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Raman study of the pressure-induced neutral-to-ionic transition in tetrathiafulvalene chloranil

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The pressure-induced phase transition from a neutral regular stack to an ionic dimerized stack (NR-ID) in the tetrathiafulvalene chloranil charge-transfer crystal has been studied by Raman spectroscopy. An accurate estimate of the change of ionicity during the phase transition is obtained from calculations of mode frequencies which are based on the trimer (NR phase) and dimer (ID phase) models of the electron–molecular-vibration interaction. The possibility of the formation of ionic dimers embedded in neutral chains as precursors of the phase change is discussed.

I. INTRODUCTION

Since the discovery of a neutral-to-ionic phase transition in mixed-stack organic charge-transfer (CT) crystals[1] tetrathiafulvalene chloranil (TTF-CA) still remains a unique material exhibiting both a pressure- and a temperature-induced phase transition to a clearly ionic ground state.[1,2] Actually, the phase transition at about 1 GPa (300 K) or 84 K (ambient pressure) involves not only the ionicity of the molecules, but also the one-dimensional stack structure, being from a quasineutral regular (NR) stack to a quasi-ionic dimerized (ID) ground state.[3–5] Evidence for other materials undergoing a similar reversible phase change came from the marked color change observed visually for a number of CT crystals under pressure.[1] However, infrared (ir) vibrational spectroscopy has failed to confirm this idea in three[6,7] out of the ten originally reported materials. Thus, TTF-CA is the only example so far that has experimentally been verified to undergo a NR-ID transition.

Several experimental and theoretical investigations of the phase transition in TTF-CA have recently been reported. On the experimental side, both temperature and pressure have been used as external parameters to drive the NR-ID transition, as studied by a variety of techniques.[3–5,8–12] On the theoretical side, the proposed phase diagrams account, in general terms, for most of the available experimental data.[13] Despite a strong effort, several aspects of the phase transition remain to be investigated. In particular, it has been suggested that the temperature- and pressure-induced transitions occur through somewhat different mechanisms.[4,14]

The present report aims to advance the discussion by presenting the results of the first high-pressure Raman investigation of TTF-CA. Single crystals under hydrostatic conditions have been used to follow the behavior of the vibrational Raman-active modes from ambient pressure up to 8 GPa. An accurate determination of the ionicity (ρ) as a function of pressure is obtained by comparing the experimental frequencies with those predicted by a semiempirical model which takes into account the perturbative effect of the electron–molecular-vibration (e-MV) interaction.[15] The pressure dependence of ρ leads to a characterization of the phase transition which agrees with that obtained through a reinterpretation of the available ir data[4] also presented here. The Raman investigation is complemented by the determination of the pressure shift of the optical-absorption edge of TTF-CA in the visible spectral range. This absorption corresponds to an intramolecular excitation of the TTF molecule and its pressure shift accounts for the striking color change during the phase transition. We suggest that the pressure-driven transition differs from the temperature-induced one in that the former has a precursor regime, probably characterized by the presence of ionic dimers embedded in the quasineutral lattice.

II. EXPERIMENT

TTF-CA single crystals were grown from solution or by co-sublimation, according to the methods described elsewhere.[5,16] Raman experiments under pressure have been performed by using a gasketed diamond-window cell[17] with pressure being calibrated by the ruby-luminescence technique.[18] The uncertainty in pressure is about 0.05 GPa. Needles of TTF-CA were loaded in a pressure medium of glycerol. Spectra were excited with a 25-mW He-Ne laser at 632.8 nm using nearly back-

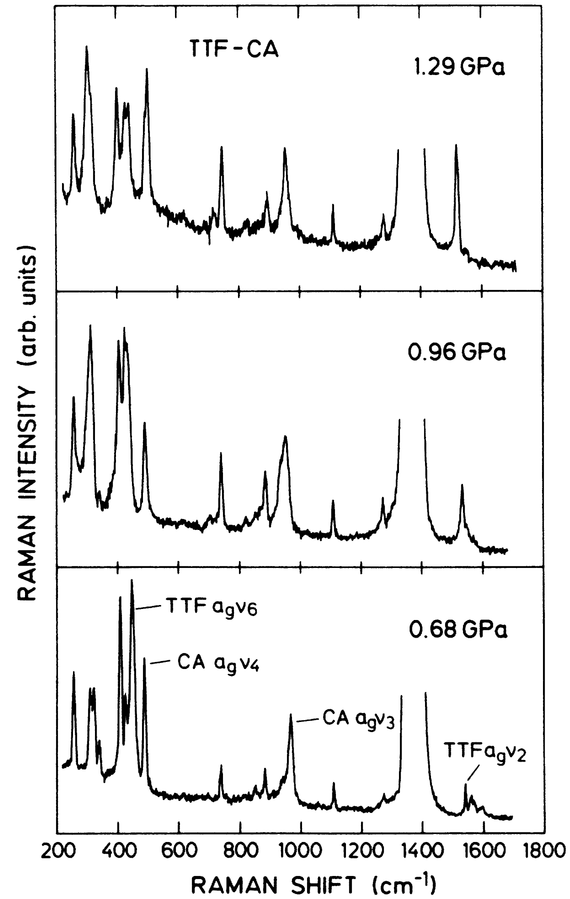

FIG. 1. Raman spectra of TTF-CA measured at different pressures. For an assignment of modes see Table I.

scattering geometry. The spectrometer was a 0.6-m grating spectrograph equipped with a subtractive-grating prefilter stage and coupled to a position-sensitive (resistive-anode type) photomultiplier system. The overall spectral resolution was about 4 cm^{-1}. The absorption-edge measurements were made with a microoptical spectrometer described earlier.[17]

III. RESULTS

Representative Raman spectra of TTF-CA at three different pressures are shown in Fig. 1. In order to avoid laser heating of the samples, a relatively large focal spot of about 200 μm has been used. Therefore, the spectral region between 1300 and ~ 1450 cm^{-1} was not accessible due to Raman scattering from the diamond windows as well as luminescence from ruby. Apart from a somewhat lower resolution, the spectra appear to be of quality equivalent to those obtainable from conventional apparatus under normal conditions. Some remarkable spectral variations due to the NR-ID transition are evident from the spectra in Fig. 1. The Raman frequencies observed from 0.5 to 1.8 GPa (i.e., from before to after the transition) are collected in Table I. The mode assignment listed in the last column of Table I follows immediately from that reported for the corresponding temperature-induced transition.[5]

The spectra in Fig. 1 refer to samples grown from solution. We have also recorded Raman spectra for samples grown by sublimation, reaching maximum pressures of about 8 GPa. Upon releasing the pressure from 3 GPa the original spectra were obtained again. After a cycle reaching a maximum pressure of 8 GPa, only some weak

TABLE I. Raman frequencies (cm^{-1}) of TTF-CA (sample from solution) at several pressures around the phase transition.

0.45 GPa	0.68 GPa	0.96 GPa	1.29 GPa	1.83 GPa	Assignment[a]
252	255	257	260	262	TTF, $a_g \nu_7$
308	308	312	305	320	TTF or CA, b_{3g}
322	320		316		CA, $a_g \nu_5$
337	340	341			CA, b_{1g}
409	409	407	403	404	CA, b_{2g}?
422	426				TTF, b_{1g}?
456	448	425 432	429	435	TTF, $a_g \nu_6$
			440	449	TTF, b_{2g}?
484	487	490	504	505	CA, $a_g \nu_4$
738	739	741	748	751	TTF, $a_g \nu_5$
	883	885	894	899	TTF, b_{1g} or b_{2g}
975	968	940 954	955	969	CA, $a_g \nu_3$
1108	1109	1109	1111	1113	TTF, $a_g \nu_4$
	1273	1274	1275	1278	TTF, b_{3g}?
1543	1542	1535	1517	1516	TTF, $a_g \nu_2$
1564 1573	1560 1570	1549	1550	1548	CA, $a_g \nu_2$
1609	1600				CA, $a_g \nu_1$

[a] Symmetry and mode numbering as in Ref. 5.

residual bands were observed. Thus, the phase transition can be considered to be essentially reversible.

Figure 2 reports the frequency variation of four important a_g bands as a function of pressure for both solution- and sublimation-grown samples. In order to compare the data directly, we have plotted the frequency differences with respect to values read at 7.9 GPa. The two types of samples exhibit quite similar behavior under pressure, in contrast to what has been observed for the temperature-induced transition.[5,9] The pressure range in which abrupt changes in the frequency *variation* are observed is 1.0–1.3 GPa for both types of samples. Furthermore, the apparently strange variation of the Raman frequencies with pressure is different from frequency shifts observed in ir spectra (e.g., Ref. 4, Fig. 2). The reason is that the totally symmetric (a_g) modes in mixed-stack CT crystals are coupled to the CT electron system (e-MV interaction).[15] This coupling has to be taken into account in the interpretation of the Raman spectra.

The shift of the visible absorption edge of TTF-CA under pressure has been measured by spotting a tiny portion of a thin single crystal. The absorbance was derived by using as reference an empty part of the cell next to the sample. For all spectra the shift of the absorption edge relative to the ambient-pressure spectrum has been determined at an optical density of 1.0. Figure 3 shows the change of the absorption-edge energy as a function of pressure. Also shown in Fig. 3 is the shift of the absorption edge of the first $\pi^* \leftarrow \pi$ transition of anthracene, as an example of the typical red-shift of -0.06 eV/GPa generally found for this type of excitation.[19] By subtracting this contribution, the shift related to the neutral-ionic phase transition is, on the whole, about 0.33 eV.

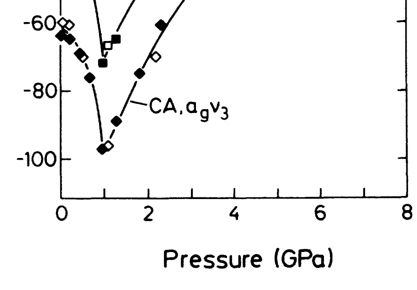

FIG. 2. Change of the Raman shift of four a_g modes of TTF-CA as a function of pressure. Frequency differences are plotted relative to their value at 7.9 GPa. Solid and open symbols refer to solution and sublimation grown samples, respectively.

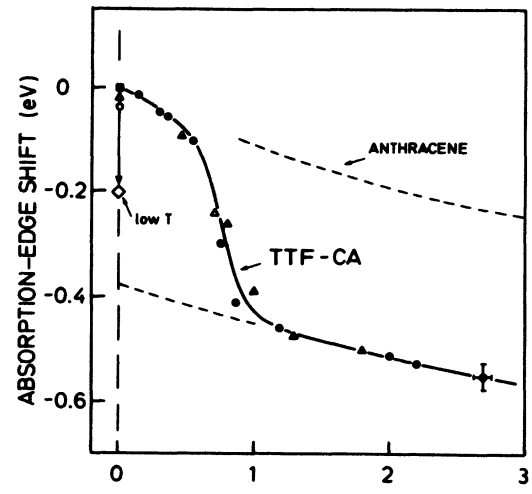

FIG. 3. Shift of the visible absorption edge of TTF-CA as a function of pressure. Solid and open symbols refer to increasing and decreasing pressure, respectively. Also indicated is the shift of the absorption edge for the temperature-induced transition in TTF-CA. The dashed line corresponds to the effect of pressure on the first singlet transition in anthracene.

A. Dependence of Raman frequencies on charge transfer

In order to (1) rationalize the apparently strange variation of the Raman frequencies in Fig. 2 and to (2) extract the charge-transfer ρ as a function of pressure from the observed frequency variation, we have to consider the effect of e-MV coupling on the totally symmetric frequencies.

The e-MV perturbed Raman frequencies are obtained from a diagonalization of a "force constant" matrix given by[15,20]

$$F_{i,i} = \omega_i^2 - \chi_v \omega_i g_i^2/\hbar \, , \tag{1a}$$

$$F_{i,j} = -\chi_v (\omega_i \omega_j)^{1/2} g_i g_j/\hbar \, , \tag{1b}$$

where i and j run over all totally symmetric modes of both electron donor and acceptor molecules, $\omega_{i,j}$ being their frequency in the absence of e-MV coupling. These frequencies are, in good approximation, linear functions of the degree of ionicity ρ: $\omega_i = \omega_i^* - \Delta\rho$, where ω_i^* is the frequency of the neutral molecule and Δ is the corresponding ionization frequency shift.[15] The e-MV coupling constants g_i are molecular quantities, transferable from one CT crystal to another,[21] and χ_v is the electronic response to the vibrational perturbation.

Equation (1) can be used in different ways depending on which kind of information one is interested in. For instance, if the e-MV perturbed experimental frequencies, ρ, and χ_v are known, the e-MV coupling constants can be estimated.[21] Alternatively, from the experimental frequencies, ρ, and the g's, one can evaluate χ_v and from this important microscopic parameters.[20] In this paper we shall instead use Eq. (1) to extract ρ as a function of pressure from the experimental frequencies.

The first problem in this process is the evaluation of χ_ν. For a regular mixed stack, such as TTF-CA before the phase transition, χ_ν could be estimated from optical spectra through the recently published valence-bond analysis of the relevant electronic structure.[20] However, such a procedure requires an accurate determination of electronic parameters, such as the charge-transfer integral, and their variation with pressure. This makes the above route rather unpractical. Thus, we prefer a semiempirical approach, based on the so-called trimer model[15] for the regular stack, which gives

$$\chi_\nu = 4\rho(1-\rho)^2/\omega_{\mathrm{CT}} \ , \tag{2a}$$

where ω_{CT} is the frequency of the charge-transfer excitation. Despite its shortcomings this model has been shown to work reasonably well.[20] For a dimerized stack such as TTF-CA in the ionic phase,[3,4] the dimer model gives[5,15]

$$\chi_\nu = 4\rho(1-\rho)/\omega_{\mathrm{CT}} \ . \tag{2b}$$

Another approximation is to disregard the coupling of the a_g modes through the e-MV interaction by neglecting the off-diagonal terms of Eq. (1) (isolated-band approximation).[3,22] In this way one essentially uses "effective" e-MV coupling constants, and a proper calibration of the system is needed.

We use the frequency variation of the Raman bands with temperature[22] and the corresponding ρ obtained from ir data to test the validity of the above semiempirical approach. For the CA $a_g\nu_3$ mode, which is well separated from the other ones, Eq. (1) gives $g = 795$ and 900 cm^{-1} for 300 and 15 K, respectively, where $\rho = 0.20$ and 0.64 and $\omega_{\mathrm{CT}} = 5320$ and 4850 cm^{-1}.[8,22] With these values we estimate the e-MV perturbed frequency as a function of ρ by taking into account the temperature variation of ω_{CT}.[8] The corresponding curves for the trimer ($\rho < 0.5$) and dimer ($\rho > 0.5$) models are reported in the upper part of Fig. 4. The crosses are the experimental data determined from Raman (frequency value) and ir (ρ value) measurements. The agreement is remarkably good, giving us confidence in the use of such a diagram to estimate ρ from the high-pressure Raman spectra.

The CA $a_g\nu_4$ and TTF $a_g\nu_6$ modes are too close in frequency and the isolated-band approximation breaks down. An improvement is obtained by considering the two modes together and solving the resulting 2×2 force-constant matrix. The corresponding curves are reported in the lower part of Fig. 4, where again the experimental behavior is given by crosses. The interaction through e-MV coupling pushes the two modes apart, thus causing their rather strange variation with ρ. One final observation concerns the fourth (TTF, $a_g\nu_2$) mode in Fig. 2. Its e-MV coupling constant is rather small[15] and therefore this mode exhibits an almost linear variation with ρ. It occurs in a spectral region where other a_g modes are expected, so that it is less useful to estimate ρ.

B. Pressure dependence of charge transfer

We are now in the position to evaluate the pressure dependence of ρ from the present Raman data. As the ρ dependence of the CA $a_g\nu_4$ mode is rather small, we use the CA $a_g\nu_3$ and TTF $a_g\nu_6$ modes only and employ the TTF $a_g\nu_2$ as a secondary, independent check. The variation of ρ with pressure so obtained is shown in Fig. 5.

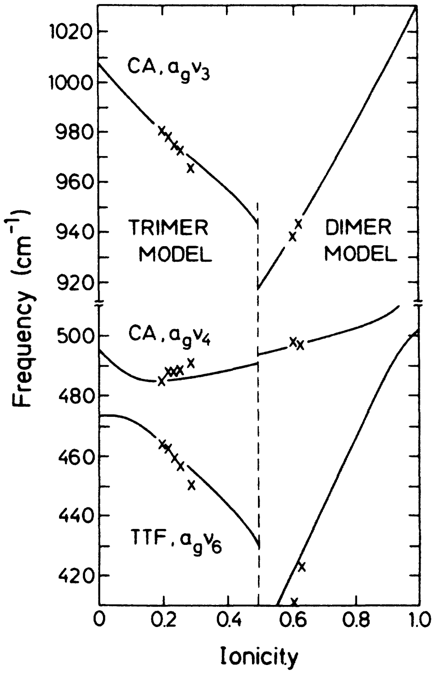

FIG. 4. Frequency of vibrational modes in TTF-CA as a function of ionicity. Solid lines refer to a semiempirical calculation using the trimer and dimer model (see text for details). Crosses refer to results derived from the experimental temperature dependence of vibrational-mode frequencies.

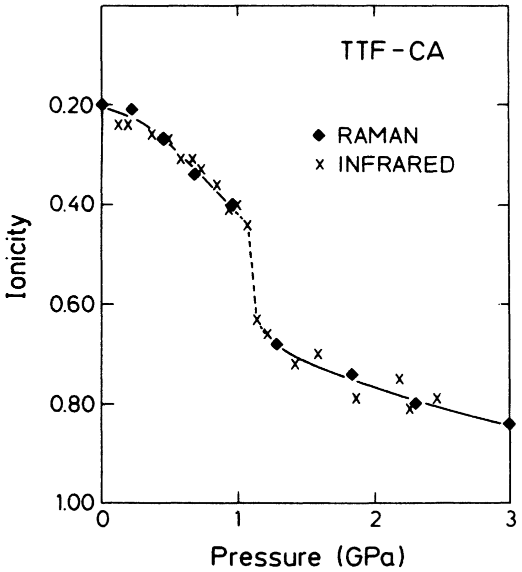

FIG. 5. Ionicity of TTF-CA as a function of pressure ($T = 300$ K). Solid symbols correspond to results derived from the present Raman data. Crosses refer to results obtained through a reinterpretation of the infrared measurements of Ref. 4 (see text). The line is a guide to the eye.

The uncertainty in the estimate of ρ is about 0.05. In the analysis we have neglected the pressure-induced frequency increase due to the overall compression.[23] This approximation should not introduce significant errors, at least for pressures below 3 GPa.

The setting of the point at 0.96 GPa requires some comments. At this pressure both the TTF $a_g\nu_6$ and CA $a_g\nu_3$ modes, which are most sensitive to the charge transfer, show a doublet structure (see Fig. 1). Only the high-frequency component of the doublet is used to evaluate ρ. Apart from this fact (to be discussed below) there is an ambiguity in the choice of the corresponding ρ (either 0.4 or 0.6) due to the cusp structure in the frequency versus ρ curves (Fig. 4). This uncertainty is removed by employing the TTF $a_g\nu_2$ and also the CA $a_g\nu_4$ modes: their frequency dependence on ρ is almost linear and the choice of $\rho=0.4$ becomes unequivocal. The different functional dependence of the frequencies of the four modes also explains why they seem to indicate different pressures for the transition, if only the position of the minima in Fig. 2 is considered. The full analysis described here actually shows that the pressure dependence of all four modes is consistent with a fairly abrupt neutral to ionic transition between about 1.0 and 1.3 GPa.

The pressure dependence of ρ given in Fig. 5 appears to be different from that reported previously.[4] In particular, according to Tokura *et al.*, TTF-CA is already ionic above about 0.7 GPa. Their analysis is based on the frequency shift of the CA $b_{1u}\nu_{10}$ mode (C=O asymmetric stretching, ir active) and a nonlinear dependence of frequency on ρ was assumed. However, in the absence of *e*-MV perturbation, one expects a linear dependence, both on theoretical[15] and experimental[24] grounds. The crosses in Fig. 5 indicate the ionicity obtained from the data of Ref. 4 by assuming a linear dependence of the C=O asymmetric stretch on ρ. The agreement with our present results becomes striking. We therefore conclude that the TTF-CA stack is still mostly neutral ($\rho \approx 0.4$) up to the critical pressure of about 1.1 GPa, where it transforms to the ionic state with $\rho \approx 0.6$.

X-ray,[25] electrical conductivity, and reflectance[14] measurements seem to indicate that there is a precursor regime to the phase transition starting at about 0.7 GPa. Also, the deviation of the absorption-edge shift from a normal behavior (Fig. 3) starts already at about 0.6–0.7 GPa, corresponding to only a small change in slope in Fig. 5. On the other hand, the absorption data are consistent with our above analysis of the Raman data concerning the termination of the phase transition at ~1.1 GPa. Thus, the behavior of TTP-CA in the 0.7–1.1-GPa pressure range requires further examination and we take a closer look at the Raman data in this pressure range. The spectra indicate that in the 0.7–1.1-GPa regime there are inhomogeneities in the sample with two species with different ρ being present. This is particularly evident from the doublet structure of both TTF $a_g\nu_6$ and CA $a_g\nu_3$ modes, not corresponding to a simple superposition of lower- and higher-pressure spectral features (see Fig. 1 and Table I). Due to the limited resolution of our experiment, only the two bands most sensitive to the degree of ionicity appear split. We notice that in the ir spectrum at 0.99 GPa reported by Tokura *et al.*, the CA $a_g\nu_3$ mode starts to appear at the same frequency (940 cm^{-1}) as the low-frequency component of the doublet observed in the Raman spectrum at 0.96 GPa. This observation indicates the presence of dimeric distortions of the lattice. It is reasonable to think that the distorted lattice is on the ionic side, and indeed from the dimer part in Fig. 4 one estimates $\rho \approx 0.6$. Thus, we suggest that in the 0.7–1.1-GPa pressure range, quasi-ionic donor-acceptor dimers are embedded in a quasineutral ($\rho=0.3-0.4$) regular lattice.

The above interpretation differs from that presented in Refs. 4 and 14 in two important aspects. First, for Tokura *et al.*, the TTF-CA crystal is already all ionic in the 0.7–1.1-GPa pressure range, whereas we believe that it is mostly neutral. Second, according to Ref. 14, the 0.7-GPa pressure marks the passage from the neutral to the ionic phase, the dimeric distortions appearing only at higher pressure. Instead, in our view, at 0.7 GPa the dimerized ionic species starts to appear in the quasineutral, regular lattice.[26] By increasing the pressure, the amount of dimeric ionic species increases somewhat, until at 1.1 GPa there is an almost abrupt transition to the fully dimerized ionic phase.

Of course, more measurements are needed to support our hypothesis about the nature of the transition regime in TTF-CA and to decide whether the spectral signatures of ionic dimerized species appearing between 0.7 and 1.1 GPa are due to ionic dimers ingrained in an otherwise neutral regular stack or to ionic dimerized stacks separating the neutral ones.[27] In any case, the inhomogeneous character of the pressure-driven transition appears to be well established now. This behavior is different from the discontinuous first-order phase change induced by temperature, which is, however, also very sensitive to the presence of defects.[2,10,28] The difference between temperature- and pressure-induced transition is not particularly surprising, as fluctuations most probably play an important role at sufficiently high temperature. An explanation of the sensitivity of the NR-ID transitions to experimental conditions (temperature, defect concentration, internal and external stress, etc.) has recently been proposed on the basis of the calculated 0 K phase diagrams of mixed-stack CT crystals.[13]

Note added. After submitting the present manuscript, a recent paper by T. Takaoka *et al.* came to our attention [T. Takaoka, Y. Keneko, H. Okamoto, Y. Tokura, T. Koda, T. Mitani, and G. Saito, Phys. Rev. B **36**, 3884 (1987)]. They report ir absorption data for TTF-CA as a function of pressure and temperature. Although the discussion is not very detailed (in particular with respect to ionicities), it seems to use that their view concerning the inhomogeneous character of the phase transition is now quite similar to the interpretation presented here.

ACKNOWLEDGMENTS

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[26] Preliminary infrared measurements performed by M. Kobayashi clearly indicate the presence of a dimeric species at ≈ 0.8 GPa.

[27] This question is not marginal, as it is related to two different microscopic mechanisms for the phase transition. [See, for instance, J. Hubbard and J. B. Torrance, Phys. Rev. Lett. **47**, 1750 (1981); N. Nagaosa, Solid State Commun. **57**, 179 (1986).] In our opinion, the time-scale reasoning adopted by Torrance *et al.* (Ref. 2) in interpreting the low-temperature ir data, which supports the second hypothesis, does not necessarily apply, because it does not take into account the coupling to the phonons yielding the dimerization. We prefer not to draw any conclusions on this question from the present data.

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