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Short communication

The infrared spectrum of YI_3 in the vapour phase

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ABSTRACT

The vibrational spectrum of the vapour phase above YI_3 was measured by infrared spectroscopy. The spectrum revealed four strong bands, three of which could be assigned to the fundamantal infrared active vibrations of the YI_3 monomer molecule. The observed frequencies agree very well with quantum-chemical calculations reported in literature. The presence of dimer molecules, the fraction of which is significant in the vapour according to literature, is also discussed in the context of assigning the fourth strong band in the experimental spectrum. Although its position matches well with a strong fundamental of the dimer, its intensity suggest a dimer fraction that is far outside the range for the other rare-earth triiodides.

1. Introduction

The thermodynamics of yttrium triiodide in the gas phase have been analysed extensively by Osina et al. [1], who performed an assessment of the monomer and dimer molecules based on available experimental literature and theoretical calculations. As comprehensively summarised by these authors, the equilibrium between crystal/liquid and the gas phase was measured experimentally by Knudsen effusion technique [2] and the molecular structure was obtained from gas-phase electron diffraction experiments [3],[4]. The monomer has a planar XY_3 structure (D_{3h}), the dimer molecules have a D_{2h} halogen-bridged X_2Y_6 symmetry [5],[6], [7],[8]. The authors completed the required data with the vibrational frequencies obtained from quantum chemical computations, and thus obtained the basic standard thermodynamic properties such as standard entropies, heat capacities and enthalpies of formation of the YI_3 and Y_2I_6 molecules. The absence of experimental data on the vibrational frequencies of the molecules is a weak spot in the analysis. Therefore it is interesting to confront the computed values with the experimental results for the infrared spectrum of the gas phase of YI_3 and add further information on the vapour composition.

2. Methods

The infrared spectrum was recorded with a BOMEM DA3.02 Fourier-transform spectrometer equipped with an optical gas-cell that was tailor made for the instrument. The HTOC-2 cell consisted of a quartz tube that was closed by two water-cooled optical windows and heated in a three-zone furnace to create a section of constant temperature of about 20 cm, as discussed in [9],[10]. In order to protect the highly hygroscopic sample, the material was loaded in the cell in an argon-filled glove box. For the experiments approximately 2–3 g of solid X-ray pure YI_3 was heated in a molybdenum boat in the centre of the cell. The gas atmosphere in the cell was argon at a pressure of 15 mbar at room temperature. The spectrum was scanned between 1200 and 1400 K; 128 scans were co-added.

The following experimental arrangements were used for the operation of the spectrometer: for the 375–100 cm^{-1} spectral range a globar light source, for the 100–25 cm^{-1} range a Hg light source and in both cases a helium-cooled germanium bolometer operating at 4.2 and 1.6 K, respectively. In the whole range Si windows were used. The spectra were recorded at 0.5 cm^{-1} resolution.

3. Results

The measured infrared spectrum of the vapour above YI_3 is shown in Figure 1. It shows four strong bands in the 25–250 cm^{-1} spectral range, at 37 cm^{-1}, 41 cm^{-1}, 165 cm^{-1} and 236.3 cm^{-1}, and a weak band at 58 cm^{-1}. The 236.3 cm^{-1} band is the strongest band and can be assigned to the asymmetric stretching vibrational mode (ν_4) of the planar XY_3 monomer, assuming the monomer is the predominant vapour species. This assumption is supported by the monomer concentration of 75 % that was cited by Hargittai [6] from unpublished gas-phase electron diffraction studies. The planar geometry of YI_3 was derived from gas-phase electron diffraction (ED) measurements by Ezhov et al. [4] as

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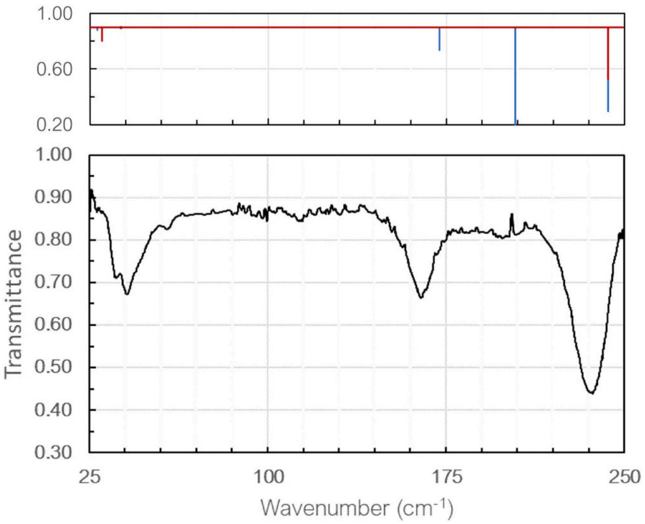

Fig. 1. The infrared spectrum (0.5 cm^{-1} resolution) of the vapour above YI_3 at T = (1300 ± 100) K. The top graph shows the band positions from the computations by Kovacs [5], normalised to the strongest intensity of the monomer (red) and dimer (blue) species.

well as by quantum-chemical (QC) calculations. In the latter work, Ezhov et al. also estimated the vibrational frequencies of the YI_3 molecule from the radial distribution function from the ED experiments. As disscussed by Hargittai, the interpretation of the results by Ezhov et al. omit the presence of the dimer and thus are subject to significant uncertainty. The value for the ν_4 frequency found here is substantially higher than the value estimated by Ezhov et al. [4]. The value is in good agreement with the values from QC calculations, 243 cm^{-1} (LANL2DZ pseudopotentials) [5], 225 cm^{-1} (LANL2DZ and SDD pseudopotentials) [8]. However, it should be noted that the QC calculations by Kovács [5] show that the dimer has a intense terminal stretching band at the same position as the monomer, thus not excluding that the vibration band found experimentally is an overlap of the two vapour species. The QC calculations also reveal a second terminal stretch of slightly stronger intensity at 204 cm^{-1}. Around this wavenumber we observe a very weak absorption band, and thus can conclude that the band at 236.3 cm^{-1} is predominantly due to the monomer.

The symmetry rules allow only two more infrared active vibrational modes for a planar XY_3 molecule, the ν_3 bending mode and the ν_1 inversion mode. Although they could be assigned to double absorption bands with substantial intensity in the 30 and 50 cm^{-1} range, this is in contrast with the computed infrared intensities [5],[8], which indicate a much lower intensity for ν_3 compared to ν_1 (1 km · mol^{-1} vs. 19 km · mol^{-1}). The small red shift between the two bands would be compatible with a hot band. The assignment of the weak band at 58 cm^{-1} to ν_3 would better fit the computed intensities. Table 1 shows an good agreement with the quantum chemical calculations, though some care needs to be taken with this assignment.

Table 1
The vibrational frequencies of YI_3 (in cm^{-1}) and comparison to literature; values in parenthesis are the relative IR intensities, scaled to 100 for the most intense band. ED, gas-phase Electron Diffraction; QC, Quantum Chemical calculations; IR, gas-phase Infrared spectroscopy. Note that we followed the frequency numbering by Kovacs [5].

	method	ν_1 (A_2'')	ν_2 (A_1')	ν_3 (E′)	ν_4 (E′)
Ezhov et al. [4]	ED	70	125	50	200
Kovacs [5]	QC/MP2	30 (26)	143 (0)	38 (1)	243 (100)
Zhang et al. [8]	QC/RHF	35 (40)	132 (7)	36 (3)	225 (100)
	QC/ B3LYP	22 (28)	138 (0)	35 (1)	236 (100)
This work	IR	41 (50)	-	58 (9)	236.3 (100)

The fourth band that we observed at 165 cm^{-1} is very strong. The QC calculations [5] indicate an intense ring stretch at 172 cm^{-1}, so it is tempting to assign it to the dimer. It is, however, not fully consistent with the QC results of the other IR active bands, as the calculated intensity is significantly less than that of the dimer band at 204 cm^{-1}, which we observe vaguely. The possibility of a combination band (e.g. $\nu_1 + \nu_3$) is not likely, as we have not observed combination bands in our work on rare earth halides [10],[11]. Alternatively, it could be due to condensed YI_3 in the colder parts of the optical cell or the cell windows, but this is not regularly observed for this group of compounds in any of the measurements on yttrium or lanthanide halides in our experimental equipment. However, if the case, the intensity of the low wavenumber bands could have been amplified by a higher background from solid state vibrations.

4. Discussion

The current results for YI_3 can be compared to those for the rare-earth triiodide group, in which experimental data exist for the ν_4 frequency of LaI_3 [11], CeI_3 [12], DyI_3 [13] and ScI_3 [14]. As expected, the value found in the current work for ν_4 of the monomer fits very well between the values of LaI_3 and ScI_3 when examining the relation with the interatomic distance (Figure 2), using the experimental ED values (LaI_3, [6]; CeI_3, [12], DyI_3, [13], ScI_3 [14]), whereas the lanthanides (La, Ce, Dy) follow a different trend showing the effect of the lanthanide contraction. A similar comparison for the low-wavenumber bend and inversion vibrations is not straightforward, as they occurred close to the detection limit in the LaI_3 IR spectrum and were not reported for ScI_3. Qualitatively, we can remark that the broad band at 25 cm^{-1} for LaI_3 is consistent with the observation of the two frequencies observed here; the shift being in line with the predictions of the QC calculations. So one can conclude, that the experimental IR data for the YI_3 molecule are fully consistent with the group 3 triiodides.

The situation is different for the Y_2I_6 dimer. YI_3 is the compound with the reported largest fraction of dimeric species in the vapour: 25 % [6], versus 4.5 % for CeI_3 [12], 17 % for DyI_3 [13] as derived from the ED analysis in all three cases at not too dissimilar temperatures. In case of CeI_3 and DyI_3 independent mass spectrometric studies have been published. Dunaev [15] confirmed the low concentration between 2 % and

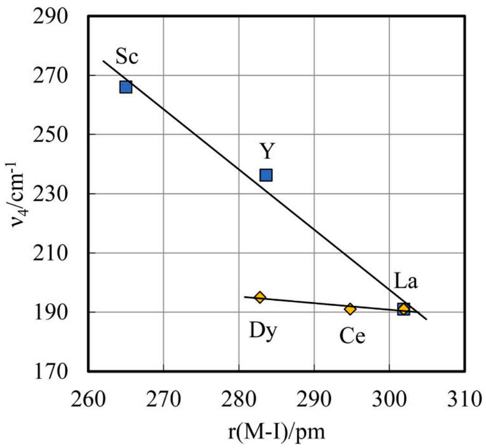

Fig. 2. The correlation between the interatomic distance (M-I) and the asymmetric stretching frequency ν_4 of the MI_3 rare-earth molecules. The black symbols show the group 3 triiodides (Sc, Y, La), the red symbols the lanthanide molecules (La, Ce, Dy). Note that the lanthanide follow a different trendline as a result of the lanthanide contraction, as a result of which the ionic radius of the Ln metals becomes smaller with increasing atomic number.

4 % for the solid range of CeI_3; Hilpert et al. [16] showed that the dimer concentration is about 9 % for DyI_3 (at 1000 K). Mass spectrometric studies for ScI_3 also indicate a dimer fraction between 3 % and 7 % [17], whereas for LaI_3 they show a concentration of less than 1 % [18]. Even for heavy LnI_3 compounds (Ln = Tb-Lu) with ionic radii close to Y^{3+} the dimer fraction found by mass spectrometry is small, i.e. less than 6 % [19],[20].

This raises the question whether the dimer concentration for YI_3 is truly 25 % as suggested in [6], because this strongly affects the interpretation of the present results. As discussed above, assigning the very strong 165 cm^{-1} band to the dimer seems to corroborate the large dimer fraction, whereas the weak intensity of the dimer band at 204 cm^{-1} suggests the contrary. On the basis of the available data for the dimer fraction in the rare-earth triiodides, summarized in the previous paragraph, we consider the latter option the most probable, assigning the band at 165 cm^{-1} to condensed material. Mass spectrometric measurements of YI_3 should resolve this issue.

Author statement

R.K. and A.B. conceived the experiment, A.B. conducted the experiment, R.K. analysed the results and wrote the first draft of the manuscript. All authors reviewed the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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