September, 1980] © 1980 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 53, 2489—2492 (1980)

Resonance Raman Spectra of Intermolecular Vibrations of Würster's Cation Dimers

Kenji Yokoyama,* Yoshitaka Tajima, Masao Tahara, and Shiro Maeda
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuda, Midori-ku, Yokohama 227

(Received March 24, 1980)

The resonance Raman spectra of some Würster's cation dimers were measured in alcohol solution at 201 K and in glassy matrix at 77 K. The spectra of the dimer of *p*-phenylenediamine cation showed the resonance enhancement of the Raman line assigned to the intermolecular stretching vibration and supported the D_{2h} symmetry for the dimer. However, for the dimer of 2,3,5,6-tetramethyl-*p*-phenylenediamine cation and *N*,*N*-dimethyl-*p*-phenylenediamine cation, it was supposed that D_{2h} symmetry was broken down in alcohol solution and in glassy matrix, because the dimers had two Raman lines in the region of the intermolecular vibration.

Resonance Raman effect is a well known phenomenon where the Raman lines related to an electronic transition show enhancement of their intensities when wavelength of an exciting line approaches to the corresponding absorption band. Recently, the authors found the resonance enhancement of the Raman lines assigned to the intermolecular stretching vibrations for the dimers of some aromatic ion radicals, *p*-phenylenediamine cation (PD^+), 2,3,5,6-tetramethyl-*p*-phenylenediamine cation ($TMPD^+$),[1] *p*-benzosemiquinone anion[2] and tetracyanoethylene anion ($TCNE^-$),[3] by the excitation at the long wavelength absorption bands characteristic of the dimer formation. These results not only indicated the strength of the intermolecular bondings directly, but brought fine informations about the behavior of dimerization, with the detailed feature of their spectra taken into account. In the present study, the resonance Raman effect of Würster's cation dimers was further reinvestigated to study the mechanism of dimerization and the relation between the nature of the intermolecular bondings and the values of force constant for the corresponding bondings of the dimers.

Experimental

PD^+ and $TMPD^+$ were prepared with Br_2, as previously reported.[1] *N*,*N*-Dimethyl-*p*-phenylenediamine bromide ($DMPD^+Br^-$) was prepared by the method of Michaelis and Granick.[4] *N*,*N*,*N*′,*N*′-Tetradeuterated PD (PD-d_4) and *N*,*N*,*N*′,*N*′-tetradeuterated TMPD (TMPD-d_4) were prepared by repeating of dissolution and crystallization in CH_3OD. Methanol and ethanol were used as solvents for measurement at 201 K. A mixed solvent, EPA (ethanol: isopentane: diethyl ether=10:1:1), was used for measurement at 77 K. The conditions of spectroscopic measurement were almost equal to the previous report,[1] except that the satellite lines of the exciting source were eliminated by using a prism system.

Results and Discussion

Figure 1 a) shows the resonance Raman spectrum of the dimer of PD^+Br^- in ethanol solution at 201 K by the excitation at the absorption band characteristic of the dimer at 605 nm.[1] A broad line at 161 cm^{-1} showed a striking resonance enhancement together with its progression, and a weak line appeared at 523 cm^{-1} in resonance condition. These Raman lines were all polarized, and the depolarization ratio of the line at 161 cm^{-1} was 0.31. Therefore, they were assigned to totally symmetric vibrations.

Kimura *et al.* studied the electronic structure of the dimer of PD^+ by using LCMO method, assuming a parallel structure of D_{2h} symmetry, as shown in Fig. 2[5] and showed that the absorption band at 605 nm characteristic of the dimer was assigned to a transition from ϕ_+ to ϕ_-, which had a transition dipole along the out-of-plane axis, z. A significant difference between ϕ_+ and ϕ_- is that ϕ_+ has a bonding character whereas ϕ_- has an antibonding character on the intermolecular bonding. Therefore, according to the Franck-Condon mechanism of Raman intensity, the resonance enhancement of the Raman line assigned

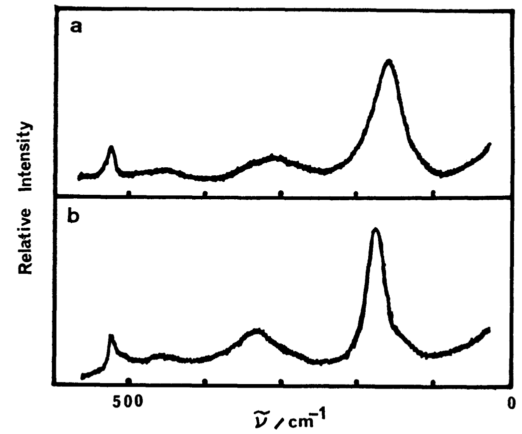

Fig. 1. Resonance Raman spectra of PD^+Br^- by the excitation with 605 nm line.
a) In ethanol solution at 201 K, b) in EPA glassy matrix at 77 K.

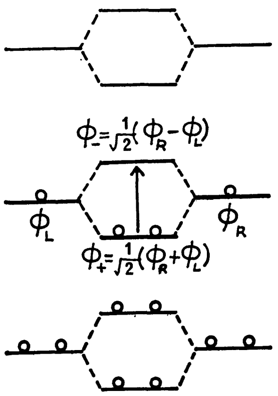

Fig. 2. MO scheme of the dimer of ion radical.

to the intermolecular stretching vibration is expected to take place by the excitation at this absorption band.

Consequently, the 161 cm^{-1} line was assigned to the intermolecular stretching vibration, as previously reported.[1] The broard line shape indicates the nature of the intermolecular vibration and the value of depolarization ratio shows the contribution of α_{zz} component to the resonance enhancement.

On the other hand, an out-of-plane NH$_2$ bending vibration may appear in the region about 200 cm^{-1},[6] while this mode probably increases in frequency when PD is converted to PD$^+$ because the conjugation between benzene ring and NH$_2$ is increased.[7,8] If the line is the out-of-plane NH$_2$ vibration, it must decrease in frequency about 6 cm^{-1} according to the deuteration. However, in the present study, the resonance Raman spectrum of the dimer of PD-$d_4$$^+$ did not show any considerable change in frequency, compared with that of the dimer of PD-$h_4$$^+$. Therefore, it was confirmed that the line observed at 161 cm^{-1} is not assigned to the out-of-plane NH$_2$ bending vibration.

Figure 3 a) shows the resonance Raman spectrum of the dimer of TMPD$^+$Br$^-$ in methanol solution at 201 K by the excitation at 605 nm. In the previous report,[1] the shoulder at 145 cm^{-1} was regarded as due to a satellite line of the exciting source. However, this shoulder did not disappear even if the satellite line was eliminated. Therefore, we have revised the assignment of this shoulder as a Raman line of the dimer of TMPD$^+$, and confirmed that the dimer of TMPD$^+$ has two lines in the region of the intermolecular vibration. Both lines at 117 and 145 cm^{-1} showed no change in spectral feature when TMPD$^+$ was converted to TMPD-$d_4$$^+$. The depolarization ratio of the band consisting of the two lines was 0.23, which is smaller than that of the dimer of PD$^+$, slightly.

Figure 3 b) shows the resonance Raman spectrum of the dimer of TMPD$^+$Br$^-$ in EPA glassy matrix at 77 K. Two lines in the region of low frequency region appeared more clearly and became to be more distiguishable from each other. Table 1 shows the observed frequencies of the Raman lines for the dimer of TMPD$^+$ at 77 K, together with those at 201 K. Both lines at 117 and 145 cm^{-1} at 201 K shifted to 128 and 156 cm^{-1} in glassy matrix, respectively. These deviations are larger than those for the lines at 250 and 655 cm^{-1}. These results mean that both lines at 117 and 145 cm^{-1} are more sensitive to the surrounding condition than the other lines, which shows that these lines relate to the intermolecular bonding closely.

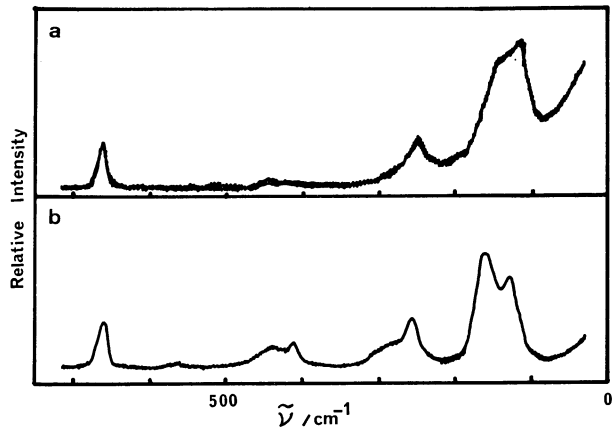

Fig. 3. Resonance Raman spectra of TMPD$^+$Br$^-$ by the excitation with 605 nm line.
a) In methanol solution at 201 K, b) in EPA glassy matrix at 77 K.

TABLE 1. THE OBSERVED FREQUENCIES AND THEIR ASSIGNMENT FOR WÜRSTER'S CATION DIMERS

Species	201 K cm^{-1}	77 K cm^{-1}	Assignment
(PD$^+$)$_2$		≈130 sh	intermolecular vibration
	161 s p	174 s p	intermolecular str.
	322 w p	343 w	161×2 and 174×2
	523 m p	521 m	ring bend.
(TMPD$^+$)$_2$	117 s p	128 s p	intermolecular vibration
	145 s p	156 s p	
	250 m p	258 m p	CH$_3$ bend.
		≈280 w	156+128=284
		415 w	156+258=414
		445 w	156×2+128=440
	655 m p	658 m p	ring bend.
(DMPD$^+$)$_2$		151 s p	intermolecular vibration
		184 s p	

s; Strong, m; medium, w; weak, sh; shoulder, p; polarized.

As shown in the previous study,[3] the resonance Raman spectra of the dimer of TCNE$^-$ showed the resonance enhancement of two lines in the frequency region of the intermolecular stretching vibration. The two lines were assigned to the respective intermolecular stretching vibrations of two kinds of the dimers, because the relative intensities of the two lines showed remarkable alternation when the counter cation was changed from Na$^+$ to Cs$^+$. However, the two Raman lines for the dimer of TMPD$^+$ did not show any considerable change of their intensities when the counter anion was changed among Br$^-$, I$^-$, and ClO$_4$$^-$. Therefore the origin of the two lines for the dimer of TMPD$^+$ must be different from that for the dimer of TCNE$^-$.

These results are interpreted reasonably by considering that D$_{2h}$ symmetry is broken down for the dimer of TMPD$^+$. When the D$_{2h}$ symmetry of the dimer is degraded, vibrations belonging to other symmetry species become totally symmetric and the transition from ϕ_+ to ϕ_- becomes to contain in-plane components beside z component. Therefore the both lines at 117 and 145 cm^{-1} were assigned to mixed modes between two intermolecular vibrations. One is surely the intermolecular stretching vibration, and the other is probably the ring tilting vibration. The break down of D$_{2h}$ symmetry for the dimer of TMPD$^+$ is probably attributed to the repulsion between the H atoms of CH$_3$ substituents of component radicals. The value of depolarization ratio, 0.23, is reasonably interpreted to be owing to the mixing of α_{xx} or α_{yy} to the scattering tensor, derived from the lowering of symmetry. The alternation of intensity for these lines at 201 K and 77 K (see Fig. 3) shows that the configuration of the dimer of $TMPD^+$ is sensitive to the surrounding condition. Figure 3 b) shows that there are some weak lines at 280, 415, and 445 cm^{-1}. These lines can be assigned to combination lines, $156+128=284$, $156+258=414$, and $156\times2+128=440$ cm^{-1}, respectively. These assignments show a good correspondence with the interpretation that both lines at 128 and 156 cm^{-1} in glassy matrix should be attributed to the same species.

Figure 1 b) shows the resonance Raman spectrum of the dimer of PD^+Br^- in EPA glassy matrix at 77 K. The spectral feature at 77 K was almost the same as that at 201 K, with slight differences that 161 cm^{-1} line was observed to increase in frequency slightly and narrow its band width, and a new weak shoulder appeared at 130 cm^{-1}. These results show that the deviation of configuration from D_{2h} symmetry for the dimer of PD^+ is slight in glassy matrix.

The resonance Raman spectra of $DMPD^+Br^-$ in EPA glassy matrix at 77 K are shown in Fig. 4. The dimer of $DMPD^+$ has the absorption band characteristic of dimerization at 680 nm.[5] As the wavelength of excitation line approached to the absorption band two Raman lines appeared with resonance enhancement, same as for the dimer of $TMPD^+$. This result indicates that the dimer of $DMPD^+$ does not take D_{2h} symmetry in glassy matrix, either. Tanaka and Sakabe reported that in the crystal of $DMPD^+Br^-$, one component cation radical was displaced relatively to the other.[7] The present result is in good agreement with their conclusion.

Table 1 shows the observed values of frequency for the dimers at 77 K, together with those at 201 K. The Raman lines in the region of low frequency were assigned to the intermolecular vibrations, as discussed above. A 250 cm^{-1} line of the dimer of $TMPD^+$ was assigned to an out-of-plane CH_3 bending vibration because the corresponding line did not appear for the dimer of PD^+. Lines at 523 cm^{-1} for the dimer of PD^+ and 655 cm^{-1} for the dimer of $TMPD^+$ were assigned to respective ring bending vibrations because they were observed for both dimers. The corresponding line for the dimer of $DMPD^+$ was not confirmed because S/N ratio was wrong. These lines at 250, 523, and 655 cm^{-1}, assigned to intramolecular vibrations, probably borrow their intensities from the intermolecular vibrations through the mixing of vibrational modes.

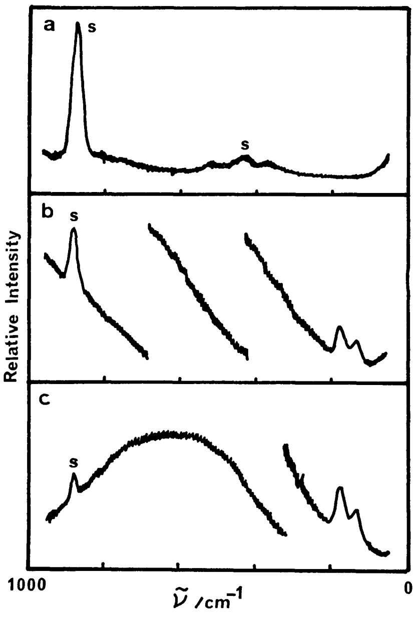

Fig. 4. Resonance Raman spectra of $DMPD^+Br^-$ in EPA glassy matrix at 77 K by the excitation with 514.5 nm a), 584 nm b), and 605 nm c) lines, respectively.
s: Solvent lines.

Table 2 shows the force constants of the intermolecular stretching vibrations of three dimers on the basis of diatomic model. The values for the dimer of $TMPD^+$ and $DMPD^+$ were derived from the averaged frequency of the two Raman lines. Nakayama and Suzuki reported that the values of enthalpies of the dimer formation, $-\Delta H$, were nearly equal for PD^+ and $DMPD^+$, 8.0 and 8.2 kcal/mol, respectively.[9] These values show a good correspondence with the values of force constants of the dimers.

Table 2. The values of force constants for the intermolecular stretching vibrations

Species	201 K	77 K
$(PD^+)_2$	0.82 md/Å	0.96 md/Å
$(TMPD^+)_2$	0.83	0.97
$(DMPD^+)_2$		1.12

It is well known that the values of force constant of the stretching vibrations are related to the corresponding bond distances among bondings with similar nature. The values of force constant for the intermolecular bonding of these ion radical dimers are 0.8—1.1 md/Å, as shown in Table 2, and their bond distances are expected to be about 3.1 Å, according to the result of X-ray study on $DMPD^+$ crystal.[7] Yada *et al.* reported that the force constant of intermolecular stretching vibration for a CT complex, trimethylamine–iodine (TMA–I_2), was 0.546 md/Å, though the corresponding bond distance was 2.27 Å.[10] The inclination of force constants between these ion radical dimers and TMA–I_2 is not parallel to that of their bond distances. Therefore the nature of intermolecular bondings of the ion radical dimers is expected to be different from that of the CT complex. On the other hand, ferrocene is a well known sandwitch type molecule and similar with the ion radical dimers because the π orbitals of aromatic rings form a kind of covalent bond, directly. For ferrocene, the metal-ring distance is 1.66 Å and the force constant of metal-ring stretching vibration is 3.07 md/Å on the basis of linear triatomic molecule model.[11,12] At least, the inclination of their force constants are parallel to that of their bond distances. This result indicates that the intermolecular bonding of the ion radical dimer is owing to the covalency between two π orbitals rather than CT interaction.

References

1) K. Yokoyama and S. Maeda, *Chem. Phys. Lett.*, **48**, 59 (1977).

2) S. Yamaguchi, K. Yokoyama, and S. Maeda, *Bull. Chem. Soc. Jpn.*, **51**, 3193 (1978).

3) K. Yokoyama, S. Maeda, C. Etoh, S. Matsuzaki, and K. Toyoda, *Bull. Chem. Soc. Jpn.*, **53**, 36 (1980).

4) L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **65**, 1747 (1943).

5) K. Kimura, H. Yamada, and H. Tsubomura, *J. Chem. Phys.*, **48**, 440 (1968).

6) G. Varsanyi, "Vibrational spectra of benzene derivatives," Academic Press, New York (1969).

7) J. Tanaka and N. Sakabe, *Acta Crystallogr., Sect. B*, **24**, 1345 (1968).

8) E. Mayer, R. B. Girling, and R. E. Hester, *J. Chem. Soc., Chem. Commun.*, **1973**, 192.

9) S. Nakayama and K. Suzuki, *Bull. Chem. Soc. Jpn.*, **46**, 3694 (1973).

10) H. Yada, J. Tanaka, and S. Nagakura, *J. Mol. Spectrosc.*, **9**, 461 (1962).

11) J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Crystallogr.*, **9**, 373 (1956).

12) E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, **10**, 307 (1958).