Bromine Isocyanate, BrNCO, and Its ¹⁵N, ¹³C, ¹⁸O Isotopically Enriched Species: Assignment of Vibrational Spectra, Force Field, and Structure

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The Raman spectrum of liquid BrNCO has been recorded at -50° C. Infrared spectra are reported for gaseous and matrix-isolated BrNCO (Nc and Ar matrices) and for the ¹⁵N, ¹³C, and ¹⁸O enriched species isolated in Ar matrices. All of the six fundamental vibrations, eight combination tones, and three overtones could be assigned. The NCO angle and the CN/CO bond length ratio of gaseous BrNCO (α (NCO) = 172°; CN/CO = 1.0457) were calculated using ν_6 of the four isotopic species. A normal coordinate analysis based on the calculated structure agrees well with the frequencies and isotopic shifts of the vibrational spectra. © 1989 Academic Press, Inc.

I. INTRODUCTION

Bromine isocyanate, BrNCO, was first prepared in 1971 by the reaction of bromine vapor with AgNCO (1) and by vacuum pyrolysis of tribromoisocyanuric acid (2). The compound is very unstable because it is easily hydrolyzed by traces of water, is polymerized in the liquid state above -50° C, and decomposes during vaporization into CO(NCO)₂, NBr₃, and Br₂. Accordingly it is very difficult to prepare the pure compound, and BrNCO is still poorly characterized. Only four of six fundamental modes of vibration have been measured and partially assigned (2, 3). The data from microwave measurements (4, 5) are insufficient to obtain definitive values for the bond lengths and angles.

The purpose of this work was to prepare BrNCO in high purity and its ¹⁵N, ¹³C, and ¹⁸O isotopical enriched species in order to study the vibrational spectra carefully. A reliable force field and some structural data were calculated from the measured vibrational frequencies.

II. EXPERIMENTAL DETAILS

1. Materials

Bromine isocyanate was prepared in a similar way to that described in (2). The vacuum pyrolysis of tribromoisocyanuric acid, $(BrNCO)_3$, was carried out in a Duran glass vessel (l = 30 cm, o.d. = 3 cm) provided with a condenser (l = 10 cm) and a tube to the vacuum line (Fig. 1). The thermolysis vessel described above was half filled with an intimate mixture of 4 g freshly prepared (BrNCO)₃ and quartz glass wool. Then the vessel was heated in vacuo (10^{-4} mbar) to 150°C for 12 hr. At 290°C (BrNCO)₃ was sublimed past the quartz glass wool and pyrolyzed to BrNCO. Unreacted

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FIG. 1. Thermolysis device.

 $(BrNCO)_3$ condensed at the water-cooled finger and monomeric BrNCO was collected in a U-trap cooled at -110° C. At the beginning of the pyrolysis yellow bromine isocyanate crystals and red bromine crystals were isolated. The reaction product was rejected until BrNCO was pure. This was the only method to obtain pure BrNCO, because bromine could not be separated from bromine isocyanate.

Isotopically enriched bromine isocyanate was obtained in a similar way by the following reaction sequences using ¹⁵NH₄Cl (95%; VEB-Berlin-Chemie, Berlin Aldershof, GDR), ¹³CO (99%; A. Hempel GmbH, Düsseldorf, FRG), and H₂¹⁸O (98%; Ventron, Karlsruhe, FRG) as starting materials:

¹⁵NH₄Cl
$$\xrightarrow{\text{NaOH}}_{200^{\circ}\text{C}}$$
 ¹⁵NH₃ $\xrightarrow{\text{COCl}_2}_{220^{\circ}\text{C}}$ (H¹⁵NCO)₃ $\xrightarrow{\text{OH}^-/\text{Cl}_2}_{(6)}$
(Cl¹⁵NCO)₃ $\xrightarrow{\text{Br}_2}_{(2)}$ (Br¹⁵NCO)₃ $\xrightarrow{290^{\circ}\text{C}}$ Br¹⁵NCO
¹³CO $\xrightarrow{\text{Cl}_2}_{h\nu}$ ¹³COCl₂ $\xrightarrow{\text{NH}_3}_{220^{\circ}\text{C}}$ (HN¹³CO)₃ $\xrightarrow{\text{OH}^-/\text{Cl}_2}_{\rightarrow}$
(ClN¹³CO)₃ $\xrightarrow{\text{Br}_2}$ (BrN¹³CO)₃ $\xrightarrow{290^{\circ}\text{C}}$ BrN¹³CO
H₂¹⁸O $\xrightarrow{\text{(ClCN)}_3}_{(7)}$ (HNC¹⁸O)₃ $\xrightarrow{\text{OH}^-/\text{Cl}_2}_{\rightarrow}$
(ClNC¹⁸O)₃ $\xrightarrow{\text{Br}_2}$ (BrNC¹⁸O)₃ $\xrightarrow{290^{\circ}\text{C}}$ BrNC¹⁸O

2. Apparatus

Volatile materials used in this work were handled in a glass vacuum line equipped with a capacitance pressure gauge (221 AHS-A-10 MKS Baratron Burlington) and valves with PTFE pistons (Young, London). The vacuum line was connected directly to an IR cell (l = 200 mm, KBr windows) by a glass tube, so it was possible to observe the effect of purifications immediately. Nonvolatile materials were handled under dry nitrogen atmosphere of a glovebox. For sealed glass tube reactions a device described in (8) has been used.

Infrared spectra of gaseous BrNCO were recorded in the range 4000–400 cm⁻¹ on a FTIR spectrometer (Nicolet MX-3600) with a resolution of 1 cm⁻¹. Infrared spectra of matrix isolated materials were obtained with a continuous flow He cryostat equipped with a copper mirror via a reflection accessory on the FTIR spectrometer Bruker IFS-113v (4000–50 cm⁻¹, resolution 0.5 cm⁻¹, He cooled Ge/Cu-detector and bolometer).

The Raman spectra were measured in the liquid phase in the range $2400-100 \text{ cm}^{-1}$ with a Coderg T 800 spectrometer using the 647.1-nm exciting line of a Kr ion laser (300 mW, resolution 4 cm⁻¹).

III. RESULTS AND DISCUSSION

Figure 2 shows IR spectra of BrNCO in the gas phase and isolated in a Ne matrix as well as a Raman spectrum of a liquid sample of BrNCO at -50° C. Table I lists all measured vibrational frequencies.

The microwave spectroscopic treatment of BrNCO indicated that the molecule is planar and excluded the configuration BrOCN (5). The latter could be confirmed by the vibrational frequencies of isotopically enriched molecules. The five inner coordinates of the BrNCO molecule are defined as follow:



1. Assignment

The irreducible representation of the vibrations of the planar BrNCO molecule (C_s symmetry) is

$$\Gamma_{\rm vib} = 5a'({\rm IR}, {\rm Ra} p) + 1a''({\rm IR}, {\rm Ra} dp). \tag{1}$$

The assignments for the six modes are based on characteristic frequencies, relative band intensities, isotopic shifts, and gas band contours. The fundamental vibrations of the NCO group are nearly decoupled from the vibrational modes belonging to the heavy bromine atom, so they can be well compared with the modes of the NCO⁻ ion in the KI matrix (9) ($\nu_3 = 2170 \text{ cm}^{-1}$, $\nu_1 = 1232 \text{ cm}^{-1}$, $\nu_2 = 629 \text{ cm}^{-1}$). The two stretching modes ν_3 and ν_1 are better called antisymmetric and symmetric, rather than the CO and CN stretching, as shown in a later section.

We conclude that the band at 2199 cm⁻¹ in the IR spectrum of gaseous BrNCO corresponds to the antisymmetric stretching vibration ν_{as} (NCO). In the IR spectrum of BrNCO isolated in a Ne matrix the band appears at 2196 cm⁻¹ and in the Raman spectrum at 2168 cm⁻¹. The symmetric NCO stretching vibration of gaseous BrNCO is found at 1294 cm⁻¹, of BrNCO isolated in Ne matrix at 1290.9 cm⁻¹, and at 1284 cm⁻¹ in the Raman spectrum of the liquid.

The bending mode of the NCO⁻ ion appears at 629 cm⁻¹ and is double degenerate. In bromine isocyanate the degeneracy of the corresponding vibration mode is removed.



FIG. 2. Vibrational spectra of BrNCO: (A) IR gas spectrum (10-cm cell with KBr windows) at 1.3 and 16.7 mbar (resolution, 1 cm^{-1}); (B) IR, Ne matrix (S/M = 1:500; 4.3 mmole matrix; resolution, 0.5 cm^{-1}) at 4.5 K; (C) Raman, liquid at -50° C (resolution, 4 cm^{-1}).

Hence one of the bands will have a' symmetry and the other a'' symmetry. In the IR spectrum of gaseous BrNCO the bands are found at 689 and 570 cm⁻¹. The assignments to symmetry classes a' and a'' may be made unambiguously from the band contours in the gas phase and from the measured isotopic shifts of BrNCO isolated in an Ar

TA	BL	Æ	Ι

IR gas	Ne matrix	┝	— Ar matri	x		Raman		
BrNCO	BrNCO	BrNCO	Br ¹⁵ NCO	BrN13CO	BrNC ¹⁸ O	BrNCO	assignment	
	4366.5 VW	4358.1	_	4244.5		_	2 v1	
	3588.9 vw	3576.5	3551.6	3480.3	3542.2		$v_1 + 2v_3$	
3472	3467.6 m	3470.0	3440.1	3405.0	3424.5		$v_1 + v_2$	
2880	2884.9 w	2876.5*	2859.5*	2807.2*	2850.7*		V1 + V3	
2710	2709.9 w	2699.6	2685.9	2635.7	2673.0	_	$v_1 + v_4$	79Br
	2708.5 W	2698.3	2684.5	2634.5	2671.6		$v_1 + v_4$	^{e1} Br
	2654.2 vw	-			-	_	$v_2 + 2v_3$	
	2563.7 w					_	2 V 2	
	2333.1 vw	2335.1	-		-		v1 + v5	
2199	2196.0 vs	2191.9	2183.9	2133.7	2169.8	2168 w	Vı	
2100	2109.6 m	2096.6*	2069.7*	2044.5*	2074.9*		BrOCN ?	
1960	1960.2 vw	1948.5	1921.9	1922.0	1924.1	_	v2 + v3	
1389	1394.6 vw	1385.4	1371.8	1361.7	1374.5	1383 w	2 v ₃	
1294	1290.9 m	1296.9	1274.2	1286.3	1273.2	1284 m	V2	
	825.7 vw	824.7	-				v ₃ + v ₅	
689	691.1 s	686.6*	679.6*	671.5*	683.0*	684 s	Va	
570	572.2 s	563.1	561.25	546.95	558.1	560 VW	٧6	
	506.0 vw	-	_	-	—	490 vs	٧4	79Br
	504.6 VW	_		-	-		V.	⁰¹Br
	137.4 w	-			-	150 s	V3	

Measured Vibrational Frequencies of Bromine Isocyanate (cm⁻¹)

*) Split due to matrix effects.

matrix. The vibration belonging to class a'' shows a change of the dipole moment parallel to the principal axis I_c and according to this a C-type band with a prominent Q branch is expected. Furthermore the isotopic shifts of this a'' mode can be calculated directly from the structure of BrNCO (see next section) and compared with the measured data. On this basis the vibrational band at 570 cm⁻¹ is assigned to $\gamma(NCO)$ (out-of-plane bending mode) and the band at 689 cm⁻¹ belongs to $\delta(NCO)$ (in-plane bending mode).

The BrN-stretching vibration is expected to show a very intense band in the Raman spectrum because of the large change of polarizability and the corresponding band in the IR spectrum should be very weak. This vibration is located at 490 cm⁻¹ in the Raman spectrum. In the IR spectrum of BrNCO isolated in a Ne matrix there is a very weak doublet at 505.9/504.5 cm⁻¹. This doublet shows that bromine having a relative ⁷⁹Br/⁸¹Br isotopic abundance of 1:1 is strongly involved in the vibrational mode. The band at the lowest energy is expected to be the BrNC bending mode. In the Raman spectrum this mode is found at 150 cm⁻¹ and in the IR spectrum of BrNCO isolated in a Ne matrix it appears at 137.4 cm⁻¹.

The remaining 11 vibrations in Table I are combination modes and overtones. As can be seen in Table I the whole vibrational spectrum of BrNCO is repeated above the fundamental v_1 . It is remarkable that the intensity of the combination mode ($v_1 + v_4$) is much greater than that of the fundamental v_4 . The overtone $2v_3$ which shows Fermi resonance with the normal mode v_2 is of special importance. Because of the Fermi resonance, the position of v_2 is disturbed in a different way for each of the ¹⁵N, ¹³C, and ¹⁸O isotopically enriched species. Thus the isotopic shifts which are necessary for the calculation of the force field cannot be deduced directly from the spectrum (see next section).

In all IR spectra there is a weak band ≈ 100 cm⁻¹ below the fundamental ν_1 which does not belong to any combination mode. This band cannot be assigned to any vibrational mode of possible thermolysis products such as HNCO, $CO(NCO)_2$, CO_2 , and NBr₂C(O)NCO. Therefore, we presume that this absorption band belongs to traces of the isomeric BrOCN. This is confirmed by the expected large ^{14/15}N- and ^{12/13}C-, but small ^{16/18}O-isotopic shift.

2. Structure of BrNCO

The fundamental v_6 can be calculated by the FG formalism using one G and one F matrix element. In principle each isotopic substitution provides additional information about the G matrix, because the F matrix is independent of the atomic masses. In the G matrix three bond lengths and two bond angles of BrNCO are included.

Starting with the structural suggestion given in (5) each of the five structural parameters of the bromine isocyanate was systematically varied. The resulting models I to V are presented in Table II. For each model the fundamental ν_6 of ⁷⁹BrNCO, ⁷⁹Br¹⁵NCO, ⁷⁹BrN¹³CO, and ⁷⁹BrNC¹⁸O was calculated by the program NCA (10). The same values resulted using the Redlich-Teller product rule (11).

The isotopic shifts Δv_6 resulting from the calculated frequencies and the measured isotopic shifts are gathered in Table II. The comparison shows that the $^{12/13}$ C-isotopic shift is independent of the structural parameters and is in excellent agreement with the measured values. Thus this value does not provide further structural information. However, the good agreement shows that the anharmonicity of the vibration can be neglected and the measured ^{14/15}N- and ^{16/18}O-isotopic shifts can also be regarded as harmonic ones. Remarkable changes in the ^{14/15}N- and ^{16/18}O-isotopic shifts are calculated if the NCO bond angle α and the CN/CO bond length ratio x are varied. Therefore, these two structural parameters can be estimated using the measured values.

by the Out-of-Plane Bending Mode (ν_6)									
		ref (5)	model	model	model	model	model	BrNCO	
			I	II	ш	IV	v	Ar matrix	
structural parameters									
d(CO) r(CN) R(BrN) α(NCO) β(BrNC)	pm pm pm •	116 123 185 175 120	120 123 185 175 120	116 <u>127</u> 185 175 120	116 123 180 175 120	116 123 185 <u>173</u> 120	116 123 185 175 <u>115</u>	170	
CN/CO		1.0603	1.0250	1.0948	1.0603	1.0603	1.0603	1.0145	
isotopic shifts ∆∨.				-calculated				obs.	
14/15N 12/13C 16/18O	cm ⁻¹ cm ⁻¹ cm ⁻¹	2.245 15.987 4.793	2.327 15.995 4.642	2.158 15.986 4.938	2.236 15.995 4.795	2.057 16.101 4.943	2.286 15.973 4.742	1.85 16.15 5.00	

TABLE II

Estimation of the Structural Parameters CN/CO and α (NCO) of BrNC
by the Out-of-Plane Bending Mode (v_6)

The variation of isotopic shifts obeys the following linear equations for small changes of α and x:

$$\Delta \nu_6(^{14/15}N) = -2.32x + 0.094\alpha - 11.75$$
⁽²⁾

$$\Delta \nu_6(^{16/18}\text{O}) = 4.21 x - 0.075 \alpha + 13.46.$$
(3)

Using the measured isotopic shifts α is calculated to be 170° and x to be 1.0145 for bromine isocyanate isolated in an Ar matrix. Since BrNCO may be distorted by the Ar matrix and there may be systematic errors in this method the whole procedure was repeated for the well-established ClNCO structure ($\alpha = 171^\circ, x = 1.0551$) (7) in order to estimate the gas phase structure of BrNCO. In Table III the essential data of CINCO for calculating the following linear equations are put together:

$$\Delta \nu_6(^{14/15}N) = -1.98x + 0.0993\alpha - 13.09 \tag{4}$$

$$\Delta \nu_6(^{16/18}\text{O}) = 4.22x - 0.0787\alpha + 13.98.$$
 (5)

Using the measured isotopic shifts, values of α of 169° and x of 1.02362 are deduced for chlorine isocyanate isolated in an Ar matrix. If the structural changes of gaseous and matrix-isolated CINCO are transferred to BrNCO α is 172° and x is 1.0457 for gaseous bromine isocyanate.

The uncertainty of this structural determination can hardly be estimated, but in any case we expect that the NCO bond angle of BrNCO should be greater than that of CINCO and the CN/CO bond length ratio should be smaller. These results are closest to structure II among the three sets given in (5).

3. Normal Coordinate Analysis

For calculating the general force field of BrNCO the fundamentals of the symmetry class $a'(v_1 \text{ to } v_5)$, isotopic data, and centrifugal distortion constants (5) are available.

Estimation of the Structural Parameters CN/CO and α (NCO) of CINCO by the Out-of-Plane Bending Mode (v_6)									
		ref (7)	model I	model II	CINCO Ar matrix				
structural parameters									
d(CO) r(CN) R(CIN) α(NCO) β(CINC)	pm pm pm •	116.2 122.6 170.5 170.87 118.83	<u>120.0</u> 122.6 170.5 170.87 118.83	116.2 122.6 170.5 <u>174.0</u> 118.83	 169 				
CN/CO		1.05508	1.02167	1.05508	1.02362				
isotopic shifts ∆vs		<u> </u>	— calculated ·		obs.				
14/15N 16/18O	cm-1 cm-1	1.804 4.976	1.870 4.835	2.102 4.740	1.65 5.00				

TABLE III

The method of calculating force constants according to Wilson's GF matrix method requires unperturbed harmonic vibrational frequencies. The measured vibrational frequencies listed in Table I are perturbed by anharmonicity and by Fermi resonance in the case of the fundamental ν_2 . Since we do not have enough measured values to calculate all the unperturbed harmonic frequencies, we corrected the frequencies using the method below.

In Table IV all measured isotopic shifts are compared with those calculated from the frequencies of the fundamentals. The differences between measured and the sum of the fundamental's isotopic shifts are indicative for influences of anharmonicity and Fermi resonance. There are very large deviations for $2\nu_3$ since these vibrations are in Fermi resonance with the fundamental ν_2 . In order to correct the $\Delta\nu_2$ values for Fermi resonance we transferred the difference between $\Delta 2\nu_3$ (measured) and $\Delta 2\nu_3$ (calculated) to $\Delta\nu_2$. The limits of error mentioned in Table IV are estimated in such a way that they increase in proportion to the amount of $\Delta\nu_2$ correction.

Because of the very low intensity of the fundamental ν_4 it was impossible to measure its absorption band in isotopical enriched samples of lower purity. However, the isotopic shifts $\Delta \nu_4$ may be estimated from $\Delta(\nu_1 + \nu_4) - \Delta \nu_1$, but we are not able to consider the influence of anharmonicity. Accordingly the values listed in Table IV having a high error limit. The isotopic shifts $\Delta \nu_5$ are not measured but calculated assuming an uncoupled BrNC-bending mode. Finally the product rule of the vibrational frequencies of the isotopic molecules $\Pi(\nu_i/\nu_{i'})$ (i = 1-5, calculated from Table IV) provides

$$\Pi(\nu[BrNCO]/\nu[Br^{15}NCO]) = 1.0534$$
(6)

$$\Pi(\nu[BrNCO]/\nu[BrN^{13}CO]) = 1.0699$$
(7)

$$\Pi(\nu[BrNCO]/\nu[BrNC^{18}O]) = 1.0726.$$
(8)

TABLE IV

Observed and Sum of the Fundamental's Isotopic Shifts Relative to BrNCO

aent	gnr	assig		v ^{16/18} O	Δ	ν ^{12/13} C	Δ v ^{12/13} C		Δ v ^{14/15} N	
				sum	obs.	sum	obs.		sum	obs.
		21			_		113.6		16.0	_
2v3	+	V1		29.3	34.3	88.4	96.2		22.0	24.9
V2	+	V1		45.8	45.5	68.8	65.0		30.7	29.9
va	+	V1		25.7	25.8	73.3	69.3		15.0	17.0
Va	+	Vi			26.6		63.9			13.7
		v,			22.1		58.2		_	8.0
٧a	+	V2		27.3	24.4	25.7	26.5		29.7	26.6
•		213		7.2	10.9	30.2	23.7		14.0	13.6
		V2	E 1≜	27.4	23.7	4.0 ± 2ª	10.6	0.5*	22.2 ±	22.7
		V3			3.6	-	15.1			7.0
		Va	F Jp	4.5	_	5.5 ± 1 ^b		10	6.0 ±	
		Va		2.3°		0.7°			1.4°	-

^a Corrected for Fermi resonance.

^b Deduced from $v_1 + v_4$.

^c From model calculations.

Using the assumed structural parameters of BrNCO isolated in a Ne matrix (R(BrN) = 185 pm, r(NC) = 121 pm, d(CO) = 116 pm, $\beta(BrNC)$ = 120°, $\alpha(NCO)$ = 171°) the corresponding products of the vibrational frequencies calculated by the program NCA (10) are

$$\Pi(\nu[BrNCO]/\nu[Br^{15}NCO])_{calcd} = 1.0602$$
(9)

$$\Pi(\nu[BrNCO]/\nu[BrN^{13}CO])_{calcd} = 1.0683$$
(10)

$$\Pi(\nu[BrNCO]/\nu[BrNC^{18}O])_{calcd} = 1.0739.$$
(11)

These numbers are in excellent agreement except those for the isotope pair ($^{14}N/^{15}N$), for which a small correction to $\Delta\nu_4(^{14/15}N)$ was applied. The final frequencies used for the normal coordinate analysis are listed in Table V.

For the calculation of the force field using the program NCA (10) the assumed structural parameters of BrNCO in a Ne matrix, the frequencies listed in Table V, and the centrifugal distortion constants (5) were used as input data. Relevant force constants were transferred from CINCO (12) and BrN (13). Interaction force constants were estimated according to Ref. (14). The normal coordinate treatment was carried out by means of a best-fit iterative procedure. The resulting force field and the potential energy distribution are shown in Table VI. These force constants were adjusted with the calculated and experimental frequencies and lay within the given limits of error (see Table V) except for ν_1 and ν_2 of the ¹⁸O isotopically enriched species. In spite of the huge quantity of input data for the force field calculation, we estimate the uncertainty of the diagonal force constants to be $\pm 3\%$.

The potential energy distribution gives a qualitative picture of each vibrational mode. The PED indicates that v_5 is largely uncoupled and is assigned as the BrNC-bending mode. It can be seen that the frequencies v_3 and v_4 are essentially pure NCO-

BrNCO 2196	Br ¹⁶ NCO			BrN13CO			BrNC ¹⁸ O			assignment	
	2188 (-8	± ±	1 1)=	2138 (-58	± ±	2 2)	2174 (-22	± ±	2 2)	۷۱	
1291	1269 (-22	± ±	0.5 0.5)	1287 (-4	± ±	2 2)	1263.5 (-27.5	± ±	1 1)	٧2	
691	684.0 (-7.0	± ±	0.2 0.2)	675.9 (-15.1	± ±	0.2 0.2)	687.4 (-3.6	± ±	0.2 0.2)	٧3	
506.0	499 (-7.0	± ±	1 1)	500.5 (-5.5	± ±	1 1)	501.5 (-4.5	± ±	1 1)	٧4	79₿r
504.6										٧4	eiBr
137.4	136.0 ^b (-1.4)	b		136.7 (-0.7)	b		134.16 (-3.3)	ь		VS	

TABLE V

Corrected Fundamental Frequencies and Isotopic Shifts (cm⁻¹) of Bromine Isocyanate

*) Values in parentheses are isotopic shifts relative to BrNCO.

b) Calculated from the best force field.

TABLE VI

Force Field for BrNCO and Potential Energy Distribution for the Fundamental Vibrations in (%)

	Force co	onstants ^{a)}						PED		
fr	fr	fa	fø	fa	_	۷1	V 2	٧a	٧.	νs
2.862	0.178	0.129	0.343	0.180	fz	-	-	20	87	
	13.501	1.023	0.348	0.388	fr	59	40	-	-	
		12.981	-0.114	0.371	fa	49	50	-	-	-
			0.378	0.062	fs	-	_		-	99
				0.717	ſa	-	-	80	-	-
Symmetr	y class a"	<u>:</u>								
foor = 0	.016									

 Porce constants in 10² N/m, bending force constants and bendingstretching constants normalized on 10⁻¹⁰ m.

bending and BrN-stretching vibrations, respectively, whereas v_1 and v_2 are strongly coupled. They can be best described as the antisymmetric and the symmetric NCO-stretching modes.

The values of 13.68×10^2 and 13.19×10^2 N/m obtained for the CN and CO stretching force constants are essentially identical, so the following resonance form is probably the major one:

$$\overline{N} = C = \overline{Q}$$

In contrast to BrNCO the difference between the CN and CO force constants observed for the isocyanate ion is larger ($f_{CN} = 14.6 \times 10^2 \text{ N/m}$, $f_{CO} = 10.9 \times 10^2 \text{ N/m}$). This can be attributed to the favorable resonance form

of this ion. The values of the interaction constant $f_{CN/CO} = 1.21 \times 10^2 \text{ N/m}$ and of the bending force constant $f_{\alpha} = 0.72 \times 10^2 \text{ N/m}$ of the NCO⁻ ion correspond closely to the values of BrNCO. The BrN force constant fits those calculated for the BrN (13) and BrNO (15) molecules.

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