Low-Frequency Laser-Excited Raman Spectral Study of the Red to Yellow Phase Transition in Mercuric Iodide[1a]

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The red to yellow phase transition occurring in solid mercuric iodide above 126° was studied by means of laser-excited Raman spectroscopy. Raman spectra of polycrystalline red and yellow mercuric iodide solid as well as the melt were recorded. Far-infrared spectra were also obtained for both solid phases. Marked changes in the spectra were related to changes in the crystal structure of the two polymorphs rather than to temperature effects. The observed spectra are discussed in terms of the nonmolecular structure of red HgI_2 and the molecular nature of yellow HgI_2. Strong Raman bands were observed in red mercuric iodide at 17.5, 29, and 114 cm^{-1} and weaker bands at 46, 142, and 246 cm^{-1}. The strong Raman bands observed in the yellow phase were at 37, 41, and 138 cm^{-1} and a weak band was at 278 cm^{-1}. Two Raman bands were observed at 41 and 138 cm^{-1} in the melt. A strong infrared absorption occurred at 110 cm^{-1} in red HgI_2, while yellow HgI_2 absorbed at 200 cm^{-1} and also had a band between 40 and 50 cm^{-1}.

Introduction

Solid HgI_2, which is colored orange-red at room temperature, undergoes a reversible phase transition to a yellow form at 126°.[2] Although this transition has been known for some time, there is a lack of Raman spectral information reported on either red or yellow crystalline HgI_2. This scarcity of spectral data is due to the previous difficulty of obtaining Raman spectra of highly colored red compounds using mercury-arc excitation. In addition, the low-frequency region of the spectrum where the internal and lattice frequencies of HgI_2 are expected was not readily accessible owing to instrumentation limitations.

The only Raman spectral data reported for HgI_2 are one band observed in the melt[3] and a band observed in the gas,[4] both assigned to the same Hg–I symmetric stretch. Far-infrared data are reported for the crystalline red form as well as solution spectra of HgI_2 in various solvents;[5,6] no data are reported for the yellow crystalline phase.

The present study was undertaken to record the laser Raman spectra of both red and yellow crystalline HgI_2 and to relate the spectra to the known crystal structures of these polymorphs. Additional spectra were recorded of HgI_2 liquid melt, as well as far-infrared spectra of red and yellow HgI_2.

Experimental Section

Mallinckrodt analytical reagent grade red HgI_2 was finely powdered and then vacuum sublimed at 100°. The Raman spectra were recorded on a Cary 81 Raman spectrometer equipped with a Spectra-Physics Model 125 He–Ne laser. The optical configuration of the sampling compartment is such that the Raman radiation from the powdered sample is observed as back-scattered radiation, i.e., viewed at 180°. Very low frequency bands observed in red HgI_2 were rerun using a Spex Industries Model 1400-11 double monochromator employing a similar He–Ne laser. This was done to rule out completely the possibility of grating ghosts as the source of the bands close to the exciting line.

A conventional Cary 81 powder sampling rod with the sample packed into a grooved end was modified to permit heating of the sample; see Figure 1. Thin asbestos film was put around the metal rod and then nichrome wire was wound over the asbestos. Another layer of asbestos was used to insulate the wire from air. The yellow form of HgI_2 was formed from the red while in the spectrometer by sending current through the nichrome wire which then acted as a resistance heater. The heat was controlled manually with a Variac and the temperature of the sample was determined by means of an iron–constantan thermocouple inserted into the sampling rod. An additional check as to the occurrence of the phase transition was the disappearance of Raman bands associated with the red HgI_2 and appearance of new bands of yellow HgI_2.

It was observed that upon initial heating of red-orange HgI_2 the color first became bright red before becoming yellow. To check for the possible existence of a new red phase, a differential thermal analysis (dta) was run on HgI_2. No new phase was seen which is in agreement with the observed Raman spectra; the color change may be due to changes in electronic absorption bands or absorption edge. The dta run, however, indicated a latent heat change at 137° rather than the lower temperature reported in the literature. When the same sample was recycled, the temperature of the change shifted to 144° indicating a possible mixture of phases after the initial phase change. Visual examination of this cycled sample revealed the presence of white or yellow occlusions.

The sluggishness of the reverse yellow to red transition was confirmed spectroscopically. After the temperature was raised above the transition point, a Raman spectrum of yellow HgI_2 was recorded. The sample was then permitted to return to room temperature without disturbing it in any other way. It was found that the yellow HgI_2 persisted for periods long enough to permit recording its spectrum at room temperature. This technique was employed to record the Raman spectrum of yellow HgI_2 unperturbed by elevated temperature. In addition, infrared spectra were run on room-temperature metastable yellow HgI_2 in the following manner. A Nujol mull of red HgI_2 was prepared and put on a polyethylene disk which acted as a substrate which was transparent in the far-infrared region. After recording the spectrum of red HgI_2, a soldering iron was used

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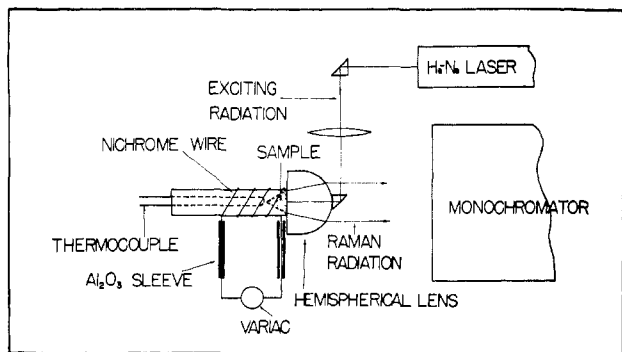(6) G. Randi and F. Gesmundo, *Atti Accad. Nazl. Lincei, Rend. Classe Sci. Fis. Mat. Nat.*, **41**, 200 (1966).

Figure 1.—High-temperature laser Raman solid sampling technique. Laser excitation is at 180°. Nichrome wire carrying current serves as heater.

locally to heat the sample on the surface of the polyethylene disk. In this manner the yellow HgI_2 could be formed without melting the polyethylene. The yellow HgI_2 remained stable on the polyethylene at room temperature long enough to permit recording its spectrum. For the region above 200 cm⁻¹ a Perkin-Elmer 225 infrared spectrometer was employed. The spectrum below 200 cm⁻¹ was run using an RIIC Model FS-620 Fourier interferometer. Poor energy and resolution only permitted examining the spectral region down to approximately 50 cm⁻¹.

A Raman spectrum of HgI_2 liquid (mp 257°) was recorded to assure the assignment of a low-frequency band as originating from an internal rather than a lattice vibration. To form the melt, a tube was constructed as shown in Figure 2. The lower part of the U tube was packed with solid HgI_2 and nichrome wire inserted through the solid and sealed to the glass with Sauereisen cement. The U tube was then put flush against the hemispherical lens of the spectrometer and current was sent through the nichrome wire until a very dark red melt was formed throughout the sample. No attempt was made to ensure a vacuum seal but the excess vapor over the melt (bp 351°) was allowed to vent through the porous Sauereisen. It was observed that when the original red-orange crystalline HgI_2 was heated through its melting point, a spectrum of colors was observed in sequence: red-orange, red, yellow, orange, deep red. Spectra were recorded at all colors; however, the only marked spectral changes occurred at the point of yellow coloration. The orange form below the melting point gave a similar spectrum to the yellow form and is probably not the orange phase recently reported.[7,8]

Both red and yellow HgI_2 are extremely strong Raman scatterers with red being stronger than yellow. The intensity of the low-frequency bands of red HgI_2 was so great that spectra could be recorded using a spectral slit width of 0.25 cm⁻¹ with minimal amplifier gain. This ability to operate using very narrow slits permitted the recording of spectra extremely close to the exciting line. The strong band observed at 17.5 cm⁻¹ in red HgI_2 is the lowest frequency Raman band ever observed in this laboratory. A report[9] of the observation of a Raman band as close as 5 cm⁻¹ to the exciting line in a crystal of $BaTiO_3$ also indicates that a strong Raman scatterer lends itself to extremely low frequency Raman spectral examination.

Operation close to the exciting line introduced the problem of distinguishing strong grating ghosts from Raman lines. To check on the location of ghosts, the laser beam was reflected into the monochromator using a mirror rather than a sample. The ghost spectrum and He–Ne emission spectrum were recorded and then the HgI_2 Raman spectrum was superimposed upon this background to ensure that the sample bands were indeed not background effects. This was then double checked by re-
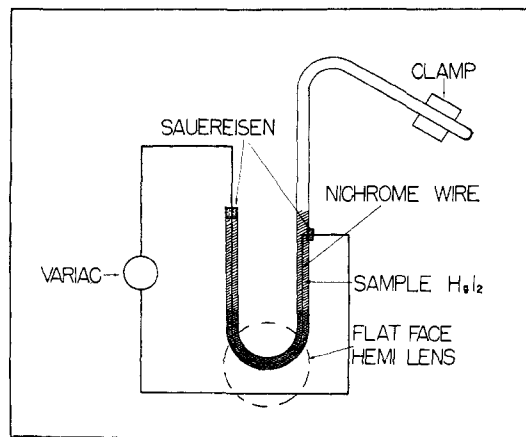

Figure 2.—Glass sample tube for observing Raman spectrum of melt. Excess vapor pressure is vented through the porous Sauereisen cement. Laser excitation is at 180°. The nichrome wire is surrounded by powdered sample.

cording the Raman and ghost spectra using a Spex double monochromator which employed different gratings from the Cary 81 laser Raman spectrometer.

Results

The Stokes and anti-Stokes spectra of both red and yellow polycrystalline HgI_2, as well as a mixture of the two, are shown in the sequence of spectra in Figure 3. (Grating ghosts are not shown and only the Stokes lines are shown for the weak bands above 200 cm⁻¹.) Since yellow HgI_2 is a relatively weaker Raman scatterer than red HgI_2, and its Raman spectrum is diminished in intensity, the amplifier gain had to be increased to observe properly its Raman spectrum.

As already discussed, the yellow to red phase transition was sluggish and the original Raman bands returned only slowly when the temperature was lowered below the transition point. This permitted recording of the yellow-phase spectrum unperturbed by elevated temperature. Increasing temperature caused the shoulder of the low-frequency doublet at 37 and 41 cm⁻¹ to smear out and become unresolved as shown in Figure 4.

Table I is a tabulation of all spectral work reported for HgI_2 gas,[4,10–12] liquid,[3] and solid,[5,6] including the

TABLE I

INFRARED AND RAMAN FREQUENCIES OF HgI₂ (cm⁻¹)

Mode	Gas^a	Melt^{b,c} Raman	Yellow solid Infrared^c	Yellow solid Raman^c	Red^d solid Infrared	Red^d solid Raman^c
						17.5
ν₂	33 (ir)	41^c	<50	37⎫ 41⎭	25	29
						46^e
					92	
ν₁	156 (R)	146, 138^c		138	102	114
					112, 110^c	142^e
					132	
ν₃	237 (ir)		200			
						226
						246^e
				278^e		

a See ref 4, 10–12. *b* See ref 3. *c* This work. *d* See ref 5, 6. *e* Weak and broad.

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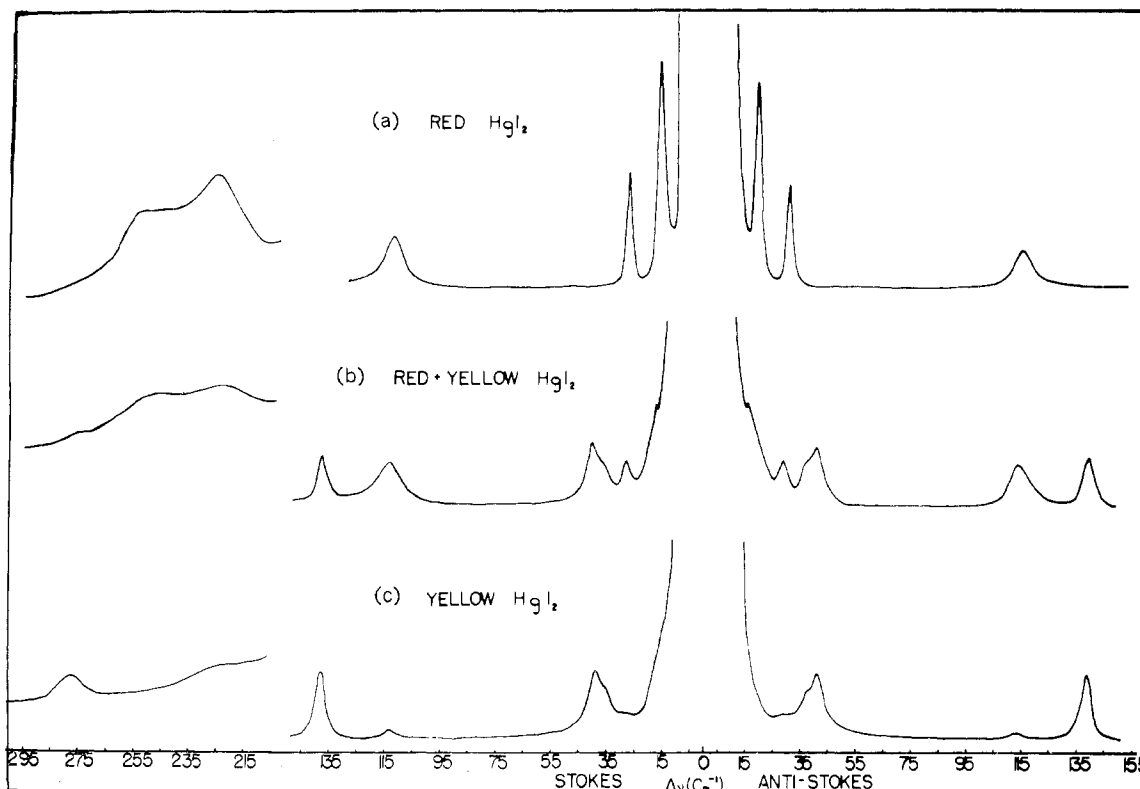(12) M. Wherli, *Helv. Phys. Acta*, **11**, 339 (1938).

Figure 3.—(a) Raman spectrum of room-temperature red HgI_2. (b) Raman spectrum of the red and yellow HgI_2 mixture at the point of incomplete phase conversion. (c) Raman spectrum of yellow HgI_2 just above the transition point. Residual trace of red HgI_2 is indicated.
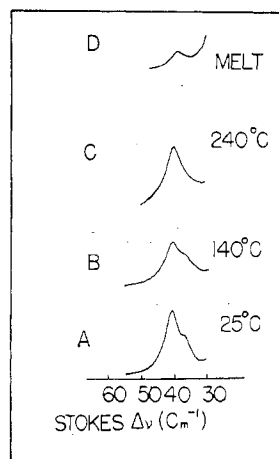

Figure 4.—(A) Spectrum of the low-frequency doublet of metastable yellow HgI_2 at room temperature. (B–D) Progressive increase in temperature removes the doublet structure but the single band is still present in melt.

present study. All solid-state work was done on either powders or mulls with no report of any single-crystal spectral results. All Raman bands in the present study were intense except shoulders at the high-frequency side of the 29- and 114-cm^{-1} bands and the bands above 200 cm^{-1}. The exact frequency of the far-infrared band near 50 cm^{-1} could not be determined owing to energy and resolution limitations.

General Discussion

The newly observed Raman frequencies of the yellow form are not merely frequency changes due to elevated temperature but rather are representative of a truly new phase. This becomes apparent from examination of the sequence of spectra shown in Figure 3. The initial spectrum is that of red HgI_2 at room temperature. Spectrum 3b is taken above 126° but at a time when there is only partial conversion to yellow HgI_2. Raman bands belonging to red HgI_2 are still present even though the temperature is elevated, while at the same time the new bands associated with yellow HgI_2 can also be seen. Thus, the two forms of HgI_2 have distinct nonsuperimposable Raman spectra. Figure 3c shows the point at which almost complete conversion to yellow HgI_2 has occurred; the red HgI_2 bands have disappeared except for some residual trace and the yellow HgI_2 spectrum predominates. The strikingly different spectrum of the two forms of HgI_2 indicates that the transition is accompanied by a marked change in structure which is certainly indicated by X-ray studies.[2,7] Examination of the yellow form in its metastable condition at room temperature reveals a similar spectrum to that at elevated temperatures except that the splitting of the band at 37 and 41 cm^{-1} is more pronounced; see Figure 4.

Spectral Analysis

Yellow HgI_2.—The free HgI_2 molecule is linear, having molecular symmetry $D_{\infty h}$. For such a molecule there are three independent fundamentals, only one of which is Raman active, the other two being infrared active.[13] The symmetric stretch, ν_1, has been found[4] at 156 cm^{-1} by Raman spectroscopy of the gas. ν_3, the antisymmetric stretch, was observed[11] at 237 cm^{-1}

in the infrared spectrum of the gas and ν_2, a degenerate bending vibration, has been determined[12] to be at 33 cm⁻¹ from analysis of the fine structure of electronic spectra of the gas.

In going from gas to the various condensed states, a modification of the fundamental frequencies is expected, based upon perturbations induced by neighboring molecules in the crystal lattice. Yellow HgI_2 is orthorhombic having space symmetry[2,7] Cmc^2 (C_{2v}^{12}) with four molecules per unit cell. The Hg–I distances of the nearest neighbors are 2.615 and 2.620 Å. These Hg–I bond lengths are equal to the sum of the covalent radii of Hg and I: $r[Hg(2)] + r[I(2)] = 1.28$ Å $+ 1.33$ Å $= 2.61$ Å.

The bonding in the crystal of yellow HgI_2 can thus be best considered molecular with distinct molecules of HgI_2 in the lattice.[2,7] In principle, it is possible to correlate the molecular vibrations of a free HgI_2 molecule with those in the crystal lattice modified by site and factor group splitting. The space group and site symmetry, C_s, of yellow HgI_2 are identical with $HgBr_2$, and, as in the latter case, two molecules in the unit cell are related to the remaining two by a simple translation such that the unit cell may be considered as having two molecules for spectroscopic purposes. The site and factor group correlations for the internal vibrations have been previously worked out.[5] These correlations predict that the internal vibrations of the free molecule all become Raman active in the crystal. Should this in fact occur in the crystalline powder, it would be expected that the normally Raman-inactive vibrations would at most be very weak if observed. Correlation or factor group splitting of Raman-active bands would be weak since these transitions depend upon changes in polarizability with respect to changes of the normal coordinate of a vibration; the effect of internal fields upon the splitting is expected to be much less than in infrared transitions where the dipole moment change may be greatly influenced by internal fields. Thus, splitting of observed Raman transitions is not normally expected to be strong in going from gas to crystalline solid. It is unlikely that ν_2, the degenerate bending mode, and ν_3, the asymmetric stretch, would become strong in intensity and be split according to the factor group scheme, whereas ν_1 the normally Raman-active symmetric stretch would be strong.

The fairly intense low-frequency doublet found at 37 and 41 cm⁻¹ would not ordinarily be expected to correspond to the normally Raman-inactive E_u mode (33 cm⁻¹) split according to site symmetry. To determine whether these were lattice vibrations or the split E_u fundamental, spectra were run on the yellow form at temperatures below the melting point and in the melt. As the temperature of the yellow phase increased, the doublet structure became smeared out (see Figure 4); finally only one band at 41 cm⁻¹ is observed in the melt. The fact that this band remains in the liquid indicates

that it is not a true lattice mode but is the normally Raman-inactive twofold degenerate bending mode which appears as a split band in the solid. The appearance of this free-molecule Raman-inactive band in the liquid indicates a breakdown in selection rules due to environmental effects. Similar observations[14] have been made in melts of $HgCl_2$ and $HgBr_2$. The persistence of low-frequency librations in liquids just above the melting point has also been reported[15] and this possibility should not be ruled out.

The enhanced intensity of this low-frequency doublet in the crystalline solid and no observation of lower frequency lattice modes may be due to interaction of the internal mode ν_2 with some low-lying lattice modes. This is not too surprising since, at such low frequencies, lattice and internal modes lose their distinction to a large extent. A low-frequency Raman band may also be increased in intensity by virtue of the inverse relationship of Raman intensity of the vibrational frequency of the Raman transition,[16] as indicated in the expression $I_\theta = K_\theta I_0 (\nu_0 - \nu)^4 / \nu [1 - e^{-h\nu/kT}]$, where I_θ is the intensity of the Stokes line at angle θ from exciting radiation, ν is the Stokes Raman frequency, ν_0 is the exciting frequency, and K_θ, h, and k are constants.

The observed strong band at 138 cm⁻¹ in the spectrum of yellow HgI_2 is assigned to the symmetric stretch ν_1 found at 155 cm⁻¹ in the gas, at 138 cm⁻¹ in the melt in this work, and at 146 cm⁻¹ as reported recently.[3] The weak band at 278 cm⁻¹ is probably an overtone of the fundamental ν_1 at 138 cm⁻¹. Its broad shape in both yellow and red HgI_2 indicates an overtone. The assignment of this frequency to ν_3, the antisymmetric stretch, is ruled out by observation of the fairly strong absorption at 200 cm⁻¹ in the infrared spectrum which is assigned to this fundamental. This band could not be observed in the melt spectrum. The poorly resolved band between 40 and 50 cm⁻¹ in the infrared spectrum is assigned to the ν_2 band also observed in the Raman spectrum.

Red HgI_2.—The correlation of the fundamental vibrations of gaseous to crystalline red HgI_2 is not as readily obtained as for the yellow phase. Red HgI_2 is tetragonal having space symmetry $P4_2/nmc$ (D_{4h}^{15}) with two molecules per unit cell. The structure is such that no distinct molecules of HgI_2 can be identified.[17] The structure may be best thought of as a nonmolecular lattice with layers of HgI_4 tetrahedra linked at some of their vertices.[7] There are four equal Hg–I nearest neighbor distances of 2.783-Å length for each HgI_4 tetrahedron which are somewhat greater than the gaseous band distances of 2.57 Å. A vibration such as the free-molecule symmetric Hg–I stretch ν_1 is normally Raman active and infrared forbidden; however, such a vibration may become infrared active in the solid

(13) G. Placzek, "The Rayleigh and Raman Scattering," University of California Radiation Laboratory Trans No. 526 (L) issued by the USAEC Division of Technical Information Extension, Oak Ridge, Tenn., 1962, p 133.
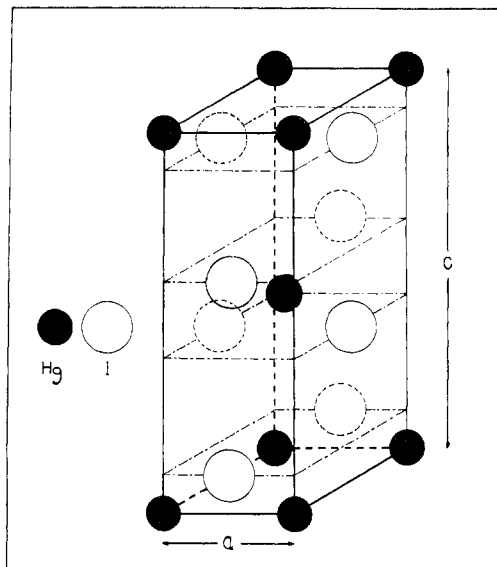
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(15) L. Blatz, *ibid.*, **47**, 841 (1967).

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(17) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry, A Comprehensive Text," Interscience Publishers, A Division of John Wiley and Sons, New York, N. Y., 1962, p 485.

Figure 5.—Tetragonal unit cell of red HgI_2 in the space group $P4_2/nmc$ (D_4h^{15}) containing two molecules of HgI_2. Hg atoms are located at sites 2a having coordinates ($^3/_4$, $^1/_4$, $^3/_4$); ($^1/_4$, $^3/_4$, $^1/_4$). I atoms are at sites 4d having coordinates ($^1/_4$, $^1/_4$, z); ($^3/_4$, $^3/_4$, $\bar{z}$); ($^1/_4$, $^1/_4$, $^1/_2 + z$); ($^3/_4$, $^3/_4$, $^1/_2 - z$), where $z = 0.39$ and the origin is at ($\bar{1}$).

form by virtue of destruction of its simple linear symmetry, as is the case in a crystal lattice of interconnected tetrahedra.

Rather than treating the vibrations as internal vibrations of simple molecular configurations, it is necessary to assume a different model. Red HgI_2 is considered as being part of a lattice structure in which Hg and I atoms occupy isolated lattice points, I atoms being located on sites having symmetry 4d or C_{2v} and Hg atoms on sites of 2a or D_{2d}. Instead of internal vibrations of HgI_2 molecules, the vibrations of lattice sites against one another are considered. According to this scheme and following the method of Bhagavantam,[18] referral to the unit cell of lattice points as shown in Figure 5 and the group character table for D_{4h} space symmetry leads to the following distribution of the allowed optical vibrations with the acoustic modes having been omitted

$$\Gamma = A_{1g} + B_{1g} + 2E_g + 2A_{2u} + B_{2u} + 3E_u$$

(18) S. Bhagavantam, *Proc. Indian Acad. Sci.*, **A13**, 543 (1941).

All the "g" modes are Raman active only, whereas $2A_{2u} + 3E_u$ are infrared active; four Raman and five infrared bands are predicted.

Previous workers[4] report a strong band in the far-infrared region at 112 cm^{-1} (confirmed in this laboratory) together with two weaker ones at 92 and 132 cm^{-1}. They made no attempt to assign these vibrational frequencies. A band was also reported[6] at 25 cm^{-1} which was correlated with the bending mode ν_2 of the free molecule and a band at 102 cm^{-1} which was assigned to the asymmetric stretch ν_3 normally at 237 cm^{-1}. Their assignment of the band at 102 cm^{-1} seems unreasonable in view of the large shift in frequency away from the free molecule. This band may be the same band as reported by Mikawa, *et al.*,[5] and found in this study, and belongs to one of the "u" modes in the lattice model just adopted.

This model predicts four Raman bands. The current work shows three strong bands at 17.5, 29, and 114 cm^{-1}, together with four broad and weak bands. The strong band at 114 cm^{-1} is probably the A_{1g} lattice mode analogous to the symmetric Hg–I stretch in a molecular model. The low-intensity bands cannot be assigned precisely, although the broad-band system at 226 and 246 cm^{-1} indicates the possibility of an overtone of 114 cm^{-1} and the combination of twice 114 + 17.5 cm^{-1}. The weak, broad shoulders on the high-frequency side of the bands at 29 and 114 cm^{-1}, which could only be observed by increasing the amplifier gain, are assigned to combinations since 46 cm^{-1} $\cong$ 29 cm^{-1} + 17.5 cm^{-1} and 142 cm^{-1} $\cong$ 114 cm^{-1} + 29 cm^{-1}. The exact frequency of these broad bands cannot be determined and hence their assignment to combinations may need modification. These broad bands also correspond to the region where yellow HgI_2 has its bands; however, superimposition of the two spectra indicates that the bands associated with the yellow form are much sharper and hence do not correspond to these weak bands of red HgI_2.

The unavailability of a good single crystal of red HgI_2 prevented an oriented crystal Raman study to determine the exact symmetry species of the observed bands.