

SELECTIVE RESONANCE RAMAN SCATTERING OF PEIERLS-HUBBARD $(\text{TTF}^+)_2$ DIMERS IN $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ AND $(\text{TTF})_2\text{W}_6\text{O}_{19}$ SALTS

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Raman investigation of Peierls-Hubbard $(\text{TTF}^+)_2$ dimers in $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ and $(\text{TTF})_2\text{W}_6\text{O}_{19}$ salts have been performed. It was found that the resonance enhancement of Raman intensity of intramolecular vibration modes exists only when the frequency of excitation light fits to the localised electron transition, however, the resonance enhancement of intermolecular modes occurs when the frequency of excitation light corresponds to the charge transfer transition.

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1. Introduction

It is well known that organic ion radicals, such as TTF^+ (tetrathiofulvalene), TCNQ^- (tetracyanoquinodimethane), CA^- (chloranil) and others, form dimers with charge transfer interaction in solid salts and in low temperature solutions. In Refs. [1, 2] experimental results of investigations of electronic absorption spectra for TTF solution and TTF salts were presented. It was experimentally confirmed that for the solution at low temperature the broad absorption band appears in the red or near-infrared region of the spectrum. This band does not exist for solutions at room temperature. This is associated with the charge transfer transition intra

(TTF⁺)₂ dimers, which are formed at low temperature. The existence of the broad band in the red or near-infrared region is an evidence for the dimer formation. The absorption spectra of TTF salts are similar to that of the low temperature solution. They also exhibit a broad absorption band with maximum in the red or near-infrared region, which is caused by the charge transfer transition, and proves for the existence of dimers in the crystal structure.

For a theoretical analysis of (TTF⁺)₂ dimers the two-site two-electron Hubbard Hamiltonian [3] can be used. This Hamiltonian treats the electron transfer and electron correlation interaction only. When adding the terms, which represent the intramolecular vibrations and linear coupling of the dimer electrons to the intramolecular vibration modes (e-mv), to the Hubbard Hamiltonian, one obtains the so-called Peierls-Hubbard model [4-7]. In Ref. [8], taking into account all possible interactions, the (TTF⁺)₂ dimers were analysed. The Hamiltonian of the dimer was obtained by adding the terms describing the intermolecular vibrations and the coupling electron-intermolecular phonon vibration modes (e-p) to the Peierls-Hubbard Hamiltonian. For a symmetric dimer of two identical radicals the existence of the selective resonance enhancement of Raman active intermolecular phonon modes was predicted. Investigations of resonance Raman scattering (RRS) of (TTF)Br salt confirmed the appearance of selective resonance enhancement of intermolecular modes by their excitation in resonance or close to resonance with charge transfer transition.

In the following sections we give a short theoretical background of the Peierls-Hubbard dimer model, and present experimental results of investigations of electronic absorption spectra and RRS for (TTF)₂Mo₆O₁₉ and (TTF)₂W₆O₁₉ salts. We also propose an explanation on the basis of the above-mentioned dimer model.

2. Theory

The model Hamiltonian for two-site two-electron dimer can be written as

$$H = H_E + H_V + H_{ev}, \quad (1)$$

where

$$H_E = -t \sum_{\sigma} (a_{1\sigma}^{\dagger} a_{2\sigma} + a_{2\sigma}^{\dagger} a_{1\sigma}) + U(n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow}), \quad (2)$$

$$H_V = \sum_i \left(\frac{\hbar\omega_i}{4} \right) (\dot{Q}_{1i}^2 + \dot{Q}_{2i}^2 + Q_{1i}^2 + Q_{2i}^2) + \sum_e \frac{\hbar\omega_e}{4} (\xi_e^2 + \xi_e'^2), \quad (3)$$

$$H_{ev} = \sum_i g_i (Q_{1i} n_1 + Q_{2i} n_2) - \sum_e \sum_{\sigma} g_e \xi_e (a_{1\sigma}^{\dagger} a_{2\sigma} + a_{2\sigma}^{\dagger} a_{1\sigma}). \quad (4)$$

$a_{n\sigma}^{\dagger}$ ($a_{n\sigma}$) is the creation (annihilation) operator for an electron of spin $\sigma = \uparrow, \downarrow$ on the molecular site $n = 1, 2$; $n_n = \sum_{\sigma} n_{n\sigma} = \sum_{\sigma} a_{n\sigma}^{\dagger} a_{n\sigma}$ is the occupation operator; t represents the electron transfer energy among adjacent sites with conserving the spin orientation ($t = \langle D^{\dagger} D^{\dagger} | H_E | D^{++} D^0 \rangle$); U is the correlation energy and is defined to be the energy while putting two spin-paired electrons on the same site; Q_{ni} , \dot{Q}_{ni} and ω_i are the dimensionless coordinate, momentum and angular frequency of i th intramolecular vibrational mode of the n th site, respectively; ξ_e , ξ_e' , ω_e are the corresponding meaning for the six external vibrations;

$g_i = (\partial \varepsilon / \partial Q_i)_0$ and $g_e = (\partial t / \partial \xi_e)_0$ represent the strengths of electron coupling with the intramolecular and intermolecular vibration modes, respectively; ε is the potential energy surface of HOMO (for cation radicals) or LUMO (for anion radicals). As follows from Eq. (1) the dimer Hamiltonian is a sum of three terms. The first term H_E is the Hubbard Hamiltonian, the second H_V represents the intramolecular and intermolecular vibrations and the last term H_{ev} describes the coupling of electrons to intramolecular vibration modes.

According to Rice [9] we introduce symmetric and antisymmetric intramolecular vibrational coordinates, $s_i = (Q_{1i} + Q_{2i})/\sqrt{2} - s_i^0$ and $q_i = (Q_{1i} - Q_{2i})/\sqrt{2}$ with $s_i^0 = -2\sqrt{2}g_i/\hbar\omega_i$. We define the displaced coordinates $u_e = \xi_e - \xi_e^0$ with $\xi_e^0 = 2g_e\rho_B/\hbar\omega_e$, where $\rho_B = \langle \sum_{\sigma} (a_{1\sigma}^{\dagger} a_{2\sigma} + a_{2\sigma}^{\dagger} a_{1\sigma}) \rangle_0$ is the ground-state expectation value of the bond-order operator. Using new coordinates s_i , q_i , u_e the Hamiltonian (1) takes the form

$$H = H_E^{\dagger} + H_V^{\dagger} + H_{e-mv} + H_{ep}, \quad (5)$$

where

$$H_E^{\dagger} = -t_1 \sum_{\sigma} (a_{1\sigma}^{\dagger} a_{2\sigma} + a_{2\sigma}^{\dagger} a_{1\sigma}) + U(n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow}) - \sum_i \frac{2g_i^2}{\hbar\omega_i} + \sum_e \frac{g_e^2 \rho_B^2}{\hbar\omega_e}, \quad (6)$$

$$H_V^{\dagger} = \sum_i \frac{\hbar\omega_i}{4} (s_i^2 + q_i^2) + \sum_i \frac{\hbar\omega_i}{4} (\dot{q}_i^2 + \dot{s}_i^2) + \sum_e \frac{\hbar\omega_e}{4} (\dot{u}_e^2 + u_e^2) + \sum_e g_e \rho_B u_e, \quad (7)$$

$$H_{e-mv} = \sum_i \frac{1}{\sqrt{2}} g_i q_i (n_1 - n_2), \quad (8)$$

$$H_{ep} = \sum_e g_e u_e \sum_{\sigma} (a_{1\sigma}^{\dagger} a_{2\sigma} + a_{2\sigma}^{\dagger} a_{1\sigma}), \quad (9)$$

$$t_1 = t + \sum_e \frac{2g_e^2 \rho_B}{\hbar\omega}.$$

It follows from (8) and (9) that the antisymmetric intramolecular vibration modes are coupled to the dimer electron only. The symmetric intramolecular modes, as previously noted [9], are completely decoupled from the electronic degrees of freedom of the dimer. In principle the symmetric vibration modes are Raman active only. It results from the above considerations and the discussion performed in [8] using RRS Albrecht vibronic model [10, 11] that, when the symmetric Peierls-Hubbard (P-H) dimer is excited in resonance or in pre-resonance with charge transfer transition, the intensity of the totally symmetric intermolecular modes is enhanced only. Conversely, no resonance intensity enhancement exists for the intramolecular modes.

3. Experimental

(TTF)₂Mo₆O₁₉ and (TTF)₂W₆O₁₉ used for investigations were prepared electrochemically. The powder of the investigated salts was mixed with KBr and from this mixture the pellets for measurements of electronic absorption spectra

were prepared. For Raman measurements the samples were obtained by mildly pressing the powder of $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ or $(\text{TTF})_2\text{W}_6\text{O}_{19}$ onto KBr disk. In all measurements the samples were placed in the chamber with a closed-cycle helium refrigerator (CTI Cryodyne model 21). Electronic absorption spectra at room temperature and at 12 K were recorded by Cary14 spectrophotometer. The instrumentation for Raman measurements consisted of a krypton ion laser (Spectra-Physics model 171), premonochromator (Anaspec 300s), double monochromator (Spex 1403), thermoelectrically cooled photomultiplier (RCA 3103A) and a photon-counting system (5C1-Ortec). The scanning of the spectra and the data acquisition were controlled by a microcomputer. The typical spectral resolution was 2 cm^{-1} . All Raman measurements were performed by keeping the samples at 12 K.

4. Results

4.1. Electronic absorption spectra

The electronic absorption spectra of crystalline $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ and $(\text{TTF})_2\text{W}_6\text{O}_{19}$ salts are presented in Fig. 1. The room temperature spectrum of $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ is composed of bands with maxima of 920, 530, 400 and 350 nm,

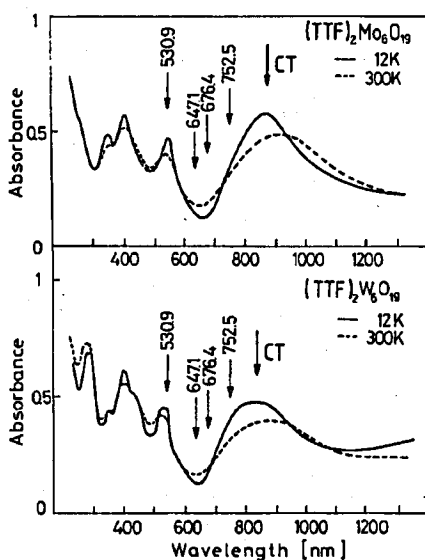


Fig. 1. Electronic absorption spectra of crystalline $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ and $(\text{TTF})_2\text{W}_6\text{O}_{19}$ powders at room (dashed line) and 12 K (solid line) temperatures.

whereas the spectrum at 12 K exhibits absorption bands with maxima of 870, 530, 400 and 350 nm. The $(\text{TTF})_2\text{W}_6\text{O}_{19}$ salt exhibits absorption bands with maxima of 870, 530, 400, 350 and 280 nm at room temperature and of 830, 530, 400, 350 and 280 nm at 12 K. The longest wavelength absorption band is associated with charge transfer transitions in the $(\text{TTF}^+)_2$ dimers. This is a distinct indication of

the existence of dimers in the investigated samples. The shorter wavelength absorption bands are attributed to the intramolecular electron transitions (localised electron (LE) transitions). Comparing these results with the electronic absorption spectrum of (TTF)Br salt [8] one can notice that the CT transition band for the investigated salts is shifted toward infrared. One may then conclude that the CT interaction in the (TTF⁺)₂ dimers formed in (TTF)₂Mo₆O₁₉ and (TTF)₂W₆O₁₉ crystals is smaller than that in (TTF)Br crystals.

4.2. Resonance Raman spectra

For Raman investigations the following Kr⁺ laser lines were used: 530.9, 647.1, 676.4 and 752.5 nm with the power equal to about 40 mW. These lines are marked by arrows on the absorption spectra. Using the 530.9 nm excitation line, a resonance with the localised electron transition takes place. The intensity of the intramolecular bands is then very strongly resonance enhanced. Figure 2a presents the obtained RRS spectrum of (TTF)₂Mo₆O₁₉ in the range of 200–1700 cm⁻¹. The

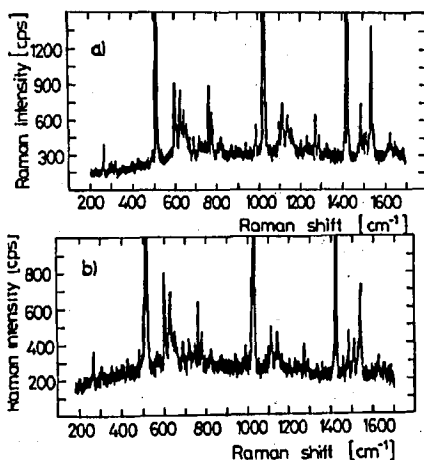


Fig. 2. Raman spectra of crystalline powders of (TTF)₂Mo₆O₁₉ (above) and (TTF)₂W₆O₁₉ (below) at 12 K in 200–1700 cm⁻¹ range obtained by using 530.9 nm excitation line.

obtained spectrum shows numerous and very strong bands. The majority of these bands can be attributed to the intramolecular vibration modes of TTF⁺ [2, 12]. The strongest bands are attributed to the following symmetric modes of TTF⁺: $a_g\nu_2$ (1537 cm⁻¹), $a_g\nu_3$ (1422 cm⁻¹), $a_g\nu_4$ (1024 cm⁻¹) and $a_g\nu_6$ (512 cm⁻¹). Their intensities are equal to 1400, 5000, 5200 and 16000 cps, respectively. To record the RRS spectrum of (TTF)₂W₆O₁₉ using for excitation the 530.9 nm laser line we obtained in the 200–1700 cm⁻¹ range very similar spectrum (Fig. 2b). Using the laser lines 647.1 and 676.4 nm we found that the Raman activity of the intramolecular modes practically disappears. This is shown for (TTF)₂Mo₆O₁₉ together with

the spectra given by intermolecular modes. For example, the intensity of the $a_g\nu_3$ band excited by 647.1 and 676.4 nm lines is about 125 and 200 times smaller, respectively, than that for the 530.9 nm excitation line.

The Raman intensity is proportional to ν^4 , where ν is the frequency of the scattered light. For the used excitation lines we obtain the following relation: $(1/\lambda_1)^4 : (1/\lambda_2)^4 : (1/\lambda_3)^4 = 100 : 45 : 38$, where λ_1, λ_2 and λ_3 are equal to 530.9, 647.1 and 676.4 nm, respectively. In order to obtain better information about the Raman activity of intermolecular modes and their dependence on the excitation wavelength the experimentally measured Raman intensities of $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ were multiplied by the adequate correction factors according to the above relation. In Fig. 3 the corrected low-frequency Raman spectra of the $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ salt are shown. The intermolecular bands observed for this salt are gathered in Table I.

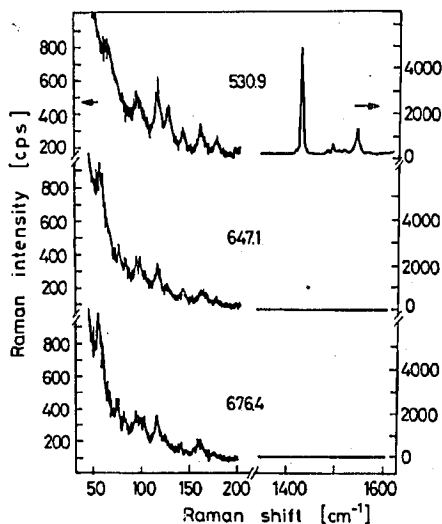


Fig. 3. Raman spectra of pure $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ powder in 20–200 cm^{-1} (left) and 1300–1600 cm^{-1} (right) ranges obtained by using indicated excitation wavelengths (nm).

We also carried out investigations of the $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ salt, using the 752.5 nm line, but we did not observe any bands. This was probably caused by a strong absorption both of the excitation and scattered light in this region of the spectrum. For the sample with smaller concentration of $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ ($(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ mixed with NH_4Cl in 1:80 weight ratio) we observed only traces of some bands comparable to the noise level.

From the investigation of $(\text{TTF})_2\text{W}_6\text{O}_{19}$ we obtained more information about the resonance enhancement of Raman scattering intensity of intermolecular vibration modes. Using pure $(\text{TTF})_2\text{W}_6\text{O}_{19}$, we have observed intermolecular bands similar to that for $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ for excitation lines 530.9, 647.1 and 676.4 nm only. However, for $(\text{TTF})_2\text{W}_6\text{O}_{19}$ mixed with NH_4Cl in the weight ratio 1:80, distinct intermolecular bands have been observed using the 752.5 nm excitation

TABLE I
Observed frequencies (cm^{-1}) in the 40–200 cm^{-1} resonance Raman spectra of $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ at 12 K for various excitation wavelengths.

Excitation wavelength [nm]	Observed frequencies [cm^{-1}]										
530.9		65			93		114	125	140	159	176
647.1	54		74	81	94	101	114	122	140	160	175
676.4	54		74	81	95	101	115		140	160	176

line. The CT transition in the $(\text{TTF})_2\text{W}_6\text{O}_{19}$ occurs as follows from the electronic absorption spectra at 830 nm, while in the case of $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ at 870 nm. Most likely it is the reason why the intermolecular bands appear while using the 752.5 nm excitation line for the $(\text{TTF})_2\text{W}_6\text{O}_{19}$ and they are not detectable for $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$. In the first case we are closer to the CT transition resonance. The normalised Raman spectra of $(\text{TTF})_2\text{W}_6\text{O}_{19}$ obtained for all four excitation wavelengths are collected in Fig. 4. For the normalization we used the 186 cm^{-1} band

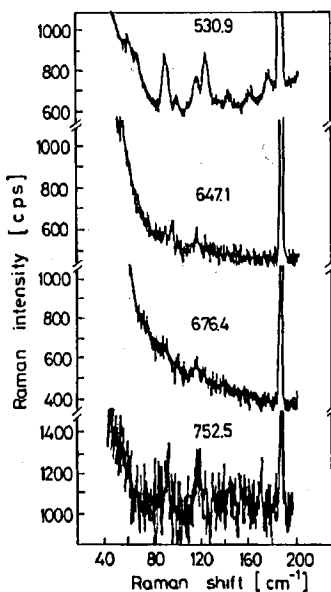


Fig. 4. Low-frequency Raman spectra of $(\text{TTF})_2\text{W}_6\text{O}_{19}$ powder mixed with NH_4Cl (1 : 80 weight ratio) obtained by using indicated excitation wavelengths (nm).

given by NH_4Cl . All observed intermolecular bands together with the normalised integrated intensities are collected in Table II. Figure 5 presents the dependence

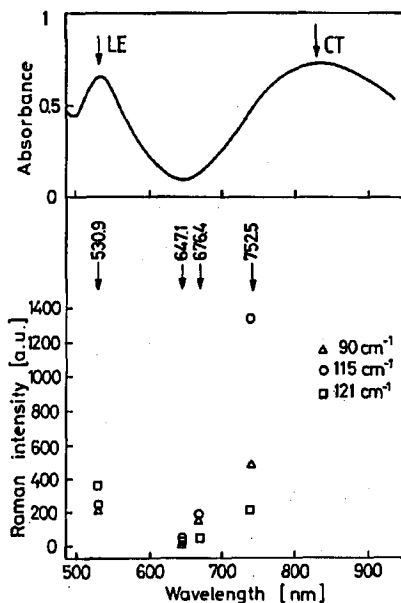


Fig. 5. Electronic absorption spectrum of $(\text{TTF})_2\text{W}_6\text{O}_{19}$ powder at 12 K (above) and the integrated intensity of its 3 Raman bands (90 , 115 and 121 cm^{-1}) obtained by using 530.9 , 647.1 , 676.4 and 752.5 nm excitation lines (below).

of the normalised integrated intensities of three intermolecular bands (90 , 115 and 121 cm^{-1}) on the excitation wavelength. Taking this dependence into account it follows that the resonance enhancement of the Raman scattering intensity of intermolecular modes is the largest for the 752.5 nm line, i.e. when the excitation light is close to resonance with CT transition. A weak resonance enhancement of intermolecular modes appears for the 530.9 nm excitation light as well, i.e. for the resonance with LE transition.

5. Conclusions

In Sec. 2 the total decoupling of electrons of the dimer from the symmetrical intramolecular vibration modes has been theoretically predicted. On this basis one should expect the Raman intensity of intramolecular modes to be enhanced only by their excitation in resonance with the localised electron transition. On the contrary, excitation in resonance with the CT transition should produce an enhancement of the intermolecular modes only. Such selective resonance enhancement occurs under restrictive conditions [8] when (i) the dimer is symmetric, i.e. the two moieties have equal electron densities and the same vibrational modes, and (ii) the CT states do not mix with the localised molecular excitation.

Experimental investigations of $(\text{TTF})_2\text{Mo}_6\text{O}_{19}$ and $(\text{TTF})_2\text{W}_6\text{O}_{19}$ satisfactorily confirm the theoretical predictions. The enhancement of the Raman intensity

TABLE II

Frequencies ν (cm^{-1}) and normalised to 186 cm^{-1} NH_4Cl band integrated intensities I of the observed bands in the $40\text{--}200 \text{ cm}^{-1}$ resonance Raman spectra of $(\text{TTF})_2\text{W}_6\text{O}_{19}$ mixed with NH_4Cl (1:80 weight ratio) at 12 K for various excitation wavelengths. The integrated intensity of the 186 cm^{-1} band given by NH_4Cl was assumed to be equal to 1000.

Excitation wavelength [nm]							
530.9		647.1		676.1		752.5	
ν	I	ν	I	ν	I	ν	I
		55	60	53	444		
61	48						
91	216	90	10	89	147	90	477
99	8	95	42	100	88		
116	244	115	54	115	176	116	1329
123	363	122	20	121	49	122	209
132	10						
142	44						
160	38						
175	71						
186	1000	186	1000	186	1000	186	1000

of intramolecular modes has been observed only in resonance with the localised electron transition. When we detune the excitation light wavelength from the resonance with LE transition, we observe a dramatic decrease in the Raman intensity of intramolecular modes. However, as follows from Figs. 4 and 5 the largest enhancement of the Raman intensity of intermolecular modes has been observed in the pre-resonance region with CT transition. A weak enhancement of the intensity of intermolecular bands has been also observed in resonance with LE transition. It was technically impossible to perform an experiment, which could confirm or exclude the existence of a weak resonance enhancement of intramolecular modes in resonance with CT transition. The probable existence of a weak enhancement of intramolecular modes in resonance with CT transition, and the observed weak enhancement of intermolecular modes in resonance with LE transition may be an evidence for feeble mixing of LE and CT states in the investigated dimers.

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References

- [1] J.B. Torrance, B.A. Scott, B. Welber, F.B. Kaufmann, P.E. Seiden, *Phys. Rev. B* **19**, 730 (1979).
- [2] R. Bozio, I. Zanon, A. Girlando, C. Pecile, *J. Chem. Phys.* **71**, 2282 (1979).
- [3] Z.G. Soos, D.J. Klein, in: *Molecular Association*, Ed. R. Foster, Academic Press, London, New York, San Francisco 1975, p. 1.
- [4] Y. Toyozawa, *J. Phys. Soc. Jpn.* **50**, 1861 (1981).
- [5] K. Nasu, Y. Toyozawa, *J. Phys. Soc. Jpn.* **51**, 2098 (1982).
- [6] K. Nasu, *J. Phys. Soc. Jpn.* **52**, 3865 (1983).
- [7] S. Weber, H. Büttner, *J. Phys. C* **17**, L337 (1985).
- [8] R. Bozio, A. Feis, I. Zanon, C. Pecile, *J. Chem. Phys.* **91**, 13 (1989).
- [9] M.J. Rice, *Solide State Commun.* **31**, 93 (1979).
- [10] A.C. Albrecht, *J. Chem. Phys.* **34**, 1476 (1961).
- [11] J. Tang, A.C. Albrecht, in: *Raman Spectroscopy. Theory and Practice*, Ed. H.A. Szymanski, Vol. 2, Plenum Press, New York 1970, p. 33.
- [12] R. Bozio, A. Girlando, C. Pecile, *Chem. Phys. Lett.* **52**, 503 (1977).