PHYSICAL REVIEW B VOLUME 20, NUMBER 6 15 SEPTEMBER 1979

Raman spectrum of potassium tetracyanoquinodimethane crystals

K. D. Truong*
Department of Chemistry, Université de Sherbrooke, Sherbrooke, Quebec J1K 2R1 Canada

Cosmo Carlone*
Department of Physics, Université de Sherbrooke, Sherbrooke, Quebec J1K 2R1 Canada

(Received 11 January 1979)

The Raman spectrum of K(TCNQ) crystals has been obtained from 30 to 2300 cm^{-1}. We have identified lattice modes at 70, 81, 110, 170, 229, and 295 (±5) cm^{-1} and 13 intramolecular modes above 300 cm^{-1}. The modes at 70, 81, and 110 cm^{-1} are probably $(\text{TCNQ})^-$ librations. The intensity of the lattice modes is independent of the laser-field orientation, indicating isotropy for the nuclear motions, but the intramolecular modes are more intense when the laser field is directed perpendicularly to the crystal axis, indicating the stacking arrangement for the TCNQ's.

I. INTRODUCTION

Potassium tetracyanoquinodimethanide, symbolized by K(TCNQ), belongs to those one-dimensional compounds in which the acceptors stack on top of each other. General reviews[1] of one-dimensional compounds and their possible arrangements[2,3] have been given. The relative simplicity of K(TCNQ), that is to say, its donor is atomic and the donor-acceptor ratio is equal to unity, is probably the reason why its properties—crystal structure,[4–7] electronic structure,[3,8–14] electrical conductivity,[15–17] magnetic susceptibility,[18–20] infrared absorption and reflection,[21] and Raman scattering[22–27]—have been studied in some detail. The Raman spectra obtained to date involved solutions or powder. The present work reports the first spectrum on crystals of K(TCNQ).

We have analyzed the Raman spectrum of K(TCNQ) from 30 to 2300 cm^{-1}, both at room temperature and at liquid-nitrogen temperature, using several lines of the argon-ion laser. We have found lattice modes at 70, 81, 110, 170, 229, and 295 cm^{-1} (the error is ±5 cm^{-1}), and 13 intramolecular modes above 300 cm^{-1}. The intensity of the lattice modes is independent of whether the electric field of the laser is directed perpendicularly to the crystal axis or parallel to it; in other words K(TCNQ) is isotropic as far as the nuclear movements are concerned. The intensity of the intramolecular modes is about 15 times stronger when the electric field is directed perpendicularly to the axis than when parallel. The anisotropy of the intramolecular modes reflects the stacking arrangement of the TCNQ's.

The modes at 70, 81, and 110 cm^{-1} are probably $(\text{TCNQ})^-$ librations.

The Raman spectrum of K(TCNQ) has been obtained[24] in compressed pellets of potassium bromide from 300 to 2300 cm^{-1}. The spectra presented in this work are significantly different from the previously published spectra. We have observed fewer intramolecular modes, their number being independent of laser line excitation, and their relative intensity being dependent only slightly on the energy of the laser lines. In our crystals, we found little evidence for the resonance Raman effect. We did, however, find that the K(TCNQ) crystals are sensitive to laser radiation and that the KBr technique perturbs the Raman spectrum slightly.

The Raman spectrum of $(\text{TCNQ})^-$ has been obtained from 200 to 2400 cm^{-1} by an electrochemical process.[25] Our spectra are much more similar to these[25] than those obtained in the pellet.[24]

II. CRYSTALLOGRAPHIC DATA

Crystals of K(TCNQ) have recently been analyzed by x-ray diffraction by Konno *et al.*[6] and Richard *et al.*[7] Let *a* be the crystal axis; then *b* and *c* are the two axes defining the plane containing the TCNQ molecules. Konno *et al.* find that K(TCNQ) is dimerized at room temperature, with eight molecules per unit cell. The lattice is monoclinic and the space group is $P2_1/n$. One half of the dimer is shown in Fig. 1, which is the view seen from the *a* axis. In this figure, the TCNQ's oriented toward the *b* axis, denoted by T_b, are inclined at 15.8° relative to the (100) plane; those oriented toward the *c* axis, denoted by T_c, are inclined at 11.3°. The K atoms do not lie in the *b*-*c* plane, but rather each K sits at the center of a distorted cube consisting of eight N atoms of different $(\text{TCNQ})^-$ radical.

Konno *et al.*[6] find that K(TCNQ) undergoes a phase change at 122 °C. Above this temperature, the TCNQ's reorient themselves, with both T_b and T_c inclined at 8.9° relative to the (100) plane. The distance between TCNQ planes is constant, i.e., mono-

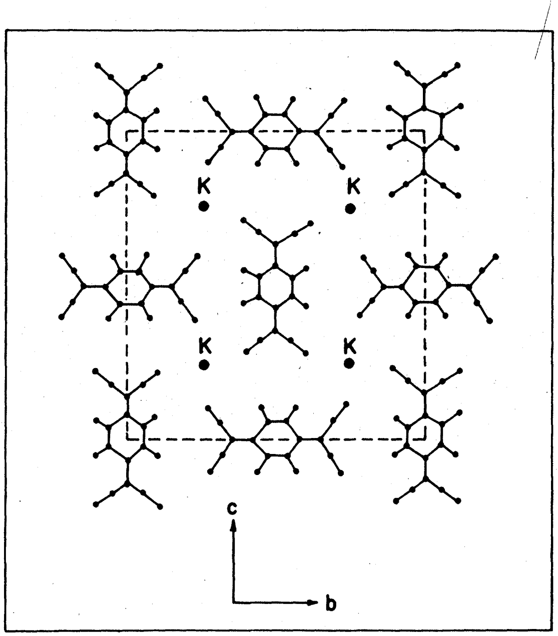

FIG. 1. Crystal structure of K(TCNQ) (Refs. 6 and 7). We do not differentiate the different atoms within the TCNQ molecule. The K atoms do not lie in the *b-c* plane; see text for details.

mer structure. The number of molecules per unit cell is two, the lattice is monoclinic and the space group is $P2_1/c$.

Richard *et al.*[7] find that at room temperature, the distance between the TCNQ planes is constant, i.e., no dimer. Figure 1 gives the Richard unit cell, in which the two T_b molecules do not quite lie in the same plane as the two T_c molecules. Each K is octahedrally surrounded by eight TCNQ nitrogen atoms. The number of molecules per unit cell is four. The lattice is monoclinic and the space group is $P2_1/c$.

From these two works, one conclusion is that K(TCNQ) exists in two forms at room temperature.

III. THEORY

If one attempts to find the normal modes for each atom in the unit cell, the results are not very useful because of the large number of atoms (one TCNQ molecule alone has 20 atoms) and because of the low symmetry in the unit cell, C_{2h}. It is found however, and we have verified it, that most transitions, particularly those above 300 cm^{-1}, that occur in the crystal of K(TCNQ) are practically identical to those of (TCNQ)$^-$ as obtained by dissolving K(TCNQ) in acetonitrile solution [this solvent was chosen because its supposed only effect is to break the weak ionic bond between K$^+$ and (TCNQ)$^-$]. The model that we use is that the (TCNQ)$^-$ is essentially a rigid body in the solid state. The Raman spectrum thus consists of intramolecular modes, i.e., those modes involving the nuclei in one (TCNQ)$^-$ and those modes which involve movements of the donors and acceptors as entities. We shall refer to the latter modes as lattice modes. The lattice modes may further be divided into those modes involving the translational degrees of freedom of K$^+$ and (TCNQ)$^-$ (phonons) and those involving the rotational degrees of freedom of (TCNQ)$^-$ about its three molecular axes (librations).

Let us consider the intramolecular modes first. The point group of the isolated (TCNQ)$^-$ molecule is D_{2h}. The representation Γ involving all 20 atoms is reducible into

$$\Gamma = 10A_g + 10B_{1g} + 6B_{2g} + 4B_{3g} + 4A_u + 6b_{1u} + 10B_{2u} + 10B_{3u} \ . \quad (1)$$

For crystals, however, the point group is C_{2h}. It is easy to show that the A_g and B_{3g} modes become A_g, and the B_{1g} and B_{2g} become B_g when D_{2h} becomes C_{2h}. One thus expects 14 A_g and 16 B_g intramolecular modes.

In considering the translational modes, one has to include the different orientations of the TCNQ molecules. The simplest unit cell of K(TCNQ) contains one T_b, one T_c, and two K atoms. This is the cell found by Konno *et al.*[6] at high temperatures. For space group $P2_1/c$, the representation at the center of the Brillouin zone, Γ, is reducible into

$$\Gamma = 3A_g + 3B_g + 3A_u + 3B_u \ . \quad (2)$$

The next simplest cell consists of 2 T_b, 2 T_c, and four K atoms, in which the T_b and T_c lie on slightly dif-

TABLE I. Complete information for the point group C_{2h} (Ref. 28).

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2,y^2,z^2,xy
B_g	1	−1	1	−1	R_x,R_y	yz,xz
A_u	1	1	−1	−1	Z	
B_u	1	−1	−1	1	x,y	

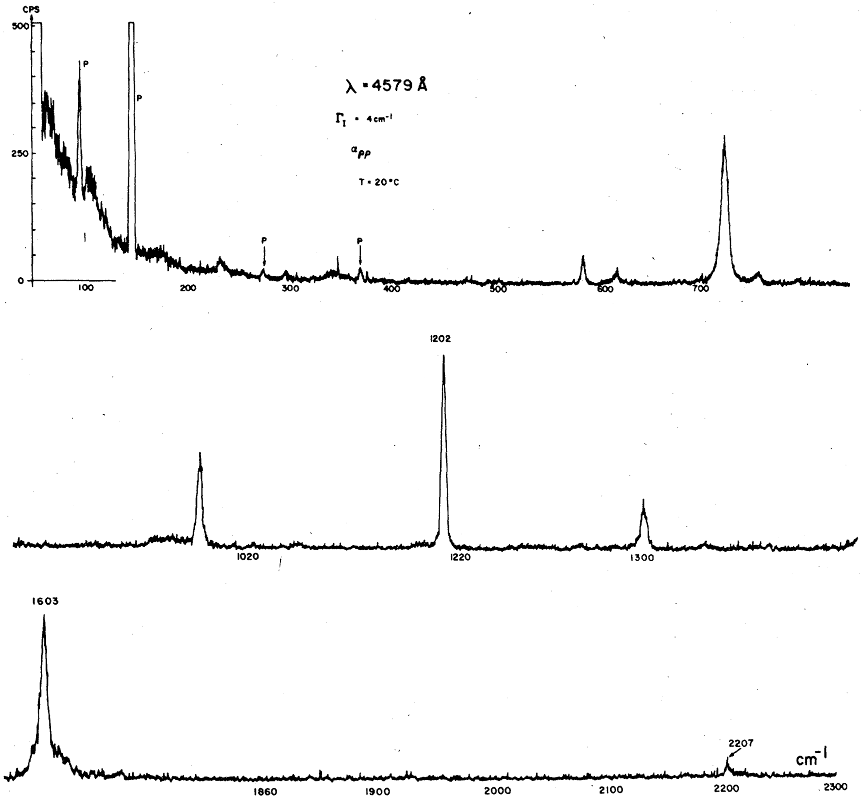

FIG. 2. Raman spectrum of K(TCNQ) crystals using the 4579-Å line. The laser electric field was perpendicular to the crystal axis (Z); the analyzer was perpendicular to the axis (ρ stands for x or y). The P indicates a plasma line. This spectrum was obtained with 2.6 mW focused on the crystal. The spectrum obtained with the 5145-Å line was similar to this, except for minor intensity differences. Γ_I is the instrument width.

ferent planes (that found by Richard *et al.*[7]). For space group $P2_1/c$,

$$\Gamma = 6A_g + 6B_g + 6A_u + 6B_u \ . \qquad (3)$$

The number of modes is essentially doubled, i.e., each mode in Eq. (2) is split because of the degeneracy with respect to labeling the T_b, T_c molecules.

An even more complicated cell consists of four T_b and four T_c and eight K's, as found by Konno *et al.*[6] at low temperatures.

$$\Gamma = 12A_g + 12B_g + 12A_u + 12B_u \ , \qquad (4)$$

i.e., a further doubling of the components. In order to make polarizability studies, we give in Table I the complete information on the C_{2h} point group.[28]

In considering the librational modes, each $(\text{TCNQ})^-$ molecule contributes three rotational degrees of freedom. As in the case of phonons, the librational modes contain structure, depending on the total number of $(\text{TCNQ})^-$ molecules in the unit cell. Since the rotations do not destroy the translational symmetry, their symmetry is g and they are all Raman active.

IV. EXPERIMENTAL

The K(TCNQ) crystals were kindly supplied to us by N. K. Hota of the Collège Militaire Royal, St-Jean, Québec. They were needle shaped, the length being about 1 cm and the thickness varying from a fraction of a millimeter to a few millimeters. All our spectra were taken at 90° scattering. The laser used was a Spectra Physics Model 170 argon-ion laser; the monochromator was a Jobin-Yvon Ramanor HG2S (f/7.8) equipped with a scrambler; the photomultiplier was a Hamamatzu R649, cooled to −20 °C, at which temperature the count was 2–3 counts per second. The intensity of the laser beam was measured with a Spectra Physics model 404 power meter. A polarization rotator was used to select the direction of the electric field incident on the crystal and a linear polarizor was used to analyze the scattered light.

The effect of the laser on K(TCNQ) crystals was

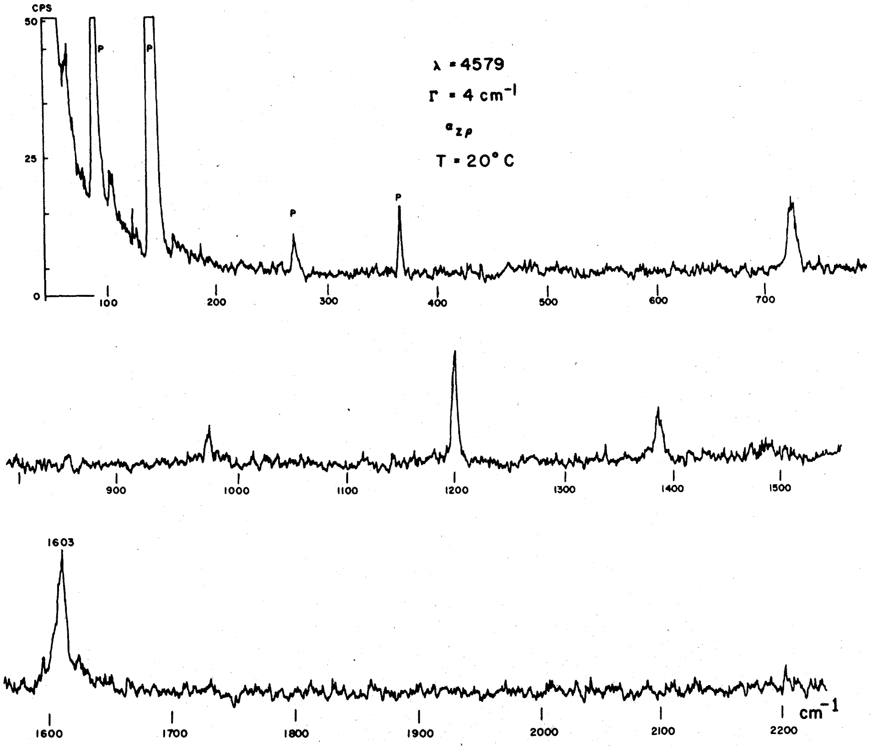

FIG. 3. Raman spectrum of K(TCNQ) in which the electric field is parallel to the crystal axis (Z). The 1202-cm^{-1} line is reduced in intensity by a factor of 15 when the electric field direction is changed from perpendicular to parallel to the axis. The laser power was the same as Fig. 2.

not negligible. The spectra shown in Figs. 2, 3, 4, and 5 were taken with 2.6 milliwatts (mW) focused on the crystal. The spectra were reproducible on the same sample as long as the laser power was a few milliwatts. K(TCNQ) crytstals, which are normally red, blacken when about 50 mW are focused on it. Figure 6 gives the spectrum of such a "burned" crystal. The new element in Fig. 6, the continuum, appeared whenever the crystal was blackened by the laser. At about 100 mW, the crystals disintegrated. We took spectra at 77 °K, finding little change in the spectra when a few milliwatts of power were used; even at this temperature, the crystals could be easily burned.

We repeated Fig. 2 using the 5145 Å line, and except for minor relative intensity differences, the spectra were identical.

In order to compare our results with those found in the literature, we obtained spectra of K(TCNQ) pressed in KBr pellets. The physical appearance of the pellets depended very much on the quality of the surfaces of the compressing discs and to a lesser extent on the humidity of the atmosphere. Figure 7 shows typical spectra. Using the pellet technique, the spectra did not depend on laser power as much, for

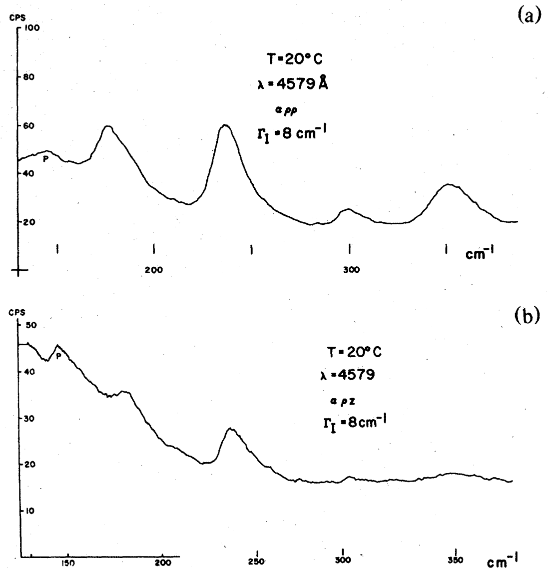

FIG. 4. Polarizability measurements from 130 to 370 cm^{-1}. Contrary to Figs. 2 and 3, the intensity of the spectrum has not changed significantly in rotating the electric field direction. The laser power was the same as in Fig. 2.

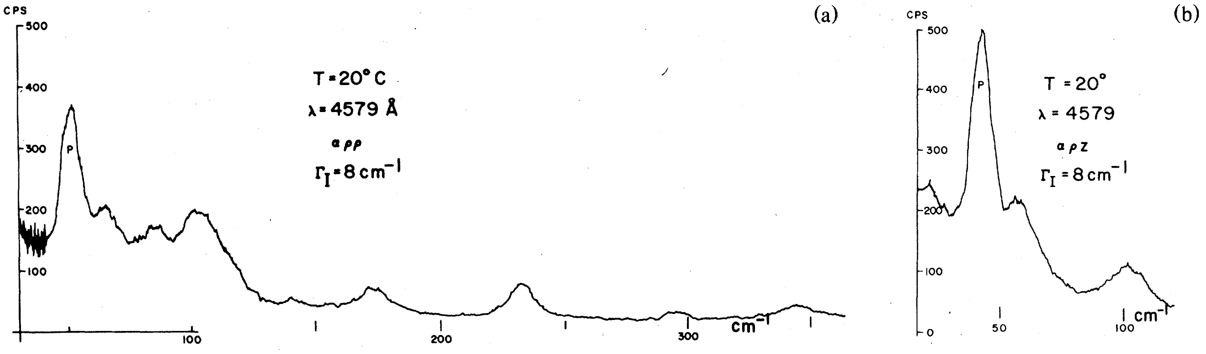

FIG. 5. Polarizability measurements from 30 to 120 cm^{-1}. Although the 81 cm^{-1} line has disappeared in (b), the intensity of the other two lattice modes is independent of laser field direction. The laser power was the same as Fig. 2. By comparing (a) with Fig. 9, the lattice modes are identified.

example the spectra of Fig. 7 were reproducible even when 350 mW reached the disc. We did not focus the laser beam when using the pellet technique.

We repeated Fig. 7 using the 5145 Å line and again found a spectrum practically identical to that of Fig. 7.

We took a Raman spectrum of K(TCNQ) dissolved in acetonitrile solution, using the 4579, 4880, and 5145 Å lines. The results are shown in Fig. 8. To remove the plasma lines close to the exciting line, we filtered the laser beam with a Jarrell-Ash 1-meter monochromator, having a band pass of a few Angstroms. Figure 9 shows the results for the solution spectra. We also repeated Figs. 4(a) and 5(a) using the filtered excitation. For the solution spectra, we measured depolarization ratios, in order to separate the A_g and B_g modes. In Figs. 8 and 9, the laser power was 30 mW and the beam was not focused.

V. OBSERVATIONS AND DISCUSSION

By comparing the crystal spectra of Figs. 2, 3, 4, and 5 with the solution spectra of Figs. 8 and 9, we can say that the transitions which are common to both are intramolecular in origin, but those which are not involve lattice modes. The lattice modes are observed by comparing Fig. 5(a) with Fig. 9. We summarize the transitions in Tables II-IV.

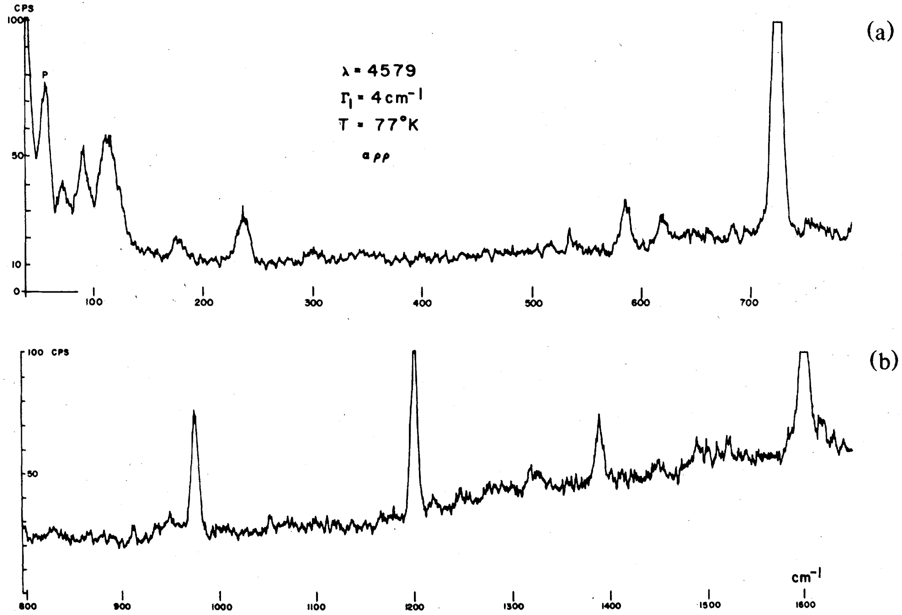

FIG. 6. This spectrum was obtained with 50 mW focused on the crystals. The continuum which increases beyond 1600 cm^{-1} was consistently found on burned crystals. The continuum was also found on previously published data (Ref. 24).

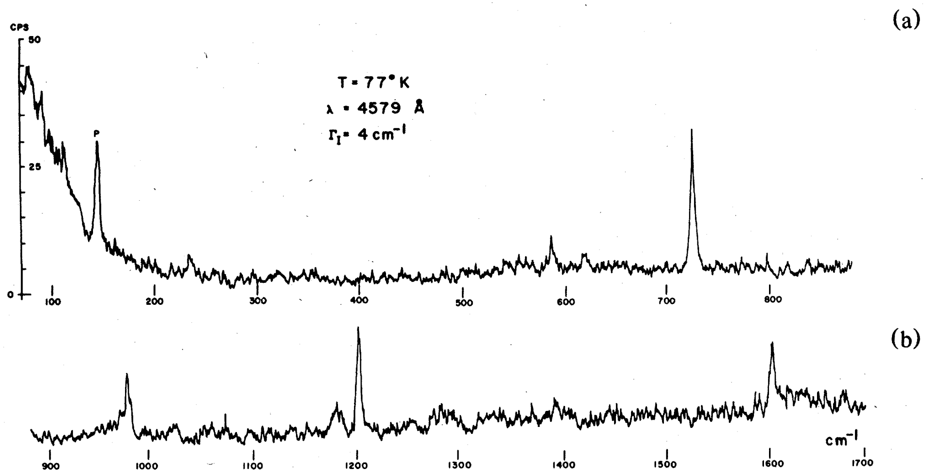

FIG. 7. Raman spectrum of K(TCNQ) in KBr pellets at 77 °K. This spectrum is not the same as the previously published pellet spectrum (Ref. 24). Our spectrum in KBr obtained with the 5145 Å is practically identical to that shown here, another difference with previously published spectra (Ref. 24).

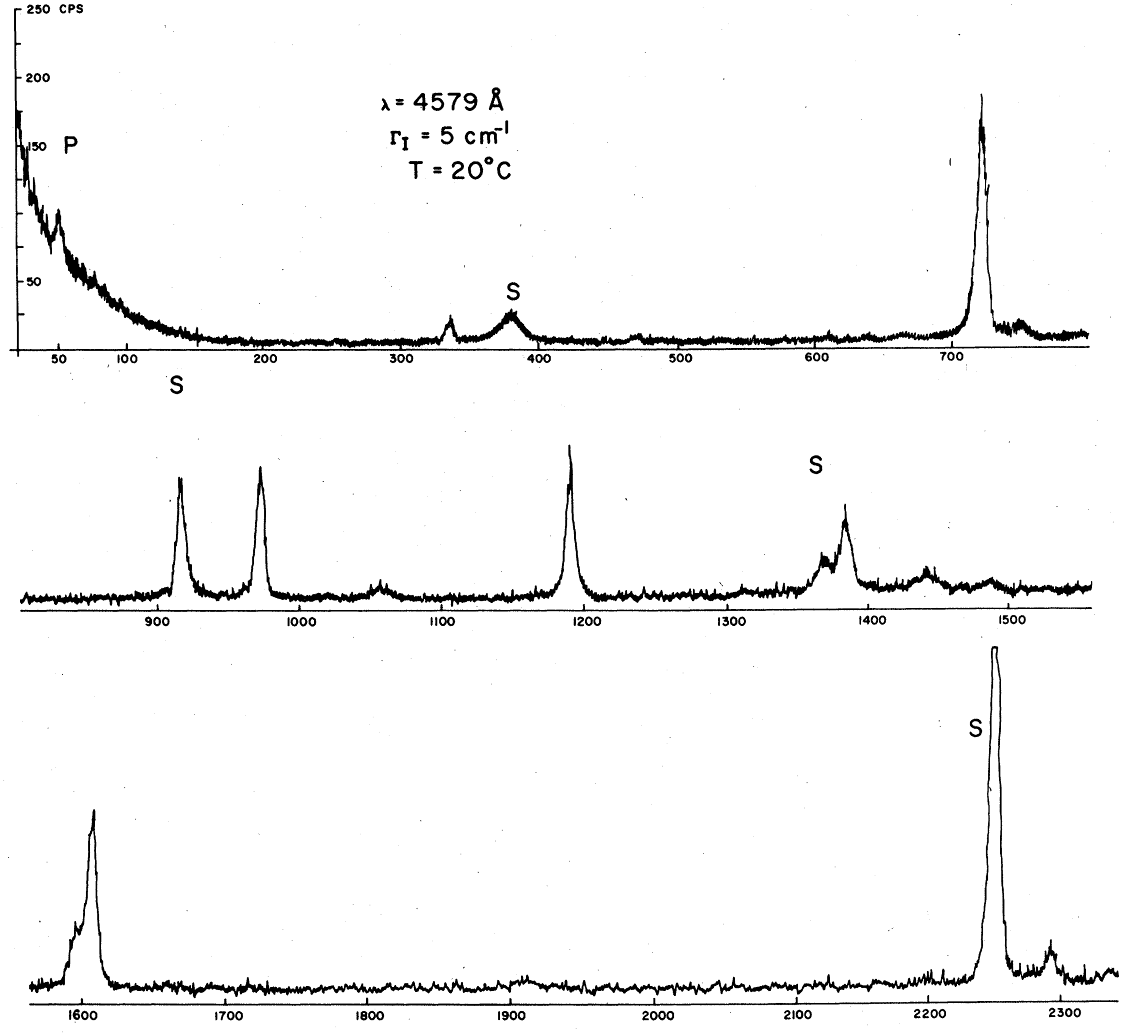

FIG. 8. Raman spectrum of K(TCNQ) as obtained by dissolving it in acetonitrile solution. *S* stands for a solvent line.

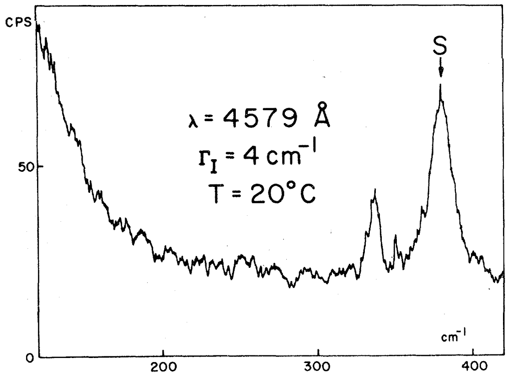

FIG. 9. Raman spectrum of $(\mathrm{TCNQ})^-$ as obtained by dissolving it in acetonitrile solution. The 341 cm^{-1} is clearly intramolecular in origin, but we find no others below this frequency. In order to remove the plasma lines, this spectrum was obtained after filtering the 4579 Å laser line with a monochrometer having a band pass of 2 Å.

There are other crystal effects on the intramolecular modes. The 1195 cm^{-1} line is shifted to 1202 cm^{-1} in the crystal and the 1615 cm^{-1} is shifted to 1625 cm^{-1}. The intensity of the 1604 and 1615 cm^{-1} line is altered in the crystal. Lastly, the $\mathrm{C}\equiv\mathrm{N}$ vibration at 2250 cm^{-1} appears shifted and very weak in the crystal, indicating the interaction with the K atoms.

The transitions at 584 and 620 cm^{-1} do not appear in the solution spectrum, but we believe they are B_{3g} out of plane intramolecular modes nevertheless. All B_{3g} modes become A_g when D_{2h} symmetry is reduced to C_{2h}. We attribute both 584 and 620 cm^{-1} to intramolecular modes, whose intensity increases in the crystal because of change of symmetry.

One might argue that the transitions below 300 cm^{-1} which do not appear in Fig. 9 are also weak B_{3g} modes whose Raman intensity has increased in the crystal form. Polarizability measurements indicate the following difference: the spectrum above 300 cm^{-1} is very much dependent on the direction of the laser field relative to the crystal axis, whereas that below 300 cm^{-1} is not. Let's denote by z the direction of the K(TCNQ) needles (z is essentially the crystallographic a axis); p stands for either x or y. When the electric field is directed perpendicularly to z, the spectrum is about 15 times stronger than when it is directed parallel to z for the intramolecular modes (Fig. 2 versus Fig. 3). However, the two spectra are about equally intense for the lower frequency modes [Fig. 4(a) versus Fig. 4(b) and Fig. 5(a) versus Fig. 7(b)]. Some lines disappear entirely, indicating their polarizability. The polarizabilities are indicated in Tables II and III.

The anisotropy of the intramolecular modes is consistent with the one dimensionality of these crystals. Moreover, that the intramolecular modes are more intense when the laser field is perpendicular to the crystal axis is also consistent with the structure of the crystals, i.e., the TCNQ planes are almost perpendicular to the crystal axis. In fact, the one dimensionality refers to the TCNQ stacking and applies to the electronic displacement along the columns. The isotropy of the collective modes indicates no reduced dimensionality for the lattice modes; in so far as the nuclear movements are concerned, these crystals are three dimensional.

Girlando and Pecile[29] have identified $(\mathrm{TCNQ})^0$ librations at 76, 97, and 105 cm^{-1}. It is reasonable to assume that the frequency of a $(\mathrm{TCNQ})^0$ libration is practically identical to that of $(\mathrm{TCNQ})^-$, so that we tentatively assign the transitions at 70, 81, and 110 cm^{-1} as $(\mathrm{TCNQ})^-$ librations. The other transitions that we observed at 170, 299, and 295 cm^{-1} were present at liquid-nitrogen temperature (Fig. 6). They could be translational modes, internal modes, or even second order.

TABLE II. The lattice modes of the K(TCNQ) crystals. The frequencies were determined by comparing Fig. 2 with Fig. 8 and Figs. 4 and 5 with Fig. 9. The species was determined by comparing Fig. 4(a) with 4(b) and Fig. 5(a) with 5(b).

$\Delta\nu$ (cm^{-1}, ±5 cm^{-1})	Polarizability	Assignment
70	x^2,xy,y^2,zx,zy	A_g [$(\mathrm{TCNQ})^-$ libration]
81	x^2,xy,y^2	A_g [$(\mathrm{TCNQ})^-$ libration]
110	x^2,xy,y^2,zx,zy	A_g [$(\mathrm{TCNQ})^-$ libration]
170	x^2,xy,y^2,zx,zy	A_g or B_g
229	x^2,xy,y^2	A_g
295	x^2,xy,y^2,zx,zy	A_g or B_g

TABLE III. Intramolecular modes of K(TCNQ) crystal.

$\Delta\nu$ (cm^{-1}) (± 3 cm^{-1})	I (relative to 10)	Assignment
345	<1	A_g
584	3	A_g
620	1	A_g
725	8	A_g
760	1	A_g
950	<1	probably B_g
980	5	A_g
1180	<1	probably B_g
1202	10	A_g
1388	3	A_g
1603	8	A_g
1625	2	A_g
2207	1	A_g

Since many workers use the KBr technique, we investigated its effect which is shown in Fig. 7. The 620 cm^{-1} line is repressed, but the 1180 cm^{-1} is enhanced. We can say that the effect of the KBr is weak. The KBr effect is, however, comparable to the effect obtained in changing the 4579 Å line with the 5145 Å line.

The spectra shown in Figs. 2 and 6 differ because of laser irradiation. The strong continuum appearing in Fig. 6, which becomes stronger beyond 1600 cm^{-1}, was found consistently on burned crystals. The continuum appeared even on crystals burned at 77 °K. The laser radiation change is more serious than that due to the KBr change.

Except for minor intensity differences, the Raman spectrum obtained with the 5145 Å line is similar to that obtained with the 4579 Å, i.e., the number of transitions observed did not depend on the laser excitation. This observation was made on spectra taken from the crystal and from the pellets; the statement applies to room-temperature spectra and liquid-nitrogen spectra. As already noted, the resonance Raman effect that we observed is comparable in magnitude to the effect of the KBr.

Our Raman spectra of K(TCNQ) are significantly different from those published by Chi and Nixon.[24] They are however more like the (TCNQ)$^-$ spectra published by Jeanmaire and Van Duyne.[25]

It is necessary to compare Raman data with infrared data when this is possible. Infrared absorption and reflectivity on K(TCNQ) has been done on polycrystalline samples pressed in KBr pellets or pressed in Nujol.[21] Although we found that our Raman spectrum of K(TCNQ) crystals was only slightly altered when we switched to the KBr technique, the method of making pellets is not unique and it is not obvious that the infrared spectrum will be altered equally slightly by the KBr. Some works[30,31] casting doubt on the pellet and Nujol techniques for the infrared exist. Nevertheless lattice modes have been tentatively assigned at 53 and 325 cm^{-1} and intramolecular modes at 106, 124, 172, 220, and 412 cm^{-1} and others with higher frequencies. Since x-ray data shows that the unit cell of K(TCNQ) has an inversion center, it is consistent that the frequencies of the lattice modes found in the infrared do not coincide with those found in the Raman. Moreover, the infrared lattice modes have their origin in translational degrees of freedom.

TABLE IV. Intramolecular modes of (TCNQ)$^-$ as obtained by dissolving K(TCNQ) in acetonitrile. The depolarization ratio indicate all these modes are A_g.

$\Delta\nu$ (cm^{-1}) (± 3 cm^{-1})	I (relative to 10)	Depolarization ratio ($\pm 5\%$)	Assignment
341	1	0.39	A_g
. . .			
. . .			
726	10	0.34	A_g
754	<1	. . .	
. . .			
980	7	0.34	A_g
. . .			
1195	7	0.31	A_g
1391	3	0.48	A_g
1604	3	0.41	A_g
1615	8	0.40	A_g
2250	. . .		A_g

VI. SUMMARY AND CONCLUSIONS

In summary: (i) We have identified lattice modes at 70, 81, 125, 170, 229, and 295 (±5) cm^{-1} and 13 intramolecular modes above 300 cm^{-1}. The modes at 70, 81, and 125 are probably (TCNQ)$^{-1}$ librations. (ii) The anisotropy of the intramolecular modes reflects the stacking structure of the TCNQ's, but the isotropy of the lattice modes indicates no reduced dimensionality for nuclear movements. (iii) K(TCNQ) crystals are sensitive to laser radiation. The Raman spectrum changes when more than 30 mW of laser power is focused on the crystal. (iv) The spectrum of K(TCNQ) is slightly modified when obtained in pellets of KBr. (v) The Raman spectrum of K(TCNQ) crystals obtained with the 4579 Å line is practically identical to that obtained with the 5145 Å line. We found little evidence of the resonance Raman effect using these two laser lines.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada and by the NRC for the Defence.

---

*Members of Groupe de recherche sur les semiconducteurs et les dièlectriques.

[1] J. Kommandeur, in *Low-dimensional Co-operative Phenomena* edited by H. J. Keller (Plenum, New York, 1974), p. 65.

[2] Z. G. Soos and D. J. Klein, in *Molecular Association,* edited by R. Foster (Academic, New York, 1975), Vol. 1, p. 1.

[3] J. Tanaka, M. Tanaka, T. Kawai, T. Takabe, and O. Maki, Bull. Chem. Soc. Jpn. 49, 2358 (1976).

[4] G. R. Anderson and C. J. Fritchie, Jr., Appl. Spectry. 17, 148 (1963).

[5] T. Hiroma and J. Kommandeur, Solid State Commun. 17, 259 (1975).

[6] M. Konno, T. Isihi, and. Y. Saito, Acta Crystallogr. Sect. B 33, 763 (1977).

[7] P. Richard, J. C. Zanghi, and J. F. Guedon, Acta Crystallogr. (to be published).

[8] Y. Iida, Bull. Chem. Soc. Jpn. 42, 637 (1969).

[9] S. Hiroma, H. Kuroda, and H. Akamatu, Bull. Chem. Soc. Jpn. 44, 9 (1971).

[10] Y. Oohashi and T. Sakata, Bull. Chem. Soc. Jpn. 46, 3330 (1973).

[11] F. B. Kaufman and I. Haller, Chem. Phys. Lett. 33, 30 (1975).

[12] J. B. Torrance, B. A. Scott, and F. B. Kaufman, Solid State Commun. 17, 1369 (1975).

[13] D. B. Tanner, G. S. Jacobsen, A. A. Bright, and A. J. Heeger, Phys. Rev. B 16, 3283 (1977).

[14] M. Michaud, C. Carlone, N. K. Hota, and J. Zauhar, Chem. Phys. 36, 79 (1979).

[15] N. Sakai, I. Shirotani, and S. Minomura, Bull. Chem. Soc. Jpn. 45, 3314 (1972).

[16] N. Sakai, I. Shirotani, and S. Minomura, Bull. Chem. Soc. Jpn. 45, 3321 (1972).

[17] S. K. Khanna, A. A. Bright, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 2139 (1974).

[18] J. G. Vegter, T. Hibma, and J. Kommandeur, Chem. Phys. Lett. 3, 427 (1969).

[19] J. C. Vegter and J. Kommandeur, Mol. Cryst. Liq. Cryst. 30, 11 (1975).

[20] Y. Lèpine, A. Caillè, and V. Larochelle, Phys. Rev. B 18, 3585 (1978).

[21] Z. Iqbal and C. W. Christoe, J. Chem. Phys. 63, 4485 (1975).

[22] A. Girlando, R. Bozio, and C. Pecile, Chem. Phys. Lett. 25, 409 (1974).

[23] R. Bozio, A. Girlando, and C. Pecile, J. Phys. Chem. 33, 1237 (1975).

[24] Cheng-Ken Chi and E. R. Nixon, Spectrochim. Acta Part A 31, 1739 (1975).

[25] D. L. Jeanmaire and R. P. van Duyne, J. Am. Chem. Soc. 98, 4029 (1976).

[26] W. T. Woznick, G. Depasquali, and M. V. Klein, Chem. Phys. Lett. 40, 93 (1976).

[27] H. Kuzmany and H. J. Stolz, J. Phys. C 10, 2241 (1977).

[28] F. A. Cotton, *Chemical Applications of Group Theory* (Interscience, New York, 1971).

[29] A. Girlando and C. Pecile, Spectrochim. Acta Part A 29, 1859 (1973).

[30] A. W. Baker, J. Chem. Phys. 61, 450 (1957).

[31] A. Tolk, Spectrochim. Acta 17, 511 (1961).