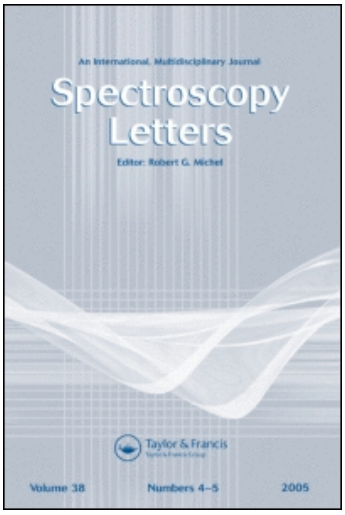

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The Raman Spectrum of Mercury (II) Iodide in High Temperature Solvents

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THE RAMAN SPECTRUM OF MERCURY(II) IODIDE IN HIGH TEMPERATURE SOLVENTS

Key words: Raman, Mercury Iodide, Cesium Nitrate, Terphenyl

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ABSTRACT

The Raman spectrum of mercury(II) iodide was observed in cesium nitrate at 430°C and in meta- and para-terphenyl at 235 and 240°C, respectively. A single strong polarized line was found at 148.5 cm^{-1}, width at half height 15 cm^{-1} in cesium nitrate, and a single line at 154.0 cm^{-1}, width at half height 7 cm^{-1} in the terphenyls. The observed spectra are not consistent with interactions of the solute and the solvents involving bonds of highly covalent character, but do not exclude other interactions.

In the course of an investigation on the nature of mercury (II) iodide species in solution in molten alkali metal nitrates, by its distribution between the salt melts and terphenyl melts[1,2], it became of interest to study by means of Raman spectroscopy the mercury(II) iodide species formed. Several such studies at

lower temperatures have already been made: in the gas phase[3], in a krypton matrix[4], in alcohols[5], tributyl phosphate[6] and dioxane[7], and in molten mercury(II) iodide[8], chloride[9] and bromide[9]. The reason for looking at the Raman spectrum in yet further media was the suggestion made on the basis of thermodynamic and kinetic data[2,10] that the mercury(II) iodide species in the alkali nitrate melts are solvated by nitrate anions, and that possibly the mixed anion tetrahedral species $HgI_2(NO_3)_2^{2-}$ is formed. Recent Raman spectrophotometric data on mixed halide anionic complexes of mercury[11] identified prominent lines of the spectrum of the species $HgBr_{\underline{n}}I_{4-\underline{n}}^{2-}$, including $HgBr_2I_2^{2-}$, so that a comparison could be made. The solubility of mercury(II) iodide in molten alkali metal nitrates is rather small, except for cesium nitrate[12], where the solubility should be sufficient for the Raman spectrum to be recorded. Also, it was concluded from vapor pressure osmometric data in aromatic solvents that dimeric species of mercury(II) halides (even a trimeric species of the iodide) are found, in which the mercury has a distorted octahedral coordination, with three halogen atoms bonded to a mercury atom in the dimer[13]. In terphenyl melts, the solubility

RESULTS AND DISCUSSION

The spectrum of mercury(II) iodide in cesium nitrate exhibits in addition to the nitrate lines at 1356, 1043 and 708 cm^{-1} expected in cesium nitrate melts[15], a single strong polarized line at 148.5 ± 0.5 cm^{-1} of full width at half height 15 cm^{-1} (Fig. 1).

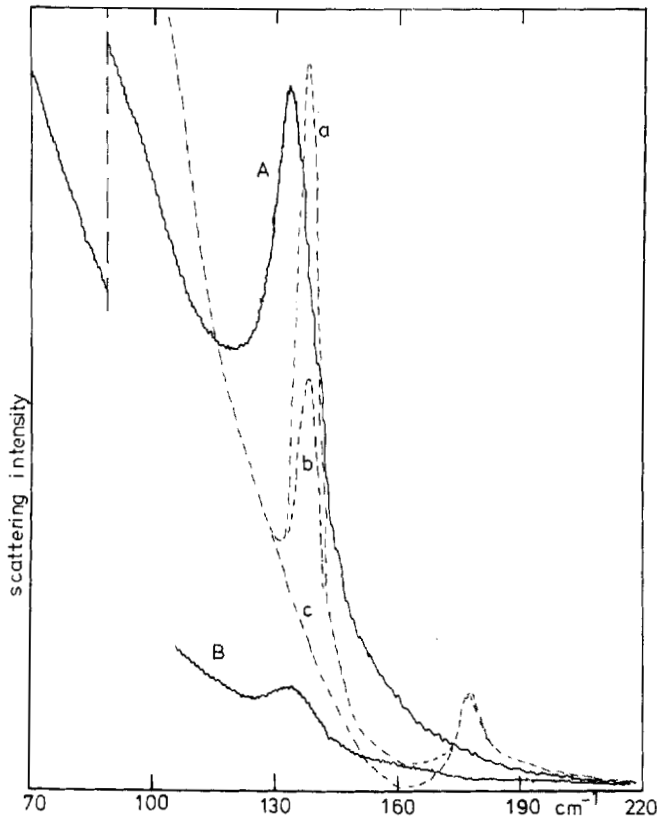

Fig. 1.

Raman spectra of HgI_2 in $CsNO_3$ at 430°C, continuous curves: A with parallel polarizer, B with perpendicular polarizer; and in p-terphenyl at 242°C, dashed curves: a with parallel polarizer, b with perpendicular polarizer, c solvent blank.

No further lines down to 75 cm^{-1} from the exciting line could be observed. The line did not change in position or in width on threefold dilution. The observed line is ascribed to ν_1, the Hg-I symmetric stretching, in a linear molecule I-Hg-I of $D_{\infty h}$ symmetry. In the terphenyl solutions, again only a single

strong, polarized line at 154.0±0.5 cm^{-1} of full width at half height of 7 cm^{-1} could be ascribed to mercury(II) iodide (Fig. 1). All the other lines observed (weak lines at 238, 273 and 405 cm^{-1} for m-terphenyl and a weak line at 218 cm^{-1} and a medium one at 407 cm^{-1} for p-terphenyl, all polarized) belong to the Raman spectra of the solvents themselves.

Matrix isolated HgI_2 molecules exhibit, similarly, a dominant line at a somewhat higher frequency (163.5 cm^{-1} for the monomer; an additional line at 158.4 cm^{-1} has been ascribed to the dimer[4]). The sensitivity to the environment in melts and solutions, reducing the frequency to 156 cm^{-1} in dioxane[7], 150 cm^{-1} in ethanol or methanol[5], 148 cm^{-1} in tributyl phosphate[6] and 146 cm^{-1} in $HgCl_2$ or $HgBr_2$[9], has already been commented on[9]. The absence of any line in the cesium nitrate medium corresponding to the Hg-O stretch observed in mercury nitrate (at 292 cm^{-1} in water, 299 cm^{-1} in benzene, 276 cm^{-1} in the anhydrous solid, 266 cm^{-1} in a $Hg(NO_3)_2 \cdot H_2O + KNO_3$ melt and aqueous solutions, or 248 cm^{-1} in acetonitrile solutions)[16] is evidence that any bonding between the the mercury(II) iodide and the nitrate in the cesium nitrate melt is predominantly ionic.

This, indeed, was initially[10] assumed concerning the postulated species $HgI_2(NO_3)_2^{2-}$, hence it is not analogous to the covalently bonded tetrahedral $HgI_2Br_2^{2-}$, which is a member of the series $HgBr_{\underline{n}}I_{4-\underline{n}}^{2-}$ (with ν_1 frequencies at 165, 144, 136, 128 and 122 cm^{-1} for $\underline{n}$ = 4,3,2,1 and 0, respectively[11]).

Interaction of the linear I-Hg-I with nitrate anions is, however, not excluded by the evidence. The situation in the cesium nitrate melt would be analogous to that of NCS-Hg-SCN in dimethylsulfoxide (DMSO) solutions[17], where the Raman spectrum showed a single Hg-S stretching frequency, interpreted as strongly bonded linear S-Hg-S, with the remaining coordination sites around the mercury occupied with weakly interacting DMSO molecules. A broad, weak feature at 202 cm^{-1} in the Raman spectrum[17], however, remained unexplained. Similarly for I-Hg-I in tributylphosphate (TBP), in addition to the 148 cm^{-1} strong sharp polarized band, a very weak band at 205 cm^{-1} was observed[6]. (No such feature could be discerned in the cesium nitrate medium). The interpretation was again in terms of an essentially linear I-Hg-I weakly interacting with TBP molecules, but a slight distortion from linearity was permitted. A similar distortion (an angle of 165°) is compatible with the short I-I distance, 0.513 nm, found by X-ray diffraction[18] in mercury(II) iodide solutions in DMSO, compared with twice the Hg-I distance, 0.260 nm. This is barely outside the error of measurement, and other explanations than bending are possible[18], but weak interactions with the DMSO molecules are confirmed. Even in an inert matrix, a slight bending of I-Hg-I (an angle of 170° is mentioned) is compatible with the spectroscopic and thermodynamic data[4].

A final consideration must be given to the dimeric species Hg_2I_4, which has been identified vibration-spectroscopically by double oven deposition in matrix isolation experiments[4]. Ther-

modynamic information[13] points to dimerization also in water for mercury(II) chloride and in aromatic hydrocarbons for the chloride and bromide, and for the iodide only at elevated temperatures where the solubility becomes sufficient. Distribution data found to be independent of solute concentration[1] in the range $5\times10^{-5} < x_{HgI_2}$ (in p-terphenyl) < 0.005 point to the mercury(II) iodide solute being in similar states of oligomerization in the terphenyl and alkali nitrate solvents, which is unlikely to be the dimer at these low concentrations. Liquid-liquid phase separation of cesium nitrate and mercury(II) iodide at a slightly higher concentration (3.75 mole%) than employed here (3.2 mole%) does indicate preferred self- rather than mutual-interactions. However, if the width of the line in cesium nitrate (15 cm^{-1}) compared with that in terphenyl (7 cm^{-1}) is ascribed to dimerization, it should have become narrower on dilution, but this was not observed.

It is concluded therefore that the Raman spectroscopic evidence points to the mercury(II) iodide species being the linear of mercury(II) iodide is much larger than in aromatic solvents at room temperature (the highest recorded is in p-xylene, being 0.0094 molal[14]), so that contrary to the case of benzene solvent[7], Raman spectra should be obtainable, to compare with expectations for the suggested species.

EXPERIMENTAL

A solution of 3.20 mole% of HgI_2 in $CsNO_3$ (0.0726m, 0.201M) was found to be orange-yellow, and stable at $430\pm3°C$, the tem-

perature of measurement (at the monotectic temperature of the system, 401°C, the solubility is[12] 3.75 mole%). A more dilute solution containing 0.99 mole% was also prepared. A solution of 10.3 mole% (0.50m) in m-terphenyl was found to be stable at 235±2°C (m.p. of solvent 87°C), where its molarity is 0.45M. Similarly, a solution of 10.3 mole% (0.50m) in p-terphenyl at 242±2°C (m.p. 213°C, density[1] at m.p. 0.981 g cm^{-3}) has a molarity of 0.47M and is stable. The samples were sealed under vacuum in test tubes, and inserted in a heated copper block with adequate heat capacity for temperature equilibrium to be attained. The Raman spectrum was excited with a Spectra-Physics Kr^+ laser at 647.1 nm, suitable for the orange melts. Excitation with an Ar^+ laser at 514.5 nm gave much reduced intensities. The spectrum was recorded with a Spex 1401 double monochromator with photon counting.

I-Hg-I, not excluding slight bending, ionic bonding to nitrate anions and dipole interactions with aromatic solvents, but covalently bonded solvates are definitely not formed.

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