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Infrared spectroscopy and thermodynamics of indium tri-iodide vapour species

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Abstract

The infrared spectra of the vapour over InI_3 were studied by matrix isolation and gas-phase techniques. The spectrum of the saturated vapour at 400 K isolated in an Ar matrix is thought to arise from dimeric as well as monomeric molecules. Four fundamental vibration frequencies were assigned to the dimer. Superheating of the vapour resulted in a decrease in the dimer relative to the monomer and, at 990 K, the appearance of InI(g). The gas-phase spectrum (at 500 K) showed the three fundamentals of the monomer and a single low-intensity absorption which could be attributed to the dimeric molecule. The thermodynamic functions of InI_3(g) and In_2I_6(g) have been calculated.

INTRODUCTION

In the event of a severe accident in a nuclear fission reactor, interaction may occur between the fission product iodine and the (In,Cd,Ag) control-rod alloy. As a consequence, many competitive reactions involving the formation of the relevant metal iodides have to be considered in the understanding of the behaviour of the radiologically hazardous iodine. Thermochemical models are commonly used to predict the speciation of iodine in the wide range of conditions that might occur in an accident sequence. In the present study we have investigated the vapour over InI_3 by matrix isolation and gas-phase infrared spectroscopy. The molecular parameters thus obtained have been used to calculate the thermodynamic properties of the vapour species InI_3 and its dimer In_2I_6.

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EXPERIMENTAL DETAILS

InI_3 was purchased from Cerac (typical purity 99.999%) and used without further purification.

The infrared spectra of the matrix-isolated species were obtained using a Bruker IFS 113v Fourier transform spectrometer and a matrix isolation apparatus developed at Winfrith Technology Centre [1]. Briefly, the sample is vaporized under vacuum from a silica furnace. The inert matrix gas (argon) is introduced throughout the experiment, so that the sample vapour molecules and matrix-gas co-condense on the deposition window which is cooled to about 12 K by a closed-cycle helium cryostat. The cryostat assembly is then rotated to bring the deposition window into the beam of the spectrometer. A silicon deposition window is used, whereas the vacuum shroud windows are made of polythene. A global light source, a Mylar beam splitter and a DTGS detector are used in measuring the spectrum.

The gas-phase infrared spectra were recorded with a BOMEM DA3.02 Fourier transform spectrometer equipped with an optical gas-cell constructed at ECN [2, 3]. The main body of the cell consists of a silica tube (95 cm long and 6 cm in diameter) which is heated in a 62.5 cm long three-zone furnace. The temperature is measured and controlled by three chromel–alumel thermocouples placed at the windings of the zones. Optical windows are mounted in water-cooled flanges at both ends of the tube.

The cell was loaded in an argon-filled glove box. The gas atmosphere in the cell was argon at a pressure of 15 mbar at room temperature. The following experimental arrangements were used for the operation of the spectrometer in the 375–25 cm^{-1} range: silicon windows, a globar or a mercury discharge light source, Mylar beamsplitters and a bolometer operating at 4.2 or 1.6 K. The spectra were recorded at 0.5 cm^{-1} resolution; 128 scans were co-added.

RESULTS AND DISCUSSION

Band assignment

Electron diffraction measurements [4, 5] of gaseous InI_3 have shown that the molecule has a planar geometry (D_{3h} point group) resulting in four fundamental modes of vibration: $\Gamma_{mol} = A_1' + A_2'' + 2E'$. The selection rules allow three infrared-active transitions. The structure of gaseous In_2I_6 has not been studied experimentally but it has been shown that solid indium(III) iodide consists of discrete In_2I_6 molecules held together by weak forces [6], being isostructural with the Al_2Cl_6 molecule in the gas phase. Such a non-planar bridge structue (D_{2h} symmetry) gives rise to

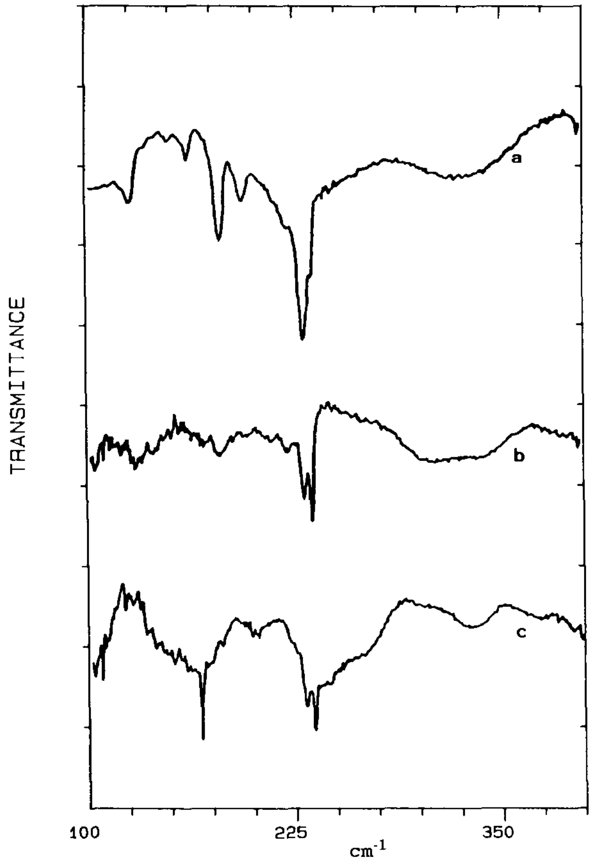

Fig. 1. Argon matrix infrared spectra from indium tri-iodide vaporization: (a) 390 K, no superheating; (b) superheated to 770 K; (c) superheated to 970 K.

18 fundamentals $\Gamma_{mol} = 4A_g + A_u + 2B_{1g} + 3B_{1u} + 2B_{2g} + 2B_{2u} + B_{3g} + 3B_{3u}$, the selection rules allowing eight infrared-active transitions.

The matrix-isolation infrared spectrum of the vapour evolved at 400 K shows six bands at 236, 231, 194, 180, 160 and 124 cm^{-1} (Fig. 1), the first two maxima partially overlapping. When the vapour was superheated to about 770 K, the intensities of most of the bands decreased significantly and the spectrum became dominated by one single band at 236 cm^{-1}. When the superheat temperature was further increased to 970 K, this band also decreased in intensity and a new, sharp band at 167.7 cm^{-1} became the dominant feature. The experiments were repeated several times, with and without superheating of the vapour, and the spectra always showed the same correlations between the bands, indicating that random variations in the procedures did not have a significant effect on the composition of the isolated vapour.

The frequencies at 231, 180, 160 and 124 cm^{-1} are close to those

TABLE 1

The IR-active wavenumbers of In_2I_6(g) in cm^{-1}

Source	Method/state [a]	ν_8	ν_9	ν_{10}	ν_{13}	ν_{14}	ν_{16}	ν_{17}	ν_{18}
Perov et al. [9]	IR/matrix	288	–	–	150	–	177	122	58
This study	IR/matrix	231	–	–	160	–	180	124	–
	IR/gas	–	–	–	–	–	175	–	–

[a] IR, infrared spectroscopy.

previously reported for InI_3 in the solid phase [7, 8] and, consequently, it is concluded that these bands are due to dimeric molecules. They are assigned to the In–I stretching modes ν_8, ν_{13}, ν_{16} and ν_{17}, respectively (Table 1). The agreement with the study by Perov et al. [9] on matrix-isolated In_2I_6 is good, except for the ν_8 band (see Table 1). Because of the differences in the intensities of the bands at 232 and 236 cm^{-1} in the experiments with and without superheating, it is concluded that the former does not belong to the dimer; it is assigned to the asymmetric In–I stretching frequency of the InI_3 molecule. The band at 167.7 cm^{-1} is assigned to molecular InI, being close to the value of 177 cm^{-1} reported for the gas [10].

The infrared spectrum of the gas phase above InI_3 in the 500–525 K range shows five strong absorption bands at 228.8, 64.5, 53.2, 48.1 and 44.3 cm^{-1} and a low-intensity band at 175 cm^{-1} (Fig. 2). The differences with the results of the matrix-isolation spectrum are distinct. The general appearence of the spectrum shows great similarity with that of the isostructural $AlCl_3$ molecule [3] i.e. sharp peaks for the ν_2 and ν_3 modes, whereas the three bands at the lowest wavenumbers form a typical PQR

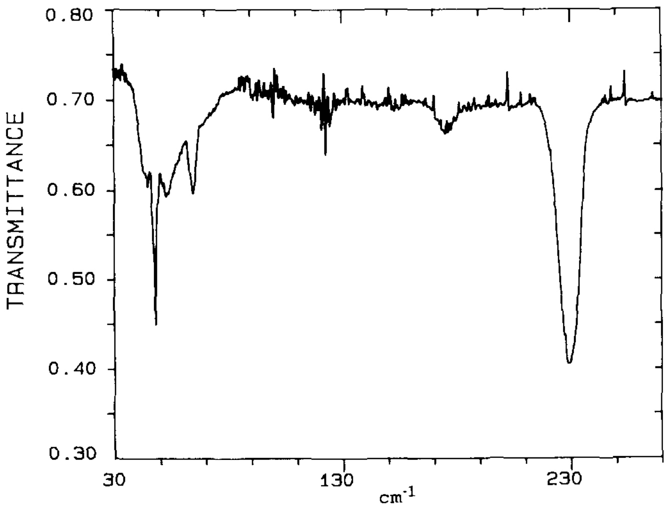

Fig. 2. The infrared spectrum of the vapour above InI_3 at 500 K.

TABLE 2

The vibrational wavenumber of InI_3(g) in cm^{-1}

Source	Method/state [a]	ν_1	ν_2	ν_3	ν_4
Beattie and Horder [11]	R/gas	151	–	–	44
Perov et al. [9]	IR/matrix		–	225	–
Selivanov and Mal'tsev [12]	IR/gas		56	–	48
This study	IR/gas		64.5	228.8	48.1
	IR/matrix		–	236	–

[a] IR, infrared spectroscopy; R, Raman spectroscopy.

structure of the ν_4 mode of a planar XY_3 molecule. We therefore conclude that the principal vapour species in these experiments is monomeric InI_3. The low-intensity band at 175 cm^{-1} does not fit in this scheme as a fundamental. It is most probably due to dimeric molecules, corresponding to the 180 cm^{-1} band found in the matrix; the more intense ν_8 dimer band is almost certainly contained within the envelope of the 228.8 cm^{-1} band. The low intensity of the dimer band indicates a minor contribution (<10%) to the vapour. The values for the fundamentals of InI_3 are in reasonable agreement with previous studies [9, 11, 12], as summarized in Table 2.

Thermodynamic properties

The ideal gas thermodynamic functions of InI_3(g) and In_2I_6(g) have been calculated from the molecular parameters shown in Table 3 by a rigid-rotor

TABLE 3

The molecular parameters used in the statistical thermodynamic calculation

	InI_3	In_2I_6
Symmetry group	D_{3h}	D_{2h}
Symmetry number, σ	6	4
M/g mol^{-1}	495.5334	991.0668
r(In–I)/nm	0.2629	0.2614
$r(In–I_{bridge})$/nm	–	0.280
$\angle$(I–In–I)/deg		130
$\angle(I_{bridge}–In–I_{bridge})$/deg		80
ν_i(degeneracy)/cm^{-1}	151, 64.5, 228.8(2), 48.1(2)	187, 134, 69, 40, 35, 114, 55, 231, 54, 15, 232, 49, 160, 49, 44, 180, 124, 59
$I_A I_B I_C/g^3 cm^6$	2.0856×10^{-110}	1.1275×10^{-108}
g_0	1	1

TABLE 4

The ideal gas thermodynamic functions of InI_3 and In_2I_6

T/K	$C_p^\ominus(T)$/ J mol^{-1} K^{-1}	$S^\ominus(T)$/ J mol^{-1} K^{-1}	$\Phi^\ominus(T)$ [a]/ J mol^{-1} K^{-1}	$[H^\ominus(T) - H(298.15\ \mathrm{K})]$/ J mol^{-1}
InI_3				
298.15	81.054	398.157	398.157	0
400	81.957	422.121	401.352	8308
500	82.377	440.459	407.406	16527
600	82.609	455.501	414.206	24777
700	82.750	468.247	421.039	33046
800	82.842	479.303	427.646	41325
900	82.905	489.064	433.938	49613
1000	82.951	497.801	439.895	57906
1200	83.010	512.931	450.845	74502
1400	83.046	525.730	460.652	91108
1600	83.069	536.821	469.496	107720
1800	83.085	546.606	477.530	124335
2000	83.096	555.360	484.883	140954
In_2I_6				
298.15	178.728	638.636	638.636	0
300	178.777	639.741	638.639	331
400	180.549	691.450	645.677	18309
500	181.390	731.839	659.018	36411
600	181.853	764.955	673.997	54575
700	182.134	793.011	689.046	72775
800	182.317	817.344	703.596	90998
900	182.443	838.826	717.451	109237
1000	182.533	858.053	730.567	127486
1200	182.650	891.344	754.673	164005
1400	182.722	919.505	776.260	200543
1600	182.768	943.907	795.725	237092
1800	182.800	965.436	813.409	273649
2000	182.822	984.698	829.592	310211

[a] $\Phi^\ominus(T) = -[G^\ominus(T) - H^\ominus(298.15\ \mathrm{K})]/T$.

harmonic oscillator approach and are listed in Table 4. For InI_3(g), the geometric parameters were taken from the electron diffraction study by Giricheva et al. [4], from the vibrational parameters of the present gas-phase results (ν_2–ν_4), and from Beattie and Horder (ν_1) [11]. The geometric parameters were estimated for In_2I_6(g) to be quite similar to those of the solid phase molecule [4]. For the vibrational contribution, the four fundamentals observed in the present study were supplemented with the solid phase data obtained by Adams and Churchill from a detailed normal co-ordinate analysis [8], which can adequately be applied to the gaseous phase in view of the close agreement between the frequencies for the matrix-isolated molecule and the condensed phase. However, the value for the ν_{10} fundamental, the ring deformation, was not included in the study of Adams and Churchill. Beattie et al. [7] obtained $\nu_{10} = 12\,\text{cm}^{-1}$ from a normal co-ordinate analysis for solid In_2I_6. In general, little is known about the ν_{10} modes in the non-planar bridged X_2Y_6 metal halides making an estimate rather difficult; this band has only been observed for Al_2Cl_6 (at $25\,\text{cm}^{-1}$). We therefore adopt the value suggested by Beattie et al. for our calculations: $S^{\ominus}(InI_3, g, 298.15\,K) = 398.2 \pm 1.5\,J\,mol^{-1}\,K^{-1}$; $S^{\ominus}(In_2I_6, g, 298.15\,K) = 638.6 \pm 6.0\,J\,mol^{-1}\,K^{-1}$, the uncertainties being estimated.

Vapour composition

Regarding the proportion of dimer in the saturated vapour above InI_3, the gas phase and matrix-isolation experiments yield different results. Whereas the in situ IR spectroscopic experiments of the gas phase indicate that the vapour at 500–525 K consists predominantly of monomeric InI_3 molecules, the inert gas matrix-isolation work shows a significant contribution of dimeric molecules to the saturated vapour at 390 K, as well as to the superheated vapour at 770 K. Part of this difference may be attributed to the influence of the difference in temperature of the experiments on the composition of the saturated vapour phase, although this would require a much more rapid decrease in the dimer fraction than that calculated from existing thermochemical data. Three additional reasons can be suggested in explanation: firstly, dimerization in the matrix sites may increase the proportion of dimer beyond the equilibrium value; secondly, the vapour may not have reached its equilibrium composition during the superheating phase of the matrix-isolation experiments; and thirdly, the pressure in the gas cell may not have reached its equilibrium value. Although in all cases efforts were made to minimize the effects, their magnitude is not known; the first two are probably responsible for most of the dimer observed in the matrix-isolation experiments in which superheating was used.

Previous studies on the vapour composition are also inconclusive. Giricheva et al. [4, 5] studied the saturated vapour above InI_3 by electron diffraction at 463 K and concluded that it consists of a mixture of monomeric (80%) and dimeric (20%) molecules, close to the results of the present gas-phase study. Smith and Barrow [13], who studied the vapour pressure of InI_3 in the 373–405 K range, did not specify the composition of the vapour, although the torsion-effusion technique they applied is excellently suited to determine the presence of polymeric molecules. Federov et al. [14] measured the vapour pressure by a transpiration technique and assumed that only dimeric molecules are present. Other studies of the vapour above InI_3 were conducted at higher temperatues at which the vapour is a mixture of I(g), I_2(g), InI(g), InI_2(g), InI_3(g) and In_2I_6(g) [15–17]. Extrapolation of the monomer/dimer equilibrium data to the temperatures of the present experiments gives monomer/dimer ratios of around 0.3, close to the matrix-isolation results. Clearly, accurate vapour density or mass-spectrometric measurements are required to elucidate this problem.

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