculation [8]. This indicates that BrCNO might exhibit quasilinear behaviour. Harmonic vibrational wavenumbers and intensities calculated at the MP2 and QCISD levels of theory for $^{79}BrCNO$ are in fair agreement with experiment. However, the BrCN bend calculated to be 177 cm^{-1} at the MP2 level and 83 cm^{-1} at the QCISD level of theory is not likely to be reliable for a molecule which is possibly quasilinear, since anharmonicities are not considered in the calculations [8].

This Letter reports the first investigation of the rotational spectrum of BrCNO. Spectral assignments of the ground vibrational state lines are presented for the bromine 79 and bromine 81 isotopomers, yielding accurate ground state constants. The observed vibrational satellite pattern of the low-lying BrCN bending mode is briefly discussed to show that the molecule exhibits quasilinear behavior. Detailed analyses of the excited vibrational state data for BrCNO and similar investigations on ClCNO and NCCNO, are in progress.

2. Experimental procedures

The rotational spectra of BrCNO were recorded at room temperature using backward wave oscillator based millimeter wave synthesizers from AMC [3], Schottky barrier diode detectors and a 2.5 m free-space glass absorption cell [9]. The output frequency of the synthesizers was phase-locked to a frequency modulated reference signal, thus providing source modulation. Two synthesizers were used to cover the spectral ranges of 52–79, 117–148 and 160–179 GHz. The operating parameters of the spectrometer were set at 25 kHz steps, a modulation frequency of 100 kHz, a modulation deviation of 250 kHz, 2f demodulation and a lock-in amplifier time constant of 100 ms, resulting in an overall time of 190 ms required per step. Spectrometer control, digital data acquisition and data reduction were carried out with computer programs from AMC and the Gießen laboratory.

BrCNO was synthesized in a flow system by gas phase pyrolysis of the volatile solid Br_2CNOH as described in the literature [7,8]. The quartz pyrolysis tube had an inner diameter of 11 mm and was heated to 1100 K along a length of 20 cm. Owing to the unstable nature of BrCNO, the furnace was located directly at the inlet of the cell and the full pumping capacity of the liquid nitrogen trapped vacuum system had to be utilized. The consumption of Br_2CNOH was ≈ 0.6 g/hour when a pressure of 0.01 mbar was maintained in the absorption cell.

3. Results

The millimeter wave spectrum of BrCNO was found to be dense due to the presence of a large number of intense vibrational satellite lines arising from an extremely low-energy BrCN bending mode ν_5. The spectrum is further complicated by the overlap of the spectra of the $^{79}BrCNO$ and $^{81}BrCNO$ isotopomers which have approximately the same natural abundance. Additional lines from the known millimeter wave spectra of HCNO [10] and HNCO [11] were also identified in agreement with the pyrolysis chemistry reported in previous work [7,8]. Isotopic shifts could be used effectively to identify the two sets of isotopomer lines for approximately one

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[3] Analytik und Meßtechnik GmbH, Stollberger Straße 4a, D-09119 Chemnitz, Germany

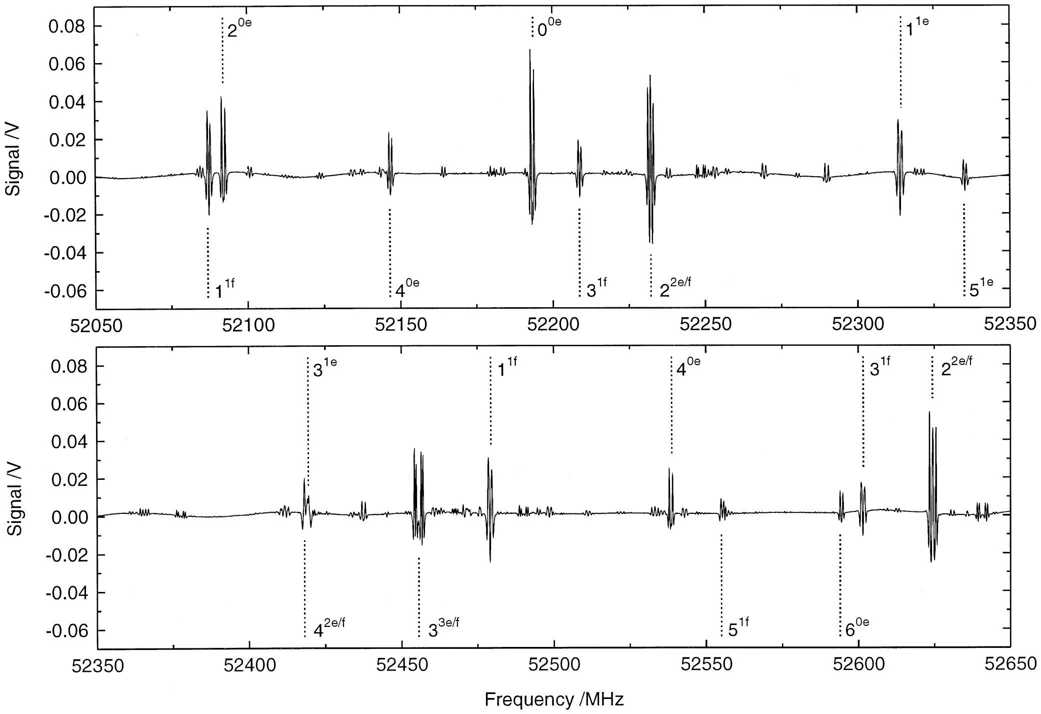

Fig. 1. The assignment of the ground state and the most intense ν_5 satellites is demonstrated for the $J = 15 \leftarrow 14$ rotational transition of the BrCNO isotopomers. The υ_5 and l_5 quantum numbers are given in the form $\upsilon_5^{l_5}$, e/f denoting the parity. ^{79}BrCNO lines are labelled above the spectrum, ^{81}BrCNO lines below the spectrum.

hundred vibrational levels, defined by the vibrational quantum number υ_5 and the vibrational angular momentum quantum number l_5. A portion of the rotational spectrum in the lower frequency range is shown in Fig. 1. The assignments of the most intense ν_5 satellite lines as well as the ground state line are shown for the $J = 15 \leftarrow 14$ rotational transition of ^{79}BrCNO. A number of the stronger ν_5 satellite lines of the ^{81}BrCNO isotopomer also appear in this spectrum. These assignments were obtained by combining information from line positions, line intensities, l-type resonance splitting and the l-dependence of the bromine nuclear quadrupole splitting [12]. The nuclear quadrupole splitting, which decreases with increasing J, was of particular importance since in the lower frequency range, it could be at least partly resolved for all l_5 states. In contrast, the l-type resonance splitting, which increases with increasing J, could only be resolved in the higher frequency range for $l_5 \leq 3$.

The first order quadrupole coupling energy of a linear molecule with one coupling nucleus[4] is given by

$$E_Q = \chi\left[\frac{3l^2}{J(J+1)} - 1\right] \times \frac{3C(C+1) - 4I(I+1)J(J+1)}{8I(2I-1)(2J-1)(2J+3)}, \qquad (1)$$

$$C = F(F+1) - I(I+1) - J(J+1),$$

where χ is the quadrupole coupling constant and I is the nuclear spin quantum number [12,13]. $I = \frac{3}{2}$ for the ^{79}Br nucleus and for the ^{81}Br nucleus. F is the total angular momentum quantum number which

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[4] The coupling of the ^{14}N nucleus is expected to be two orders of magnitude smaller than that of the Br nuclei and could not be observed in the present spectra.

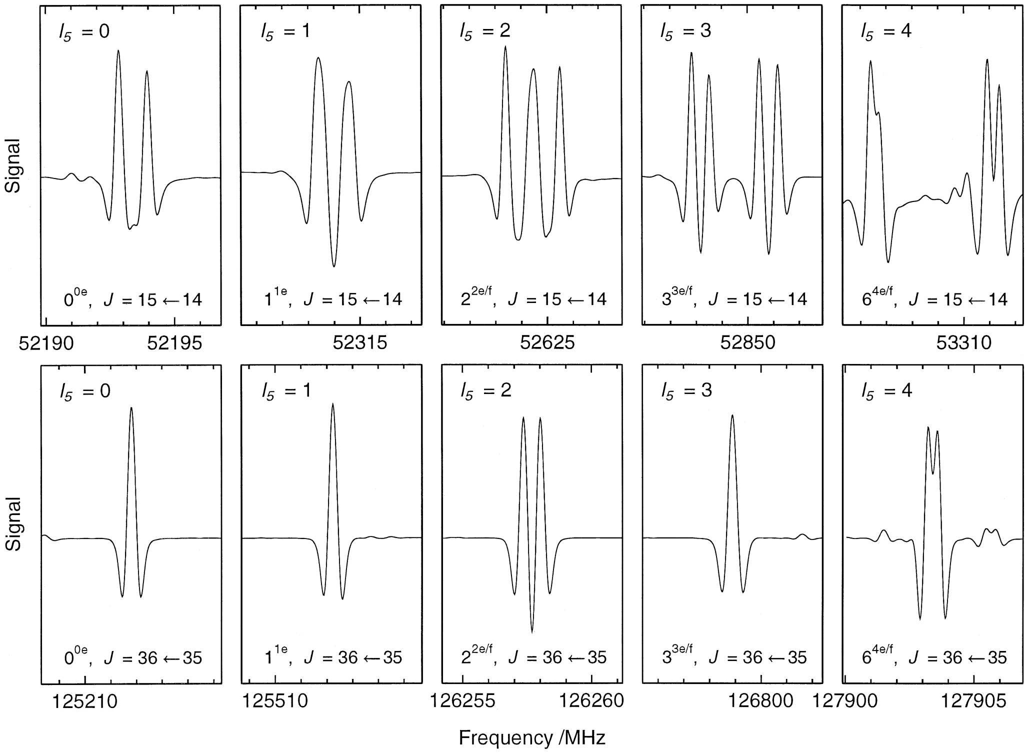

Fig. 2. The nuclear quadrupole splitting of the $J = 15 \leftarrow 14$ transitions and of the $J = 36 \leftarrow 35$ transitions is shown for ^{79}BrCNO in several $\upsilon_5^{l_5}$ vibrational states to demonstrate the l_5 dependence of the splitting. Note that the splitting of the $J = 36 \leftarrow 35$ transition in the 2^2 vibrational state arises from l-type resonance, while that of the 6^4 vibrational state is still quadrupole splitting.

results from the coupling of J to I. For ^{79}BrCNO and for ^{81}BrCNO, it can take the values $J + \frac{3}{2}$, $J + \frac{1}{2}$, $J - \frac{1}{2}$ and $J - \frac{3}{2}$. The selection rules are $\Delta J = +1$, $\Delta I = 0$ and $\Delta F = 0, \pm 1$, but in the case of BrCNO, only the four $\Delta F = +1$ components have appreciable intensity in the investigated frequency range. The frequency expression for a hyperfine transition therefore is

$$\nu = \nu_0 + \left[E_Q(J+1, I, F+1) - E_Q(J, I, F) \right]. \quad (2)$$

The hypothetical unsplit frequency ν_0 of each transition would be observed without quadrupole coupling [12]. For $l_5 = 0$, the $F = J + \frac{3}{2}$ component of a transition coincides with the $F = J + \frac{1}{2}$ component and the $F = J - \frac{1}{2}$ component with the $F = J - \frac{3}{2}$ component, whereas all four components are observed at different frequencies for $l_5 > 0$. However, in some cases even at the lowest investigated frequencies only two or three components could be resolved. In the frequency range above 117 GHz, no hyperfine structure at all could be resolved for $l_5 \leq 3$. For the ground state and some ν_5 vibrational satellites of ^{79}BrCNO, the nuclear quadrupole splitting of the $J = 15 \leftarrow 14$ transition and the splitting of the $J = 36 \leftarrow 35$ transition are shown in detail in Fig. 2.

Eq. (2) was used to determine χ values from least-squares fits of the nuclear hyperfine components observed for the lowest $J + 1 \leftarrow J$ rotational transition. For the ground states of ^{79}BrCNO and ^{81}BrCNO, the fits gave $\chi = 656.8(88)$ and $551(10)$ MHz, respectively. For each rotational transition, the center frequencies ν_0 were calculated using these values of χ and Eq. (2). The center frequencies of the ground state transitions of ^{79}BrCNO and ^{81}BrCNO are listed in Table 1. They were least-squares fit to the usual frequency equation for a linear molecule [13],

$$\nu_0 = 2B_0(J+1) - 4D_0(J+1)^3 + H_0(J+1)^3 \times \left[(J+2)^3 - J^3 \right]. \quad (3)$$

Table 1
Rotational transition frequencies of ^{79}BrCNO and ^{81}BrCNO in the vibrational ground state

Transition	^{79}BrCNO		^{81}BrCNO	
$J+1 \leftarrow J$	ν_0 (MHz) [a]	$\Delta\nu$ (kHz) [b]	ν_0 (MHz) [a]	$\Delta\nu$ (kHz) [b]
$15 \leftarrow 14$	52193.3163	-1.0		
$16 \leftarrow 15$	55672.1923	-6.3	55257.2877	-6.0
$17 \leftarrow 16$	59150.9396	-1.0	58710.1143	-9.8
$18 \leftarrow 17$	62629.5630	4.6	62162.8180	-7.9
$19 \leftarrow 18$	66108.0481	1.9	65615.3853	1.7
$20 \leftarrow 19$	69586.3434	2.0	69067.7719	6.5
$21 \leftarrow 20$	73064.4866	-4.5	72519.9969	-5.8
$22 \leftarrow 21$	76542.4722	1.6	75972.0740	1.9
$34 \leftarrow 33$	118262.0171	4.6	117380.9249	-1.3
$35 \leftarrow 34$	121737.0524	-2.2	120830.0940	-1.0
$36 \leftarrow 35$	125211.8073	-3.1	124278.9816	-4.6
$37 \leftarrow 36$	128686.2703	-6.6	127727.5870	-5.0
$38 \leftarrow 37$	132160.4454	-9.4	131175.9065	1.6
$39 \leftarrow 38$	135634.3139	3.2	134623.9153	-1.6
$40 \leftarrow 39$	139107.8628	5.0	138071.6206	-1.2
$41 \leftarrow 40$	142581.0993	5.9	141519.0058	-2.7
$42 \leftarrow 41$	146054.0049	8.5	144966.0813	8.5
$47 \leftarrow 46$	163413.3111	-9.3	162196.2881	1.2
$48 \leftarrow 47$	166884.0967	2.8	165641.2405	-1.1
$49 \leftarrow 48$	170354.4784	-7.2	169085.8231	-5.8
$50 \leftarrow 49$	173824.4898	1.2	172530.0254	-8.3
$51 \leftarrow 50$	177294.1000	5.1	175973.8520	4.3

[a] The center frequencies, ν_0, were calculated for each transition using the χ values obtained from a hyperfine fit of the lowest frequencytransition and Eq. (2). See text.

[b] $\Delta\nu$ is ν_0 minus the frequency calculated from Eq. (3) using the constants in Table 2.

Table 2 summarizes the spectral constants obtained from these fits for the two isotopomers.

4. Discussion

The observed rotational spectra of ^{79}BrCNO and ^{81}BrCNO are consistent with the type of rotational spectrum one would expect for a quasilinear molecule. A comparison of the pattern presented by the rotational constants in excited states of the lowest-lying bending mode of BrCNO with the corresponding patterns of HCNO [10,14] and of OCCCO [15] shows that BrCNO is more similar to OCCCO than to HCNO. This is confirmed by a preliminary analysis of the vibrational dependence of the *l*-type doubling constant q_5 which is plotted in Fig. 3. All the currently available information strongly suggests that BrCNO is much further from the linear limit than HCNO and perhaps more so than OCCCO [2]. Hence, BrCNO should have a value for the quasilinearity parameter γ_0 [16] that is roughly equal to the value -0.20 found for OCCCO [15], which means that BrCNO is the most quasilinear polar molecule known.

Table 2
Rotational and centrifugal distortion constants of ^{79}BrCNO and ^{81}BrCNO in the vibrational ground state

	^{79}BrCNO	^{81}BrCNO
B_0 (MHz)	1739.930 07(10) [a]	1726.961 86(11)
D_0 (Hz)	339.88(68)	335.10(74)
H_0 (μHz)	758 (14)	747 (15)
σ (kHz) [b]	6.8	7.1

[a] Quantities in parentheses are one standard deviation.

[b] σ is the standard deviation of the least-squares fit.

The fundamental transition frequency ω_5 of the low-lying BrCN bending mode can be roughly estimated from the relation

$$\omega_5 = f\frac{B_0^2}{q_5}, \qquad (4)$$

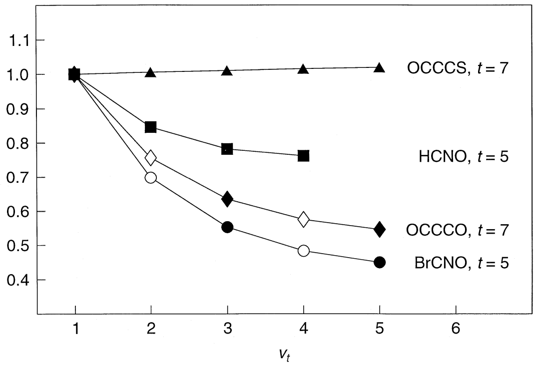

Fig. 3. The vibrational dependence of the l-type doubling constant q_t is shown for the lowest-lying bending mode ν_t of the linear molecule OCCCS and of the quasilinear molecules HCNO, OCCCO and BrCNO. All values are normalized to the l-type doubling constant in the first excited bending state. The open symbols indicate interpolated values.

where B_0 is the ground state rotational constant and q_5 is the l-type doubling constant for the first excited state of the bending mode ν_5 [13]. From the splitting of the l-type doublets in the rotational spectrum, q_5 of ^{79}BrCNO was found to be 5.52 MHz. The constant f, which is ≈ 2 for a harmonic bending potential, has empirically been found to decrease with increasing quasilinearity of the molecule. A value of $f = 1.32$, calculated for OCCCO [15], was used as an approximation of f for BrCNO. Using these constants, ω_5 of ^{79}BrCNO is calculated to be 24.15 cm^{-1}. Relative intensity measurements are in agreement with this estimate which is only slightly larger than the 18.18 cm^{-1} found for OCCCO [17]. However, this value is much lower than the harmonic wavenumbers obtained from the ab initio calculations [8].

Another indication of quasilinearity in BrCNO comes from an estimate of the Br–C internuclear distance. In HCNO, it was found that the r_s H–C internuclear distance is 1.027 Å [18], which must be compared with 1.063 Å in HCN [19]. It is abnormally short due to the effect of the large amplitude bending motion of the hydrogen atom. So far, the ^{79}Br^{13}CNO or ^{81}Br^{13}CNO ground state rotational constants needed to determine an r_s Br–C internuclear distance are not available. However, it is possible to obtain an estimate by fixing the C–N and N–O distances at the HCNO values of 1.169 and 1.199 Å, respectively, and adjusting the Br–C distance to get agreement with the ^{79}BrCNO and ^{81}BrCNO ground-state rotational constants. Using the HCNO values for BrCNO seems reasonable since the C–N distances of 1.155 Å in HCN is not very different from the value of 1.158 Å determined for BrCN [20]. The calculations give Br–C distances of 1.732 and 1.739 Å for ^{79}BrCNO and ^{81}BrCNO, respectively, which are indeed significantly shorter than the Br–C distance of 1.790 Å found for BrCN.

According to recent results, the vibrational satellite pattern of the low-lying ClCN bending mode in ClCNO is remarkably similar to that of the BrCN bending mode in BrCNO. This strongly indicates that ClCNO, like BrCNO, is an extremely quasilinear molecule, both definitely more quasilinear than HCNO. The rotational constants of the ground states of ^{35}ClCNO and ^{37}ClCNO are found to be 2 572.781 23(26) and 2 511.445 82(37) MHz, respectively. The pattern found for the low-lying CCN bending mode of NCCNO, however, exhibits only slight deviations from the linear limiting case, suggesting that NCCNO is significantly less quasilinear than HCNO. A detailed analysis of the data for ClCNO and NCCNO will be published separately.

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