

FOURIER TRANSFORM DETECTION OF THE VIBRATION-ROTATION BANDS OF IF

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High resolution absorption spectra of the IF molecule in the $X^1\Sigma^+$ ground state have been observed with the Kitt Peak Fourier transform spectrometer in a F_2/I_2 flame. Accurate wavenumber measurements ($\pm 0.0002\text{ cm}^{-1}$) were made for the 1-0, 2-1 and 2-0 bands and molecular constants were derived.

1. Introduction

Evidence for the existence of the IF molecule was first obtained by Durie [1] from emission spectra of fluorine/iodine flames. He later analyzed high resolution spectra of $B^3\Pi_0-X^1\Sigma^+$ (called $A^3\Pi_0-X^1\Sigma^+$ by Durie) transition and derived the first set of constants for the ground state [2]. Improved measurements and Dunham analyses for this transition have been made by laser-induced fluorescence [3,4]. What is now called the $A^3\Pi_0-X^1\Sigma^+$ transition was first seen by Birks et al. [5] and recently analysed in more detail by McFeeters et al. [6] Nicolai and Heaven have observed the metastable $A'^3\Pi_2$ state in argon matrices [7].

The first observation of the IF vibration-rotation spectrum was made by Magg et al. [8] using diode laser absorption spectroscopy. Two groups made the initial studies on the pure rotation spectrum of IF [9,10], and accurate values for the $X^1\Sigma^+$ rotational constants have been derived from these millimeter wave spectra by Hoeft and Nair [11]. The IF molecule was the last of the non-radioactive diatomic interhalogens to be discovered because it rapidly disproportionates at room temperature into I_2 and IF_5 [12].

Recent interest in IF has centered around the possibility of an B-X IF visible chemical laser. So far, pulsed [13,14] and cw [15] optically pumped B-X

lasers and a fast TEA discharge D'-A' laser [16] have been reported. The extensive infrared vibration-rotation measurements reported in this paper will facilitate the development of infrared diagnostics for the IF chemical laser.

2. Experimental

The IF molecule was produced by burning iodine vapor in fluorine. Since IF is not stable, it was necessary to use a flow reactor. The reactor was a Pyrex pipe (1.2 m long and 7.5 cm inner diameter) with three ports for admission of the reactants and exhausting of the spent gases. It contained a multipass white cell optical system with gold-coated mirrors. During our study, the system was aligned for 16 transversals yielding an optical path length of about 19.5 m, although the effective path length may be somewhat shorter due to inefficient mixing of the reactants.

Fluorine (5% in argon) was admitted through the port located near one end of the reactor. Iodine vapor (from a flow of argon over solid iodine) was admitted by way of a port at the center of the reactor and the spent gases removed through a port near the opposite end of the reactor. Flow rates were not monitored, but adjusted by the strength of the IF absorption. The best IF spectrum was obtained with a total cell pressure of 12.5 Torr and it was used for measurement of the IF lines. A similar spectrum with a total pressure of 2.4 Torr, although weaker in IF,

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was useful in understanding the molecular linewidths.

Absorption spectra were taken with the McMath Fourier transform spectrometer of the National Solar Observatory at Kitt Peak. The background continuum was provided by a tungsten glower. Each spectrum consisted of 12 scans coadded over a period of about one hour. The unapodized resolution was 0.0053 cm^{-1} with liquid helium cooled As:Si detectors, KCl beamsplitters, and a bandpass from 500 to 1450 cm^{-1} . The lower wavenumber limit of this bandpass was set by the detector band gap and KCl transmission while an uncooled InSb filter in front of the spectrometer established the upper wavenumber limit. The optical path between the light source and the spectrometer was purged with dry nitrogen to minimize atmospheric CO_2 and H_2O absorptions.

The spectra were calibrated from absorption spectra taken with the reactor filled with about 0.7 Torr of N_2O gas. A very small correction ($<0.0001\text{ cm}^{-1}$) was determined using wavenumbers for N_2O from the literature [17], and applied to the raw Fourier transform measurements. The signal-to-noise ratio was about 35:1 for the stronger lines in the 1-0 band. Since the IF linewidths were about 0.007 cm^{-1} , the resulting absolute wavenumber accuracy for strong lines is about 0.0002 cm^{-1} .

3. Results and analysis

A computer code called DECOMP, developed by J.W. Brault of the National Solar Observatory, was used to analyze the data. Line lists were made and the line profiles fitted to Voigt functions. Most of the strong lines were found to be essentially Gaussian. Some channeling was present in the spectrum because the input and output windows of the cell were made of unwedged KBr. This sinusoidal ripple in the base line was removed in DECOMP by Fourier transformation, elimination of the offending frequency components, and then performing an inverse Fourier transformation.

Analysis started from the values for the lines of the 1-0 and 2-1 bands given by Magg et al. [8]. It was then straightforward to calculate the position of the 2-0 band and locate its lines. A search for the lines of the 3-2 band was unsuccessful.

Table 1 lists all the lines observed. A combination of weakness and interfering molecular absorptions near the band gap made accurate measurement of the low J lines not possible, so the calculated values (in parentheses) have been included in table 1. The entire P branch of the weaker 2-1 band was not measured, although present, because it was badly blended with a complex band system due to IF_3 , or, possibly IF_2 . The P(27) line of the 1-0 band was coincident with a Q branch head of the unknown absorber, and thus was not measured.

The strongest lines of the 1-0 band, around $J=22$, had peak absorptions of about 75%. The intensity ratio of the 1-0 to the 2-1 band was about 3.52, while the overtone 2-0 band was about 15.1 times weaker than the 1-0.

The lines of table 1 were reduced to two sets of equivalent constants. In table 2 the standard spectroscopic parameters were derived for $v=0, 1$ and 2, while table 3 provides the Dunham coefficients. In both fits the hyperfine-free microwave and millimeter wave transitions found in Hoeft and Nair's paper [11] were included.

4. Discussion

An interesting comparison of diode and Fourier transform spectroscopies can be made with these data. Our data cover 15 of the 18 lines measured by Magg et al. by diode spectroscopy [8]. The difference between them is $0.16(50) \times 10^{-3}\text{ cm}^{-1}$, but five lines differ by more than the standard deviation. Throughout this paper one standard deviation error in the least significant digits is provided in parentheses. The largest difference, $1.39 \times 10^{-3}\text{ cm}^{-1}$, is for the P(11) lines of the 1-0 band. The only high J line observed by Magg et al. [8], R(85) of 1-0 band, is somewhat suspect since it lies nearly 0.006 cm^{-1} away from its expected position and should be much weaker than the next lower J , R(51), that they observed. This single dubious line greatly affects their higher order Dunham constants.

These two data sets and constants illustrate an important advantage of Fourier transform spectroscopy. In Fourier transform spectroscopy all of the line positions are measured in a single experiment and so form a coherent set. In contrast each line

Table 1

The vibration-rotation lines of the $X^1\Sigma^+$ ground state of the IF molecule. The line positions in parentheses were not be measured, but were calculated from the Dunham fit. The values following the measured wavenumbers are the calc. - obs. values

J	1-0		2-1	2-0	
	P(J)	R(J)	R(J)	P(J)	R(J)
0	-	(604.52946)	(598.24363)	-	(1202.21931)
1	(603.41813)	(605.07949)	(598.78988)	(1201.11174)	(1202.76180)
2	(602.85683)	605.62690(116)	(599.33235)	(1200.54667)	(1203.29675)
3	602.28923(-256)	606.16808(-15)	(599.87103)	(1199.97409)	(1203.82416)
4	601.72275(-25)	606.70643(-50)	(600.40592)	(1199.39401)	1204.34513(111)
5	601.15046(-2)	607.24169(-15)	600.93504(-198)	(1198.80642)	1204.85560(-73)
6	600.57420(-3)	607.77270(-26)	601.46320(-111)	1198.21258(125)	1205.36229(121)
7	599.99429(3)	608.30051(22)	601.98670(-110)	1197.60913(38)	1205.85844(18)
8	599.41061(4)	608.82385(4)	602.50759(12)	1196.99853(-15)	1206.34758(-29)
9	598.82323(7)	609.34334(-18)	603.02292(-40)	1196.38235(122)	1206.82936(-54)
10	598.23232(27)	609.85934(-8)	603.53477(-58)	1195.75694(83)	1207.30405(-30)
11	597.63691(-33)	610.37135(-14)	604.04372(18)	1195.12332(-29)	1207.77071(-49)
12	597.03863(-10)	610.87980(6)	604.54694(-96)	1194.48437(72)	1208.23073(27)
13	596.43694(42)	611.38414(-2)	605.04805(-36)	1193.83646(23)	1208.68243(31)
14	595.83078(14)	611.88462(-11)	605.54467(-41)	1193.18156(21)	1209.12645(29)
15	595.22073(-34)	612.38147(1)	606.03766(-22)	1192.51953(50)	1209.56255(-5)
16	594.60753(-30)	612.87435(1)	606.52696(13)	1191.84923(-3)	1209.99126(-14)
17	593.99027(-64)	613.36332(-5)	607.01139(-52)	1191.17228(24)	1210.41290(31)
18	593.37043(9)	613.84849(-4)	607.49246(-65)	1190.48668(-72)	1210.82598(-15)
19	592.74600(-10)	614.32966(-16)	607.97054(11)	1189.79583(51)	1211.23264(60)
20	592.11811(-10)	614.80718(-5)	608.44420(33)	1189.09636(54)	1211.63061(32)
21	591.48711(44)	615.28068(-8)	608.91346(5)	1188.38989(100)	1212.02061(-28)
22	590.85168(19)	615.75043(2)	609.37909(3)	1187.67529(74)	1212.40401(18)
23	590.21235(-32)	616.21599(-17)	609.84069(-11)	1186.95250(-30)	1212.77914(4)
24	589.57032(10)	616.67791(-10)	610.29867(4)	1186.22365(1)	1213.14656(-14)
25	588.92420(6)	617.13581(-15)	610.75300(46)	1185.48724(16)	1213.50709(47)
26	588.27423(-20)	617.58984(-15)	611.20288(35)	1184.74244(-68)	1213.85868(-16)
27	(587.62111)	618.04005(-6)	611.64815(-43)		1214.20288(-50)
28	586.96429(11)	618.48622(-8)	612.09078(7)		1214.54024(4)
29	586.30391(27)	618.92848(-8)	612.52837(-51)		1214.86959(27)
30	585.63917(-33)	619.36683(-5)	612.96255(-56)		1215.19140(67)
31	584.97148(-28)	619.80120(-6)	613.39270(-68)		1215.50354(-87)
32	584.30016(-27)	620.23172(4)	613.82036(67)		1215.81056(21)
33	583.62559(8)	620.65808(-7)	614.24235(31)		1216.10826(-31)
34	582.94737(37)	621.08064(-2)	614.65992(-48)		1216.39883(-20)
35	582.26497(5)	621.49928(8)	615.07465(-14)		1216.68267(92)
36	581.57926(-1)	621.91366(-10)	615.48546(28)		1216.95751(81)
37	580.88933(-72)	622.32412(-22)	615.89156(-3)		1217.22352(-37)
38	580.19517(-210)	622.73089(-5)	616.29441(42)		1217.48255(-75)
39	579.50123(30)	623.13336(-17)	(616.69237)		1217.73370(-123)
40	578.80137(33)	623.53221(8)	617.08608(-67)		1217.97921(44)
41	578.09825(65)	623.92643(-28)			1218.21313(-169)
42	577.39041(-20)	624.31734(5)			1218.44334(28)
43	576.68032(23)	624.70388(4)			1218.66314(-34)
44	575.96636(33)	625.08636(0)			
45	575.24809(-35)	625.46465(-19)			
46	574.52725(-8)	625.83962(33)			
47	573.80197(-73)	625.20964(-5)			
48	573.07457(1)	626.57625(22)			
49	572.34253(-37)	626.93829(-2)			
50	571.60778(4)	627.29682(29)			

Table 1
Continued

<i>J</i>	1-0		2-1	2-0	
	P(<i>J</i>)	R(<i>J</i>)	R(<i>J</i>)	P(<i>J</i>)	R(<i>J</i>)
51	570.86909(2)	627.65060(-6)			
52	570.12716(25)	628.00075(3)			
53	569.38047(-79)				
54	568.63271(59)				
55	567.87824(-126)				
56	567.12327(-12)				
57	566.36403(21)				
58	565.60025(-52)				
59	564.83391(-35)				

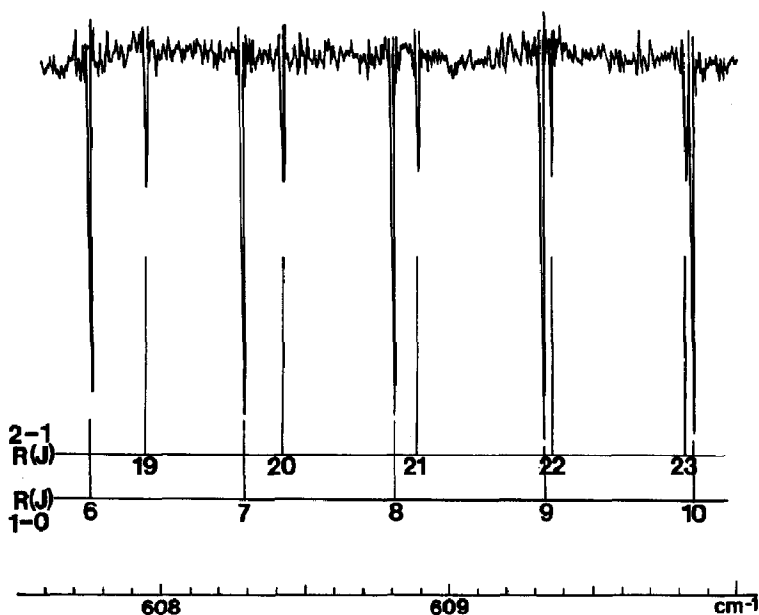


Fig. 1. Portion of the R branch region of the 1-0 and 2-1 vibration-rotation bands of IF.

Table 2
The molecular constants for the X $^1\Sigma^+$ state of IF in cm^{-1}

Constant	$v=0$	$v=1$	$v=2$
T_v	-	603.975675(29)	1201.669286(35)
B_v	0.278773440(48)	0.276894649(51)	0.275010810(51)
$D_v \times 10^7$	2.35780(85)	2.36687(88)	2.37698(87)

measured with a diode laser constitutes a separate experiment with independent statistical and systematic errors.

Since we observed only three vibrational levels,

$v''=0, 1, 2$, only two vibrational constants Y_{10} (ω_e) and Y_{20} ($-\omega_e x_e$) could be determined from our measurements (table 3). However, Gouédard et al. [4] have determined accurate term values (± 0.003

Table 3
The Dunham coefficients for the $X^1\Sigma^+$ state of IF in cm^{-1}

Dunham coefficient	Value
Y_{10}	610.257739(82)
Y_{20}	-3.141032(28)
$Y_{01} \times 10$	2.79710942(55)
$Y_{11} \times 10^3$	-1.873743(69)
$Y_{21} \times 10^6$	-2.524(25)
$Y_{02} \times 10^7$	-2.35365(80)
$Y_{12} \times 10^{10}$	-8.04(63)
$Y_{22} \times 10^{11}$	-5.2(28)

cm^{-1}) for $v''=8-19$ by laser excitation spectroscopy. When our vibrational intervals were combined with these high term values, and improved vibrational expression for the ground $X^1\Sigma^+$ state was found:

$$G(v) = 610.242499(323)(v + \frac{1}{2}) - 3.129329(184)(v + \frac{1}{2})^2 - 2.4588(304) \times 10^{-3}(v + \frac{1}{2})^3 - 3.724(195) \times 10^{-5}(v + \frac{1}{2})^4 - 1.2642(431) \times 10^{-6}(v + \frac{1}{2})^5 \quad (\text{cm}^{-1}).$$

A coherent set of Fourier transform measurement can also be invaluable for the determination of parameters which depend on intensities or lineshapes. The IF rotational temperature of 354 ± 6 K was derived from a Boltzmann plot of the absorbances [18]. Rotational lines of the R branch with $J > 43$ or $J < 13$ were not used because of low intensities and blending with other absorption features. Since many lines of the P branch were affected by other strong molecular absorptions, they were not used to determine the temperature, but do show a similar trend. The intensity difference (Herman-Wallis effect [19]) between the R and P branches is not significant enough for a determination of transition moment to be made. The linear Herman-Wallis factor α ($F_{10} = 1 + \alpha m$, $m = J + 1$ for R branch lines and $m = -J$ for P branch lines) can be calculated from the observed dipole moment of 1.948(20) D [20] and the ab initio value [21] of the dipole moment derivative, 11.50 D/Å (see, for example, ref. [22]). The small α value of 0.000325 accounts for our inability to find a Herman-Wallis effect. The ab initio

value of the dipole moment derivative [21] is unusually large but the theoretical value for the dipole moment, 1.87 D, is in good agreement with the experimental value of 1.948(20) D. The large dipole moment derivative originates from the strong ionic character of the IF bond [21].

Infrared absorption measurements can only provide estimates for molecular concentrations if the infrared transition dipole moment is available. In the case of the transient IF, there have been no measurements but the theoretical value of the dipole moment derivative yields the rather large value of 0.472 D for the fundamental band and $2^{0.5} \times 0.472$ D = 0.668 D for the 2-1 hot band [22,23]. The error in these values is hard to assess since the error in the theoretical dipole moment derivatives is unknown but $\pm 10-20\%$ represents a reasonable guess.

The relative transition dipole moments for the 2-1 and 1-0 bands allows a vibrational temperature of 360 ± 10 K to be derived from the ratio of the absorbances (0.178) of the R(22) lines of these two bands [22,23]. The vibrational and rotational temperatures are the same within experimental error, both slightly above room temperature, presumably because the reaction exothermicity has not been completely transferred to the surroundings.

The fundamental band transition dipole moment of 0.472 D for the fundamental band results in a vibrational band strength (S_v) of $1060 \text{ cm}^{-2} \text{ atm}^{-1}$ at 354 K [23]. The value for the 2-0 overtone is $39 \text{ cm}^{-2} \text{ atm}^{-1}$ at 354 K using the observed ratio (27.1) of the 1-0 and 2-0 absorbances for the R(22) line. The observed peak absorption of the R(22) line of the 1-0 band yields an estimate of 1.2×10^{13} molecules of IF/ cm^3 for the average concentration [23]. This number represents a lower limit because of the uncertainties in determining the effective path length, which is smaller than the geometric path length.

Another interesting feature of these spectra was the linewidth of the IF lines. None of the IF lines in our spectra showed ringing near the base line. Ringing is caused by the $\sin x/x$ instrumental profile of the Fourier transform spectrometer and would be seen if the absorption lines were appreciably narrower than the resolution width. An average linewidth was derived from the 30 of the strongest lines of the 1-0 R branch. The observed linewidth was $7.17(26) \times 10^{-3} \text{ cm}^{-1}$ for the 12.5 Torr spectrum and

$6.03(29) \times 10^{-3} \text{ cm}^{-1}$ for the 2.4 Torr spectrum. There was no systematic variation of the linewidth with J . These widths, which are substantially greater than the $5.3 \times 10^{-3} \text{ cm}^{-1}$ resolution width, could be due to Doppler broadening, collisional broadening or unresolved hyperfine structure. The Doppler full width at half maximum calculated at the measured rotational temperature is only $0.7 \times 10^{-3} \text{ cm}^{-1}$, and would not vary with pressure. The magnitude of unresolved hyperfine structure, due to the large iodine quadrupole coupling constant [9], is more difficult to assess, but it also will not depend on pressure. The observed increase of average width with total pressure thus appears to be the result of collisional broadening by a mixture of argon and reactant gases. A crude estimate of $0.0003 \text{ cm}^{-1}/\text{Torr}$ (10 MHz/Torr) for the pressure broadening coefficient is consistent with these data.

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References

- [1] R.A. Durie, *Proc. Phys. Soc. (London)* A 63 (1950) 1292; *Proc. Roy. Soc. A* 207 (1951) 388.
- [2] R.A. Durie, *Can. J. Phys.* 44 (1966) 337.
- [3] T. Trickl and J. Wanner, *J. Mol. Spectry.* 104 (1984) 174.
- [4] G. Gouédard, N. Billy, B. Girard and J. Vigué, *Mol. Phys.* 62 (1987) 1371.
- [5] J.W. Birks, S.D. Gabelnick and H.S. Johnston, *J. Mol. Spectry.* 57 (1975) 23.
- [6] B.D. McFeeters, E.A. Walters and P.J. Wolf, *J. Mol. Spectry.* 135 (1989) 1.
- [7] J.P. Nicolai and M.C. Heaven, *J. Chem. Phys.* 87 (1987) 3304.
- [8] U. Magg, H. Birk, K.P.R. Nair and H. Jones, *Z. Naturforsch.* 44a (1989) 313.
- [9] E. Tiemann, J. Hoeft and T. Topping, *Z. Naturforsch.* 28a (1973) 1405.
- [10] J.C. McGurk and W.H. Flygare, *J. Chem. Phys.* 59 (1973) 5742.
- [11] J. Hoeft and K.P.R. Nair, *Z. Physik D* 8 (1988) 85.
- [12] E.H. Appelman and M.A.A. Clyne, *J. Chem. Soc. Faraday Trans. I* 71 (1975) 2072.
- [13] S.J. Davis and L. Hanco, *Appl. Phys. Letters* 37 (1980) 692.
- [14] S.J. Davis, L. Hanco and R.F. Shea, *J. Chem. Phys.* 78 (1983) 172.
- [15] S.J. Davis, L. Hanco and P.J. Wolf, *J. Chem. Phys.* 82 (1985) 4831.
- [16] M. Diegelmann, H.P. Griencisen, K. Hohla, X.-J. Hu, J. Krasinski and K. L. Kompa, *Appl. Phys.* 23 (1980) 283.
- [17] G. Guelachvili and K.N. Rao, *Handbook of infrared standards* (Academic Press, Orlando, 1986).
- [18] G. Herzberg, *Spectra of diatomic molecules*, 2nd Ed. (Van Nostrand Reinhold, New York, 1950).
- [19] R. Herman and R.F. Wallis, *J. Chem. Phys.* 23 (1955) 637.
- [20] K.P.R. Nair, J. Hoeft and E. Tiemann, *Chem. Phys. Letters* 60 (1979) 253.
- [21] S.A. Kucharski, J. Noga and R.J. Bartlett, *J. Chem. Phys.* 88 (1988) 1035.
- [22] J.B. Burkholder, P.D. Hammer, C.J. Howard, A.G. Maki, G. Thompson and C. Chackerian Jr., *J. Mol. Spectry.* 124 (1987) 139.
- [23] M.A.H. Smith, C.P. Rinsland, B. Fridovich and K.N. Rao, in: *Molecular spectroscopy: modern research*, Vol. 3, ed. K.N. Rao (Academic Press, Orlando, 1986).