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1975 J. Phys. B: At. Mol. Phys. 8 2841

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Rotational analysis of the C $^1\Pi-x$ $^1\Sigma^+$ system of indium monofluoride

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Received 13 May 1975, in final form 9 July 1975

Abstract. Indium monofluoride was excited in a high-frequency discharge and the C-x system was photographed at a reciprocal dispersion of 0.3 \AA mm^{-1} using a plane-grating spectrograph. Rotational analyses of the 0,0 1,0 2,2 3,3 4,4 2,4 3,5 4,6 and 5,7 bands have been carried out and the following molecular constants have been evaluated.

$$\begin{array}{ll} B'_e = 0.2670(\pm 3) \text{ cm}^{-1} & B''_e = 0.2628(\pm 4) \text{ cm}^{-1} \\ \alpha'_e = 0.0050(\pm 4) \text{ cm}^{-1} & \alpha''_e = 0.0020(\pm 1) \text{ cm}^{-1} \\ D'_e = 3.65(\pm 5) \times 10^{-7} \text{ cm}^{-1} & D''_e = 2.5(\pm 3) \times 10^{-7} \text{ cm}^{-1} \\ \beta'_e = 0.5(\pm 2) \times 10^{-7} \text{ cm}^{-1} & \beta''_e = 0.2(\pm 1) \times 10^{-7} \text{ cm}^{-1} \\ r'_e = 1.9672(\pm 3) \text{ \AA} & r''_e = 1.9853(\pm 2) \text{ \AA} \end{array}$$

The r''_e value agrees with the microwave absorption value 1.9854 \AA .

1. Introduction

The spectrum of indium monofluoride was studied by Welti and Barrow (1952), Barrow *et al* (1954) and Barrow *et al* (1955). Welti and Barrow carried out the vibrational analyses of the A-x, B-x and C-x systems of InF in absorption. Barrow *et al* (1954) repeated the vibrational analyses for the emission spectrum. Further Barrow *et al* (1955) carried out the rotational analyses of the A-x and B-x systems. They were not able to resolve the bands of the C system and carry out the rotational analysis, however from the data on the origin of the band heads they calculated the rotational constants for the C-x system. Lovas and Törring (1969) studied the microwave absorption spectra of InF and evaluated the molecular constants. In the present study, the rotational analysis of a number of bands in the C-x system of InF has been carried out and the results are reported here.

2. Experimental technique

Pure indium fluoride was kept in a conventional quartz discharge tube. The molecule was excited in a high-frequency discharge (10–15 MHz) having an output of 125 W. A two metre plane-grating spectrograph (Carl-Zeiss) was used to record the spectrum. An exposure time of two hours was sufficient to record a satisfactory spectrogram in the eleventh order. Reciprocal dispersion of 0.3 \AA mm^{-1} was obtained and the resolution was about 3×10^5 . Ilford N-40 plates were used to record the spectrum. Measurements were made on an Abbe comparator using iron arc lines as standards.

3. Experimental results

Well resolved rotational structure of the 0, 0 and 0, 2 sequences were obtained on the spectrogram. The 0, 1 sequence was overlapped by higher members of the 0, 0 sequence and hence analysis of that sequence was not possible. In the 0, 0 sequence the 0, 0 1, 1 2, 2 3, 3 and 4, 4 bands were found suitable for measurement and in the 0, 2 sequence the 2, 4 3, 5 4, 6 and 5, 7 bands were suitable. The reproductions of the 0, 0 and 2, 4 bands are given in figures 1 and 2 (plates).

4. Rotational analysis

The 0, 0 and 2, 4 bands of the c-x system of InF show some peculiar structure. Bands form a head in the R branch and degrade towards the longer wavelength side although $B'_v > B''_v$. Two Q heads were observed corresponding to a change in degradations. There is a tendency to form a P head because of convergence for low J values, but for high J values lines in the P branch diverge. This phenomenon is seen distinctly in the case of the 0, 0 band.

The Q branch of the 0, 0 band was not resolved due to the small $(B'_0 - B''_0)$ value and the change in degradation. The analysis was carried out for the R and P branches. Since the zero gap is resolved, the numbering of the P branch was straightforward. The numbering of the R branch was fixed so that $\Delta_2 F(J)/J + \frac{1}{2}$ plotted against $(J + \frac{1}{2})^2$ gave a straight-line graph (figure 3).

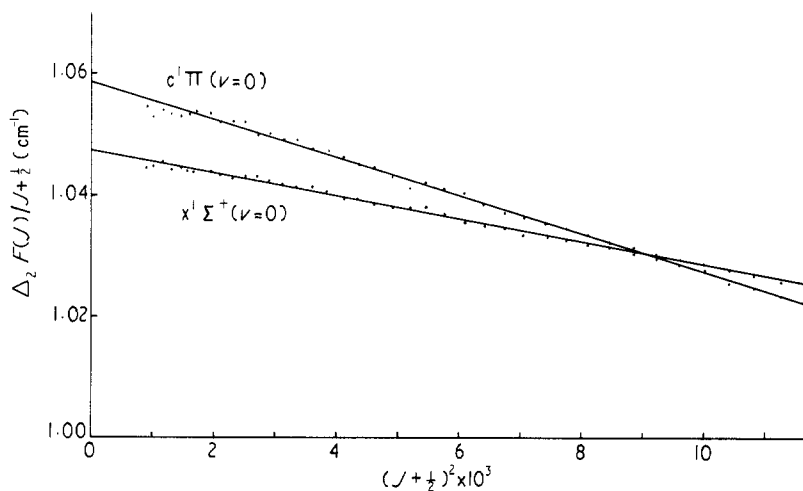


Figure 3. Determination of B and D values for the 0, 0 band of the c-x system.

The 1, 1 band has a clear degradation towards the longer wavelength side and the P, Q and R branches were well resolved. The numbering of the R branch lines was performed as usual. Lines in the P branch were fixed from the combination relations for $\Delta_2 F$ and $\Delta_1 F$.

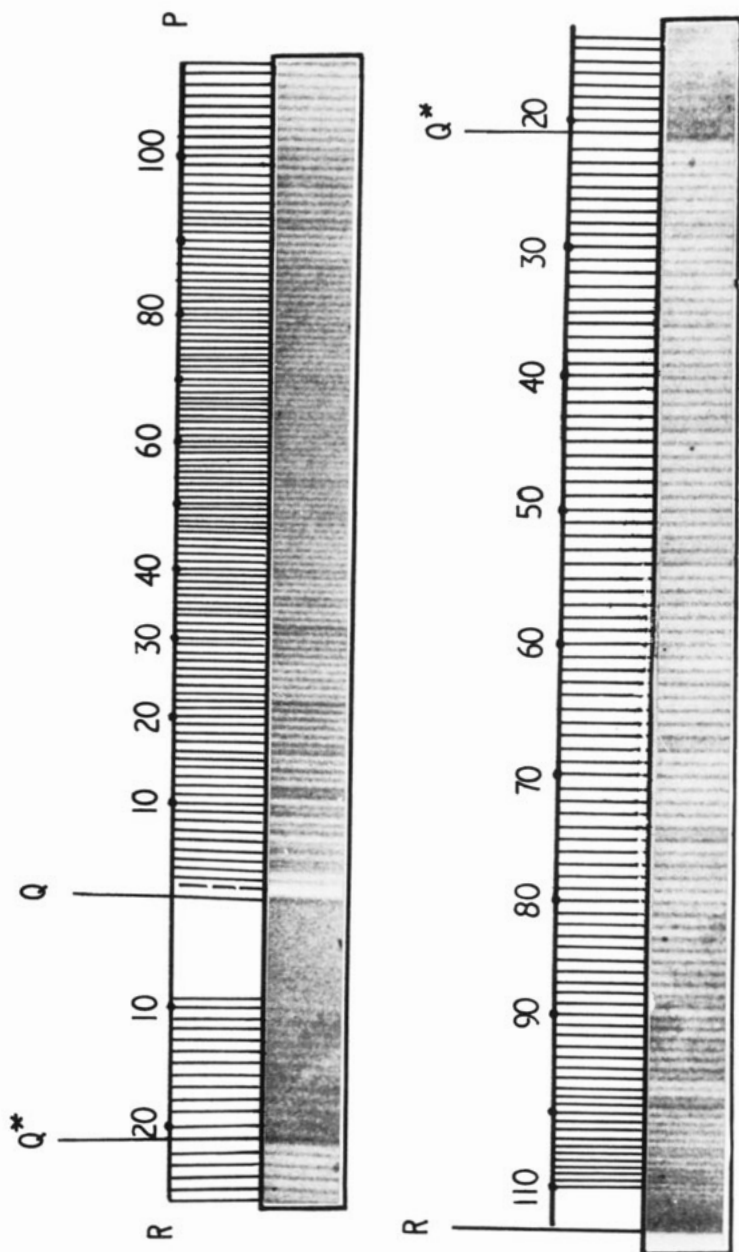


Figure 1. 0, 0 band of the c-x system of InF recorded at a dispersion of 0.3 \AA mm^{-1} .

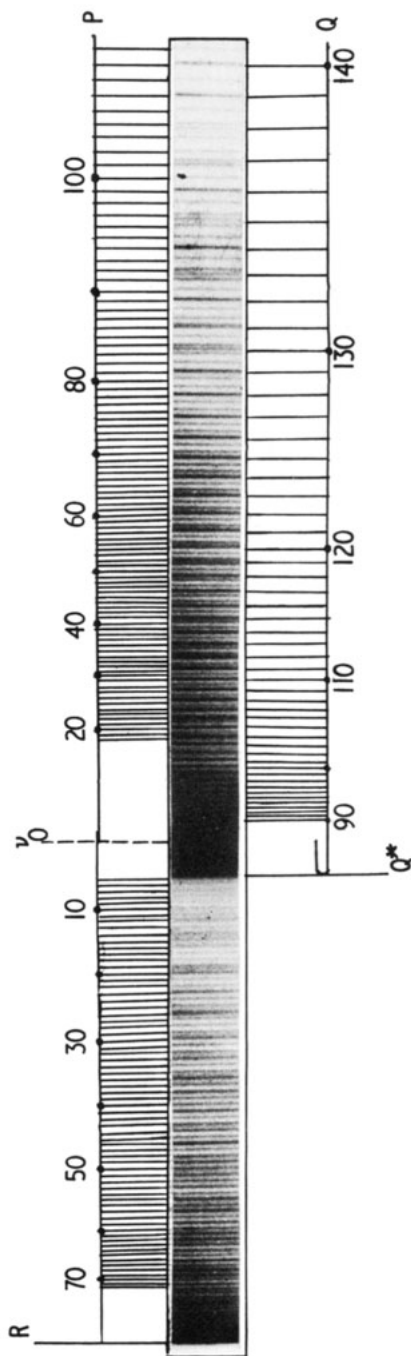


Figure 2. 2, 4 band of the C-X system of InF recorded at a dispersion of 0.3 \AA mm^{-1} .

The analysis of the 2, 2 band was carried out on similar lines to that for the 1, 1 band. Since the returning branch of the red-degraded 3, 3 band is very weak, analysis was carried out using the P and Q branch lines. The Q branch was extrapolated to zero and approximate numbering was given. The correct numbering was fixed from the combination relation between the lines of the P and Q branches. Analysis of the 4, 4 band was similar to that for the 3, 3 band.

In the 0, 2 sequence, rotational analyses were done for the 2, 4 3, 5 4, 6 and 5, 7 bands. Analyses were carried out by comparing the common states of bands in the 0, 2 and 0, 0 sequences. The 5, 7 band was analysed by methods similar to those followed for the 3, 3 and 4, 4 bands.

The band origins, ν_0 , for all bands were determined graphically (from the graph of $R(J-1)+P(J)$ plotted against J^2) and are given in table 1. Table 2 gives the molecular constants obtained from the present analysis.

Table 1. Band origins of some bands in the 0, 0 and 0, 2 sequences of InF c-x system.

| v', v'' | Band origin (cm^{-1}) |
|-----------|----------------------------------|
| 0, 0 | 42772.26 (± 3) |
| 1, 1 | 42688.87 (± 4) |
| 2, 2 | 42591.66 (± 3) |
| 3, 3 | 42478.88 (± 2) |
| 4, 4 | 42344.27 (± 3) |
| 2, 4 | 41558.21 (± 4) |
| 3, 5 | 41454.40 (± 2) |
| 4, 6 | 41342.62 (± 3) |
| 5, 7 | 41208.35 (± 4) |

Figures in parentheses give the estimated error in the last significant figure.

Table 2. (a) B and D values of the InF c-x system for different vibrational levels. (b) Rotational constants for the InF $c^1\Pi-x^1\Sigma^+$ system.

| v | B_v' (cm^{-1}) | B_v'' (cm^{-1}) | $D_v' \times 10^7$ (cm^{-1}) | $D_v'' \times 10^7$ (cm^{-1}) |
|-----|--------------------------------|---------------------------------|--|---|
| 0 | 0.2647(± 3) | 0.2619(± 2) | 3.9(± 1) | 2.5(± 1) |
| 1 | 0.2598(± 2) | 0.2601(± 3) | 4.0(± 3) | 2.5(± 1) |
| 2 | 0.2559(± 4) | 0.2582(± 4) | 4.5(± 3) | 2.7(± 1) |
| 3 | 0.2510(± 4) | 0.2559(± 3) | 5.2(± 6) | 2.7(± 1) |
| 4 | 0.2457(± 3) | 0.2545(± 5) | 5.8(± 4) | 2.9(± 2) |
| 5 | 0.2410(± 4) | 0.2528(± 4) | 6.4(± 5) | 3.2(± 3) |
| 6 | — | 0.2510(± 2) | — | 3.8(± 6) |
| 7 | — | 0.2493(± 4) | — | 4.0(± 1) |

| | B_e (cm^{-1}) | α_e (cm^{-1}) | $D_e \times 10^7$ (cm^{-1}) | $\beta_e \times 10^7$ (cm^{-1}) | r_e (\AA) |
|---------------|-------------------------------|------------------------------------|---|---|---------------------------|
| $c^1\Pi$ | 0.2670(± 3) | 0.0050(± 4) | 3.65(± 5) | 0.5(± 2) | 1.9672(± 3) |
| $x^1\Sigma^+$ | 0.2628(± 4) | 0.0020(± 1) | 2.5(± 3) | 0.2(± 1) | 1.9853(± 2) |

Figures in parentheses give the estimated error in the last significant figure.

5. Results and discussion

A graph of rotational constants B_v plotted against v shows a crossing corresponding to the vibrational level $v = 1$ (figure 4). From the graph it is clear that all except the 0, 0 band must be degraded to the longer wavelength side. However from the spectrogram we see a longer wavelength degradation for the 0, 0 band and the formation of an R head. This can be explained as follows.

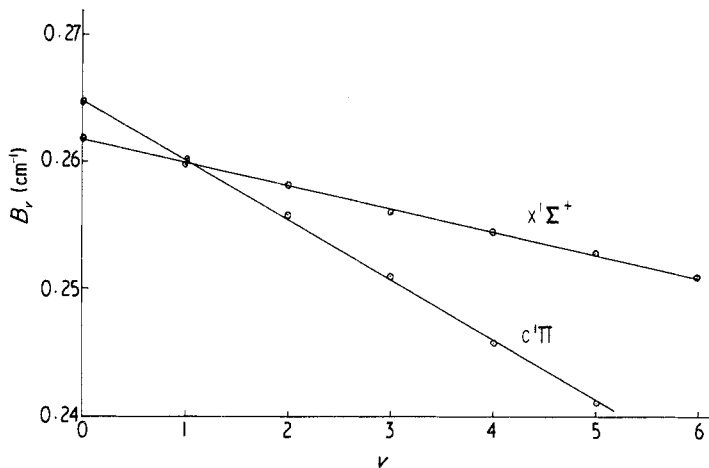


Figure 4. Graph of B_v plotted against v for the $c^1\Pi$ and $x^1\Sigma^+$ states.

Initially the band tends to degrade to the violet and to form a P head and a violet-degraded Q head. Due to the effect of a large difference in the D terms ($D'_0 > D''_0$), $\Delta_2 F'(J) - \Delta_2 F''(J)$ changes sign after $J \sim 96$, as seen clearly from the graph (figure 3). This results in a change in degradation and a head is formed in the R branch as well as a second head designated as Q^* in the Q branch. These features are clearly seen on the spectrogram. The spacing in the P branch passes through a minimum as the lines tend to converge at lower J values and then diverge at higher values. For the unresolved band an intensity maximum rather than a sharp head would therefore be observed.

A graph of $P_{3,3}(J) - P_{3,5}(J)$ plotted against $J(J+1)$ gave the value for $G''(5'') - G''(3'')$ as 1024 cm^{-1} as the intercept and $P_{2,4}(J+1)$ plotted against $J(J+1)$ gave the value for $G'(2') - G'(4')$ as 789 cm^{-1} . These values agree with those calculated using the constants from the previous vibrational analysis (Barrow *et al* 1954). From the slopes of the graph we get α''_e as $0.0020 (\pm 1) \text{ cm}^{-1}$ and α'_e as $0.0050 (\pm 4) \text{ cm}^{-1}$. The r''_e value of $1.9853 (\pm 2) \text{ \AA}$ is in good agreement with the microwave absorption value of 1.9854 \AA (Lovas and Törring 1969).

Since the system was observed in absorption by Welti and Barrow (1952), the lower state must be the ground state which was fixed by Welti and Barrow as the $^1\Sigma^+$ state arising from the configuration $z\sigma^2 y\sigma^2 w\pi^4 x\sigma^2 ^1\Sigma^+$. By the excitation of an electron from the $x\sigma$ orbital to a $v\pi$ orbital, the resulting configuration $z\sigma^2 y\sigma^2 w\pi^4 x\sigma v\pi$ gives two excited states $^3\Pi$ and $^1\Pi$. The transition $^3\Pi - x^1\Sigma^+$ was attributed to the A and B systems. The present analysis suggests that the C-x system may be attributed to the $^1\Pi - x^1\Sigma^+$ transition.

Acknowledgments

The authors (VPN and MNK) are grateful to the University Grant Commission for financial assistance.

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