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BRIEF REPORTS

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Fluctuation effects on the Raman scattering from the charge-density-wave system TTF-TCNQ

Y. Lin and J. E. Eldridge

Physics Department, University of British Columbia, Vancouver V6T 1Z1, Canada

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The resonant Raman spectrum of TTF-TCNQ has been measured from room temperature to 10 K, using a Fourier Raman spectrometer. Only features due to the TCNQ molecule are observed. New Raman lines appear at temperatures below 150 K as the fluctuating charge-density wave (CDW) occurs. The intensity of the new Raman lines increases with decreasing temperature. In addition to the Raman allowed modes, we observe numerous lines originating from the usually infrared-active-only modes, which become Raman active via the Fröhlich interaction in the fluctuating and static CDW phases. The appearance of the strong out-of-plane intramolecular B_{3u} vibrational modes of TCNQ confirms an earlier x-ray study that found that the CDW on the TCNQ chain involved such an out-of-plane distortion of the TCNQ molecule. The condensation of the longitudinal acoustic phonon is also observed in the Raman spectrum. [S0163-1829(98)01328-9]

Many quasi-one-dimensional materials show unusual phenomena resulting from the electron-phonon interaction. It is well known that a Peierls phase transition or charge (spin)-density-wave (CDW and SDW) instability will occur below the three-dimensional ordering transition T_{3D} in these materials because of the $2k_F$ distortion, where k_F is the wave vector at the Fermi surface.¹ Recently studies²⁻⁴ have been reported on the fluctuation effect of the CDW between the temperature T_{3D} and T_{CDW}^{MF} , the mean-field transition temperature. This mean-field transition temperature T_{CDW}^{MF} can be estimated from the relation $2\Delta = 3.52k_B T_{CDW}^{MF}$, the well-known BCS relation between the zero-temperature CDW gap Δ and the transition temperature. Δ can usually be found from infrared or tunneling measurements below the metal-insulator transition temperature T_{3D} . Fluctuations play a very important role in the dynamic properties such as the increase in both the dc (Ref. 2) and frequency-dependent conductivity.^{3,4} In this paper we show that the fluctuations are also able to affect the observed resonant Raman scattering from a CDW system.

TTF-TCNQ (tetrathiafulvalene tetracyanoquinodimethane) is a low-dimensional charge-transfer salt, which was for a time the best synthetic organic conductor. It consists of parallel segregated stacks of TTF^+ and $TCNQ^-$ mol-

ecules, along which the electrical conductivity is high. The charge transfer between the molecules is incomplete leading to the formation of an incommensurate CDW, with wave vector $0.295b^*$, as the temperature is lowered. The electrical conductivity increases upon cooling, until at 53 K there is a metal-insulator transition caused by the condensation of the CDW on the TCNQ stacks. This is followed at 49 K by the condensation on the TTF stack and at 38 K a first-order phase transition established a three-dimensional CDW with components $4a \times 3.4b \times c$.

In this paper we report a resonant Raman scattering study on TTF-TCNQ from room temperature down to 10 K. We observe many forbidden Raman lines due to usually-infrared-active intramolecular phonon modes. These are probably becoming Raman active through the Fröhlich interaction.⁵ These new low-temperature lines persist in the fluctuation regime above T_{3D} up to T_{CDW}^{MF} . We have been able to observe almost *all* of the TCNQ intramolecular modes of vibration, both the Raman active and the infrared active. (None of the TTF modes are seen since it is not resonant with the infrared laser.) By far the strongest features are due to the out-of-plane TCNQ B_{3u} modes, with the most intense one of these being the low-frequency out-of-plane distortion of the quinoid ring. This has been shown in a

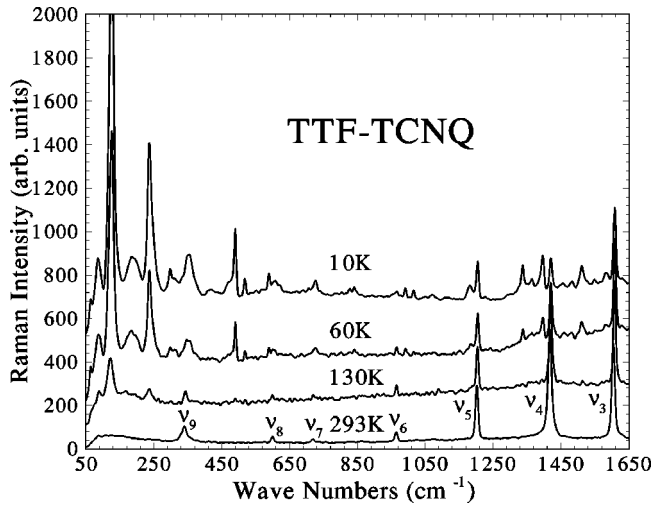


FIG. 1. Raman spectra of TTF-TCNQ between 50 and 1650 cm^{-1} at temperatures 10, 60, 130, and 293 K. Seven of the ten totally symmetric (A_g) modes, which are the room-temperature Raman features, have been labeled (ν_3 - ν_9).

previous x-ray study⁶ to be a strong component of the CDW distortion.

The Raman measurements were performed with a Bruker RFS 100 Fourier Raman spectrometer, which operates with an infrared diode-pumped Nd:YAG laser with a wavelength of 1064 nm. The laser power was 60 mW. An Air Products Heli-Tran refrigerator was used. At each temperature we performed 10 runs of 400 scans each, taking a total of approximately 2 h, and with a resolution of 4 cm^{-1} . The measurements were repeated with the three different isotopic analogs, in which the four hydrogen atoms were substituted by deuterium on either the TTF or the TCNQ molecule, or in both.

In our preliminary communication⁷ of some of these data we described some of the other spectra that were run as checks on possible experimental effects. These included single-crystal spectra instead of powders, freshly prepared samples of both TTF-TCNQ and TSeF-TCNQ, and runs using a Janis dewar in which superfluid helium surrounds the sample.

The temperature dependence of the Raman spectra between 50 and 1650 cm^{-1} is shown in Fig. 1. The room temperature Raman features are due to seven of the ten totally symmetric A_g modes^{7,8} of the TCNQ molecule, with which the Nd:YAG 1064-nm Raman laser frequency is resonant. ν_1 (A_g) and ν_{10} (A_g) were not observed, and ν_2 (A_g) is outside the frequency range plotted. When the temperature is decreased, new Raman lines appear and become stronger with decreasing temperature. Figure 2 shows the Raman spectra of TTF(h_4)-TCNQ(h_4) and TTF(h_4)-TCNQ(d_4) at 10 K. With the aid of the measured deuterium-isotope frequency shifts, we were able to assign all of our measured Raman features in Tables I and II. Some Raman lines have one or more shoulders, which have been fitted with several Lorentzians, from which we have determined the resonant frequencies.

It is straightforward to assign eight of the ten in-plane totally symmetric A_g vibrational modes, which are the only Raman features at room temperature. The 10-K spectrum

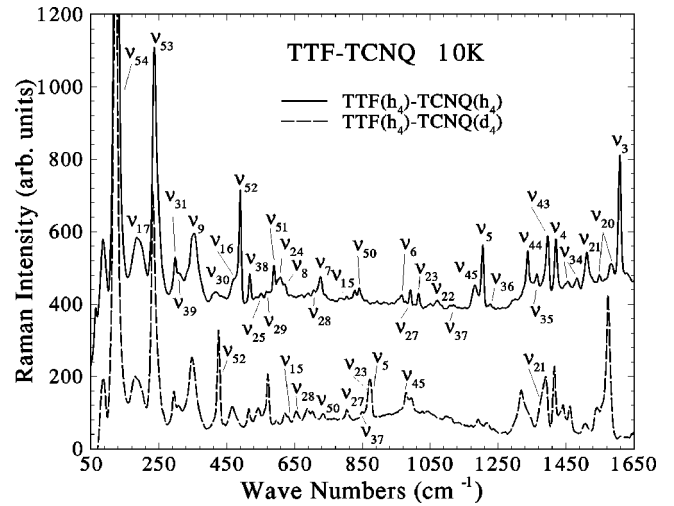


FIG. 2. Raman spectra of TTF(h_4)-TCNQ(h_4) and TTF(h_4)-TCNQ(d_4) between 50 and 1650 cm^{-1} at 10 K. The Raman lines of TTF(h_4)-TCNQ(h_4) have been assigned and labeled by comparison with the data from Refs. 8–10. The Raman lines, which have a large deuterium-isotope frequency shift, have also been labeled in the spectrum of TTF(h_4)-TCNQ(d_4). The line at 86 cm^{-1} right below ν_{54} (B_{3u}) is an atmospheric line.

contains several strong lines at low frequency with the strongest at 125 cm^{-1} , the next at 236 cm^{-1} , and a third at 489 cm^{-1} . These three, along with two other weaker lines at 589 and 840 cm^{-1} have been assigned to the out-of-plane B_{3u} intramolecular vibrational modes of TCNQ. We note that these strong B_{3u} modes are usually infrared-active only. All of the other smaller features have also been assigned by comparison with the data from Refs. 8 and 9. The lowest Raman peak has a frequency of 63 cm^{-1} , which is the same as that of the longitudinal-acoustic phonon observed by neutron scattering.¹¹

We will now discuss the following issues raised by the

TABLE I. Frequencies (cm^{-1}) and assignments of the *out-of-plane* vibrational modes of the TCNQ molecule in TTF-TCNQ at 10 K, by comparison with the room-temperature data from Ref. 9.

Symmetry	ν	TTF- h_4	TTF- h_4	Expt.	TCNQ- h_4	Ref. 9
		TCNQ- h_4	TCNQ- d_4		$\Delta\nu$	
B_{1g}	ν_{17}	186	179	7	169	8
	ν_{16}	469	466	3	428	4
	ν_{15}	804	631	173	816	178
B_{2g}	ν_{31}	297	294	3	300	9
	ν_{30}	412				
	ν_{29}	567	558	9	593	11
	ν_{28}	706	655	51	752	58
	ν_{27}	991	804	187	1002	173
B_{3u}	ν_{54}	125	122	3	103	2
	ν_{53}	236	232	4	225	5
	ν_{52}	489	426	63	483	60
	ν_{51}	589	571	18	585	20
	ν_{50}	840	734	106	836	104

TABLE II. Frequencies (cm^{-1}) and assignments of the *in-plane* vibrational modes of the TCNQ molecule in TTF-TCNQ at 10 K, by comparison with the room-temperature data from Ref. 8.

Symmetry	ν	TTF- h_4	TTF- h_4	Expt.	TCNQ- h_4	Ref. 8
		TCNQ- h_4	TCNQ- d_4		$\Delta\nu$	
A_g	ν_9	347	347	0	337	0
	ν_8	621	620	1	613	1
	ν_7	726	702	24	725	24
	ν_6	964			978	8
	ν_5	1204	875	329	1196	325
	ν_4	1420	1416	4	1391	2
	ν_3	1608	1574	34	1615	34
	ν_2	2212	2212	0	2206	0
B_{3g}	ν_{45}	1180	979	201	1183 ^a	227 ^a
	ν_{44}	1336	1318	18	1326 ^a	18 ^a
	ν_{43}	1395	1390	5	1398 ^a	7 ^a
B_{1u}	ν_{25}	550	542	8	541	13
	ν_{24}	607	597	10	600	-2
	ν_{23}	1015	869	146	987	161
	ν_{22}	1070	1043	27	1008	34
	ν_{21}	1511	1380	131	1361	139
	ν_{20}	1548	1507	41	1504	43
		1582	1541	41		
	ν_{19}	2185	2185	0	2181	2
B_{2u}	ν_{39}	308	308	0	301	2
	ν_{38}	517	515	2	498	2
	ν_{37}	1117	847	270	1125	270
	ν_{36}	1226	1292	34	1210	29
	ν_{35}	1364	1334	30	1358	38
	ν_{34}	1455	1441	14	1540	30
	1482	1461	21			

^aData measured at 77 K from Ref. 10.

results: (i) the fluctuation of the CDW at low temperatures, (ii) the appearance of the Raman scattering originating from the infrared-active-only modes, (iii) the out-of-plane distortion of the TCNQ molecule in the CDW phase, and (iv) the condensation of the longitudinal-acoustic phonon.

Infrared measurements^{12,13} have determined a low-temperature gap of approximately 290 cm^{-1} , which starts to develop in the temperature range $T_{3D} < T < T_{CDW}^{MF}$, as a result of fluctuations. From the relation $2\Delta = 3.52k_B T_{CDW}^{MF}$, T_{CDW}^{MF} is calculated to be 120 K. Upon lowering the temperature below T_{CDW}^{MF} , one-dimensional fluctuations start to occur first, which then change over to two and three-dimensional fluctuations until T_{3D} , the actual temperature of the Peierls transition.

Figure 3 shows the integrated intensities of the lines assigned to $\nu_{54}, \nu_{53} (B_{3u})$ modes, the two strongest Raman lines at 10 K, as a function of temperature. One can see that ν_{53} is still present at 130 K and ν_{54} at 170 K. The fluctuating CDW produces the lines as well as the three-dimensionally ordered CDW. The temperature limit around 150 K would seem to correspond to the $2k_F$ diffuse x-ray and neutron scattering, rather than the $4k_F$ scattering, since Pouget

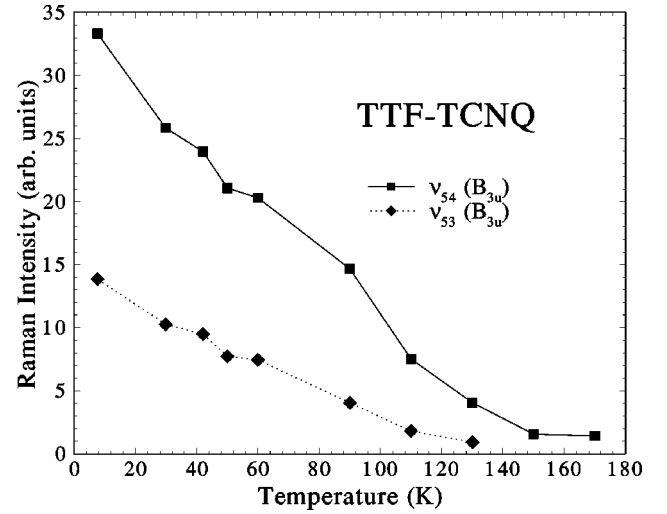


FIG. 3. The integrated intensity of the Raman lines assigned to $\nu_{54}(B_{3u})$ and $\nu_{53}(B_{3u})$ modes as a function of temperature.

*et al.*¹⁴ found that the $4k_F$ x-ray scattering was still clearly visible at 220 K whereas that due to the $2k_F$ scattering disappeared at 150 K. The T_{CDW}^{MF} inferred from the infrared measurements is lower than the value measured here and from the $2k_F$ x-ray measurements. Within the accuracy of the data there is no indication from Fig. 3 of the phase transitions at 54, 49, or 38 K.

In Fig. 1 and 2, we observe many new Raman lines from usually infrared-active-only modes, below T_{CDW}^{MF} . The Fröhlich electron-phonon interaction below T_{CDW}^{MF} induces the CDW fluctuation. It is natural to consider the Fröhlich interaction to be the cause of the additional lines. Forbidden Raman scattering by infrared-active-only LO phonons has been observed for many materials.^{15,16} This scattering does not follow the selection rules for zone-origin phonons. The forbidden LO scattering may arise from the intraband matrix elements of the Fröhlich electron-phonon interaction if the dependence of these matrix elements on the phonon wave vector q is taken into account. The matrix elements⁵ between the electronic states l and j such that $k_j = k_l - q$ are

$$\langle n+1, j | H_F | n, l \rangle = C_F \left[\frac{\delta_{jl}}{|q|} + \langle j | \frac{q \cdot p}{|q|} | l \rangle (1 - \delta_{jl}) \right],$$

where C_F is the Fröhlich constant and k, p are the photon wave vector and momentum, respectively. The third term is the nonvanishing term of the lowest order when there is a center of inversion and describes first-order intraband scattering of LO phonons. Because it is zero for $q=0$ this term is often referred to as dipole “forbidden.” Under resonance condition, however, this term can become considerable even for the small q imparted to the phonon by the incident laser in a first-order process.

A number of facts support the Fröhlich model: (i) the strong electron-phonon interaction developed below T_{CDW}^{MF} , (ii) the presence of a center of inversion in TTF-TCNQ (iii) the Nd:YAG laser is resonant with the TCNQ molecule, (iv)

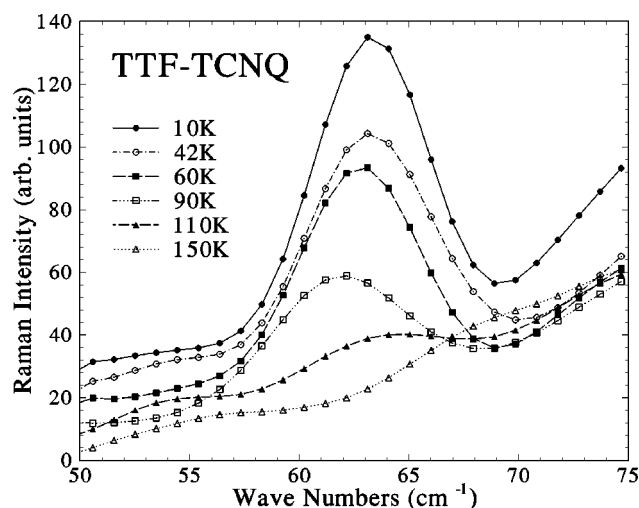


FIG. 4. Temperature dependence of the Raman scattering from TTF-TCNQ at 63 cm^{-1} .

the resonance enhancement of the forbidden Raman lines makes them stronger than the allowed phonons, (v) the frequencies of three of the B_{3u} modes observed here are higher than the frequencies measured by Bozio and Pecile¹⁷ in powders of TTF-TCNQ at 23 K by infrared absorption. The latter of course are the transverse-optic (TO) frequencies, which are necessarily lower than the longitudinal-optic (LO) frequencies involved in the Fröhlich mechanism. Bozio and Pecile report frequencies of 834 , 575 , and 477 cm^{-1} for ν_{50} , ν_{51} , and ν_{52} respectively, whereas we measure 840 , 589 , and 489 cm^{-1} (see Table I), a good indication that they are LO modes. ν_{53} , however, is not as clear. We measure only 236 cm^{-1} here, whereas Bozio and Pecile report 237 cm^{-1} and an earlier infrared paper by us reported 240 cm^{-1} for both polarizations.¹⁸ (Furthermore the assignment was confirmed by the correct 4 cm^{-1} isotope shift.¹⁸) Unfortunately in neither Ref. 17 or Ref. 18 was ν_{54} observed, or any other ungerade TCNQ modes.

Bouveret and Megtert⁶ in 1989 performed an experiment using a conventional rotating-anode x-ray source and many hours of data collection to improve the structural determination of the lowest-temperature phase by including the possibility of low-frequency intramolecular distortions. They found that the TTF molecules displayed no significant distortions and mainly slid upon their mean molecular plane. With TCNQ, however, they found a large out-of-plane intramolecular distortion which involves a substantial displace-

ment of the quinoid ring perpendicular to the mean molecular plane. From Fig. 2 and Table I, we can see that the low frequency out-of-plane vibrational modes are much stronger than other modes. $\nu_{54}(B_{3u})$, which is the assignment of the most intense line at 125 cm^{-1} , is the out-of-plane bend of the quinoid ring and is the lowest frequency B_{3u} mode. $\nu_{53}(B_{3u})$, the second strongest line at 236 cm^{-1} , is the out-of-plane bend of the quinoid wing of the TCNQ molecule. Thus we find a large out-of-plane distortion of the TCNQ molecule in the CDW phase below $T_{\text{CDW}}^{\text{MF}}$, which is consistent with the x-ray result.⁶

The Peierls distortion in TTF-TCNQ is accompanied by the condensation of a transverse acoustic (TA) phonon^{11,19} which is not observed here since it has a frequency below 50 cm^{-1} , which is in the range removed by our Raleigh line filter. The neutron scattering study¹⁹ revealed that the $2k_F$ satellites arising from the condensation of the longitudinal part of the $2k_F$ anomaly correspond to the same modulation of the lattice as the $2k_F$ satellites originating from the condensation of the $2k_F$ transverse-acoustic anomaly. The longitudinal-acoustic (LA) phonon is observed to be at 63 cm^{-1} at temperatures between 60 and 150 K.¹¹ We also observe a very weak Raman line at 63 cm^{-1} . The temperature dependence of this line is shown in Fig. 4. We can see that the intensity goes down as the temperature goes up. The line disappears around 150 K. This temperature dependence of the intensity enables us to consider this mode to be the LA phonon observed by neutron scattering.

In summary, we have studied the Raman spectra of TTF-TCNQ at room temperature down to 10 K. The Nd:YAG laser is resonant with the TCNQ molecule. Many new lines appear at temperatures below $T_{\text{CDW}}^{\text{MF}} = 150 \text{ K}$ as the fluctuating CDW occurs. The intensity of these lines increases with decreasing temperature. There is no clear indication of the phase transitions at 38, 49, and 53 K. We have assigned the new lines according to the deuterium-isotope frequency shifts. In the fluctuating CDW phase the Fröhlich electron-phonon interaction is the probable cause of the appearance of Raman-forbidden scattering originating from the infrared-active-only modes. The strong out-of-plane vibrational Raman modes correspond to the large out-of-plane distortion of the TCNQ molecule, which is in agreement with the x-ray results. We also observe in the Raman spectra the condensation of the longitudinal acoustic phonon.

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