The Diode Laser Spectrum of Iodine Fluoride (IF) in the Ground Electronic State

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To Professor Helmut Dreizler on the Occasion of his 60th Birthday

The infrared absorption spectrum of the gas phase IF molecule in its ground state has been observed for the first time, using a diode laser spectrometer. The wavenumbers of transitions in the $v = 1 \leftarrow 0$, and $v = 2 \leftarrow 1$ bands have been measured with a nominal accuracy of ± 0.001 cm^{-1}. These data were fitted along with the recently published microwave spectrum to produce an improved set Dunham Y-parameters. Also the coefficients of the Dunham potential function for the electronic state of IF were determined by a direct fit to the experimental data.

Introduction

As has been demonstrated in numerous publications, diode laser spectroscopy provides a means of obtaining highly accurate infrared data. We have recently applied this technique to a number of diatomic metal hydrides in the gas phase [1–8] and were able to determine the most accurate set of molecular parameters available to date for all these molecules. In the present paper we report the first observation of the infrared spectrum of the IF molecule in its ground electronic state.

The optical spectrum of the IF molecule was first observed in flames by Durie [9]. Since then there have been a number of studies of the electronic spectra of this molecule [10–16]. The ground state rotational spectrum was first observed by Tiemann et al. [17] and independently by McGurk and Flygare [18]. Recently Nair and Hoeft [19] extended these measurements into the mm-wave region and thus improved the accuracy of the number of the molecular parameters.

Although the measurement of microwave or mm-wave spectra allows pure rotational parameters to be determined with admirable precision, no direct information can be obtained about the vibrational contributions to the potential function. Under these circumstances, the procedure usually adopted is to use various approximate relationships to estimate the values of some of the vibrational parameters from well-determined rotational constants.

Even the high resolution optical spectra of Trickl and Wanner [14] did not furnish enough data to enable all the primary, ground state parameters to be determined independently, and these authors resorted to the use of approximate relationships to obtain values for inaccessible parameters.

The aim of the present work was to measure sufficient infrared transitions in the ground electronic state to allow a consistent set of Dunham Y-parameters to be determined without resort to approximations. In addition, it was decided to determine the coefficients of the Dunham potential function by a direct fit to the experimental data.

Experimental

Measurements were carried out on an IF sample which was produced directly within an absorption cell. Several grams of elemental iodine were placed in a 12 mm o.d. quartz tube 1 meter long, which was closed with two KBr windows. A slow stream of SF_6 gas was passed over the iodine at a total pressure of about 1 mbar. A microwave cavity was positioned around the main tube just in front of the iodine mound. Fluorine atoms were generated by a microwave discharge in the SF_6 gas. This set-up produced sufficient IF to allow absorption lines to be easily observed with a single pass of the laser beam down the axis of the cell.

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Table 1. Experimental data on the ground state of IF.

a) This work (in cm^{-1})

$v = 1 \leftarrow 0$		$v = 2 \leftarrow 1$	
P(6)	600.5741 (−02)	P(17)	587.7714 (00)
P(11)	597.6383 (10)	R(13)	605.0484 (−01)
P(16)	594.6079 (01)	R(25)	610.7523 (−03)
P(17)	593.9908 (−01)	R(26)	611.2030 (04)
P(27)	587.6214 (02)	R(33)	614.2424 (01)
R(12)	610.8799 (01)		
R(13)	611.3843 (01)		
R(19)	614.3292 (−06)		
R(26)	617.5901 (01)		
R(34)	621.0812 (04)		
R(42)	614.3168 (−08)		
R(51)	627.6509 (−05)		
R(85)	637.2240 (02)		

b) Microwave data from reference [19] (in MHz)

	$v=0$	$v=1$	$v=2$
$J = 1 \leftarrow 0$	16714.83 (02)		
$J = 2 \leftarrow 1$	33429.44 (−01)	33204.15 (−01)	32978.23 (02)
$J = 16 \leftarrow 15$	267321.57 (01)	265518.70 (−01)	263710.98 (00)
$J = 17 \leftarrow 16$	284013.27 (−01)	282097.71 (01)	280176.93 (00)

Table 2. Dunham coefficients determined for the ground state of IF (in cm^{-1}).

	Present study	Ref. [14]	Ref. [19]
Y_{10}	610.24128 (81)	610.2265 (31)	(609.69) [b]
Y_{20}	−3.12840 (29)	−3.1253 (10)	(−3.120) [b]
$Y_{30} \cdot 10^3$	−2.61 [a]	−2.61 (10)	–
$Y_{40} \cdot 10^5$	−5.83 [a]	−5.83 (45)	–
$Y_{01} \cdot 10$	2.79711060 (4)	2.7970959 (5)	2.7971104 (15)
$Y_{11} \cdot 10^3$	−1.873775 (24)	−1.87215 (4)	−1.873760 (80)
$Y_{21} \cdot 10^6$	−2.5485 (64)	−2.7165 (66)	−2.549 (13)
$Y_{31} \cdot 10^8$	−4.75 [a]	−4.75 (40)	–
$Y_{02} \cdot 10^7$	−2.35569 (64)	(−2.3507) [b]	−2.3548 (10)
$Y_{12} \cdot 10^{10}$	−7.66 (22)	−12.641 (14)	−7.9 (12)
$Y_{03} \cdot 10^{14}$	0 [c]	(−8.571) [b]	(−8.596) [b]

[a] Constrained at the value of Trickl and Wanner [14].
[b] Calculated from approximate relationship.
[c] Constrained to zero.

The diode laser spectrometer used was based on the laser head assembly of Spectra Physics with diodes from the same company. Measurements were carried out to a nominal accuracy of 0.001 cm^{-1} using a calibrated confocal étalon with a FSR of 0.009811 cm^{-1} in conjunction with accurately measured absorption lines. A single diode which operated in the relevant spectral region gave fairly good coverage (with gaps) of the region from 585 cm^{-1} to 640 cm^{-1}. Absolute wavenumber calibration was carried out using accurately known absorption lines of CO_2 and N_2O [20].

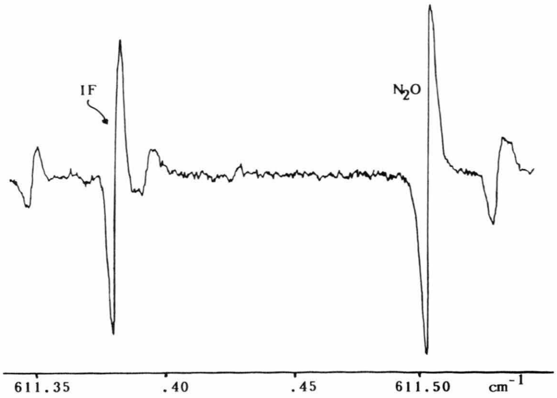

Fig. 1. The absorption spectrum of IF and N_2O (as calibrant) near 611.5 cm^{-1}. The IF line indicated in the figure was identified as the R(13) transition of the fundamental band. The remaining lines arise from N_2O which was used to make absolute wavenumber measurements. The strong line to the high frequency side of the figure is at 611.50536 cm^{-1} [20].

The diode laser beam was passed axially through the cell on to a HgCdTe infrared detector. Signals were processed by source modulation of the diode laser at 5 kHz followed by phase sensitive detection.

Spectra and Analysis

An example of the signals observed with IF is shown in Figure 1. The relevant data available in the literature [14, 19] were of sufficiently high quality to allow assignment of the absorption lines to be made without difficulty. A total of 20 rovibrational transitions were measured in the $v = 1 \leftarrow 0$ and $v = 2 \leftarrow 1$ bands. These are listed together with their assignments in Table 1. The microwave data of Hoeft and Nair [19] are also listed in this table for completeness.

These data were treated in two ways:

1. They were fitted to the usual Dunham [21] expression for the energy levels of a diatomic molecule:

$$F = \sum_{ij} Y_{ij} (v + \tfrac{1}{2})^i \, [J(J+1)]^j \, .$$

The Dunham Y-parameter fitted and the values obtained for IF are shown in Table 2. The values for these parameters available at the beginning of this work are included in Table 2 for comparison.

2. Since it is well-known (e.g. [21–23]) that the above procedure results in more parameters being fitted than are necessary, we also adopted the approach used by Maki and Lovas [22, 23] and fitted the

ω_e	610.2771 (17) cm^{-1}
B_e	0.279711420 (20) cm^{-1}
a_1	−3.435165 (41)
a_2	7.2688 (17)
a_3	−13.031 (12)

Table 3. Coefficients of the Dunham potential function.

experimental data directly to the Dunham potential function [21]

$$U_J = a_0\,\xi^2\,(1 + a_1\,\xi + a_2\,\xi^2 + a_3\,\xi^2 + \ldots)$$
$$+ B_e\,J(J+1)(1 - 2\xi + 3\xi^2 - 4\xi^3 + \ldots),$$

where $a_0 = \omega_e^2/4\,B_e$ and $\xi = (r - r_e)/r_e$.

In this case the variables fitted are ω_e, B_e, a_1, a_2, and a_3, and the values obtained are shown in Table 3.

Discussion

The main advantage of the Dunham expression for the term values of the rotating, vibrating, diatomic molecule is ease of computation. However, as Dunham himself recognised [21], this expression results in the introduction of redundancy (i.e. more parameters are used than really necessary). Moreover, the existence of explicit, approximate relationships between various Y-parameters has been used by many authors as a means of calculating higher-order Y's from those determined from their experimental data. These computed values were then fixed in the final fitting of the data and the experimentally accessible Y's redetermined. This is usually done in order to "up-grade" the ability of the set of parameters to predict transitions with higher quantum numbers than those measured. While this sort of approximation is undoubtedly of values in circumstances where lines with high quantum numbers have to be assigned, without this experimental necessity, this seems to be a pointless and subjective exercise. When all is said and done, the Y's are no more than fitting parameters.

The procedure adopted here was to use the minimum number of Y-parameters which were required to reproduce the data-set given in Table 1. In this case, the seven Y's listed with a standard deviation in the first column of Table 2 were found to be necessary. Since we only have data over states with vibrational quantum numbers up to $v = 2$, no pure vibrational Y's above Y_{20} were required to fit the data. However, in order to allow direct comparison between our values of Y_{10} and Y_{20} and those of Trickl and Wanner [14] we constrained Y_{30} and Y_{40} to the values determined experimentally by these authors.

The fit of the data of Table 1 to the Dunham potential function is carried out over the relationships between the Y-parameters and the coefficients of the function given by Dunham [21].

The superiority of this procedure is demonstrated by the fact that the residuals of a fit which included only five variables (ω_e, B_e, a_1, a_2 and a_3) were identical to those produced with the seven Y's.

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