2680 © 1987 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 60, 2680—2682 (1987) [Vol. 60, No. 7

Raman Spectra of the Organic Conductor, (TTM-TTF)I$_{2.47}$

Kikujiro Ishii,* Hideyuki Nakayama, Peiji Wu,† Takehiko Mori,†
Toshiaki Enoki,† Kenichi Imaeda,† Gunzi Saito,††
and Hiroo Inokuchi†
Department of Chemistry, Faculty of Science, Gakushuin University,
Mejiro, Toshimaku, Tokyo 171
†Institute for Molecular Science, Myodaiji, Okazaki 444
††Institute for Solid State Physics, The University of Tokyo,
Roppongi, Minatoku, Tokyo 106

(Received February 16, 1987)

Synopsis. The Raman spectra of a highly conductive molecular complex of the title were measured. The I_3^- symmetric stretching band and its well-known overtones were observed, indicating that the formula for this complex should be written as (TTM-TTF)$(I_3)_{0.823}$. A brief discussion is given comparing the spectra of the present complex with those of TMA-I-TCNQ and (BEDT-TTF)$_2$I$_3$ complexes.

Organic conductors containing trihalide ions have attracted the attention of many workers[1] since the discovery of the ambient pressure organic superconductor, β-(BEDT-TTF)$_2$I$_3$.[2] The intermolecular interactions through the sulfur atoms of BEDT-TTF(hereafter, ET) may, of course, be important in endowing this crystal with high conductivity. However, the role played by I_3^- ions should not be overlooked, since some similar ET complexes containing similar halide ions have been found to become superconducting.[3]

The structure and various properties of the iodine complex of TTM-TTF, tetrakis(methylthio)tetrathiafulvalene, were previously reported.[4] TTM-TTF has eight sulfur atoms, similarly to ET. The iodine complex, (TTM-TTF)I$_{2.47}$, is metal-like at room temperature, but becomes insulating at low temperatures below 100 K. The iodine atoms were found to make a fairly ordered sublattice which is incomensulate to the TTM-TTF lattice. However, the structure of the iodine sublattice has not yet been clarified.

In this note, we report on the Raman spectra of (TTM-TTF)I$_{2.47}$. The results comprise essentially the typical resonance Raman spectra of I_3^- ions.[5] Thus, the formula for the present complex should be written as (TTM-TTF)$(I_3)_{0.823}$. The frequencies and the band structures found for the I_3^- bands of the present complex are significantly different from those of the ET-complexes.[6] A brief discussion is given regarding the vibrational state of I_3^- ions.

Experimental

Black thin plate crystals of (TTM-TTF)I$_{2.47}$ were obtained by previously described methods.[4] These were apparently bundles of needle crystals. The crystal b axis is known to correspond to the needle axis.[4]

The Raman spectra were measured with a SPEX 1403 monochromater equipped with a Hamamatsu R-649 photomultiplier. Data were recorded with a convensional photoncounter in combination with a personal computer. An Oxford DN1704 cryostat was used between 89 K and room temperature. The samples were mounted in a nitrogen atmosphere. The 501.7 nm line from an NEC GLG-3201 Ar-ion laser was used as the excitation source with a grazing angle of about 20°. The Raman light was collected in the direction perpendicular to the incident light. To avoid any decomposition of the sample by the local heating, the incident light was attenuated to a power below 3 mW for measurements at low temperatures and below 1 mW at room temperature. The sample temperature was estimated with an alumel-chromel thermocouple which was placed near the sample surface.

Results and Discussion

Figure 1 shows the wide-scan spectrum at 89 K with the incident-light polarization parallel to the b axis and a spectral resolution of 1.8 cm^{-1}. A series of bands (No. 1—5) are seen with almost the same separations of about 108 cm^{-1}; the wavenumber of each band is listed in Table 1. For bands 1 and 2, solid curves were drawn for eyes guides. Some strong and sharp bands observed in addition to bands 1—5 are the plasma lines coming from the Ar-ion laser.

Bands 1—5 can obviously be assigned to the fundamental and overtone bands of the symmetric stretching mode of I_3^- ions.[5] The unusually strong intensities of the overtone bands, and the fact that

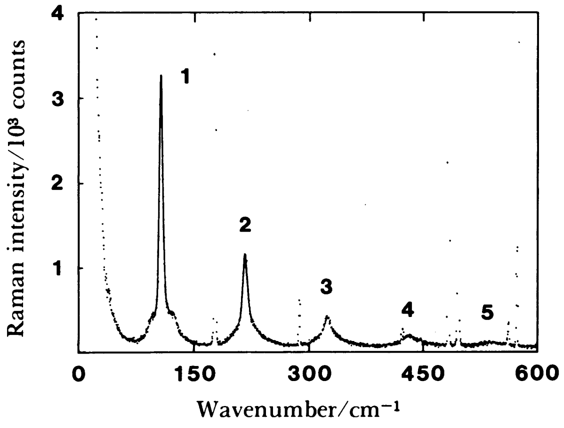

Fig. 1. Raman spectrum of (TTM-TTF)I$_{2.47}$ complex at 89 K.

Table 1. Raman Frequencies of the Fundamental and Overtone Bands (cm^{-1})

(TTM-TTF)I$_{2.47}$ (89K)	107.0 109.7	$216._7$	324	432	≈538
TMA-I-TCNQ (15K)[7]	110	218	327	435	544

only the I_3^- bands and no TTM-TTF band was observed, are attributed to the resonance Raman effect.[5] The fact that the spectra were observed with b-polarized incident light and not with the polarization perpendicular to this, indicates that the I_3^- ions exist with their molecular axis parallel to the b axis. This is because the intensity is enhanced by resonance with the electronic transition $\sigma_g \rightarrow \sigma_u^*$.[7] These results are in accordance with the result of the X-ray analysis.[4]

Details of band 1, measured with a spectral resolution of 0.6 cm^{-1}, is presented in Fig. 2. Band 1 apparently comprises two substructures. By assuming Lorentzian shapes, their frequencies were estimated to be 107.0 and 109.7 cm^{-1}, respectively, and the apparent width of either substructure to be 2.8 cm^{-1}. One possibility of the cause of this splitting is a factor-group splitting due to intermolecular interactions between I_3^- ions in the iodine sublattice. However, the polarization behaviors of the above substructures are almost the same, and we could not obtain any experimental evidence of this possibility. The fact that the structure of the iodine sublattice is inferred to be complicated, with 16 I_3^- ions in the unit cell and incommensurate to the TTM-TTF sublattice,[4] also excludes the above possibility of a simple factor-group splitting. Another possibility is that there exist roughly two kinds of I_3^- ions in the crystal, although a variety of environments of I_3^- ions must exist owing to the incommensuration. The relative ratio of the intensities of the substructures is about 2.5. This is not a ratio simply related to the structure of the iodine sublattice, and might manifest slightly different resonance effects for the different I_3^- ions.

The overtone frequencies are almost multiples of that of band 1. However, these frequencies are slightly larger than the multiples of the frequency of the main substructure of band 1. Bandrauk et al.[8] observed a regular sequence of overtone frequencies of I_3^- bands for TMA-I-TCNQ with a slight indication of anharmonicity (Table 1). In their case, the higher-order Raman processes could be assigned to multi-quantum excitations in the same vibrational mode. However, for explaining the frequencies of our overtones, we must assume that not the main substructure of band 1 but the smaller substructure gives the second-order band, or that the second-order process involves both the two modes which give these two substructures, respectively. Note that the peak frequency of band 2, 216.7 cm^{-1}, is comparable with the sum of 107.0 and 109.7 cm^{-1}, the frequencies of the substructures of band 1. An example, in which the peak of a second-order Raman band is located at a frequency higher than twice the most prominent fundamental band, is found for crystalline iodine.[9] In this case, the apparent shape of the second-order band is interpreted by a double phonon generation on the factor-group-splitted two phonon branches in the whole area of the Brillouin zone. In our case, the vibrations participating the higher-order Raman processes might not be those arising from the factor-group splitting. However, it is very likely that these processes involve the vibrations on different molecules or the vibrations delocalized over the molecules.

Figure 3 shows the temperature dependences of the frequencies of bands 1 and 2. As the temperature is raised, both bands decrease their frequecies almost monotonically within the experimental error. Such temperature shifts of low-frequency intramolecular vibrations are considered to occur by a coupling with the lattice vibrations and sometimes seen for molecular crystals. It has been inferred in connection with the metal-insulator transition around 100 K that the degree of the charge transfer would be slightly changed depending on the temperature.[4] The present Raman results do not answer this problem, but we can say that the vibrational states are not greatly affected by the temperature change.

The frequency of the fundamental band observed here is slightly smaller than of I_3^- in solution[5] or in TMA-I-TCNQ,[8] but it is not unusual as compared with other semicondutive iodine complexes.[7] Recently, the corresponding frequencies of the α and β forms of ET-iodine complexes were found to be 117 and 122 cm^{-1}, respectively at 80 K.[6] These are remarkably larger than those of other I_3^- complexes, and considered to manifest a tight crystal field around the I_3^- ions in these complexes.

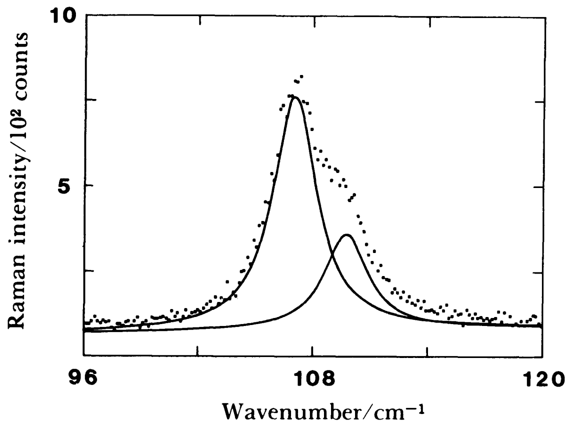

Fig. 2. Detail of band 1 with the resolution of 0.6 cm^{-1}. Solid lines are the assumed substructures.

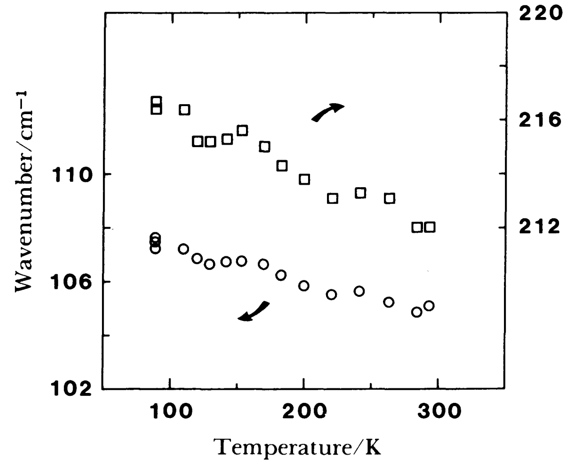

Fig. 3. Temperature dependences of the frequencies of bands 1 and 2.

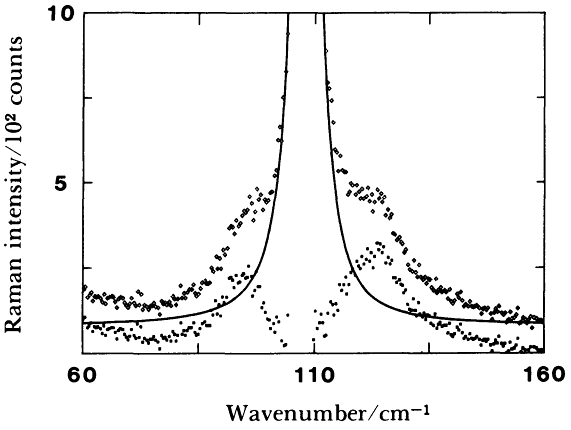

Fig. 4. Structure of the side bands accompanying band 1. Solid line is the assumed band shape of band 1, and closed squares are the difference spectrum giving the side bands.

Two side bands appear at the tail of band 1 (Fig. 1). This feature is very similar to that of TMA-I-TCNQ.[8)] Similar side bands were also observed for the ET-complexes, and were attributed to the coupled excitations between the stretching and librational modes of I_3^- ions.[6)] These assignments are plausible since the separations of the bands from the fundamental band are almost the same as the low-frequency bands appearing around 30 cm^{-1} in their spectra. In the cases of (TTM-TTF)$I_{2.47}$ and TMA-I-TCNQ, the separations of the side bands from the fundamental band are much smaller. Details of the side bands of our complex at 89 K are presented in Fig. 4, in which the spectrum is decomposed by assuming a Lorentzian shape for the fundamental band. The frequencies of these side bands were estimated to be 94 and 123 cm^{-1}, respectively. Then, the separations from the main substructure of band 1 are 13 and 16 cm^{-1}, respectively. No band appears in the 30 cm^{-1} region in both the (TTM-TTF)$I_{2.47}$ and TMA-I-TCNQ spectra. Thus, it is very likely that the librational frequencies of I_3^- ions in these complexes are as small as 15 cm^{-1}, much smaller than those in the ET-complexes. This indicates a large difference between the crystal fields in these two types of complexes.

The superconduction mechanism in the ET-complexes has not yet been clarified. However, it is likely that the Coulomb field produced by the halide ions or their large polarizability play important roles in the superconduction. Thus, it is worth noting that the frequencies of the optical phonons involving I_3^- ions in the ET-complexes are much larger than those in (TTM-TTF)$I_{2.47}$ or TMA-I-TCNQ, which are insulating at low temperatures.

References

1) See for instance, P. C. W. Leung, T. J. Emge, A. J. Schultz, M. A. Beno, K. D. Carlson, H. H. Wang, M. A. Firestone, and J. M. Williams, *Solid State Commun.*, **57**, 93 (1986).

2) E. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin, and L. I. Buravov, *Pis'ma Zh. Eksp. Teor. Fiz.*, **39**, 12 (1984); see also, K. Murata, M. Tokumoto, H. Anzai, H. Bando, G. Saito, K. Kajimura, and T. Ishiguro, *J. Phys. Soc. Jpn.*, **54**, 2084 (1985).

3) H. H. Wang, M. A. Beno, U. Geiser, M. A. Firestone, K. S. Webb, L. Nunez, G. W. Crabtree, K. D. Carlson, J. M. Williams, L. J. Azevedo, J. F. Kwak, and J. E. Schirber, *Inorg. Chem.*, **24**, 2465 (1985).

4) P. Wu, T. Mori, T. Enoki, K. Imaeda, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **59**, 127 (1986).

5) W. Kiefer and H. J. Bernstein, *Chem. Phys. Lett.*, **16**, 5 (1972); K. Kaya, N. Mikami, Y. Udagawa, and M. Ito, *ibid.*, **16**, 151 (1972).

6) S. Sugai and G. Saito, *Solid State Commun.*, **58**, 759 (1986).

7) M. Mizuno, J. Tanaka, and I. Harada, *J. Phys. Chem.*, **85**, 1789 (1981).

8) A. D. Bandrauk, K. D. Truong, C. Carlone, and S. Jandl, *Chem. Phys. Lett.*, **95**, 78 (1983).

9) B. V. Shanabrook and J. S. Lannin, *Solid State Commun.*, **38**, 49 (1981).