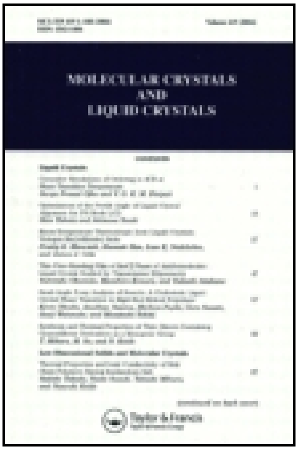

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Structure and Dynamics of the Iodine Column in the Polyiodine Canal Complex: $(\mathrm{Benzophenone})_9(\mathrm{KI})_2\mathrm{I}_7\mathrm{CHCl}_3$†

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$(\mathrm{Benzophenone})_9(\mathrm{KI})_2\mathrm{I}_7\mathrm{CHCl}_3$ belongs to a group of polyiodine complexes between iodine and benzophenone which exhibits the unusual property of a large frequency dependent conductivity, thus, indicating a major contribution due to ionic conductivity. Resonance Raman spectroscopy is used to investigate the structure and dynamics of the iodine column. It is found that the potassium complex contains two types of iodine species: I_3^- and $\mathrm{I}_3^-/\mathrm{I}_2$ complex. A temperature dependence study reveals no phase transition below room temperature, however considerable anharmonicity as well as structural disorder exist in the iodine column. Substitution of cations from K^+ to NH_4^+ and Na^+ has small effect on the iodine interactions. However, replacing K^+ with Li^+ has a profound effect on the iodine column which now shows the presence of I_5^- species in a relatively ordered structure. Although the substitution of the solvent molecule does not influence the nature of the iodine species, it does appear to affect the degree of disorder in the iodine column of the potassium complex.

INTRODUCTION

The polyiodine complexes have drawn considerable attention during recent years. The interest has been twofold: (i) Many of these complexes show high electrical conductivity. Much earlier, Little speculated that the iodine chain compound with a polar organic host would be an attractive model systems for high temperature superconductivity.[1] (ii) These complexes also exhibit unus-

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ual and varied structural properties in regards to the iodine-iodine interaction topology.

(Benzophenone)$_9$(KI)$_2$I$_7$CHCl$_3$ (abbreviated BIKI) belongs to a group of polyiodine complexes between iodine and benzophenone. Despite many unusual and highly interesting properties, it virtually went unnoticed since first being reported by Clover in 1904.[2] Labes group has revived the interest in this complex by reporting an extensive study of condutivity and other physical measurements on this system.[3,4] This complex is different from most polyiodine complexes in the sense that it exhibits a large frequency dependent conductivity and, thus, a major contribution is due to ionic conductivity. The objective of the present paper is to utilize Resonance Raman spectroscopy to obtain information on the structure and the dynamics of the iodine species present in these complexes. An integral part of this report is to correlate our spectroscopic findings with the x-ray diffraction structural studies of Coppens[5,6] and Leung as well as with the various physical measurements reported by Labes *et al.*[3,4]

To elucidate the nature of the iodine column the following was studied: (i) the resonance Raman spectra were obtained to characterize the nature of the iodine species; (ii) a temperature dependence was conducted to investigate the nature of anharmonic interactions in the iodine column, the role of disorder and the possibility of any structural phase transition; (iii) in an effort to understand the role of the solvent, we also study the nature of the iodine column in BIKI crystal grown from five solvents; (iv) complexes can also be obtained by changing the cation from K^+ to NH_4^+, Na^+ or Li^+. We investigate the effects of these substitutions and the substitutional disorder (mixed crystals) on the structure and dynamics.

EXPERIMENTAL

The components of BIKI were mixed in stoichiometric amounts. The solvent was added until the components were dissolved. Slow evaporation of solvent yields crystals with a shiny, metallic luster.

Fresh crystals of these complexes were cleared to expose the face perpendicular to the iodine column. The Raman spectra were obtained on a Spex model 14018 double monochromator with holographic gratings. The 5145 Å line of a Coherent Radiation argon ion laser or a tunable dye laser was used as the excitation source. Two types of scattering geometries were used. A backscattering geometry was used to obtain spectra at room temperature. A 90° scattering with both the excitation beam and the scattered beam being in the horizontal plane was used to obtain spectra at various temperatures. This geometry proved to be suitable for the sample in a Janis Supervaritemp cryostat where cooling was provided by a flow of liquid nitrogen or liquid helium. The temperature was measured using a chromel-constantan thermocouple. Method of detection was photon counting, signal averaging or direct current.

Precautions were taken to prevent laser damage to these crystals. At room temperature we used less than 5 milliwatts of power. At lower temperatures, we could use higher laser power. For each complex studied, we determined the upper limit of laser power before thermal dissociation was observed. Also the beam was partially defocused in order to reduce the cross sectional power density.

RESULTS AND DISCUSSION

The temperature dependence study of BIKI from room temperature to 42°K is shown in Figure 1. In the region 70 cm^{-1} to 230 cm^{-1} BIKI exhibits two transitions, at 108 cm^{-1} and 167 cm^{-1}. They are assigned as the resonance enhanced modes of the iodine column. At room temperature these bands are considerably broad (FWHH $\simeq$ 20 cm^{-1} for the 167 cm^{-1}). In going to helium temperatures there is no change in the spectral features. The transitions show practically no frequency shift but there is a considerable sharpening of the bands (FWHH $\simeq$ 10 cm^{-1}). These widths are still considerably greater than what is observed for most vibrational transitions (both lattice and internal modes) at helium temperatures. The observation of the temperature dependence behavior is interpreted as follows. The system does not exhibit any phase transition between room temperature and 42°K. This result is consistent with the temperature dependence study of conductivity reported by Labes *et al.*[3,4] They observe a fairly uniform activation behavior from 70°K to 298°K ($E = 0.026$ eV). However, an abrupt change in the activation energy is observed around room temperature. The activation energy between 298°K to 330°K was found to be 0.55 eV. As the present study has focused only in the temperature range below room temperature, it is not possible to comment on the nature of this abrupt change. The frequencies of the iodine bands do not reveal any shifts as the temperature is lowered. The temperature dependence of the vibrational frequency is derived from two conceptually different types of anharmonic contributions: (i) thermal expansion of the lattice; (ii) other anharmonic interactions. There are many cases where, even though the lattice is highly anharmonic, the two contributions are of opposite sign and nearly cancel each other.[7] In order to draw conclusion regarding the anharmonicity of the motion, one has to separate the two contributions. One method of estimating the contribution due to the thermal expansion is to use the data on the pressure dependence of the vibrational frequency in conjection with the data on the thermal expansion and the compressibility. The absence of any pres-

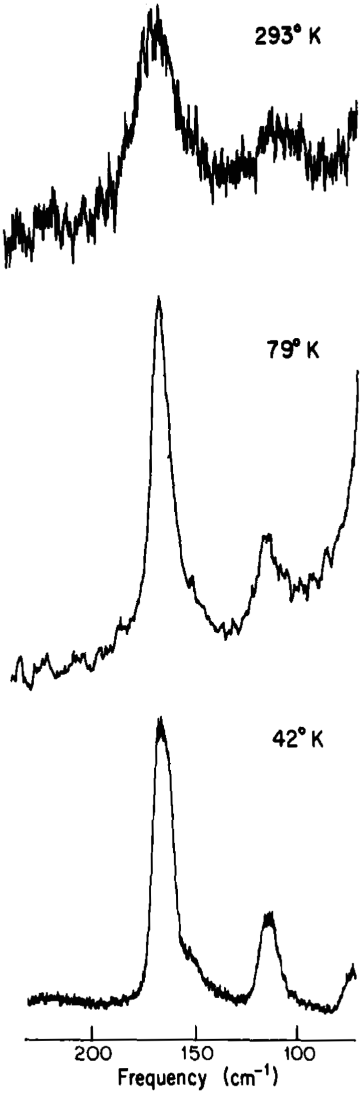

FIGURE 1 The Resonance Raman spectra in the region 70 cm^{-1} to 230 cm^{-1} for BIKI crystals at several temperatures are displayed.

sure dependence data on this system, as well as the lack of data on the thermal expansion of the BIKI crystal preclude any definite conclusion that can be derived regarding the anharmonicity using the temperature dependence of the vibrational frequency. However, the observed lack of any appreciable shift of the iodine frequencies, when the temperature is changed, may be interpreted that the nature of the iodine-iodine interaction (thus, the structure of the iodine species) does not change as a function of temperature. The thermal line broadening (related to T_2 relaxation of the iodine motions)[7] reveal considerable anharmonic interactions in the iodine column. However, as was pointed out earlier, there appears to be considerable width even at helium temperature which we relate to the presence of structural disorder in the iodine column. Our study of structurally disordered organic solids have shown that both the anharmonic interaction (other than thermal expansion) and the disorder contribute to the line width (T_2 relaxation) of the vibrational transition.[7–9] However, generally only the anharmonic contribution shows a temperature dependence.[8]

Now, we proceed to discuss the nature of the iodine species present. The Raman frequencies of the various iodine species in known polyiodine complexes have been reported by Marks.[10] In this review article, he reports a strong band at 162 cm^{-1} for a symmetric I_5^- and a strong band at 113 cm^{-1} for a symmetric I_3^-. Recently Teitelbaum *et al.*[11] have reported a Raman study of 2 Perylene • 3 I_2 complex where they see two prominent bands at 175 cm^{-1} and 115 cm^{-1}. These authors have suggested that two I_2 units are weakly coordinating and distorting an I_3^- ion. Thus, the presence of the species (I—I)$_2$---I--I—I was suggested to form by weak interactions between I_2 and I_3^-. In the BIKI system, the bands are at 167 cm^{-1} and 108 cm^{-1}. Thus the I_2 stretching frequency is further shifted to a lower value (167 cm^{-1} compared to 215 cm^{-1}). Actually, the value is much closer to the band observed for a symmetric I_5^-. This may indicate a stronger interaction between I_2 and I_3^- units compared to that observed in the 2 Perylene • 3 I_2 complex. Our results can be interpreted in terms of two models: (i) the presence of both symmetric I_5^- (167 cm^{-1}) band and I_3^- (108 cm^{-1}) band; (ii) that some of the I_3^- species are interacting with I_2 and forming an unsymmetric I_5^- species of the nature (I—I---I--I—I)$^-$.

BIKI, has been reported to have a repeating unit of I_{18}^{4-}. In view of this stoichiometry, the first model would require 3 I_5^- units per I_3^- unit. Note in figure 1 that the intensity of 167 cm^{-1} band is much stronger than the intensity of the 108 cm^{-1} band. The reflection spectra of BIKI reported by Mizuno and Tanaca[12] also suggest the presence of a symmetric I_5^- chain which favors the first model.

The second model, to account for the observed stoichiometry, would require the presence of both I_3^-/I_2 complex and I_3^-. We prefer this second model because when the sample is irradiated with a higher laser power, the relative intensity of the 167 cm^{-1} band exhibit a decrease with respect to the 108 cm^{-1} band. At the same time a band at ~218 cm^{-1} appears to grow in intensity. The band at 218 cm^{-1} is assigned to the I_2 species which can form when the complex I_2/I_3^- undergoes thermal dissociation. Additional support of this second model comes from the observed average iodine-iodine distances.[5,6] An idealized model for the iodine column has a 55.26 Å repeat distance with a formula unit of I_{18}^{4-}. When one considers the average distances in I_2 (2.67 Å), I_3^- (2.90 Å) and I_5^- (3.17 and 2.82), the best combination to obtain this 55.26 Å length would consist of 4 I_3^- and 3 I_2 molecules.

Support for this second model comes from our investigation of BIKI at various excitation wavelengths. Using a tunable dye laser, the relative intensity of the bands at 167 cm^{-1} and 108 cm^{-1} were studied at varying excitation wavelengths between 15880 cm^{-1} to 19430 cm^{-1}. If the iodine present in BIKI is of two entities, I_3^- and I_5^-, then one would expect a change in the relative ratios because each species has a different electronic absorption maxima. No observable change was found in the relative intensities for the two bands. Of course, the lack of any selective resonance enhancement can also be interpretted in terms of a broad absorption band which may arise from charge delocalization in the iodine column. This charge delocalization may be responsible for the broad metallic reflection which cover the visible spectral range. In order to investigate this aspect additional experiments are planned using photoacoustic spectroscopy.

To determine the effect of the solvent molecule on the iodine-iodine interactions, BIKI was grown from five solvents: chloroform, ether, methylene chloride, acetone and acetonitrile. The crystals obtained from these solutions were similar in color and habit. The spectra of these samples at 97°K (Band pass ~2 cm^{-1}) are shown in Figure 2. The frequencies of the major transitions did not appear to change. The solvent methylene chloride appeared to have the greatest effect on the iodine-iodine interactions. Not only is there a substantial increase of the width but there is a formation of a shoulder (175.5 cm^{-1}). While the crystals grown in acetonitrile also show the formation of a shoulder, this feature is now observed at a lower frequency (155.0 cm^{-1}) relative to the 162 cm^{-1} transition. It appears that these two solvents have caused the greatest perturbation on the iodine-iodine interaction. Crystals grown in acetone appeared to be most ordered with a FWHH of 8.4 cm^{-1}, followed by ether and chloroform. We conclude that although the solvent has no effect on the iodide species present in BIKI, it appears to affect the degree of disorder along the iodine chain and to some extent, the iodine-iodine interaction.

We have conducted studies on $(Benzophenone)_9(MI)_2I_7CHCl_3$ where $M^+ = NH_4^+, Na^+$. The spectra of these complexes are compared in figure 3. The complex formed with the NH_4^+ cation (BINI) shows transitions at 110 cm^{-1} and 165 cm^{-1} where as for the complex formed with the Na^+ cation (BINaI), the transitions are observed at 112.5 cm^{-1} and 164.5 cm^{-1}. The spectral features of these two complexes resemble that observed for BIKI. These results suggest that cation substitution from NH_4^+, to K^+ or to Na^+ has a small effect on the nature of the iodine-iodine interactions.

When Li^+ is substituted for K^+, a new stoichiometry is found:[6] $(Benzophenone)_4(LiI_5)$ (abbreviated BILI). While this newest complex is also grown from chloroform solution, the solvent molecule is not included in this lattice.[6]

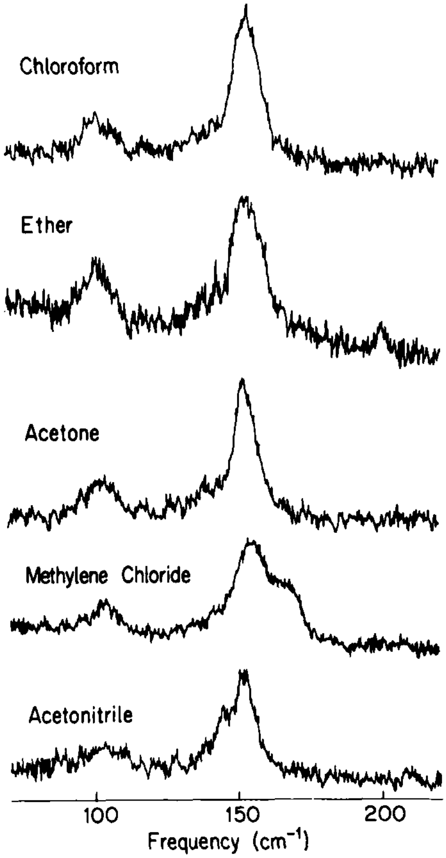

FIGURE 2 The 97°K Raman spectra of BIKI crystals grown from different solvents.

BILI has a different color and habit than BIKI. The spectra of this new complex are also shown in Figure 3. Differences in the spectra and, thus, in the iodine interaction between BILI and BIKI are evident. For BILI, there is a doublet with values of 153 cm^{-1} and 167 cm^{-1}. The transitions are considerably sharper than that observed for BIKI. This observation is indicative of a more ordered structure. The difference in the iodine species between BILI and BIKI may arise from the difference in the co-ordination of the Li^+ and the K^+.

BILI is unique not only in color and spectral features but also in that a spectrum may be obtained from the metallic side. BILI was mounted on a goniometer and the signal was observed at four angles; 0°, 45°, 90° and 180°. The relative intensities of these two peaks remained constant at the different angles and were identical to that observed for the face perpendicular to the iodine column. These results are indicative of the two dimensional structure of the

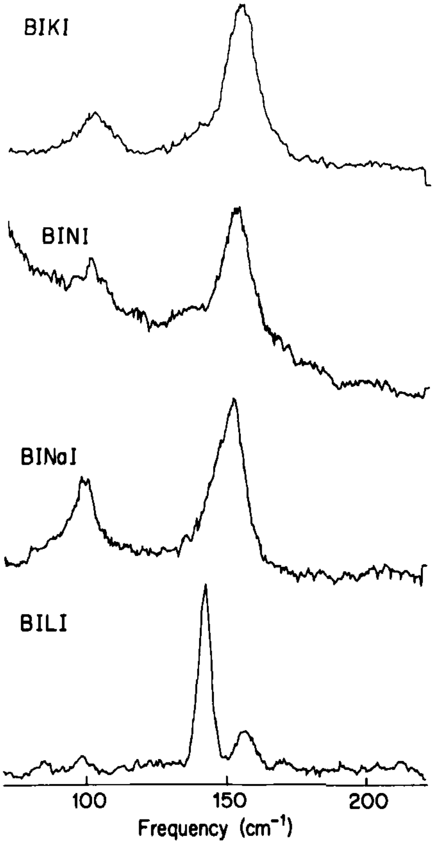

FIGURE 3 Raman spectra at 97°K of the complexes (Benzophenone)$_9$(MI)$_2$I$_7$CHCl$_3$ with M$^+$ = K$^+$, NH$_4^+$ and Na$^+$ are displayed together with that of (Benzophenone)$_4$ (LiI$_5$).

iodine column. Crystallographic data confirmed the two dimensional data of BILI.[6] The crystallographic work of Leung[6] *et al.* shows that BILI contains I$_5^+$ ions which are strongly bent with an angle of 105° at the central iodine atom and an asymmetry in the I—I distances.

It should be noted that two bands are observed for BILI. BILI contains an unsymmetrical I$_5^-$ species. In CsI$_3$, the triiodide units are distorted (I—I = 2.83(2) and 3.03(2) Å). In the Raman spectrum of CsI$_3$, the lower symmetry gives rise to two ν_{I-I} bands.[10] We believe that the two bands observed for BILI are a result of the unsymmetrical nature of the iodine species.

Crystals were grown with 50% molar concentration of NH$_4$I and KI or 50% molar concentration of NaI and KI. The spectra of these two complexes showed a small difference in frequency. The FWHH were nearly identical. An attempt was made at growing a 50% molar concentration of KI and LiI. After the solvent evaporated, BILI and BIKI had segregated.

CONCLUSIONS

The summary of our findings is as follows. Our temperature dependence results of BIKI show that the structure of the iodine species does not change as a function of temperature. No phase transition is observed below room temperature. The broad nature of these transitions in BIKI show considerable anharmonic interactions and disorder in the iodine column. The nature of the iodine species can be explained by the presence of both I_3^-/I_2 complex and I_3^-. This model would be consistent with the observation of thermal dissociation of the I_2/I_3^- complex. In addition, the two transitions in BIKI show no change in relative intensity with varying excitation wavelength.

The solvent substitution does not change the nature of the iodine species present in BIKI, but it does appear to affect the degree of disorder along the iodine chain. Complexes obtained by changing the cation from K^+ to NH_4^+, Na^+ are identical in the nature of the iodine species present. On the other hand, Li^+ yields a complex with a different iodine species. Substitutional disorder (mixed crystals) with respect to the cation has no significant effect on the nature of the iodine-iodine interactions or the degree of disorder along this chain.

Acknowledgments

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References

1. W. A. Little, *Phys. Rev.*, **134**, A1416 (1964).
2. A. M. Clover, *Am. Chem. J.*, **31**, 256 (1904).
3. H. I. Kao, Ph.D. Thesis, Temple University, Philadelphia.
4. M. M. Labes, M. Jones, H. I. Kao, L. Nichols and C. Hsu, *Mol. Cryst. Liq. Cryst.*, **52**, 115 (1979).
5. P. Coppens, Abstract, ACS Meeting, Honolulu, 1979.
6. P. Leung, R. F. Boehme and P. Coppens, companion paper.
7. P. N. Prasad, *Mol. Cryst. Liq. Cryst.*, **58**, 39 (1980).
8. P. N. Prasad and R. V. Smith, *J. Chem. Phys.*, **71**, 4646 (1979).
9. J. C. Bellows and P. N. Prasad, *J. Chem. Phys.*, **70**, 1864 (1979).
10. T. J. Marks, *Annals New York Acad. of Sci.*, 594 (1978).
11. R. C. Teitelbaum, S. L. Ruby and T. J. Marks, *J. Am. Chem. Soc.*, **101**, 7568 (1979).
12. M. Mizuno and Tanaca, Abstract, ACS Meeting, Honolulu, 1979.