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Assignment of the lattice modes in TCNQ⁰ single crystals

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A complete assignment of the six librational modes of the TCNQ⁰ crystal has been made employing both polarized Raman spectroscopic measurements and lattice dynamical calculations. Agreement between theory and experiment is good and modes at 40.5, 74.5, and 96 cm⁻¹ are assigned as *A_g* active and those at 63, 75.5, and 104 cm⁻¹ are *B_g* active. The lattice modes are found to be clearly separated from the molecular modes. The study emphasizes the importance of crystal optics and quality in the measurement of the polarized Raman spectra of biaxial crystals.

I. INTRODUCTION

The study of intermolecular potentials has been an active area of research for many years. Perhaps the most effective approach for their calculation has involved using the parametrized Buckingham or Lennard-Jones potentials.^{1,2} These functions, which are employed to calculate interatomic interactions between molecules, are used widely and are appropriate to many different systems. The parameters are almost exclusively obtained from the consideration of the structure and energetics of organic molecular crystals. Interestingly, these same crystal systems have not received a great deal of attention with regard to their lattice dynamics. This is curious since the forces holding the lattice together are particularly simple when compared to other systems. An explanation for this probably lies in the complicated nature of the basis, although application of the rigid body approximation can yield exceedingly useful results.

A research effort directed at understanding the lattice dynamical properties of molecular crystals has been undertaken in our laboratory. Particular interest has been directed at understanding the anharmonicity of the potential in organic molecular solids. A new spectroscopic approach to this problem, piezomodulated Raman spectroscopy, has been developed.³ It is sensitive to the anharmonic interactions in a crystal and can be used to examine the anisotropy of the potential. In particular, it has been shown that this approach provides a direct observation of coupling between vibrational modes in the molecular crystal lattice.

A molecular crystal well-suited to this investigation is 7,7,8,8-tetracyanoquinodimethane (TCNQ⁰). Solid state interactions in crystals of TCNQ⁰ and its salts are of interest because of the metallic and semiconducting properties that these solids exhibit.⁴⁻⁶ In addition, the possibility of significant coupling between external and internal vibrational modes in the TCNQ⁰ lattice has been raised in studies using Raman spectroscopy. The interpretation of the results, however, has not been unambiguous, especially when trying to assign the Raman active lattice modes. A set of assignments has been proposed in a report of polarized Raman spectra of the TCNQ⁰ single crystal, but it was suggested therein that extensive coupling between the lattice modes and low frequency intramolecular vibrations prevented the identifica-

tion of pure lattice modes.⁷ Indeed, the polarization data for two of the assigned lattice modes were actually found to be more characteristic of intramolecular modes. The existence of coupling has been confirmed in temperature⁸ and pressure⁹ dependent Raman studies of TCNQ⁰ crystals. In the latter study, two vibrational bands were observed in the gas phase Raman spectrum of TCNQ⁰ below 100 cm⁻¹, implying that intramolecular modes are present in the low frequency portion of the spectrum. Since this region is normally occupied by the lattice modes in molecular crystals, the gas phase results suggest that a demarcation in frequency between the external and internal vibrational modes in TCNQ⁰ is not possible. Such a conclusion casts further doubt on the lattice mode assignments proposed for TCNQ⁰.

Clarification of the lattice dynamics of the TCNQ⁰ crystal is clearly needed. Before piezomodulated Raman spectroscopy in the low frequency region can be effectively employed, it is desirable to identify, to the greatest extent possible, the Raman active lattice modes. With this intent, we present here the polarized Raman spectra of TCNQ⁰ single crystals measured at room temperature for six different polarization configurations. The results are found to differ significantly from the data reported previously and offer a new assignment of the lattice modes in TCNQ⁰. To elucidate the data and to assist in an understanding of the actual motions of the molecules, a lattice dynamical calculation for TCNQ⁰ has also been performed.

In the following section of the paper, the experimental procedure is described and the crystal structure and symmetry are considered. The results of the experiments are presented next, subsequent to which is given a detailed discussion of the lattice mode assignments using the data and results of the lattice dynamical calculation.

II. EXPERIMENTAL

Single crystals of TCNQ⁰ were obtained by slow evaporation of acetone solutions at room temperature. The spectra were taken with the crystals mounted in a 90° scattering geometry. For four of the six polarization configurations, the naturally occurring (010) and (001) faces of TCNQ⁰ were oriented perpendicular to the directions of the incident and scattered light, respectively. However, for the other two configurations, it was necessary to use the face parallel to the *bc** plane of the crystal, where *c** is the appropriate reciprocal

^{a)} Work completed in partial fulfillment of requirements for the Ph.D. at the University of Nebraska-Lincoln.

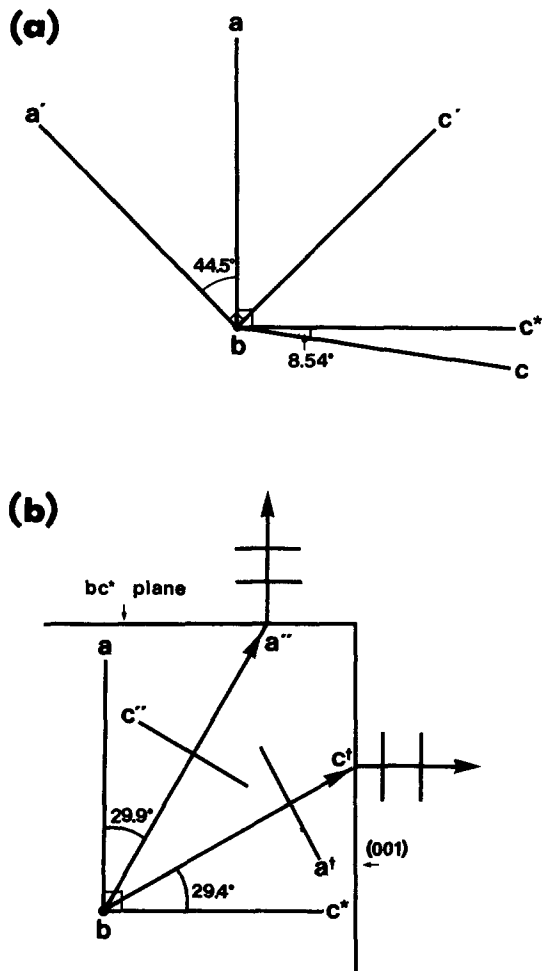


FIG. 1. The reference axial system used in the Raman experiment viewed down the twofold b axis. In (a) the a' , b , and c' principal axes are shown relative to the a , b , and c^* crystallographic axes of the TCNQ⁰ lattice. The a'' , c'' , c^\dagger and a^\dagger directions indicated in (b) correspond to the actual ray and polarization directions of scattered light inside the crystal that is detected along the a or c^* axes and polarized perpendicular to the b axis.

lattice vector. This face was cut by means of a wire saw and then smoothed using an LKB Ultrame III 8800 ultramicrotome. Finally, the surface was rendered suitable for taking spectra by polishing it on a cloth with a slurry of 0.05 μm micropolish in water until it was transparent and nearly specular.

The spectra were measured using the 5145 \AA line of a single moded, Coherent CR-6 argon ion laser. The power of the beam at the sample was 15 mW. A polarization rotator controlled the polarization of the incident beam and the scattered light was analyzed by a Polaroid sheet. An iris placed just prior to the analyzer minimized the detection of mixed polarizations in the measured spectra. The scattered light was then focused through a polarization scrambler onto the entrance slit of a SPEX model 1400-II double monochromator equipped with holographic gratings. The signal from a cooled, Hamamatsu R928 photomultiplier tube was amplified by means of lock-in detection and the data were stored by computer. The spectra were digitally recorded from 5 to 190 cm^{-1} at 1 cm^{-1} intervals. The spectral bandpass was 1.4 cm^{-1} and the measured frequencies have an accuracy of $\pm 1 \text{ cm}^{-1}$.

The choice of the reference axial system and polarization configurations used in measuring the single crystal Raman spectra of TCNQ⁰ is very important because of the significant effects of the crystal optics on the incident and scattered light. By employing configurations in which the exciting laser beam does not undergo depolarization or a change in ray direction upon entering the crystal, mixing of polarizations in the spectra is avoided and a full vertical image of the beam inside the sample can be focused onto the monochromator slit for maximum throughput of the scattered light. This was achieved by choosing the principal axes of the polarizability ellipsoid of the TCNQ⁰ crystal to be the reference system, with polarization configurations $b(a'a^\dagger)c^\dagger$, $b(c'a^\dagger)c^\dagger$, $b(c'c'')a''$, $a(bb)c^*$, $b(a'b)c^*$, and $b(c'b)c^*$ (see Fig. 1). The principal axes, denoted a' , b , and c' , were determined from previous spectroscopic work.^{7,10}

For the first three configurations, which detected scattered light polarized perpendicular to the b axis, it was necessary to take into account a deviation in ray and polarization direction. The refractive indices for the a' and c' axes at 5145 \AA were determined from reflection spectroscopy to be 1.78 and 3.40, respectively.¹¹ These values were then used to calculate the altered polarization and ray directions inside the crystal for light having its wave normal oriented along the c^* or a axis and polarization perpendicular to the b axis. The results are diagrammed in Fig. 1(b). Light collected in the c^* direction with polarization along a actually comes from light inside the crystal that was scattered in the c^\dagger direction with polarization along a^\dagger . In a similar manner, light collected along a with polarization along c^* outside the crystal originates from a beam inside the crystal traveling along the a'' direction with polarization along c'' . An important consequence of specifying the polarizations using the direction of the electric vector of the light internal to the crystal is that the relative intensities of the bands in the Raman spectrum so described will be the same regardless of the directions specified for the incident and scattered light.

To aid the interpretation of the spectral data, all six spectra were placed on the same intensity scale. This was accomplished for the $b(a'a^\dagger)c^\dagger$, $b(c'a^\dagger)c^\dagger$, $b(a'b)c^*$, and $b(c'b)c^*$ spectra by measuring each of them using the same crystal in the same position and orientation, while changing only the polarization rotator and/or the analyzer in between measurements. In a similar manner, the $b(c'c'')a''$ spectrum was measured relative to the $b(c'b)a$ spectrum. Since the crystal optics in TCNQ⁰ dictate that the intensities of the $b(c'b)a$ and $b(c'b)c^*$ spectra be nearly identical, the $b(c'b)a$ spectrum was used as an intensity reference to scale the $b(c'c'')a''$ spectrum to the first four spectra. Finally, it was not possible to measure the $a(bb)c^*$ spectrum relative to a reference spectrum. Therefore, it was scaled to the other spectra solely from a consideration of the sensitivity settings of the detection electronics used in the different measurements with all other experimental conditions held constant. Since it did not employ a reference, this last method of scaling is only an approximation.

Identification of the lattice modes in a molecular crystal requires a knowledge of the crystal structure and its symmetry. TCNQ⁰ crystallizes in the $C2/c$ space group with four

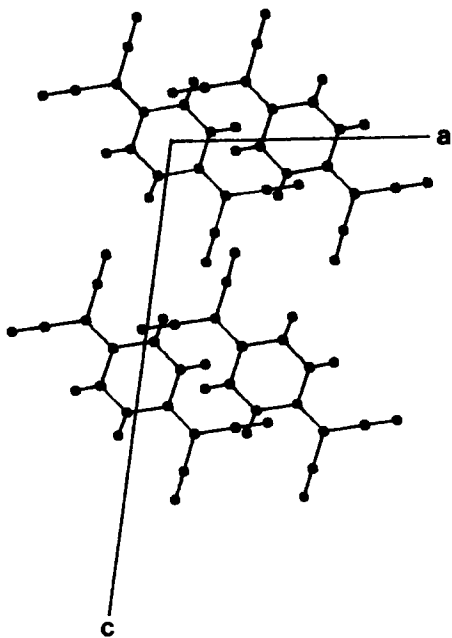


FIG. 2. Projection of the TCNQ⁰ unit cell onto the (010) plane. The two molecules on the left have their centers at $b = 0$, while those on the right are displaced one-half of a lattice translation up the b axis.

molecules in the crystallographic unit cell¹² (see Fig. 2). To determine the number of lattice modes, however, one must consider only the two molecules found in the primitive unit cell. A symmetry analysis then predicts that there will be nine optical lattice modes, six being Raman active and the remaining three infrared active:

$$\Gamma = \underbrace{3A_g + 3B_g}_{\text{Raman}} + \underbrace{2A_u + B_u}_{\text{Infrared}}.$$

Of the six polarization configurations used in our experiments, Raman selection rules for a monoclinic crystal predict that the three modes of A_g symmetry will be observed only in the $b(a'a')c^\dagger$, $a(bb)c^*$, $b(c'c'')a''$, and $b(c'a^\dagger)c^\dagger$ spectra (hereafter referred to as A_g spectra), while the three having B_g symmetry should be seen only in the $b(a'b)c^*$ and $b(c'b)c^*$ spectra (hereafter referred to as B_g spectra). On the other hand, the intramolecular vibrational modes may be observed in both the A_g and B_g spectra, depending on the symmetry of the mode and the polarization configuration of the given spectrum. The molecular symmetries of these modes may be determined by comparing the relative intensities of their bands in the various polarization configurations, called polarization data, to theoretical relative intensities derived using the oriented gas approximation. For the purpose of discussion, the predicted oriented gas relative intensities, as well as symmetry and vibrational mode designations, will be taken from Ref. 7. Factor group symmetries will be expressed in upper case letters and molecular group symmetries in lower case letters.

III. RESULTS

The polarized Raman spectra of TCNQ⁰ initially showed severe variability in intensity for the bands near 40

and 75 cm^{-1} relative to the other bands observed in the spectra. An example is shown in Fig. 3. In the two spectra shown, the relative intensities of the bands at 63 and 104 cm^{-1} remain the same while the intensities of those at 40.5 and 75.5 cm^{-1} change radically. The intensities of these latter two bands were found to be dependent both on the crystal used in the measurement and the positions of the incident and scattered beams on the crystal faces. The causes of these fluctuations in intensity were the presence of internal defects in the crystal and the poor quality of the crystal surfaces due to films, "hopper growth",¹³ and surface roughness. These effects caused the incident and scattered light in the Raman experiment to be depolarized. As a result, modes of one particular symmetry, especially those displaying very intense peaks, would give rise to additional bands or add intensity to existing bands in spectra of another symmetry where they were not allowed. This has been a source of difficulty in the polarized Raman spectra of several different molecular crystals and probably has been the reason for the observation of the 40.5 cm^{-1} band in both A_g and B_g spectra of TCNQ⁰ by previous investigators.^{7,14} Care was taken to use single crystals of TCNQ⁰ which had very clean, specular faces and no visible defects, but even under these conditions some of the more intense peaks still gave rise to small structures in spectra in which they were forbidden. Such an observation could also be the result of using a nonzero collection angle for the scattered light.

Since the polarized Raman spectrum is very sensitive to both the surface and bulk quality of the crystal used, the integrity of the spectra obtained from the crystals cut to create a face parallel to the bc^* plane was of particular concern. To assure the quality of the $a(bb)c^*$ spectrum, a measurement was taken in another configuration having the incident and scattered light polarized along the b axis. In this experiment, the incident beam entered the (001) face approxi-

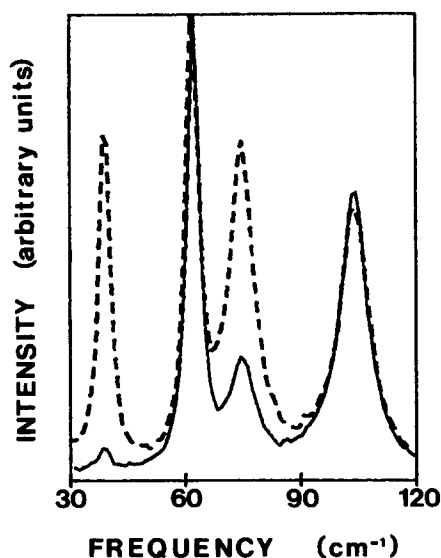


FIG. 3. An example of the effects of crystal imperfections on the $b(a'b)c^*$ Raman spectrum of a TCNQ⁰ single crystal. The spectra shown were measured from different locations of the same crystal without changing the crystal orientation. Rayleigh scattering from crystal defects was observed visually for the incident laser beam position used in the spectrum indicated by the broken line.

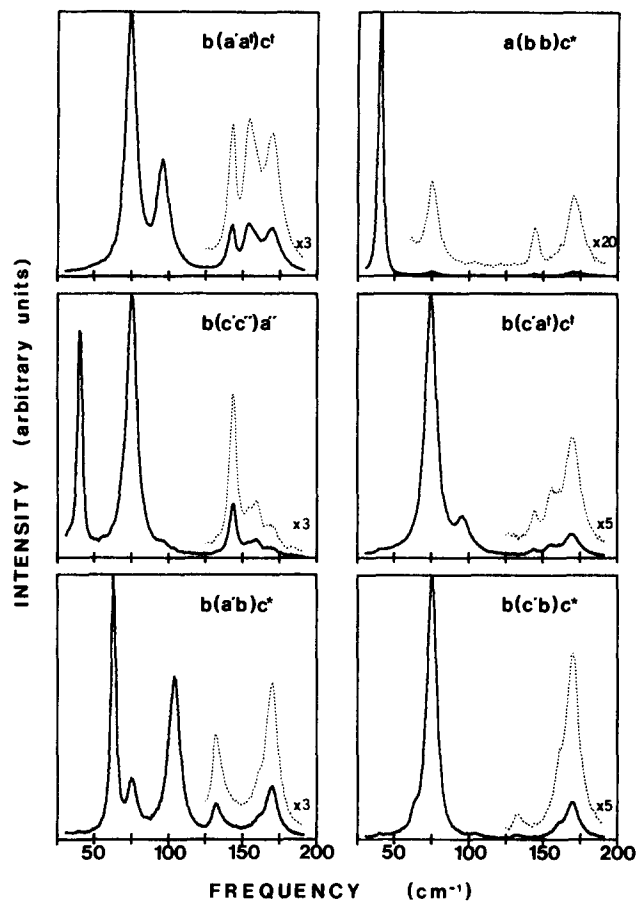


FIG. 4. Polarized Raman spectra of the TCNQ⁰ single crystal in the low frequency region. The intensity scale in each spectrum has been normalized to its tallest peak.

mately 60° from the normal and the scattered light was collected normal to the incoming light. This configuration maintained the polarization of the light along the *b* axis despite entry and exit from the crystal which was off the normal to (001). The (*bb*) spectra in the two configurations were identical, indicating that the cut surface was of sufficient quality to prevent the appearance in the *a*(*bb*)*c** spec-

trum of bands having a different polarization.

To determine the quality of the *b*(*c'c''*)*a''* spectrum, the *b*(*c'b*)*a* spectrum was taken using the same crystal orientation. Should the cut face be sufficiently free of defects, the relative intensities of the bands in the *b*(*c'b*)*a* spectrum would be the same as those observed previously in the *b*(*c'b*)*c** spectrum using naturally occurring faces. The relative intensities in the two spectra were found to be the same, except for a small band which appeared near 40 cm⁻¹ in the spectrum involving the cut face. It was concluded that the *b*(*c'c''*)*a''* spectrum might contain some structure due to intense modes having *B_g* symmetry, but the amount would be small enough so as not to hinder the assignments of the lattice modes.

The polarized Raman spectra of TCNQ⁰ for the six polarization configurations are shown in Fig. 4. In each spectrum, the intensity scale has been normalized to the tallest peak. Only the frequency region from 30 to 190 cm⁻¹ has been plotted since no peaks could be observed between 5 and 30 cm⁻¹ for any of the polarizations. In all, 12 bands can be observed and their frequencies have been tabulated in Table I. In general, the frequencies are in agreement with those reported in other Raman studies of TCNQ⁰.^{7-9,14-16} Nevertheless, there are some important differences. A previously unreported shoulder can be seen around 137 cm⁻¹ in the *b*(*a'b*)*c** and *b*(*c'b*)*c** spectra. A more significant difference concerns the intense peak observed near 75 cm⁻¹. A reproducible difference of approximately 1 cm⁻¹ was observed between the frequencies of the peak measured in spectra of different symmetries. In the *A_g* spectra the peak is located at 74.5–75 cm⁻¹, while in the *B_g* spectra it is seen at 75.5–76 cm⁻¹. Even though the accuracy of the reported frequencies is ± 1 cm⁻¹, the error in their difference is estimated to be less than 0.5 cm⁻¹.¹⁷ The fact that the measured frequencies in the *B_g* spectra were always higher than those observed in the *A_g* spectra also supports the existence of this difference.

The relative peak intensities of the bands in the Raman spectra are listed in Table I. The intensity values were determined with the spectra for all six polarization configurations on the same scale to allow for comparisons between spectra.

TABLE I. Polarized Raman spectra of TCNQ⁰ single crystals.

Frequency (cm ⁻¹)	Relative peak height ^a (arb. units)					
	<i>b</i> (<i>a'a</i>) <i>c</i> †	<i>a</i> (<i>bb</i>) <i>c</i> *	<i>b</i> (<i>c'c''</i>) <i>a</i> ''	<i>b</i> (<i>c'a</i>) <i>c</i> †	<i>b</i> (<i>a'b</i>) <i>c</i> *	<i>b</i> (<i>c'b</i>) <i>c</i> *
40.5	...	4100	478	w	w	w
63	1668	sh
74.5	1672	74	558	298
75.5	350	680
96	721	...	w	44
104	1010	w
132	184	9
137	sh	sh
144	292	37	107	7
154	302	...	(27)	(10)
160	sh	sh	(32)	sh	sh	sh
170	271	62	(15)	22	297	92

^a The values listed for all six polarization configurations are based on the same intensity scale. Values in parentheses indicate the band significantly overlaps neighboring bands. Weak bands are denoted by w and shoulders by sh.

Since it can be shown¹⁸ that the relative intensities of the bands observed in the $b(a'a^{\dagger})c^{\dagger}$, $b(c'a^{\dagger})c^{\dagger}$, $b(a'b)c^*$, and $b(c'b)c^*$ spectra are not altered when the scattering configuration is reversed, one can compare the relative intensities in any one of these spectra with those reported for the corresponding spectrum measured by Girlando and Pecile using a reversed, 90° scattering geometry.⁷ However, the ratio of intensities *between* spectra of different polarization configurations cannot be compared to the ratio between spectra of the corresponding reversed configurations without correcting for the effects of the crystal optics on the incident and scattered light.

The agreement of the relative intensities in the two sets of spectra is qualitative with two important exceptions. In the $b(a'b)c^*$ spectrum, the bands at 63 and 104 cm^{-1} are relatively much more intense than previously reported, and the bands at 40.5 and 75.5 cm^{-1} are relatively much weaker. The second difference deals with the mode at 40.5 cm^{-1} . This band is extremely intense in the $a(bb)c^*$ spectrum and is also seen in the $b(c'c'')a''$ spectrum. However, the band is, for all practical purposes, absent from the other four spectra. This is in contrast to the data of Girlando and Pecile, who did see a very strong peak at 41 cm^{-1} in the $b(c'c')b$ forward scattering spectrum, but did not report any bands below 300 cm^{-1} in the $c^*(bb)c^*$ forward scattering spectrum. On the other hand, they did measure peaks at 41 cm^{-1} in all four of their right angle scattering spectra. While some intensity is seen near 40 cm^{-1} in our $b(a'b)c^*$, $b(c'b)c^*$, and $b(c'a^{\dagger})c^{\dagger}$ spectra, it is very small and is attributed to a mixing of polarizations. Since the 40.5 cm^{-1} mode is so intense, a portion of its intensity could easily appear in spectra of other polarizations due to a nonzero collection angle for the scattered light and imperfections in the crystal. Such an effect has been demonstrated above.

IV. DISCUSSION

The assignment of the Raman active lattice modes in TCNQ⁰ from the spectral data reported here appears to be straightforward. In the $b(a'a^{\dagger})c^{\dagger}$, $a(bb)c^*$, $b(c'c'')a''$, and $b(c'a^{\dagger})c^{\dagger}$ spectra, three distinct bands are observed in the region below 120 cm^{-1} at 40.5, 74.5, and 96 cm^{-1} . These are assigned to the three lattice modes of A_g symmetry. In the $b(a'b)c^*$ and $b(c'b)c^*$ spectra, three more bands appear in this same region at 63, 75.5, and 104 cm^{-1} . These correspond to the three lattice modes having B_g symmetry.

The interpretation of these assignments in light of previously published data requires some discussion. The assignment of the 96 and 104 cm^{-1} bands to lattice modes of A_g and B_g symmetry, respectively, agrees with the earlier assignment by Girlando and Pecile.⁷ However, the band at 63 cm^{-1} was not considered in their vibrational mode assignments, even though it was observed. Its assignment here as a lattice mode of B_g symmetry is based on its low frequency and its appearance only in the B_g spectra. The fact that it displays a very intense peak in the $b(a'b)c^*$ spectrum makes it imperative to consider such an assignment.

The band at 40.5 cm^{-1} has been difficult to assign because it has exhibited characteristics of both an intramolecu-

lar mode and a lattice mode in prior Raman studies. The observation of a 40 cm^{-1} band in the gas phase Raman spectrum implied that its origin was molecular.⁹ However, it has been shown in a mass spectroscopic study of TCNQ⁰ that dimers do exist in the gas phase.¹⁹ It was determined in the study that the dimers formed before the ionization process and were tightly enough bound for a fraction of them to exist even after electron impact. While the percentage of dimers observed in the mass spectrum relative to the monomer peak was quite small, it is probable that under normal conditions the amount increases significantly. From this evidence, the 40 cm^{-1} band seen in the gas phase Raman spectrum of TCNQ⁰ can be attributed to an intermolecular mode in the dimer. The molecular masses and intermolecular force constants existing in such a dimer would easily account for a frequency at 40 cm^{-1} .²⁰ Moreover, if the molecular motions in this dimer mode were similar to those involved in the 40.5 cm^{-1} lattice mode of TCNQ⁰, the resulting Raman intensity would be large, as observed for the lattice mode, and a peak could be seen in the gas phase spectrum even with a relatively small fraction of dimers present.

The appearance of the 40.5 cm^{-1} band in both the A_g and B_g Raman spectra of the TCNQ⁰ single crystal measured previously⁷ was recognized as not consistent with a lattice mode assignment, but it was felt that a mode with such a low frequency could not be intramolecular. As a result, it was attributed to a lattice mode in TCNQ⁰, but the determination of its symmetry was uncertain. From the results presented here, the 40.5 cm^{-1} mode is assigned as a lattice mode of A_g symmetry. Observations of this band in B_g spectra have been explained by a mixing of polarizations arising from crystal imperfections.

The bands near 75 cm^{-1} have been reported as a single peak in earlier Raman studies of TCNQ⁰.^{7,8,14-16} The peak observed in the polarized Raman study of the single crystal was assigned to a lattice mode even though, like the 40.5 cm^{-1} mode, it appeared to be intramolecular based on interpretation of the polarization data.⁷ The present study, however, suggests that the 74.5 and 75.5 cm^{-1} bands should be considered as two separate modes directly assigned as lattice vibrations of A_g and B_g symmetry, respectively, which is consistent with the polarization data. Just as was seen in the case for the 40.5 cm^{-1} band, a peak near 76 cm^{-1} in the gas phase Raman spectrum of TCNQ⁰ also suggested an intramolecular mode assignment, but this peak can be attributed to the presence of dimers as well, since rigid molecule dimers have a total of three torsional degrees of freedom. Furthermore, it is possible that the dimers do not have inversion symmetry, in which case the low frequency Raman bands seen in the gas phase spectrum could also arise from translational degrees of freedom.

Since the two bands near 75 cm^{-1} lie so close together, but in spectra of different symmetry, the possibility that they represent an intramolecular mode which displays a Davydov splitting must be considered. Low frequency, Raman active intramolecular modes have been predicted for TCNQ⁰ from calculations of both the in-plane and out-of-plane fundamentals. A Urey-Bradley force field,¹⁵ a modified Urey-Bradley force field,¹⁶ and a valence force field^{7,21} have been used in the in-plane calculations, and a Urey-

Bradley force field without any modifications¹⁵ was used for the calculation of the out-of-plane vibrational frequencies. In all of the calculations, a least squares fit to experimental data was used to refine the force constants.

Four Raman active intramolecular modes, two out-of-plane and two in-plane, have calculated frequencies below 150 cm⁻¹. The $\nu 17 b_{1g}$ and $\nu 30 b_{2g}$ out-of-plane modes were calculated at 137 and 138 cm⁻¹, respectively, by Futamata *et al.*¹⁵ It was suggested that either of these modes could correspond to the 154 or 168 cm⁻¹ bands that they observed in the Raman spectrum. Girlando and Pecile assigned the band they saw at 169 cm⁻¹ in their polarized Raman spectrum to the $\nu 17$ mode, in accordance with Futamata's suggestion. Our results also confirm this assignment. However, the possibility of the band at 154 cm⁻¹ being the $\nu 30$ mode is less certain, since polarization data do not support it. Polarization data preclude the assignment of the bands near 75 cm⁻¹ to the $\nu 30$ mode as well. In addition, in the assignments of the out-of-plane modes made thus far, the observed frequencies are, in general, significantly higher than the calculated ones, especially for the modes at frequencies below 600 cm⁻¹. This suggests that the out-of-plane force constants may have been underestimated. Indeed, the lack of sufficient observed data was reported to have hindered the refinement of the force constants used in the calculation.¹⁵ As a result, the bands observed near 75 cm⁻¹ in the polarized Raman spectrum of TCNQ⁰ apparently are too low in frequency to be assigned to either of the out-of-plane intramolecular modes calculated below 150 cm⁻¹.

Several investigators have calculated the in-plane intramolecular vibrational modes in TCNQ⁰.^{7,15,16,21} The reliability of the intramolecular mode assignments from the single crystal measurement of Girlando and Pecile suggests that the three calculations^{7,15,21} that involved a least squares refinement using their data set should be considered in the discussion. These calculations predicted two in-plane modes for TCNQ⁰ in the frequency region below 150 cm⁻¹. One of these modes, $\nu 10$, has a_g symmetry with a frequency at 126,⁷ 127,¹⁵ or 144²¹ cm⁻¹, depending on the calculation. It has been assigned to the 144 cm⁻¹ band measured in the TCNQ⁰ single crystal. A weak band observed at 145 cm⁻¹ in the gas phase Raman spectrum of TCNQ⁰ provides further support for this molecular mode assignment. It has been previously pointed out that dimers exist in the gas phase. Nevertheless, intramolecular modes must still be present and are expected to have no substantial difference in frequency for either dimers or monomers. It is unlikely that there would be any dimer mode of such high frequency. In the powder Raman spectra of salts of the TCNQ⁻ anion,²² a band seen at 148 cm⁻¹ is also assigned to $\nu 10$, since the calculated frequency for this intramolecular mode in the anion is approximately the same as in the neutral molecule. Hence, the assignment of the $\nu 10$ intramolecular mode calculated in TCNQ⁰ below 150 cm⁻¹ is consistent.

The band at 144 cm⁻¹ has also been assigned from single crystal polarized Raman spectra as an A_g lattice mode.⁷ The assignment was based, in part, on the Raman spectrum of TCNQ⁰ powder at 100 K, in which this band apparently split into two bands located at 145 and 151 cm⁻¹. It was concluded that at room temperature, the peak observed at

144 cm⁻¹ resulted from two overlapping bands: one arising from an intramolecular mode having a frequency which showed almost no change with temperature, and another arising from a lattice mode whose frequency changed significantly with temperature. However, it has been shown in a temperature dependent Raman study of TCNQ⁰⁸ that the low temperature band seen at 151 cm⁻¹ actually results from a decrease in frequency of the band observed at room temperature near 154 cm⁻¹. Therefore, the 144 cm⁻¹ band should only be assigned as an intramolecular mode of TCNQ⁰.

The other low frequency in-plane vibration predicted for TCNQ⁰ that is Raman active is a b_{3g} mode with designation $\nu 49$. It has been calculated at 93,⁷ 109,¹⁵ or 125²¹ cm⁻¹, but has not yet been assigned. If the bands observed near 75 cm⁻¹ in both the A_g and B_g spectra of TCNQ⁰ are due to an intramolecular mode, then apparently the only possible assignment would be the $\nu 49$ in-plane mode. However, such an assignment may not be consistent with Raman spectral data of the TCNQ⁻ anion. Calculation and experiment have demonstrated that for the energy region below 700 cm⁻¹, the in-plane intramolecular modes in TCNQ have nearly the same frequencies in the anion as in the neutral molecule.^{21,22} The $\nu 49$ mode in TCNQ⁻ has already been assigned to the 98 cm⁻¹ band in the single crystal Raman spectrum of the potassium salt.²³ The band was observed only in the spectra in which both the incident and scattered radiation were polarized in the plane of the TCNQ⁻ anion. It also showed a 7 cm⁻¹ shift to lower energy in the spectrum of the deuterated anion, lending additional support to its assignment as the $\nu 49$ in-plane molecular mode. There is some uncertainty in interpreting the data, since some bands assigned to out-of-plane intramolecular modes also appeared in the in-plane Raman spectrum. Nevertheless, if the assignment for the $\nu 49$ mode in the TCNQ⁻ anion is correct, the $\nu 49$ band in the Raman spectrum of the neutral molecule would be expected in the region between 90 and 110 cm⁻¹. No such intramolecular band has been seen for TCNQ⁰ in this region. Perhaps this is because the band is very weak in the neutral molecule and overlaps with the nearby 96 and 104 cm⁻¹ lattice modes. Whatever the case, it seems that the bands near 75 cm⁻¹ are again, too low in frequency to be assigned to the $\nu 49$ intramolecular vibration.

In an effort to further characterize the low frequency intramolecular modes in TCNQ⁰, an examination of the Raman spectra of its charge transfer complexes with anthracene (A) and tetrathiafulvalene (TTF) is helpful. Anthracene does not have any Raman active intramolecular vibrations in the frequency region below 200 cm⁻¹,^{24,25} while single crystal and powder Raman spectra indicate that TTF may have only one or two.²⁶⁻²⁸ Therefore, the bands observed below 200 cm⁻¹ in crystals of these charge transfer complexes of TCNQ⁰ which are not attributed to lattice modes, or, in the case of TTF-TCNQ, to intramolecular modes of the donor molecule, can be assigned as vibrational modes of the TCNQ⁰ molecule.

The Raman spectrum of A-TCNQ²⁹ has bands at 22, 37, 45, 52, 62, and 72 cm⁻¹ which can be attributed to the six Raman active lattice modes predicted from symmetry considerations of the crystal structure.³⁰ The low values for the

TABLE II. Assignment of lattice modes^a in TCNQ⁰.

	Factor group symmetry	Exptl data			Calcd data 0 K This work	Exptl data 298 K This work
		298 K		30 K/(77 K)		
		Ref. 7	Ref. 15	Ref. 15		
Raman active	A_g	76/41	...	43	41.7	40.5
	B_g	41/76	...	66	71.9	63
	A_g	97	...	80	75.3	74.5
	B_g	105	...	80	93.5	75.5
	A_g	144	...	103	103.9	96
	B_g	133	...	109	120.4	104
IR active	A_u	...	39	(41)	48.2	...
	A_u	...	62	(66)	63.5	...
	B_u	...	77	(84)	76.2	...

^aFrequencies are given in cm^{-1} .

lattice mode frequencies are no doubt due to the weak association in the A-TCNQ complex, as evidenced from the large interplanar spacing (3.5 Å) in the crystal and separation of the molecular components during recrystallization. Three additional bands, which are very weak compared to the lattice modes, are observed at 134, 142, and 164 cm^{-1} . All of them can be attributed to molecular modes in TCNQ⁰.

In the Raman spectrum of TTF-TCNQ, six bands were observed below 100 cm^{-1} .²⁸ Five of them were assigned as lattice modes and the remaining one was ascribed to the amplitude mode of the charge density wave in this complex. Three bands were reported above 100 cm^{-1} , at 142, 164, and 182 cm^{-1} . The authors associated the first and last bands with the $\nu_{10} a_g$ and $\nu_{17} b_{1g}$ modes of TCNQ⁰, respectively, in accordance with previous intramolecular mode assignments for TCNQ⁰.

The foregoing identification of low frequency intramolecular modes in TCNQ⁰ from Raman spectra of its charge transfer complexes is consistent with Raman data of the TCNQ⁰ crystal. Furthermore, the absence of an intramolecular mode near 75 cm^{-1} confirms the assignment of the 74.5 and 75.5 cm^{-1} bands in the single crystal spectrum of TCNQ⁰ to A_g and B_g lattice modes, respectively.

The assignments of the remaining bands observed in our polarized Raman spectra of TCNQ⁰ should also be considered. The results discussed above confirm the previous assignments of the 144 and 170 cm^{-1} bands to the $\nu_{10} a_g$ and $\nu_{17} b_{1g}$ molecular modes in TCNQ⁰. Futamata *et al.* have suggested that the band at 132 cm^{-1} could be assigned to the $\nu_{49} b_{3g}$ intramolecular mode. The band seen at 134 cm^{-1} in the A-TCNQ Raman spectrum is in agreement with a molecular mode assignment. Polarization data from the single crystal Raman spectrum of TCNQ⁰ do not support the b_{3g} symmetry, however, since the band is only seen in B_g spectra. It is possible that the ν_{49} mode interacts significantly with other vibrational modes in the crystal, resulting in the relative intensities observed at 132 cm^{-1} in the B_g spectra.

It has been suggested that the two overlapping bands measured at 154 and 160 cm^{-1} in the Raman spectra of TCNQ⁰ represent strongly coupled vibrational modes in the crystal.⁸ An assignment of the 160 cm^{-1} band to the $\nu_{30} b_{2g}$ intramolecular mode is supported by the fact that the frequency of this band is practically unchanged at low tempera-

ture.⁸ Additional evidence is seen in a corresponding band at 164 cm^{-1} in the Raman spectra of both A-TCNQ and TTF-TCNQ, which has already been attributed to an intramolecular mode in TCNQ⁰. The band at 154 cm^{-1} , on the other hand, only appears in the A_g spectra and may be attributed to an overtone of either the 74.5 or 75.5 cm^{-1} lattice modes. Likewise, the weak shoulder observed in the B_g spectra at 137 cm^{-1} may arise from a combination band of the 63 and 74.5 cm^{-1} lattice modes.

V. LATTICE DYNAMICAL CALCULATION

The usefulness and applicability of theoretical calculations in the study of lattice dynamics in molecular crystals is well established. In the present study, the symmetries and frequencies determined for the lattice modes of TCNQ⁰ from a lattice dynamical calculation are helpful in confirming the assignments which have been made. The results obtained from such a calculation can also be used to predict the mechanical properties of the molecular crystal lattice.³¹ A lattice dynamical calculation for TCNQ⁰, which included the internal vibrational modes of the molecule, has been performed by Morawitz.³² However, the symmetries of the resulting lattice modes were not specified, making it difficult to compare the calculated frequencies to our polarized experimental data. Assignments of previously measured Raman frequencies in TCNQ⁰ to the calculated ones were proposed in the study, but they were not complete.

We have performed a lattice dynamical calculation for TCNQ⁰ using the rigid molecule approximation to determine the frequencies, symmetries, and eigenvectors of the lattice modes. The details of the method employed are discussed elsewhere.^{31,33} Integral to the success of the calculation is the minimization of the 6-exp-1 atom-atom intermolecular potential used to derive the lattice force constants under the harmonic approximation. The potential was determined using 92 TCNQ⁰ molecules and was minimized relative to the unit cell constants a , b , c , and β , and the three Euler angles which specify the orientation of the molecules in the cell. The minimized potential that was used was found to reproduce these seven parameters to within 2% of the experimental values obtained from x-ray diffraction data and gave a heat of sublimation for the crystal which was

TABLE III. Lattice mode eigenvectors^a in TCNQ⁰.

Calculated frequency (cm ⁻¹)	T _a	T _b	T _c	R _a	R _b	R _c
41.7	0.0	0.0	0.0	-0.989	-0.088	0.122
48.2	0.961	0.0	0.276	0.0	0.0	0.0
63.5	0.276	0.0	-0.961	0.0	0.0	0.0
71.9	0.0	0.0	0.0	0.242	-0.821	0.517
75.3	0.0	0.0	0.0	-0.394	0.695	-0.601
76.2	0.0	1.0	0.0	0.0	0.0	0.0
93.5	0.0	0.0	0.0	0.001	0.375	0.927
103.9	0.0	0.0	0.0	0.497	0.394	0.773
120.4	0.0	0.0	0.0	0.828	0.263	0.496

^aThe eigenvectors are expressed in the *abc** crystallographic axial system. Translational displacements along these axes are given by the *T* coordinates and librational displacements about the axes are given by the *R* coordinates. The eigenvectors have been normalized to a single molecule.

within experimental error of the measured value.³⁴ The intermolecular force constants subsequently obtained were then used in constructing the dynamical matrix. The resulting eigenvalue problem was solved for a wavevector at the Brillouin zone center to give the three acoustic modes and nine optical modes allowed in the TCNQ⁰ crystal.

The symmetries, frequencies, and spectral activity of the nine optical modes calculated for the TCNQ⁰ lattice are listed in Table II. The experimental assignments of the Raman active lattice modes which have been proposed in this work show very good agreement with the calculation. Keeping in mind that the calculation is performed for a crystal at *T* = 0 K, it is expected that the experimental frequencies of the lattice modes will approach the calculated frequencies in spectra taken at low temperature. Futamata *et al.* have recorded the Raman spectrum of TCNQ⁰ powder at 30 K. Their results show that for nearly all of the modes, the frequencies hover near or approach the 0 K calculated values for the lattice mode frequencies. Unfortunately, no polarized Raman data are available for TCNQ⁰ at low temperature. As a result, only one band is observed near 75 cm⁻¹. It is not unlikely that the two lattice modes we assign at 74.5 and 75.5 cm⁻¹ will have similar shifts in frequency as the temperature is lowered. Therefore, the two modes probably cannot be resolved in an unpolarized spectrum.

The infrared spectrum of TCNQ⁰ in the low frequency region has been recorded by several groups and the reported frequencies are essentially the same for each measurement.^{15,16,35,36} A representative set of IR active mode frequencies, measured at room and liquid nitrogen temperatures, has been included in Table II. A possible assignment of the IR active lattice modes is indicated in the table, although this is based on frequency values only, since polarized IR data are not available for TCNQ⁰ in the low frequency region. Once again, agreement between experiment and theory is evident.

From our lattice dynamical calculation, we have also obtained the eigenvectors for the lattice modes which enable us to determine the vibrational motions of the TCNQ⁰ molecules for each mode. Since the molecules lie at centers of inversion in the lattice, the Raman active modes are purely librational, while the IR active modes are exclusively trans-

lational. The eigenvectors for the molecule at the origin of the unit cell are reported in Table III in the *abc** crystal axial system. As is observed in other molecular crystals,³⁷ the axes of libration for the Raman active modes do not coincide with the three symmetry axes in the TCNQ⁰ molecule. The two modes of highest frequency calculated at 103.9 and 120.4 cm⁻¹ involve in-phase and out-of-phase librations about an axis approximately along the long axis of the TCNQ⁰ molecules. The moment of inertia about this axis of the molecule is the lowest of the three possible inertial moments and thus would be expected to give rise to the lattice modes having the highest frequencies. The modes calculated at 71.9 and 75.3 cm⁻¹ arise from librations about axes which are inclined at 18° and 31°, respectively, from the perpendicular of the molecular plane. Finally, the modes at 41.7 and 93.5 cm⁻¹ involve librations about axes which are nearly perpendicular to each other and lie in the molecular plane between the long and short axes of the molecule.

As a rough test of the validity of the eigenvectors, the relative intensities for each Raman active lattice mode in the six scattering configurations used in the polarized Raman experiment were calculated using previously described methods.³⁷⁻³⁹ The oriented gas model was employed and the

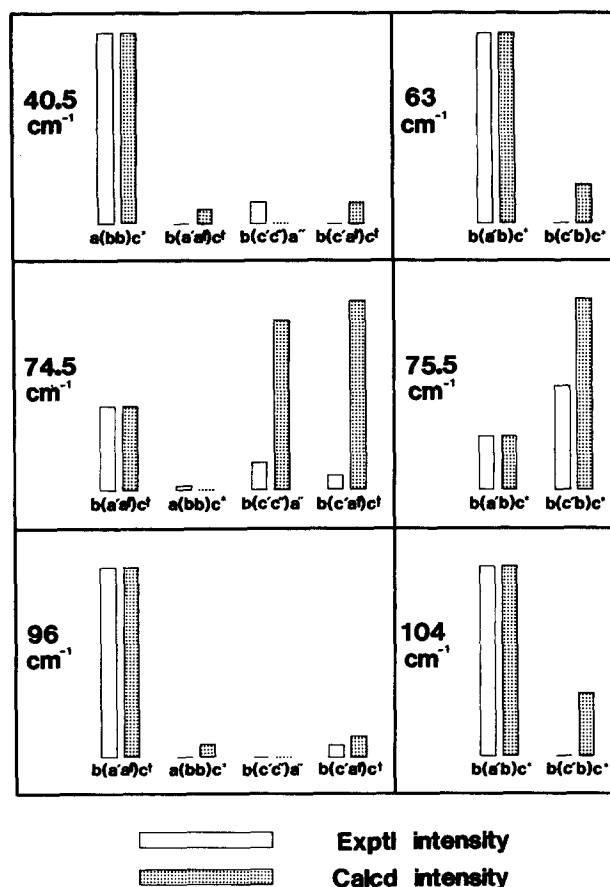


FIG. 5. Comparison of the experimental and calculated relative intensities of each Raman active lattice mode for the spectra in which it is allowed by symmetry. The intensity scale for each mode is arbitrary and comparison of the relative intensities has been achieved by equating the experimental and calculated intensities indicated in the first polarization configuration shown for that mode. Weak or undetected experimental intensities are represented by the solid lines, while very small calculated intensities are represented by the dotted lines.

values for the molecular polarizability tensor for TCNQ⁰ were taken from a MINDO/3-FP calculation.⁴⁰ The effects of reflection at the crystal surfaces involved in the various scattering configurations were included in calculating the relative intensities.¹⁸ The results are displayed in Fig. 5 in which the experimentally measured peak heights for a given lattice mode are compared to its theoretical intensities. The scale for the experimental relative intensities for each mode has been set arbitrarily. The calculated relative intensities for each mode have in turn been scaled by equating the experimental and calculated intensities indicated in the first polarization configuration shown for that mode. Qualitative agreement is observed for five of the six Raman active lattice modes in TCNQ⁰. This is quite satisfactory, especially when considering the approximations used in the calculation. It is particularly interesting to examine the agreement between theory and experiment for the 40.5 cm⁻¹ A_g lattice mode, in which extremely great intensity is seen in the a(bb)c* spectrum and relatively little intensity is observed in the other spectra. Such an observation emphasizes the importance of measuring polarized single crystal Raman spectra in a sufficient number of polarization configurations in order to locate all of the vibrational bands present in the crystal.

VI. CONCLUSION

This polarized Raman and lattice dynamical study of the TCNQ⁰ single crystal provides a complete assignment of the Raman active lattice modes and offers assignments for low frequency intramolecular modes that were previously unassigned. The A_g lattice modes have been identified at 40.5, 74.5, and 96 cm⁻¹, and the B_g lattice modes at 63, 75.5, and 104 cm⁻¹. Additional bands at 132, 144, 160, and 170 cm⁻¹ are associated with vibrational modes of the TCNQ⁰ molecule. It is possible to regard the external and internal vibrational modes in the crystal as being substantially separated although some coupling is probable.

The agreement of the lattice dynamical calculation for TCNQ⁰ with the experimental results suggests that even though coupling between vibrational modes in the TCNQ⁰ crystal is likely, it is not so significant as to prevent any understanding of the lattice dynamics using the harmonic and rigid molecule approximations. The success of the calculation opens the way for the determination of the mechanical and transport properties of the TCNQ⁰ lattice. In addition, it provides a starting point from which data obtained from piezomodulated Raman spectroscopy of TCNQ⁰ can be interpreted. Indeed, the failure of the harmonic and rigid molecule models to consider coupling in the TCNQ⁰ lattice can be accounted for by the piezomodulated Raman experiment through its determination of the coupling constants described in the theory.

Finally, the observations made in this study accentuate the need for attention to unique aspects of the polarized Raman investigations of highly anisotropic molecular single crystals. Factors such as the bulk and surface quality of the crystal, the position and orientation of the crystal, the optical effects on the exciting and scattered light within the crystal, and the number of different polarization configurations employed in the Raman experiment are crucial to the proper

identification of the various vibrational modes that exist in the solid.

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