The Fourier Transform IR Spectra of ClF and BrF

H. Bürger and P. Schulz
FB 9 – Anorganische Chemie, Universität – Gesamthochschule, Wuppertal, West Germany

E. Jacob and M. Fähnle
MAN Technologie, München, West Germany

Z. Naturforsch. **41a,** 1015–1020 (1986); received April 17, 1986

Fourier transform infrared spectra of ClF and BrF have been measured with a resolution of $0.04\ \text{cm}^{-1}$ in the region of the fundamental and first overtone with an accuracy of 2 and $4 \times 10^{-3}\ \text{cm}^{-1}$, respectively. The rotational structure was resolved up to $J'' = 58/62$ (ClF/BrF), and ν_0 values have been obtained from rotational analyses of the v $1 \leftarrow 0$, $2 \leftarrow 1$, $2 \leftarrow 0$ and, in part, $3 \leftarrow 1$ and $3 \leftarrow 0$ vibrational bands. These have been employed to obtain the hitherto most accurate ω_e, $\omega_e x_e$ and (for ClF) $\omega_e y_e$ values. From the rotational analyses, B_e, α_e, γ_e, D_e and β_e have been derived.

1. Introduction

The diatomic interhalogen molecules ClF and BrF, highly reactive and corrosive species, have been the subject of numerous investigations. While ClF has been reported to be a stable compound which is commercially available, BrF could only be detected spectroscopically because of its rapid decomposition to Br_2 and BrF_3 [1, 2].

Both molecules have been intensively studied by electronic [3–9], mw [10–13] and mmw spectroscopy [14], but only few reports deal with the infrared spectra. Most of the information on the vibrational levels stems from the analysis of electronic spectra measured in absorption and emission. The rotational structure of the fundamental and the first overtone of ClF have been partly resolved with a resolution of $0.4\ \text{cm}^{-1}$, and rotational analyses have been performed which yielded band origins, ω_e and $\omega_e x_e$ values for both isotopic species [15]. The experimental data were reexamined later, and slightly different ω_e and $\omega_e x_e$ values were derived [16]. Experimental evidence claimed for the IR detection of BrF, however, is dubious firstly because of the position and shape of the weak absorption, and secondly because of the overlap with BrF_3 absorption [17]. In contrast to ClF [15], any infrared feature unambiguously attributable to BrF has not yet been reported. The vibrational parameters presently accepted for ClF are an order of magnitude less accurate than can be achieved by FTIR spectroscopy. Since no direct measurements are available for BrF, the most accurate data come from a merge of high resolution electronic spectroscopy investigations [7, 8].

In the following we report on the FTIR spectra of pure ClF and BrF, the latter prepared according to a new procedure [18] without any major IR-absorbing contaminants present in the cell, in the region of the fundamental and first overtone. Some features of the second overtone of ^{35}ClF have been detected as well. The resolution of the spectra, $0.04\ \text{cm}^{-1}$, the relative accuracy ($< 1 \times 10^{-3}\ \text{cm}^{-1}$) and absolute wavenumber accuracy ($1-2 \times 10^{-3}\ \text{cm}^{-1}$) combined with the sensitivity of the measurement permit a determination of the rovibrational parameters of ClF and BrF with higher precision than hitherto available.

2. Experimental

Materials: All materials were handled in a well conditioned and He leak tight stainless steel vacuum system. ClF (Ozark-Mahoning) was purified by fractional condensation through traps kept at −120, −142 and −196 °C. Only the material kept in the −196° trap was used. Br_2 (Merck, p.A.) was dried over P_4O_{10} and distilled in vacuo, the middle fraction being collected and sealed off in a Pyrex bulb attached to a stainless steel bellow valve.

Reprint requests to Prof. Dr. H. Bürger, Universität – Gesamthochschule Wuppertal, Gaußstr. 20, D-5600 Wuppertal 1.

0340-4811 / 86 / 0800-1015 $ 01.30/0. – Please order a reprint rather than making your own copy.

F_2 (purity > 99.98%) was obtained by fractional distillation of technical grade fluorine (Kali-Chemie) using low-temperature distillation equipment (MAN Technologie). BrF was synthesized in the IR absorption cell [18] by slow addition of F_2 to a tenfold excess of Br_2. After 20 min only BrF was detected by FTIR spectroscopy as absorbing species, with traces of CF_4 formed by the reaction of BrF with the Teflon gaskets.

A stainless steel absorption cell, optical pathway 150 mm, inner diameter 35 mm, equipped with AgCl windows, Teflon gaskets and a Nupro bellow valve was used. Before filling the cell was passivated, either 18 h with 300 mbar ClF, or twice for 24 h with 130 mbar Br_2 and 13 mbar F_2. With these precautions ClF and BrF did not decompose for hours.

Infrared spectra: Measurements on ClF and BrF in the overtone region were performed at pressures of 70 and 13 mbar (in the presence of ca. 100 mbar Br_2), respectively, while the more intense fundamentals were recorded at pressures of ca. 20 and 5 mbar after the volatile products had been partly pumped off.

Infrared spectra were recorded with two different interferometers. Both the overtones and fundamentals of ClF and BrF were measured with a Nicolet Series 7199 interferometer equipped with a KBr beam splitter and an MCT type B detector. 500 to 1000 scans were collected for an optical retardation of 20.25 cm; the resolution of the unapodized spectra was 0.040 cm^{-1}. The actual line width (FWHM) was of the order of 0.042 cm^{-1} both for the fundamental and the first overtone, and no pressure broadening was revealed even at the highest pressures employed. The region of the fundamental was in addition investigated with a Nicolet Series 8000 Vacuum interferometer equipped with a 3 μ Mylar beam splitter and a Cu:Ge detector operating at 4.2 K. Typically 250 scans were collected, and a resolution (FWHM) of 0.045 cm^{-1} was achieved.

Positions of absorption maxima were interpolated to 4 digits after the decimal point and carefully calibrated with H_2O and CO_2 lines (Vacuum interferometer) [19], while N_2O lines [20, 21] were used for the calibration of the purged 7199 instrument. The absolute wavenumber accuracy in the region of the fundamental is $\pm 1 \times 10^{-3}$ cm^{-1}, and $\pm 2 \times 10^{-3}$ cm^{-1} in the region of the overtone. Though we did not detect any significant systematic line shifts in spectra recorded at different pressures, we have doubled the calibration error to account for possible pressure shifts. Lines due to 3ν of ^{35}ClF and $3\nu-\nu$ of ^{37}ClF were too weak to be picked by the peak-finder routine; they were evaluated visually, and their accuracy is only $\pm 10 \times 10^{-3}$ cm^{-1}.

3. General

The fundamentals and the overtones appear as typical Σ vibrations of linear molecules with a gap at ν_0 and well isolated lines in the P and R branches, Figs. 1 and 2. Due to the isotopic effect, two independent systems appear in ca. 3:1 and 1:1 intensity ratios in ClF and BrF respectively. Blending by overlap of rotational lines is modest for ClF, while it is more important for BrF, though even here blending for the cold bands is restricted to a few lines. Due to positive $(B_e - B_v)$ values, the separation of the lines decreases with increasing wavenumber, the R branches becoming denser with increasing J, and a band head is evident in the overtone of ^{35}ClF near 1560 cm^{-1}, Figure 2. The spectra are accompanied by hot bands. With Boltzmann factors of 2.4 and 4.0% at 298 K, the hot bands ν 2 ← 1 and 3 ← 1 are expected to have intensities of 4.8 and 8.0 and 7.2 and 12% for ClF and BrF respectively. The hot bands were clearly discernible for the fundamentals and the overtone of ^{35}ClF, but very weak for ^{37}ClF and not visible for the overtone

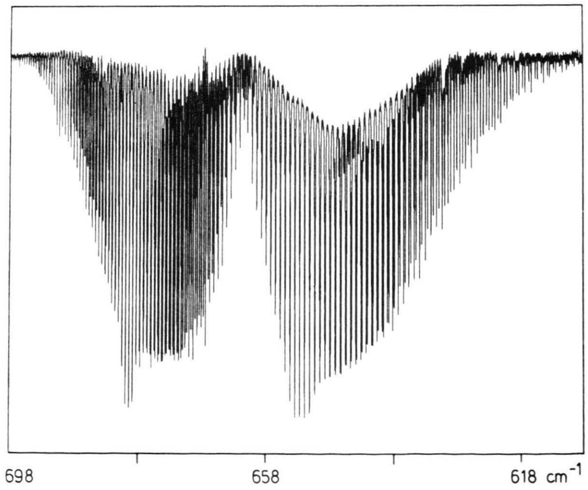

Fig. 1. Survey spectrum of BrF in the region of the fundamental. 15 cm cell, 13 mbar, resolution 0.04 cm^{-1}. The Q branch near 630 cm^{-1} is due to CF_4.

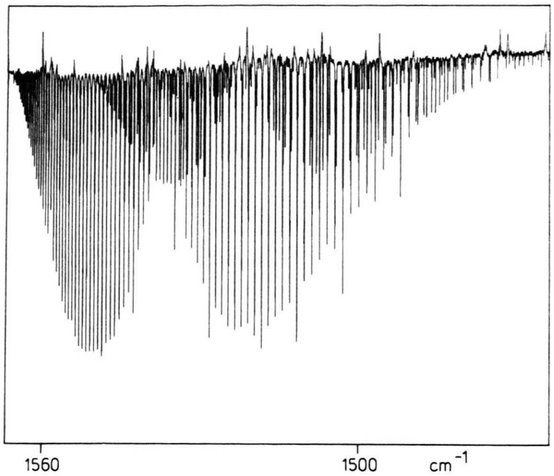

Fig. 2. Survey spectrum of ClF in the region of the first overtone. 15 cm, 70 mbar, resolution 0.04 cm^{-1}. Negative peaks are due to atmospheric H_2O absorptions.

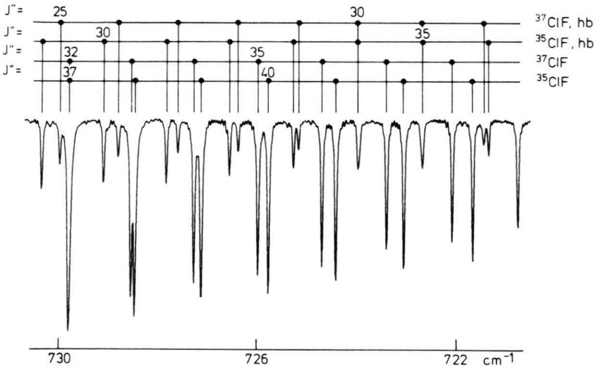

Fig. 3. Detail of the spectrum of ClF in the region of the fundamental. 15 cm cell, 70 mbar, resolution 0.04 cm^{-1}. Assignments are indicated.

of BrF. A detail of the spectrum of the fundamental of ClF with assignment of cold and hot lines is shown in Figure 3.

The rotational lines were numerically fitted by least squares methods to a quintic polynomial

$$\nu^{\mathrm{P,R}} = a_0 + a_1 m + a_2 m^2 + a_3 m^3 + a_4 m^4 + a_5 m^5$$

with $m = -J''$ and $J'' + 1$ in the P and R branches respectively. Neglecting contributions from sextic coefficients, the coefficients a_0 to a_4 have the usual meaning

$$a_0 = \nu^0, \qquad a_3 = -2(D'_J + D''_J),$$

$$a_1 = (B' + B''), \qquad a_4 = -(D'_J - D''_J).$$

$$a_2 = (B' - B'' - D'_J + D''_J),$$

The highest J'' values of measured lines were 58, 52 and 63 for ^{35}ClF, ^{37}ClF and BrF respectively. Slightly blended lines were given lower weights in the polynomial refinement. Lists of observed and calculated transition wavenumbers have been deposited as supplementary material [22]. The parameters derived from the coefficients of the polynomials are set out in Table 1.

It turned out that $a_5 = 3(H'_J + H''_J)$ and hence $\bar{H}_J = 1/2(H'_J + H''_J)$ could not be determined with significance, but from the standard deviation an upper limit of 1×10^{-12} cm^{-1} may be deduced for H_J. Therefore, excited state parameters were only evaluated up to quartic terms.

For the experimentally less well determined systems constraints were introduced which reduced the uncertainties determined for the free parameters. Such constraints concern parameters (B'', D''_J, $D'_J - D''_J$) which were available with higher significance from the analysis of other systems. The results of the constrained fits are also listed in Table 1. We have intentionally not merged our data with eventually more precise mw and mmw data in order not to make our results dependent on others though this might improve the significance of some parameters.

The averaged excited state parameters set out in Tables 2 and 3 were employed in the calculation of the equilibrium parameters according to the usual formulae

$$E_v = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 [+ \omega_e y_e(v + 1/2)^3 \text{ where appropriate}],$$

$$B_v = B_e - \alpha_e(v + 1/2) + \gamma_e(v + 1/2)^2,$$

$$D^v_J = D^e_J - \beta_e(v + 1/2).$$

For this purpose, hot band shifts were employed because they are essentially independent of calibration errors and pressure shifts, as well as $(B' - B'')$ and $(D'_J - D''_J)$ values.

4. Results and Discussion

The final excited state molecular parameters determined in the present study are set out in Tables 2 and 3. The equilibrium $^{35/37}$Cl and $^{79/81}$Br isotopic shifts, 7.471 and 1.606 cm^{-1}, respectively, are in perfect agreement with the calculated values, 7.485 and 1.607 cm^{-1}. The vibrational parameters

Table 1. Molecular parameters of ClF and BrF from polynomial fits (cm^{-1}).

	ν_0	B''	$(B'-B'')\times 10^3$	$D_J''\times 10^7$	$(D_J'-D_J'')\times 10^9$	$\bar{H}_J\times 10^{13}$	$\sigma\times 10^4$	No. of data
^{35}ClF								
v 1 ← 0	773.49879(15)	0.514311(3)	− 4.35810(27)	9.000(7)	4.75(9)		6.6	89
	773.49879(15)	0.514312(5)	− 4.35809(28)	9.010(30)	4.76(10)	2(5)	6.6	89
v 2 ← 1	763.44318(18)	0.509965(7)	− 4.3935(7)	9.18(4)	5.1(5)		9.8	51
v 2 ← 0	1536.94320(14)	0.514300(4)	− 8.7541(4)	8.986(16)	9.19(26)		5.9	70
v 3 ← 1	1516.7273(5)	0.509953 fix	− 8.8292(14)	9.05 fix	9.5 fix		12.8	23
	1516.7271(8)	0.509980(27)	− 8.829(6)	9.4(3)	9.(9)		11.7	23
v 3 ← 0	2290.2244(22)	0.514311 fix	−13.191(7)	9.00 fix	14.5 fix		66	24
	2290.225(4)	0.51431(12)	−13.19(4)	8.2(39)	0 fix		66	24
^{37}ClF								
v 1 ← 0	766.20325(14)	0.504553(3)	− 4.2353(3)	8.668(9)	4.21(14)		6.1	74
	766.20325(14)	0.504551(5)	− 4.2353(3)	8.65(4)	4.21(14)	−5(8)	6.1	74
v 2 ← 1	756.33964(27)	0.500311(8)	− 4.2685(12)	8.71(5)	4.9(9)		10.8	37
v 2 ← 0	1522.54232(21)	0.504525(5)	− 8.5032(7)	8.517(27)	9.5(5)		6.6	57
v 3 ← 1	1502.727(3)	0.500318 fix	− 8.5929(12)	8.7101 fix	8.42 fix		78	22
	1502.728(3)	0.50040(15)	− 8.598(13)	9.9(22)	0 fix		74	22
^{79}BrF								
v 1 ← 0	662.30460(18)	0.3545219(29)	− 2.61150(29)	4.012(7)	1.94(9)		6.6	88
	662.30449(20)	0.354528(6)	− 2.6113(3)	4.05(3)	2.02(11)	7(6)	6.5	88
v 2 ← 1	654.7081(11)	0.351910 fix	− 2.6285(12)	4.0314 fix	1.94 fix		31.3	23
	654.7125(15)	0.351967(29)	− 2.653(6)	4.39(11)	1.4(4)		17.2	23
v 2 ← 0	1317.0095(6)	0.354522 fix	− 5.2389(8)	4.012 fix	3.88 fix		30.9	55
	1317.0108(11)	0.354497(24)	− 5.239(4)	3.75(15)	5.3(25)		28.4	55
^{81}BrF								
v 1 ← 0	660.73343(14)	0.3528304(22)	− 2.59180(22)	3.988(5)	2.12(6)		5.6	82
	660.73344(15)	0.352830(4)	− 2.59182(25)	3.986(23)	2.11(8)	0(4)	5.6	82
v 2 ← 1	653.1712(16)	0.350239 fix	− 2.6026(20)	4.0092 fix	2.12 fix		46.3	25
	653.173(3)	0.35017(8)	− 2.611(11)	3.3(4)	7(7)		29.4	25
v 2 ← 0	1313.9072(4)	0.3528304 fix	− 5.2020(7)	3.988 fix	4.24 fix		19.7	54
	1313.9072(8)	0.352836(16)	− 5.2019(29)	4.02(10)	4.2(20)		19.3	54

Table 2. Molecular parameters of ClF (cm^{-1}).

		^{35}ClF	^{37}ClF
ν_0	obs.[a]	773.4988(20)[a]	766.2033(20)
$2\nu_0$	obs.	1536.9432(40)	1522.5423(40)
	calc.[b]	1536.9420(52)	1522.543(14)
$3\nu_0$	obs.	2290.224(10)	–
	calc.	2290.224(9)	2268.931(29)
ω_e		783.4534(24)	775.9822(56)
$\omega_e x_e$		4.9487(6)	4.8656(25)
$\omega_e y_e$		− 0.0176(1)	− 0.0147(5)
B_0		0.5143064(30)	0.5045462(30)
B_e		0.5164805(31)	0.5066588(31)
$\alpha_e\times 10^3$		4.3385(8)	4.2159(10)
$\gamma_e\times 10^5$		− 1.93(4)	− 1.88(5)
$D_J^e\times 10^7$		8.976(7)	8.647(9)
$\beta_e\times 10^9$		− 4.75(9)	− 4.21(14)

[a] Quoted standard deviation (in parentheses) of ν_0 values includes possible errors by calibration and pressure shift.

[b] Calculated from ω_e, $\omega_e x_e$ and $\omega_e y_e$.

Table 3. Molecular parameters of BrF (cm^{-1}).

		^{79}BrF	^{81}BrF
ν_0	obs.[a]	662.3046(20)	660.7334(20)
$2\nu_0$	obs.	1317.0095(40)	1313.9072(40)
	calc.[b]	1317.0127(56)	1313.9046(71)
ω_e		669.9011(23)	668.2956(26)
$\omega_e x_e$		3.7983(6)	3.7811(8)
B_0		0.3545219(29)	0.3528304(22)
B_e		0.3558215(30)	0.3541197(23)
$\alpha_e\times 10^3$		2.5953(10)	2.5743(7)
$\gamma_e\times 10^6$		− 8.1(5)	− 8.8(3)
$D_J^e\times 10^7$		4.002(7)	3.977(5)
$\beta_e\times 10^9$		− 1.94(9)	− 2.12(6)

[a] Quoted standard deviation (in parentheses) of ν_0 values includes possible errors by calibration and pressure shift.

[b] Calculated from ω_e and $\omega_e x_e$.

Table 4. Comparison of vibrational parameters of ClF and BrF (cm^{-1}).

	^{35}ClF	^{37}ClF	^{79}BrF	^{81}BrF
ω_e	783.4534(24) [a]	775.9822(56)	669.9011(23)	668.2956(26)
	786.147(30) [16]	778.684(60) [16]	669.881(18) [7]	668.275(18) [7]
	783.553(30) [14]	776.067(30) [14]	669.823(4) [8]	668.227(4) [8]
	783.2(3)		669.679(28) [14]	668.067(28) [14]?
$\omega_e x_e$	4.9487(6)	4.8656(25)	3.7983(6)	3.7811(8)
	6.161(15) [16]	6.058(25) [16]	3.797(65) [7]	3.779(65) [7]
	5.045(87) [14]	5.026(84) [14]	3.753(2) [8]	3.739(2) [8]
	4.8(1) [4]		3.863(76) [14]	3.844(78) [14]
$\omega_e y_e$	– 0.0176(1)	– 0.0147(5)	–	–
	– 0.03(1) [4]		– 0.0087(3) [8]	– 0.0078(3) [8]
$\omega_e z_e \times 10^4$			– 1.6(1) [8]	– 2.0(1) [8]
B_e	0.5164805(31)	0.5066588(31)	0.3558215(30)	0.3541197(23)
	0.51650500(33) [14]	0.50668189(33) [14]	0.35584941(23) [14] [b]	0.35414461(23) [14] [b]
	0.5164802(7) [10]	0.5066578(7) [10]	0.3558331(20) [13]	0.3541290(23) [13]
			0.3558193(12) [8]	0.3541193(12) [8]
$\alpha_e \times 10^3$	4.3385(8)	4.2159(10)	2.5953(10)	2.5743(7)
	4.432465(17) [14] [b]	4.20186(16) [14] [b]	2.5972(3) [14] [b]	2.5786(3) [14] [b]
			2.5826(12) [8]	2.5703(13) [8]
$\gamma_e \times 10^6$	–19.3(4)	–18.8(5)	– 8.1(5)	– 8.8(3)
	–17.35(6) [14] [b]	–16.70(5) [14] [b]	– 6.72(15) [14] [b]	– 6.66(15) [14] [b]
			–10.60(11) [8]	–10.25(11) [8]
$D_J^e \times 10^7$	8.976(7)	8.647(9)	4.002(7)	3.977(5)
	8.976(7) [14] [b]	8.639(7) [14] [b]	4.019(3) [14] [b]	3.981(3) [14] [b]
$\beta_e \times 10^9$	– 4.75(9)	– 4.21(14)	– 1.94(9)	– 2.12(6)
	(+)4.7(7) [14] [b]	(+)4.3(7) [14] [b]	(+)2.2(4) [14] [b]	(+)2.2(4) [14] [b]

[a] Data without quoted reference are from this study. – [b] Dunham coefficients.

may be compared with the presumably best presently available data from other sources, Table 4. Values by Coxon [16], which are based on IR measurements [15] are erroneous because of a misassignment of the v 2 ← 0 transition and insufficient resolution. Later, ω_e and $\omega_e x_e$ were calculated from B_e and D_e obtained by millimeter wave spectra [14], and agreement with our measurements within 0.1 cm^{-1} is noted. Data related to the $B \rightarrow X$ emission spectrum of ClF [4] and merged with absorption data for the same transition [23] agree within their quoted standard deviation with our data which, to conclude, are more precise by more than one order of magnitude than any of the previously reported data.

A similar situation is met for the vibrational parameters of BrF. From an analysis of the $B \leftarrow X$ absorption spectrum studied with high resolution [7], ω_e and $\omega_e x_e$ values were obtained which agree within one of their quoted standard deviation with the more precise values of the present investigation, and the standard deviations of the vibrational term values G_1'' and G_2'' appear to be underestimated [7]. A merge of the absorption data [7] with emission lines measured under high resolution provided improved vibrational parameters which were fitted up to fourth order [8]. These parameters reproduce our v 1 ← 0 and 2 ← 0 measurements to within 0.02 cm^{-1}. Finally, values obtained via the relation $(4 B_e^3 / D_e)^{1/2}$ and based on mmw data should be mentioned [14], which for ^{81}BrF apparently contain a clerical error. The ω_e values are by about 0.22 cm^{-1} smaller than ours.

For the rotational parameters of ClF and BrF, the available millimeter wave data of Willis and Clark [14] should be the most accurate source. Our B_e values for ClF are in agreement with previous mw measurements [10] which, with a clerical error (Y_{01} of ^{37}ClF), are quoted in the compilation by Lovas and Tiemann [24], but both data are ca. 2.5×10^{-5} cm^{-1} (ca. 0.8 MHz) smaller than the data of [14]. A similar inconsistency is noticed for the B_e data of BrF, where, in addition, merged data from high resolution electronic spectra are available [8]. For ClF the α_e and γ_e values of the present study are larger than those of [14], while for BrF our α_e and γ_e

values are between those previously reported [8, 14]. Agreement is found for D_e, while the β_e values of the present study are more accurate by a factor of about 5 than the best data hitherto available [14].

In conclusion, the present study provides the most accurate vibrational parameters and β_e values for the different isotopic species of ClF and BrF in the $X^1\Sigma^+$ electronic state. These rely on directly measured vibrational transitions. Furthermore, D_e data which are in full agreement with previous values and of comparable accuracy are furnished. A discrepancy between the present rotational parameters and those following from millimeter wave spectra [14] is revealed while consistency with the more relevant data from other sources is noted.

Acknowledgements

We wish to thank M. Betzel for assistance. Financial support by the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich 42 is gratefully acknowledged.

[1] L. Stein, in: Halogen Chemistry, Vol. 1 (V. Gutmann, ed.), Academic Press, London 1967.

[2] A. J. Downs and C. J. Adams, in: Comprehensive Inorganic Chemistry, Vol. 2, Pergamon Press, Oxford 1973.

[3] I. S. McDermid, J. Chem. Soc. Faraday Trans. II **77,** 519 (1981).

[4] R. D. Coombe, D. Pilipovich, and R. K. Horne, J. Phys. Chem. **82,** 2484 (1978).

[5] A. L. Wahrhaftig, J. Chem. Phys. **10,** 248 (1942).

[6] M. A. A. Clyne, A. H. Curran, and J. A. Coxon, J. Mol. Spectrosc. **63,** 43 (1976).

[7] J. A. Coxon and A. H. Curran, J. Mol. Spectrosc. **75,** 270 (1979).

[8] J. A. Coxon and M. A. Wickramaaratchi, J. Mol. Spectrosc. **87,** 85 (1981).

[9] M. A. A. Clyne, J. A. Coxon, and L. W. Townsend, J. Chem. Soc. Faraday Trans. II **68,** 2134 (1972).

[10] D. H. Gilbert, A. Roberts, and P. A. Griswold, Phys. Rev. **76,** 1723 (1949).

[11] D. F. Smith, M. Tidwell, and D. V. P. Williams, Phys. Rev. **77,** 420 (1950).

[12] J. McGurk, C. L. Norris, H. L. Tigelar, and W. H. Flygare, J. Chem. Phys. **58,** 3118 (1973).

[13] K. P. R. Nair, J. Hoeft, and E. Tiemann, J. Mol. Spectrosc. **78,** 506 (1979).

[14] R. E. Willis Jr. and W. W. Clark III, J. Chem. Phys. **72,** 4946 (1980).

[15] A. H. Nielsen and E. A. Jones, J. Chem. Phys. **19,** 1117 (1951).

[16] J. A. Coxon, Chem. Phys. Lett. **33,** 136 (1975).

[17] L. Stein, J. Amer. Chem. Soc. **81,** 1273 (1959).

[18] E. Jacob and M. Fähnle, to be published.

[19] J. Kauppinen, K. Jolma, and V.-M. Horneman, Appl. Optics **21,** 3332 (1982).

[20] K. Jolma, J. Kauppinen, and V.-M. Horneman, J. Mol. Spectrosc. **101,** 278 (1983).

[21] J. S. Wells, A. Hinz, and A. G. Maki, J. Mol. Spectrosc. **114,** 84 (1985).

[22] Lists of observed and calculated transition wavenumbers may be obtained from Fachinformationszentrum Energie – Physik – Mathematik, D-7514 Eggenstein-Leopoldshafen, West Germany, on submission of the name of the authors, the literature reference and the registry number IRD-100 22.

[23] W. Stricker and L. Krauss, Z. Naturforsch. **23a,** 1116 (1968).

[24] F. J. Lovas and E. Tiemann, J. Phys. Chem. Ref. Data **3** (1974), pp. 663 and 640.