November, 1990] © 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 3277—3281 (1990) 3277

Behavior of I_2 and I_3^- Molecular Units Near the Crystal Surface of CsI and Related Polyiodides. Raman-Spectroscopic Studies

Kazumasa Odagi, Hideyuki Nakayama, and Kikujiro Ishii*
Department of Chemistry, Gakushuin University,
Mejiro 1-5-1, Toshimaku, Tokyo 171

(Received May 31, 1990)

Raman spectra of CsI_3 and Cs_2I_8 crystals were measured for the samples whose structures were carefully examined. The surface of Cs_2I_8 samples was found to turn into CsI_3 when they were kept in air. The heating effect of laser irradiation was shown to change the spectra of Cs_2I_8 samples to those of CsI_3. These results imply that diffusion of iodine molecules occurs in polyiodide crystals. Then, we monitored the reaction of CsI crystals with iodine vapor, and found that iodine makes the layers of CsI_3 and Cs_2I_8 on the surface of CsI crystals. It was also found that nearly free I_3^- ions are generated near the surface of samples during both the thermal decomposition of Cs_2I_8 and the reaction of CsI with iodine vapor.

Iodine forms polyatomic ions represented by I_n^- (n=3,5,7,···). These ions are called polyiodide ions and have been inferred to exist, for example, in a mixed solution of KI and I_2 in water.¹⁾ A variety of molecular conformations of polyiodide ions have been found to exist in solid states.²⁾ Raman and Mössbauer spectroscopies have been shown to be useful in studying the structure of polyiodide ions.²⁾

In the Raman spectroscopy of crystals containing polyiodide ions, the most serious problem is that the crystals have almost black colors and hence absorb the excitation-laser light. This brings about an experimental restriction that the excitation-light power must be kept very low to avoid local heating and decomposition of the sample. The Raman measurements on these crystals are also difficult because of the fact that the thickness, through which the excitation or scattered light can pass, is small. This means that an observed spectrum reflects the structure near the surface which is sometimes different from that of the bulk. Therefore, we must be careful of the structure near the surface when we interpret Raman spectra of polyiodide crystals.

In the course of a Raman study of CsI_3 crystals, we were involved in a problem of irreproducibility of spectra. It was found later that the composition of the sample was sometimes not of the expected CsI_3 but of Cs_2I_8, and that the surface of Cs_2I_8 crystals was changed by exposure to air or by laser irradiation. Then, we studied carefully structures and Raman spectra of cesium polyiodide crystals.

In this paper, we first report the Raman spectra of CsI_3 and Cs_2I_8 crystals whose structures were carefully examined. It is next shown that the spectra of Cs_2I_8 crystals are changed by the increase in the laser-light power. Another spectral change is shown to occur when CsI crystals are exposed to iodine vapor. These results indicate that the diffusion of iodine molecules easily occurs near the surface of iodide crystals. It is pointed out that nearly free I_3^- ions are generated during the process of the structural transformation near the surface.

Experimental

CsI (reagent grade, Yanagishima Pharmaceutical Co.) was used for syntheses without purification. Iodine (reagent grade, the same company) was purified by sublimation. CsI_3 was crystallized from an equimolar solution of CsI and I_2 in ethanol.³⁾ Cs_2I_8 was synthesized from CsI and iodine in water in a sealed glass tube.⁴⁾ Large colorless crystals of CsI were obtained from its aqueous solution by slowly evaporating water in nitrogen atmosphere at room temperature.

Powder X-ray diffraction patterns of the samples were measured with a Rigaku 2027 diffractometer. Thermal properties were studied by differential scanning calorimetry (DSC) with a Du Pont 910 calorimeter.

Raman measurements were carried out at room temperature with the same apparatus as reported in our previous paper.⁵⁾ The 514.5 nm radiation from an Ar^+-ion laser was used as the excitation light except in the measurement on I_3^- ions in solution. The 441.6 nm radiation from an He-Cd laser was used in the latter measurement. Laser power was measured with a power meter, Japan Lasers Co., JLP-03. The geometry of back-scattering was used in the measurements on crystalline samples, but the crystal faces of the samples were not identified. The scattered Raman light with all polarizations was collected. The spectrum of I_3^- ions in solution was measured in a glass capillary using a methanol solution of KI and I_2 with the concentrations of 0.7 and 2×10^{-3} mol dm^{-3}, respectively. The other conditions of the measurement will be described later individually.

Results and Discussion

Syntheses of CsI_3 and Cs_2I_8 and Decomposition of Cs_2I_8 in Air. It has been reported⁶⁾ that CsI_3 crystals were synthesized by the reaction between CsI and I_2 in water with a little excess amount of I_2. We first tried this method to make CsI_3. Some of the crystals thus obtained gave the Raman spectra reported for CsI_3.²⁾ However, we observed different spectra for some other crystals similarly obtained. We noticed that the latter spectra were similar to that reported for Cs_2I_8.⁷⁾ It was verified by X-ray diffraction and DSC that most of the crystals obtained by the above synthesis were Cs_2I_8. Then, it was inferred that the surface of Cs_2I_8 turned into CsI_3 by exposure to air and that only the substance near the surface contributed to the Raman spectra.

To make sure the structure of the samples, we carefully prepared CsI_3 and Cs_2I_8 crystals by employing the synthesis methods described in the experimental section. The powder X-ray diffraction patterns of the products (Patterns C and A in Fig. 1) coincided with the data calculated from the crystallographic data of CsI_3 and Cs_2I_8, respectively.[3,4] CsI_3 showed no anomaly in the DSC pattern below 210 °C, around which it decomposed giving an exothermic peak.† Cs_2I_8 showed a small endothermic peak around 140 °C, and then, it gave an exothermic peak around 210 °C similarly to CsI_3. These thermal behaviors of CsI_3 and Cs_2I_8 are in harmony with the reported ones.[4,6]

We next studied the decomposition of Cs_2I_8 crystals by X-ray diffraction. Pattern A in Fig. 1 is for a freshly prepared powder sample of Cs_2I_8, and B is for the same sample 30 min later. There appear some new peaks indicated by arrows in Pattern B. These are just the peaks attributed to CsI_3 as seen in Pattern C. Thus, it was verified that Cs_2I_8 crystals turn into CsI_3 in air. This result is easily understood from the crystal structure of Cs_2I_8 in which I_2 molecular units exist between the I_3^- units.[4] These I_2 units are inferred to sublime easily into air. Since the Raman spectra of such substances are dominated by the structure near the surface, we thus found the reason why we observed the spectra of CsI_3 for the samples which had the strucutre of Cs_2I_8 in the bulk.

Raman Spectra of CsI_3 and Cs_2I_8 Crystals. The Raman spectra of CsI_3 and Cs_2I_8 crystals were measured for the samples carefully prepared as described above. To avoid the decomposition of the samples by the irradiation of laser light, the light power was kept at about 1 mW with a focusing radius of about 0.1 mm. In the case of Cs_2I_8, in addition, the measurement was performed without taking the sample out of the glass tube for the synthesis. Figure 2 shows the spectra thus obtained as well as the spectrum of I_3^- ions in the solution.

The Raman band at 110 cm^{-1} of the I_3^- ions in solution (Spectrum C) arises from the symmetrical stretching vibration, and the band around 220 cm^{-1} is its overtone.[8] The bands of CsI_3 (Spectrum A) around 100 cm^{-1} and that of Cs_2I_8 (Spectrum B) at 104 cm^{-1} are

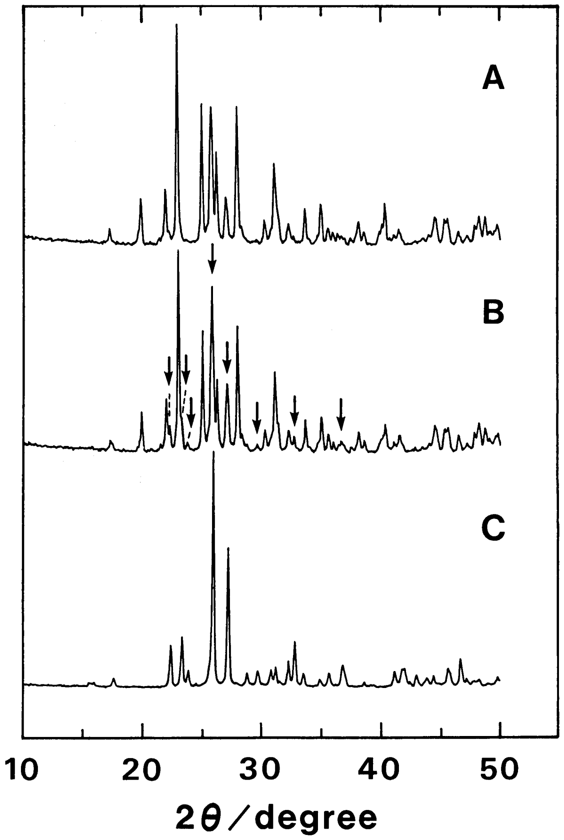

Fig. 1. X-Ray powder diffraction patterns recorded against the diffraction angle 2θ; A: freshly prepared sample of Cs_2I_8, B: the same sample 30 min later, C: CsI_3.

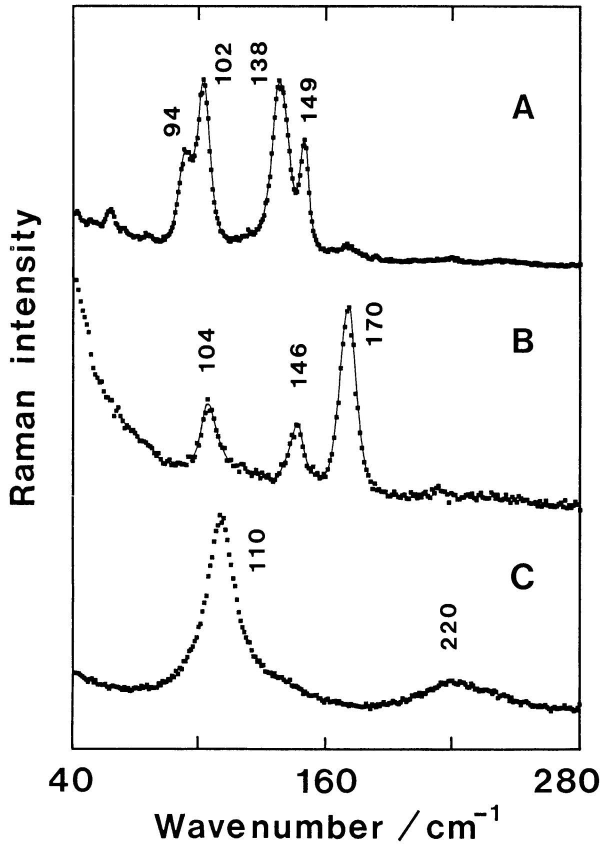

Fig. 2. Raman spectra of A: CsI_3, B: Cs_2I_8, and C: a solution of KI and I_2 in methanol. Spectrum C was measured with the 441.6 nm radiation from an He-Cd laser. All other spectra were measured with the 514.5 nm radiation of an Ar^+-ion laser.

---

† The reaction between the aluminum container for the measurement and the iodine which evaporated from the sample is considered to have given the exothermic peak.

attributed to the corresponding modes. The bands of CsI_3 around 140 cm^{-1} and that of Cs_2I_8 at 146 cm^{-1} are, on the other hand, attributed to the antisymmetrical stretching vibrations of I_3^- units. These antisymmetrical vibrations are Raman active because the I_3^- units have highly asymmetric bond distances in these crystals.[3,4]

The band of Cs_2I_8 at 170 cm^{-1} is attributed to the I_2 unit inserted between two I_3^- units. The wavenumber of this band is smaller by 10—19 cm^{-1} than the corresponding bands of the iodine crystal.[9] This implies that the I_2 unit in the Cs_2I_8 crystal slightly bears negative charge, and is in accordance with the longer bond distance of I_2, 2.83 Å,[4] than that in the iodine crystal, 2.715 Å (at 110 K).[10] The features of the spectra of Cs_2I_8 were reproduced with samples immersed in carbon tetrachloride which was nearly saturated with iodine. This verifies that Spectrum B in Fig. 2 is not affected by the heating effect of laser light.

The splittings of the bands of CsI_3 are explained in terms of the strong interactions between the I_3^- units in this crystal.[3] The corresponding splittings of Cs_2I_8 are not observable at room temperature. This is in harmony with the fact that the interaction between two I_3^- units is blocked by the central I_2 unit.[4] The Raman spectra of CsI_3 and Cs_2I_8 crystals shown in Fig. 2 are essentially the same as those reported for these crystals,[2,7] although nothing has been described about the detail of the samples in these papers.

Change in Raman Spectra of Cs_2I_8 Samples with Increase in Excitation Laser Power. As previously described, we sometimes observed strange spectra for Cs_2I_8 samples. To clear up the cause of this, we measured the spectra of Cs_2I_8 crystals by changing the incident laser power. These measurements were carried out without taking the samples out of the glass tube. The light powers indicated below are corrected for the attenuation by the glass wall. Figure 3 shows a representative series of the results.

Spectrum A obtained with a laser power of 1.2 mW is essentially that of Cs_2I_8, although the intensity of the 146 cm^{-1} band is relatively small compared with those of the 104 and 170 cm^{-1} bands. The band observed at 213 cm^{-1} is a resonance fluorescence band of I_2 vapor[11] which is considered to have existed in the glass tube.

When the laser power was increased to 1.9 mW, the spectrum suddenly changed showing a strong band at 110 cm^{-1} (Spectrum B). Judging from the high intensity of its overtone similar to Spectrum C in Fig. 2, Spectrum B in Fig. 3 is considered to arise from I_3^- ions with almost a symmetric structure. If I_3^- ions were accommodated in some regular crystal lattices containing Cs^+ ions, they would tend to have distorted structures such as are in fact seen in CsI_3 and Cs_2I_8 crystals. Therefore, the I_3^- ions giving Spectrum B in Fig. 3 may be rather free I_3^- ions in a disordered region generated by the heating effect of the laser light. However, these I_3^- ions are considered not to be as free as in solutions, since they seem to show a resonance Raman effect with the 514.5 nm excitation. This inference is based on the fact that symmetric I_3^- ions in many crystalline substances show the resonance Raman effect at 514.5 nm[12] while those ions in solutions do not show this effect prominently at this wavelength.[8]

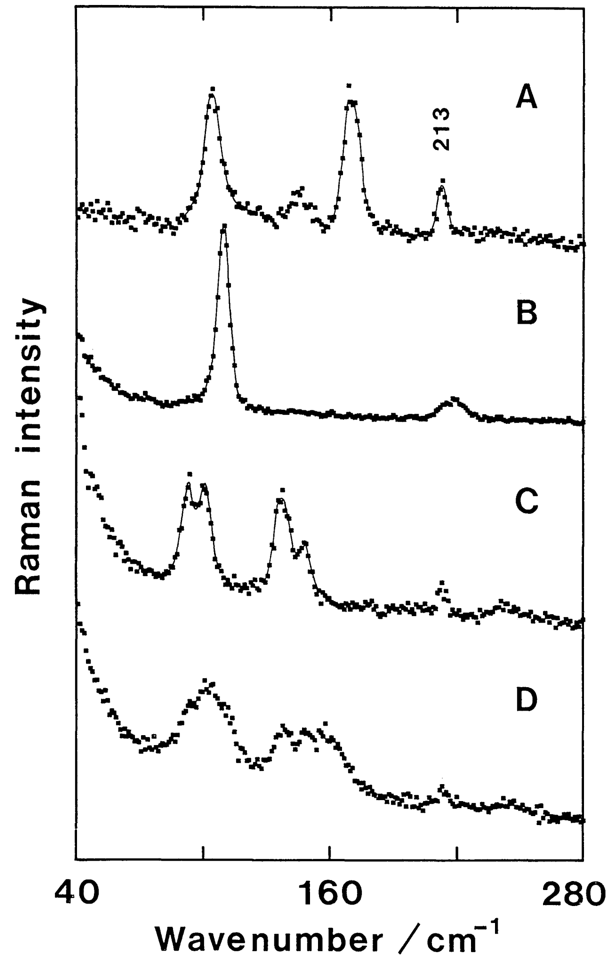

Fig. 3. Change of Raman spectra of a Cs_2I_8 sample with the increase of the incident laser power; A: 1.2 mW, B: 1.9 mW, C: 2.2 mW, and D: 3.3 mW.

On increasing the laser power to 2.2 mW, we observed Spectrum C in Fig. 3 which is similar to that of CsI_3 (Spectrum B in Fig. 2). Therefore, the iodine content in the laser-irradiated region is considered to have decreased by losing the I_2 units of the Cs_2I_8 crystal. The spectrum was broadened as shown by Spectrum D when the laser power was increased to 3.3 mW. At this stage, the laser-light scattering from the sample surface became unstable, which suggests an unstable local structure of the surface. No reproducible spectrum was obtained after this.

The above evolution of Raman spectra of Cs_2I_8 samples by the increase in the laser power was almost reproducible, although the laser power at which each spectral feature was observed was different for different samples, probably depending on the surface state and/or the condition of the laser forcusing. Thus, we verified another reason why we sometimes observed irreproducible Raman spectra for polyiodide crystals when we were not careful enough about the condition of the laser irradiation. The above results are also important in that they indicate that the diffusion of I_2 molecules occurs rather easily in polyiodide crystals and that nearly free I_3^- ions appear during the structural transformation of the polyiodide lattices.

Diffusion of I_2 Molecules into CsI Crystal—*In Situ* Observation by Raman Spectra. Since it was found that the diffusion of I_2 molecules occurs rather easily near the surface of polyiodide crystals, we next tried to monitor their diffusion into CsI crystals. The experiment was performed using an evacuated glass tube with two parts separated by a breakable seal made of a thin glass capillary. A large colorless crystals of CsI and a powder of iodine were set separately in these two parts. A Raman measurement was performed *in situ* through the glass wall. The laser power was about 1 mW except for the measurement of the final spectrum. Figure 4 shows the spectra thus obtained.

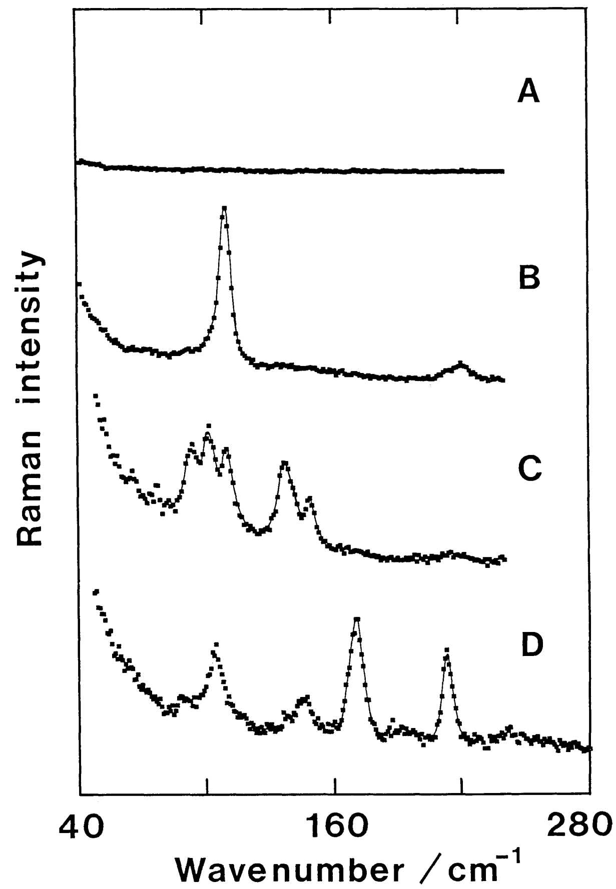

Fig. 4. Evolution of Raman spectra of a CsI sample exposed to iodine vapor; A: before the start of the reaction; B: 4 h, C: 12 h, and D: four months, after the start, respectively. Spectra A, B, and C were obtained with a laser power of 1 mW, while Spectrum D was obtained with that of 0.4 mW.

The original CsI crystal does not give Raman bands due to its symmetry as shown by Spectrum A. The reaction between the CsI crystal and iodine vapor was initiated when the breakable seal was broken. Then, the CsI crystal started to color. First, it was pale yellow, and a small band appeared at 110 cm^{-1}. Its intensity continued to increase as shown by Spectrum B (4 h after the start). After this, new bands appeared in the 100 and 140 cm^{-1} regions, and the band at 110 cm^{-1} began to decrease its intensity. Spectrum C shows the state of the sample 12 h after the start. The spectra which were dominated by the bands in the 100 and 140 cm^{-1} regions were observed for a long time even four months after the start as far as we used a laser power of 1 mW. However, with a smaller laser power (0.4 mW), we observed Spectrum D four months after the start.

The 110 cm^{-1} band seen in Spectrum B in Fig. 4 is obviously attributed to the symmetric I_3^- ions (Spectrum C in Fig. 2) which are not fixed in the cesium iodide lattice. These ions are considered to be produced by the reaction between I^- in CsI and the adsorbed I_2 molecules. The color change from colorless to brown is explained in terms of the production of I_3^- ions.

The new bands seen in Spectrum C are obviously the same as those seen for the CsI_3 crystal (Spectrum A in Fig. 2). Therefore, the spectral change from B to C implies that a regular lattice of CsI_3 was built when a certain amount of I_3^- ions were produced on the surface of the sample. Such a layer of CsI_3 is considered to increase its thickness as I_2 molecules diffuse into the bulk of the CsI crystal.

Spectrum D in Fig. 4 is almost the same as that of Cs_2I_8 (Spectrum B in Fig. 2) except the band at 213 cm^{-1} arising from the fluorescence of iodine vapor.[11] Since the Raman light was focused at a small orifice before it was introduced into the monochromator, this fluorescence came from iodine vapor near the forcusing point of the sample surface. By our experience in the experiment on the laser-power dependence of the spectra, the very sensitive laser-power dependence at this stage is considered to indicate that a very thin layer of Cs_2I_8 had been developed on the surface.

By cleaving the sample four months after the start, a black layer with a thickness only of several ten microns was found to have been produced on the surface. This layer is considered to be made mainly of CsI_3. Then, the thickness of the Cs_2I_8 layer which had been produced on the top of the sample surface is inferred to be the order of micron.

The absorption of halogen gases by alkali-halide crystals has been studied by weighing the mass of samples, and the absorption rate of iodine has been found to be very small.[13] Our results qualitatively confirm these observations. However, the importance of our results is that the reaction at the crystal surface was monitored by observing Raman spectra, and that the generation of nearly free I_3^- ions was found to occur in the initial stage of the reaction between CsI and iodine vapor. These I_3^- ions are considered to be placed in a disordered environment and gradually make the crystalline layer of CsI_3. Then, a thin layer of Cs_2I_8 is considered to be made finally when the supply of iodine vapor exceeds the diffusion of iodine into the bulk of the sample. The fact that the fluorescence of iodine vapor was observed under the condition in which the spectra of Cs_2I_8 were observable (see also Spectrum A in Fig. 3), supports this inference on the steady state of the iodine vapor pressure near the focusing point.

The authors thank Professor Masahiro Kotani for permitting them to use the He-Cd laser. They also thank Ms. Hitomi Watanabe and Mr. Gako Araki who checked the reproducibility of the reaction between CsI and iodine vapor. The X-ray and thermal measurements were carried out at Instrument Center, Institute for Molecular Science.

References

1) See, for instance, W. L. Jolly, "The Chemistry of the Nonmetals," Princeton-Hall, Inc., Englewood Cliffs (1966).

2) T. J. Marks and D. W. Kalina, "Extended Linear Chain Compounds," ed by J. S. Miller, Plenum Press, New York (1982), Vol. 1, p. 197.

3) J. Runsink, S. Swen-Walstra, and T. Migchelsen, *Acta Crystallogr., Sect. B*, **28**, 1331 (1972).

4) E. E. Havinga, K. H. Boswijk, and E. H. Wiebenga, *Acta Crystallogr.*, **7**, 487 (1954).

5) H. Nakayama and K. Ishii, *Chem. Phys.*, **114**, 431 (1987).

6) A. I. Popov and R. E. Buckles, *Inorg. Synth.*, **5**, 167 (1957).

7) T. J. Marks, *Ann. N. Y. Acad. Sci.*, **313**, 594 (1978).

8) 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).

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

10) F. van Bolhuis, P. B. Koster, and T. Migchelsen, *Acta Crystallogr.*, **23**, 90 (1967).

11) R. B. Kurzel and J. I. Steinfeld, *J. Chem. Phys.*, **53**, 3293 (1970).

12) See, for instance, K. Ishii, H. Nakayama, P. Wu, T. Mori, T. Enoki, K. Imaeda, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **60**, 2680 (1987), and the references cited therein.

13) H. W. Cremer and D. R. Duncan, *J. Chem. Soc.*, **1933**, 181.