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The infrared spectrum and vapour pressure of lead diiodide

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Abstract

The infrared spectrum of lead diiodide vapour was measured at 775 K and values were assigned to the fundamental vibrational frequencies. The results were used with other known molecular parameters to calculate the thermal functions of the gas. The vapour pressure over the solid was measured by the Knudsen effusion technique in the temperature range 580 to 621 K. The results were subjected to a second-law and third-law analysis and the enthalpy and entropy of sublimation were calculated.

Keywords: Infrared spectroscopy; Knudsen effusion; Lead diiodide; Thermochemical properties

1. Introduction

The number of accurate investigations of the properties of metal iodides has been consistently less than for metal fluorides and chlorides. Nevertheless the application of metal iodides in halide lamps and metal production (van Arkel-de Boer process) and their importance in nuclear technology [1,2] make accurate evaluation of their thermodynamic properties desirable. Lead diiodide, in particular, has been used in metal halide lamps designed for sunbathing and photocopying purposes. Also, metal iodides such as PbI_2 are being considered as iodine sources in investigations of the transmutation of the long-lived ^{129}I isotope [3].

The present study of the gaseous phase of the compound PbI_2 involved measuring the infrared spectrum of the gas to determine the values of the fundamental vibrational frequencies of the molecule, from which the thermal functions have been calculated. We

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also studied the vapour pressure using the Knudsen effusion technique to resolve the apparent contradiction of a number of studies of the vapour pressure, which fall into two distinct groups as may be seen from the recent assessment by Gurvich et al. [4].

2. Experimental

2.1. Sample characterization

The lead diiodide was purchased from Cerac, quoted as being typically 99.999% pure. X-ray diffraction analysis showed the sample to be phase pure. Chemical analysis at our institute gave for the lead content (44.73 ± 0.15%) (calculated 44.94%) and for the iodine content (55.03 ± 0.18)% (calc. 55.06%). Lead was analysed by complexometric titration with standard EDTA, iodine by argentometric titration with standard $AgNO_3$ solution. The sample was stored in an argon glove box in which loading of the equipment was performed.

2.2. Infrared spectrum

The infrared spectrum of the vapour above solid lead diiodide was recorded using a BOMEM DA3.02 Fourier transform spectrophotometer equipped with a laboratory-built optical cell as described elsewhere [5, 6]. In brief, the cell consisted of a silica tube (length, 95 cm; diameter, 6 cm) which was heated by a tube furnace. The furnace was divided into three zones which were programmed individually to control the temperature in the central region. Approximately 4 g of the sample was heated in a gold boat in the center of the cell. The temperature of the cell was measured with three chromel–alumel thermocouples placed at the windings of the zones. The windows were made of silicon and had a 1° wedge shape for minimum radiation reflection. They were mounted in water-cooled flanges at both ends of the cell.

The spectrum of lead diiodide was recorded using the following experimental set-up: (i) for the 25–100 cm^{-1} range a mercury lamp as the radiation source and a germanium bolometer operating at a temperature of 1.6 K as detector (ii) in the 70–375 cm^{-1} range a globar lamp as radiation source and a bolometer operating at 4.2 K. The spectra were measured to a resolution of 0.5 cm^{-1} and 128 scans were co-added.

2.3. Vapour pressure

The vapour pressure measurements were made using the Knudsen effusion weight loss technique using a Cahn vacuum balance (type D101). Essentially, the sample was placed in a molybdenum effusion cell with a hemispherical orifice and suspended from the balance using molybdenum wire. The cell was surrounded by a quartz tube which was in turn surrounded by a tube furnace. As before, the furnace was divided into three independently controllable regions to provide accurate control of the temperature of the cell. The top of the quartz tube was cooled by passing water around it. The vacuum balance was zeroed with a counter-weight equal in mass to the initial cell, sample and suspension wires hung from the other arm. The quartz tube was evacuated to a pressure of about 5×10^{-4} Pa with a Balzers turbo-molecular pump (type TSH 180H).

For the temperature measurements a chromel–alumel thermocouple was used; this was verified by comparison to a calibrated platinum–rhodium thermocouple. The end of the thermocouple was covered with a dummy Mo cell which was suspended next to the Knudsen cell in the tube. A Eurotherm temperature-controller was used to program the desired temperatures for a run of the experiment. The loss of weight as a function of time and temperature were recorded and processed using linear regression. The vapour pressure was calculated using the Knudsen equation as given below:

$$p = \frac{1}{A_0 W} \frac{\mathrm{d}w}{\mathrm{d}t} \left(\sqrt{\frac{2\pi kT}{M}} \right) \tag{1}$$

In the equation p is the vapour pressure, A_0 is the orifice area, W is the Clausing factor, $\mathrm{d}w/\mathrm{d}t$ is the rate of weight loss, M is the molecular mass, and T is the absolute temperature. The effective orifice area of the cell, $Ca = A_0 W$, was determined by calibration with cadmium, using the vapour pressures calculated from the thermodynamic functions from CODATA Key Values [7] as the reference.

The performance of the experimental set-up, as used here, was checked by measuring the vapour pressure of zinc. Our experimental results gave for the enthalpy of sublimation (130.7 ± 0.1) kJ mol^{-1}, which is in excellent agreement with the CODATA value (130.4 ± 0.4) kJ mol^{-1} [7].

3. Results and discussion

3.1. Spectral interpretation

Electron diffraction [8] and theoretical studies [9–12] have demonstrated that the PbI_2 molecule adopts a bent structure with a bond angle of approximately 100°. Bent triatomic molecules have three modes of vibrational freedom, all of which are infrared-active. Therefore we would expect to see two stretching (symmetric and asymmetric) and one bending vibrational band in the spectrum of lead diiodide.

The infrared spectrum of PbI_2 as shown in Fig. 1, exhibited a strong peak at approximately 160 cm^{-1}. Judging from the width and the flattened shape, this band is most likely due to the superposition of the two stretching frequencies. By the use of the spectral deconvolution technique, a mathematical means of reducing the band width [13], it was possible to separate the two superimposed peaks. We thus obtained 163 cm^{-1} as the value for the ν_1 symmetric stretching frequency and 154 cm^{-1} as the value for the asymmetric ν_3 mode. These values are in excellent agreement with the results of Zaitsev et al. [14] for PbI_2 isolated in low-temperature Ar matrix, $\nu_1 = 158$ cm^{-1} and $\nu_3 = 163$ cm^{-1}.

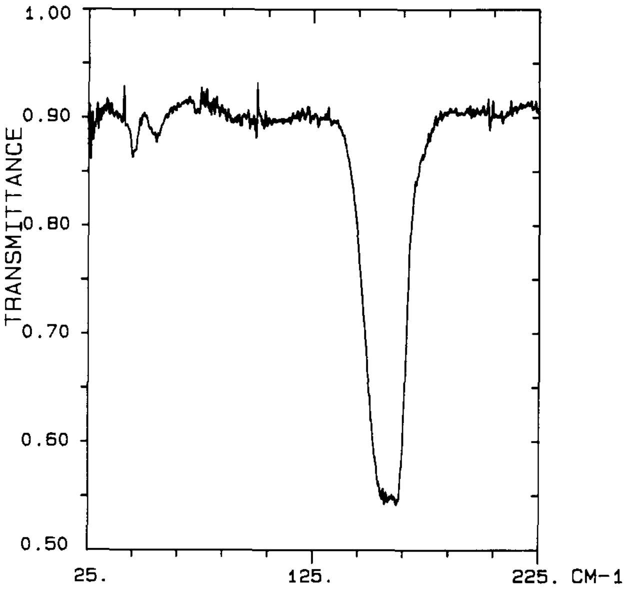

Fig. 1. The infrared spectrum (0.5 cm^{-1} resolution) of PbI_2(g) at 775 K.

In one of the two runs for the 100 to 25 cm^{-1} range two low intensity peaks were observed at 45 and 55 cm^{-1}, respectively. As only one absorption band (the ν_2 bending frequency) is expected in this range, the assignment is not straightforward. Three possible explanations can be given for the present observation: (i) one of the bands is an impurity and is therefore not part of the spectrum of PbI_2; (ii) one of the bands is a hot band, arising from the high population of the vibrational states at the temperature of the experiment; (iii) the two bands are the branches of PR rotational structure. On the basis of theoretical consideration concerning band shapes and anharmonicity [15], we tend to favour option (i) and from a comparison of the bending frequencies of SnX_2 and PbX_2 halides, we conclude that $\nu_2 = 45$ cm^{-1}. This tentative assignment is supported by the results of Zaitsev et al. [14] who found a single band at 43 cm^{-1} in the spectrum of gaseous PbI_2, which they attributed to the ν_2 bending frequency.

The Raman spectrum of the compound has been measured by Beattie and Perry [16] but they found their spectrum too complex to analyze at that time. Unfortunately no numerical results were reported by these authors which can be compared with the present results. The results of recent theoretical calculations [9, 10], as summarized in Table 1, are in reasonable agreement with the experimental data.

The thermal functions of lead diiodide were calculated using our values for the vibrational frequencies in combination with the other molecular parameters as obtained by Demidov et al. [8] and shown in Table 2. The calculations were made using the rigid-rotor/harmonic oscillator approximation, assuming that none of the excited electronic levels was occupied. The results are shown in Table 3.

Table 1
The vibrational frequencies of PbI_2 (/cm^{-1})

Authors	Method/state	ν_1	ν_2	ν_3
Nizam et al. [9]	Pseudo-potential	170.4	55	162.5
Zaitsev et al. [14]	IR/Ar matrix	158	–	163
	IR/Xe matrix	158	–	153
	IR/gas	–	43	–
Ramondo et al. [10]	ab initio	145	50	132
Howard [12]	ab initio	151.8	52.8	154.8
	ab initio	157.1	54.9	164.3
	ab initio	161.1	52.7	165.5
This study	IR/gas	154	45	163

Table 2
Input parameters for thermal function calculations for PbI_2

Parameter	Value
Group symmetry	C_{2v}
Symmetry number, σ	2
r(Pb–I)/pm	280.4 ± 0.4
Bond angle/°	99.7 ± 0.8
$I_A I_B I_C/g^3\,cm^6$	3.063×10^{-111}
Vibrational frequencies/cm^{-1}	154, 44, 163
Molecular mass/g mol^{-1}	461.009

Table 3
The thermodynamic functions of PbI_2(g)

T/K	C_p°/(J mol^{-1} K^{-1})	$S^\circ(T)$/(J mol^{-1} K^{-1})	$\phi(T)$[a]/(J mol^{-1} K^{-1})	$\{H^\circ(T) - H^\circ(298.15\,K)\}$ /(J mol^{-1})
298.15	57.382	355.189	355.189	0
300	57.392	355.544	355.190	106
400	57.741	372.109	357.446	5865
500	57.905	385.013	361.716	11648
600	57.995	395.579	366.506	17444
700	58.049	404.524	371.315	23246
800	58.085	412.277	375.961	29053
900	58.109	419.120	380.384	34863
1000	58.127	425.244	384.569	40675
1200	58.150	435.844	392.258	52303
1400	58.163	444.809	399.142	63934
1600	58.172	452.576	405.346	75568
1800	58.178	459.428	410.982	87203
2000	58.183	465.558	416.139	98839

[a] $\phi(T) = -\{G^\circ(T) - H^\circ(298.15\,K)\}/T$.

3.2. Vapour pressure analysis

The results of the vapour pressure measurements of PbI_2 are given in Table 4. All measurements were made below the melting point. Using the method of least squares with no weighting factors, the Clausius–Clapeyron equation for the vapour pressure of PbI_2 was calculated as:

$$\log(p/\mathrm{Pa}) = -(8691 \pm 84)(T/\mathrm{K})^{-1} + (13.814 \pm 0.140) \qquad (2)$$

A third-law analysis, using the thermal functions derived from a recent enthalpy increment study of our laboratory [17], yields: $\Delta_{\mathrm{sub}}H^\circ(298.15\,\mathrm{K}) = (170.9 \pm 0.1)$ kJ mol^{-1} which is in reasonable agreement with the second law value (173.1 ± 1.6) kJ mol^{-1}, the quoted errors being the statistical values. Similarly the second-law entropy at the mean temperature of the measurement $\Delta_{\mathrm{sub}}S^\circ(600\,\mathrm{K}) = 168.6$ J mol^{-1} K^{-1} agrees reasonably with the value calculated statistically, $\Delta_{\mathrm{sub}}S^\circ(600\,\mathrm{K}) = 165.0$ J mol^{-1} K^{-1}.

Using third-law and second-law methods the enthalpy of sublimation of PbI_2(g) was calculated using data from previous studies [18–22] carried out on the vaporization of lead diiodide, the results being shown in Table 5.

Three studies have been made over the solid phase [18–20], as shown in Fig. 2. Our results are in good agreement with the results of Niwa et al. [19] made by the same technique, but we are suspicious of these results since the authors did not make corrections for the non-ideality of their effusion cells. The values for the enthalpy of sublimation at standard temperature from the second/third-law analysis from our study are higher than those derived from the results by Duncan and Thomas [18] who used a modified Knudsen effusion technique. As stated by these authors, one of the major problems with this apparatus was the method of temperature measurement. In addition, the rate of weight loss was not actually measured but simply the total weight loss for an extended period where the heating and cooling of the cell are included. The third-law result that we quote from Hilpert et al. [20] is given only as an approximate

Table 4
Experimental vapour pressures of PbI_2(s)

T/K	$(\mathrm{d}W/\mathrm{d}t)/(\mathrm{kg\,s^{-1}})$	p/Pa	$\Delta_{\mathrm{sub}}H^\circ(298.15\,\mathrm{K})/(\mathrm{kJ\,mol^{-1}})$
579.7	-4.35×10^{-8}	0.068	170.89
600.3	-1.40×10^{-7}	0.221	170.82
610.5	-2.40×10^{-7}	0.384	170.80
620.8	-4.05×10^{-7}	0.652	170.83
585.0	-5.48×10^{-8}	0.086	171.24
595.2	-1.02×10^{-7}	0.161	171.00
605.6	-1.81×10^{-7}	0.288	170.95
615.9	-3.08×10^{-7}	0.494	170.96
608.6	-2.12×10^{-7}	0.338	170.94
598.3	-1.22×10^{-7}	0.194	170.94
587.8	-6.92×10^{-8}	0.109	170.88

Table 5
The molar enthalpy and entropy of sublimation of PbI_2

Author	Method[a]	T/K	$\Delta_{sub}H^\circ$(298.15 K)/ (kJ mol^{-1})		$\Delta_{sub}S^\circ(T)$/ (J mol^{-1} K^{-1})	
			2nd law	3rd law	Exp.	Calc.
Jellinek and Rudat [21]	T	923–1073	165.5 ± 3.0	170.2 ± 0.4	103.1	107.9
Niwa et al. [19]	K	579–650	166.4 ± 1.0	171.2 ± 0.2	156.6	164.3
Duncan and Thomas [18]	K	563–613	165.2 ± 1.8	165.8 ± 0.1	165.4	164.9
Abakumov and Malyshev [22]	S	900–1150	182.5 ± 1.0	166.6 ± 3.8	121.7	106.6
Hilpert et al. [20]	M	474–582	167.7 ± 1.3	(165.8 ± 0.2)[b]	167.8	164.8
This study	K	598–640	173.1 ± 1.6	170.9 ± 0.1	168.6	165.0

[a] M, mass spectrometry; K, Knudsen effusion; T, transpiration technique; S, static method.
[b] This value is given only as an approximate value (see text).

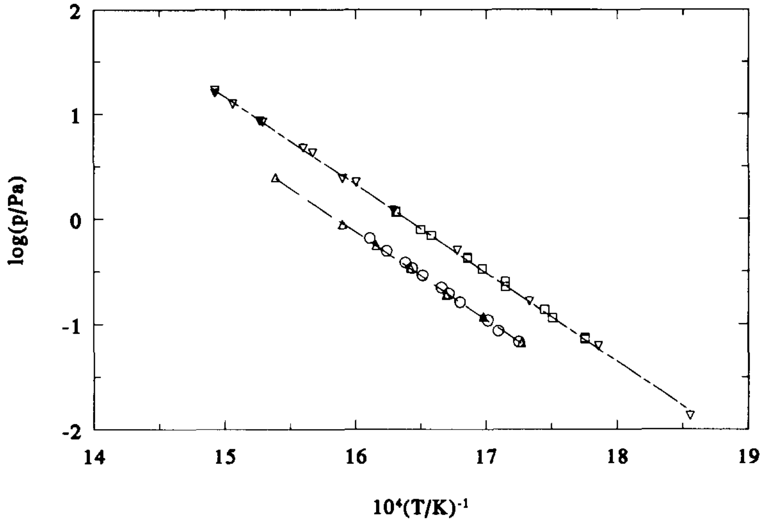

Fig. 2. The vapour pressure of PbI_2; Δ, Niwa et al. [19]; ∇, Duncan and Thomas [18]; □, Hilpert et al. [20]; ○, this study.

value since they used the absolute pressure results of Duncan and Thomas for the pressure calibration of their mass spectrometric experiment. Their second law value is intermediate between our result and that of Duncan and Thomas.

The vapour pressure over liquid PbI_2 has been measured by Jellinek and Rudat [21] and Abakumov and Malyshev [22]. The former authors report only four data points; their third-law enthalpy of sublimation is in reasonable agreement with the results of the present study but their second/third-law agreement is poor. Abakumov and Malyshev [22] measured the pressure of the lead diiodide in a similar temperature range to that of the Jellinek and Rudat study. We would tend to treat the results of Abakumov and Malyshev as rather suspect since the calculated third-law values for the standard enthalpy of sublimation showed large temperature-dependence as well as poor second/third-law agreement.

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