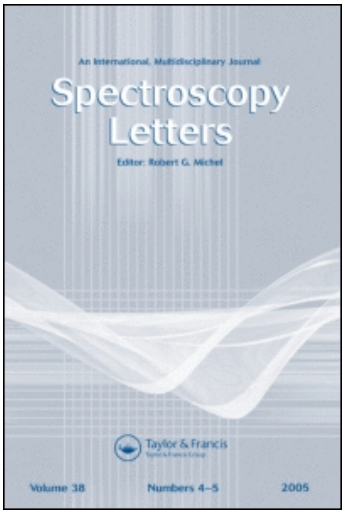

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RAMAN STUDY OF $InCl_3$

Key Words: Raman Spectra; Indium Trichloride

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Abstract

The Raman spectra of a crystalline powder of $InCl_3$ and of a de-ionized water solution show the presence of four bands at 300.0, 289.2, 115.6 and 87.1 cm^{-1}, thus suggesting that $InCl_3$ is not a perfectly planar molecule.

Introduction

The two most plausible models for $InCl_3$ are the pyramidal and the plane symmetrical forms, belonging to point groups C_{3v} and D_{3h} respectively. In both cases, there are four fundamentals. For C_{3v}, they are of species $2A_1 + 2E$ and all would be infrared and Raman active. For D_{3h}, they are of species $A_1' + A_2'' + 2E$: the totally symmetric vibration (A_1') would be

inactive in the infrared and the antisymmetric vibration (A_2") would be inactive in the Raman effect.

Greenwood et al [1] reported that the vibrational spectrum of polycrystalline $InCl_3$ has three Raman active bands at 279, 127 and 87 cm^{-1} and two infrared active bands at 235 and 119 cm^{-1}. Brinkman et al [2] found three distinct Raman bands at 276, 122 and 84.5 cm^{-1} and also observed the presence of an uncertain and weak Raman band at 163 cm^{-1}. Beattie et al [3] also studied the Raman spectra of polycrystalline $InCl_3$ and their results support the observations of Greenwood et al.; they proposed that $InCl_3$ is made up of octahedrally co-ordinated indium with adjacent octahedra sharing the edges. The three degress of freedom of a Cl atom, linked to two In atoms, were assigned to stretching and deformation modes at 279 cm^{-1} and 127 cm^{-1} respectively. The 87 cm^{-1} band was assigned to either a deformation or to the movement of an In atom in the plane containing In atoms, while maintaining the centre of symmetry. From the molecular point of view, this motion of the In atom suggests that the molecule might not be perfectly planar. Givan and Loewenschuss [4] reported the Raman and infrared spectra of monomeric $InCl_3$ in solid krypton at 20 K. Their observations under their experimental conditions support the D_{3h} planar geometry for the $InCl_3$ molecule. In an attempt to clarify the situation, we have re-investigated the Raman spectrum of $InCl_3$.

Experimental Method

Light from an argon-ion laser was focused on the crystalline powdered sample held in a glass capillary. The laser was operated in the 200 mw range. The scattered light was collected by a f/11 system and brought to a double grating

monochromator, the spectral slit width being 1 cm^{-1}. Photon-counting detection techniques were used, and the output signal was stored in a multichannel analyzer. The dark noise of the cooled RCA-31034 photomultiplier was 5 cps. The digital circuitry generating the pulses for the stepping motor of the grating drive also controlled the channel advance of the MCA. In order to average over system instabilities, the spectral region was scanned rapidly (0.5 cm^{-1}/sec) and repetitively (of the order of 8 times). Experiments were also performed on 54%, 25%, and 12% solutions of $InCl_3$ in de-ionized water in a single pass liquid cell. The observed spectra are shown in Figures 1, 2, 3, and 4. The dispersion is 2 cm^{-1}/channel.

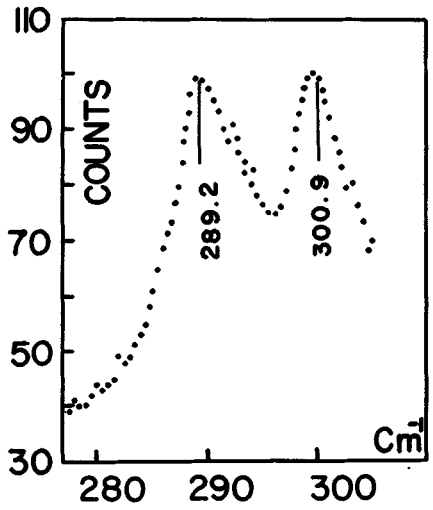

Fig. 1. The 289.2 and 300.9 cm^{-1} Raman bands of polycrystalline $InCl_3$ (smoothed data).

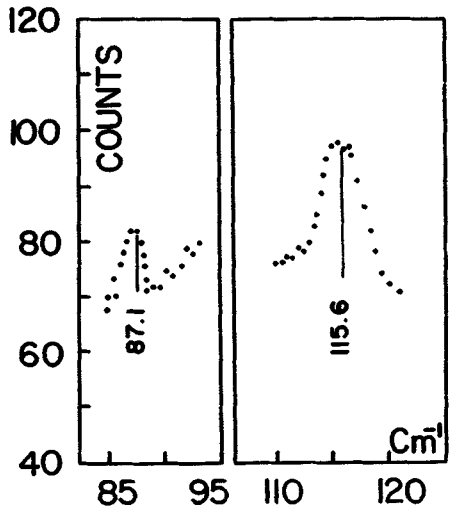

Fig. 2. The 87.1 and 115.6 cm^{-1} Raman bands of polycrystalline $InCl_3$ (smoothed data).

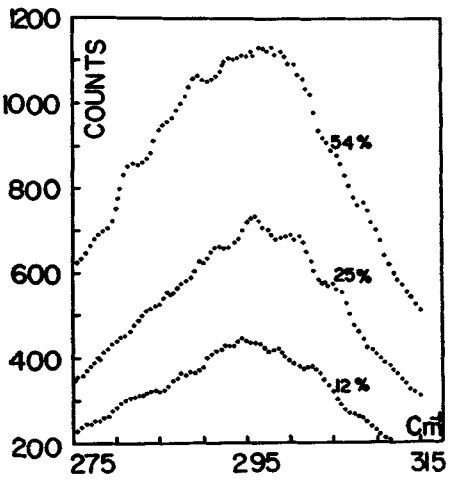

Fig. 3. Raman spectrum of 54%, 25% and 12% $InCl_3$ solutions in deionized water in the 275-315 cm^{-1} region.

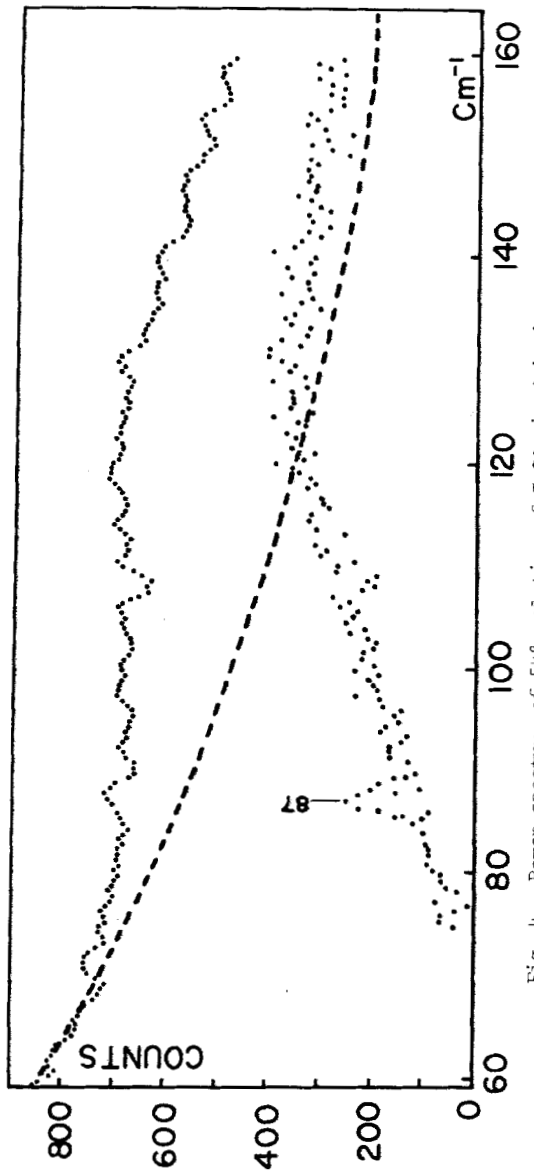

Fig. 4. Raman spectrum of 54% solution of $InCl_3$ in deionized water in the 60-160 cm^{-1} region. The upper dots are the raw data, the dashed line is the background and the lower dots give the difference curve.

Analysis of Data

As is evident from Figures 1 and 2, the Raman bands of crystalline $InCl_3$ are relatively sharp. Figures 3 and 4 show that in the spectrum of $InCl_3$ solution, there are no sharp peaks, but rather very broad asymmetric structureless bands. This asymmetry in the profiles led us to suspect that they might result from the overlapping of several components. In order to facilitate the analysis, the raw data were first smoothed, using the method of Savitzky and Golay [5], and then the spectra were divided into 30-230 cm^{-1} and 200-400 cm^{-1} regions.

Because the 200-400 cm^{-1} region in the solid contains two bands, an attempt was made to fit the observed spectrum of the solutions to the sum of two Lorentzians. A non-linear least squares fitting technique was applied using as initial estimates the frequencies from the spectrum of crystalline $InCl_3$ [6]. The frequencies of the peaks, their half widths (HWHM) and their relative intensities were determined. The reduced χ^2 for the 54%, 25%, and 12% solutions were 1.73, 1.38, and 1.73, respectively. The observed bands could indeed be obtained by summing two components at frequencies closely corresponding to those found in the spectrum of the polycrystalline solid (Figure 5).

The 30-230 cm^{-1} region contains a broad structure superimposed on a strong background which undergoes an exponential decay from near the laser frequency. This background was subtracted and the difference curve was smoothed using a quadratic polynomial over 25 channels. For all three solutions, the final curve showed a broad peak around 120 cm^{-1}. Only in the case of the 54% solution was there evidence of a weak sharp peak at 87.1 cm^{-1}. The results are summarized in Table 1.

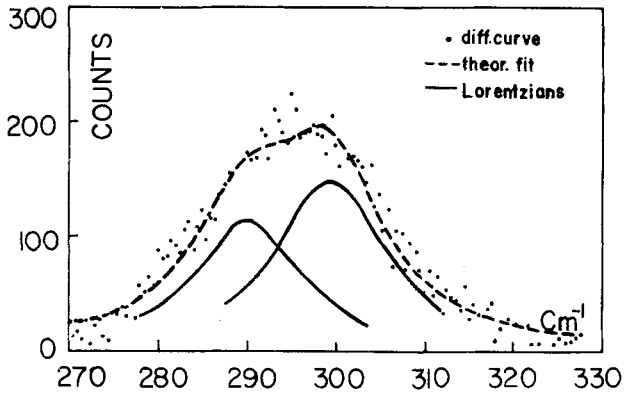

Fig. 5. Raman spectrum of the 54% solution of $InCl_3$ in deionized water in the 270-330 cm^{-1} region. The dots represent the difference curve between the raw data and the background, the heavy lines are the Lorentzians determined in the fitting process, and the dashed line is the sum of the two Lorentzians.

Results and Discussion

The Raman spectrum of crystalline $InCl_3$ powder has four distinct bands at 300.9, 289.2, 115.6, and 87.1 cm^{-1}. Of these, the first three bands are present in the Raman spectrum of the 54%, 25%, and 12% solutions of $InCl_3$ in de-ionized water. The fourth band appears as a weak sharp feature in the 54% solution spectrum, but is very weak and difficult to distinguish from the background in the case of 25% and 12% solutions. The frequencies of the solid and solution spectra are in reasonable agreement indicating that $InCl_3$ molecule retains its structure in the solution form.

Greenwood et al [1] and Brinkman et al [2] have observed only three Raman bands at 279, 127, and 87 cm^{-1}, which correspond to our 289.2, 115.6 and 87.1 cm^{-1} bands. The 300.9

Table 1. Raman Frequencies for $InCl_3$ Obtained by Curve Fitting to the Observed Spectra.

Sample		200-400 cm^{-1} region		30-230 cm^{-1} region	
		1st peak	2nd peak	3rd peak	4th peak
Crystalline Powder		300.9	289.2	115.6	87.1
54%	Solution in de-ionized water.	298.6[a]	284.7[a]	[120][b]	87
25%		298.5[a]	285.9[a]	[120][b]	[ ][c]
12%		299.4[a]	289.9[a]	[120][b]	[ ][c]

a - Non-linear least squares fitting.

b - broad feature around 120 cm^{-1}, exact location of peak not possible to determine.

c - weak feature difficult to separate from the background.

cm^{-1} Raman band, however, has not been observed before. The 289.2 and 115.6 cm^{-1} bands are the stretching modes and the 87.1 cm^{-1} deformation motion is caused by the in-plane movement of the In atom (plane containing In atoms). The depolarized spectrum of the 54% solution indicates that the 289.2 and 300.9 cm^{-1} bands are strongly polarized. Hence, the 289.2 cm^{-1} band is due to symmetric stretching and the 300.9 cm^{-1} band must be due to some symmetric vibration of the In atom. The presence of the 300.9 and 289.2 cm^{-1} band in the spectrum of the solution suggests that the 300.9 cm^{-1} band is not splitting due to the crystal structure.

Givan and Loewenschuss [4] in their study of $InCl_3$ in a krypton matrix have observed three Raman bands: at 394 cm^{-1}, a triplet due to Cl isotopes at 352.5; 349.0; 345.8 cm^{-1} and a third band at 98.5 cm^{-1}. The position of these bands is not in agreement with the other data including the present study on the crystalline powder and de-ionized water solutions.

Our observations suggest that $InCl_2$ is not rigorously planar.

Acknowledgements

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