The Tricyanomethanide Ion: An Infrared, Raman, and Tunneling Spectroscopy Study Including Isotopic Substitution

K. W. Hipps* and A. T. Aplin

Department of Chemistry and Chemical Physics Program, Washington State University, Pullman, Washington 99164-4630 (Received: May 8, 1985)

The tricyanomethanide ion (TCM), $C(CN)_3^-$, and its isotopomers, $C(CN)_2(^{13}CN)^-$ and $C(CN)_2(C^{15}N)^-$, were studied experimentally by Raman, IR, and tunneling spectroscopy in the frequency range from about 80 to 4000 cm^{-1}. The primary focus of the present paper is on the ion and its K salt, but Co and Mn complex data are also reported. An 11-parameter empirical force field provided a 2-cm^{-1} standard deviation fit to all the normal modes of the ion. While many of our assignments agree with those of previous studies (done without isotopic substitution), there are a few differences. In particular, the inactive a_2' mode is definitively assigned through the use of tunneling spectroscopy. We also performed ab initio calculations at the 4-31G SCF level to determine the geometry and 11 of the quadratic force constants of the ion. The calculated geometry is in good agreement with that of the KTCM salt, but the calculated force constants are about 25% too large.

Introduction

Percyanocarbanions were first introduced as a class of molecular systems by the monumental work of Middleton and his colleagues at Du Pont in the late 1950's.[1,2] Generally, they fall into two classes, those which are radicals like tetracyanoethylene anion,[3,4] and those which form nonradical anions like tricyanomethanide.[5-9] Several of these radical anions are well-known for their strong EPR spectra and their appearance in electrochemical and surface reduction studies. The excellent work of Devlin and his co-workers,[3,4] for example, has greatly clarified our understanding of the vibrational spectra of the radical anions. The nonradical anions have received considerably less attention. In this paper, we focus on the paired electron percyanocarbanion, tricyanomethanide (TCM).

Our original interest in percyanocarbanions stems from the intense fluorescence and exceedingly strong Raman spectrum of the pentacyanopropenide ion.[10-13] By using an SCF force field scaling algorithm, we were able to determine the normal coordinates of pentacyanopropenide (PCP). These normal coordinates and a theoretically calculated excited-state geometry were then used to reproduce the rich vibronic structure observed in the pentacyanopropenide emission. We also found that CsPCP forms a crystal in which sheets of planar PCP ions occur. More recently, we have discovered that the dianion, 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide (DTP), both fluoresces and phosphoresces, with the long-lived (about 0.5 s) decay having greatest intensity.[14] Crystal structures of salts of the DTP dianion show that it is not planar, but somewhat folded due to steric effects overriding the tendency to planarity inherent in the strongly de-

localized π structure.[15,16] In order to fully understand the nature and origin of the observed changes in electronic and vibronic properties of percyanocarbanions as a function of size, it is imperative that we have the fullest possible understanding of the smallest members of this class of ion. Thus, we turned our attention to the tricyanomethanide ion.

The tricyanomethanide ion (TCM) was first synthesized by Schmidtmann in 1896,[17] but the best preparation procedure is due to Trofimenko et al.[18] Long, Carrington, and Gravenor[7] reported the first NaCl region IR and Hg arc Raman spectra of the potassium salt of TCM. They correctly assigned all but one of the allowed fundamentals and correctly inferred the structure of the ion to be D_{3h}. Miller and Baer[6] remeasured the Raman and IR of KTCM in the 70-5000-cm^{-1} region. They modified (incorrectly in our opinion) several of Long's original assignments. Mayer et al.[5] remeasured the IR and Raman spectra of KTCM and fit a 9-parameter potential function to the data. They have a complete (and we believe correct) assignment of all allowed modes, but were unable to differentiate between two solutions giving significantly different values for the forbidden a_2' mode. The more recent analysis by Kireeva et al.,[8] and of Pentin,[9] are flawed by misassignments. In none of these studies have isotopic species been used to allow the potential function to be more completely determined and the assignments made more firmly.

Crystal structures for the Na and K salts[19,20] of TCM are now available. These studies reveal that the ion is nearly planar with some distortion from D_{3h} site symmetry. It is generally assumed that this distortion is due to crystal packing forces. There is more than one ion per unit cell so that factor group splittings of vibrational bands are possible. From the number of bands observed in the isotopic species, however, we discount their significance.

In this work we will address the questions of the location of all fundamentals of TCM, and the ground-state symmetry of the free ion. We will use isotopic and cation substitution data from three vibrational spectroscopies to obtain firm assignments for all fundamentals. These data will be used in conjunction with the ab initio SCF calculated structure and both semiempirical and empirical potentials to determine the principal potential constants for the ion.

(1) Middleton, W. J. U. S. Patents 2 766 243 and 2 766 246, 1976.

(2) Middleton, W. J.; Little, E. L.; Coffman, D. D.; Englehart, V. A. *J. Am. Chem. Soc.* **1958**, *80*, 2795. See this entire issue— Middleton's group filled it with papers on cyanocarbanions.

(3) Khatkale, M. S.; Devlin, J. P. *J. Phys. Chem.* **1979**, *83*, 1636.

(4) Hinkel, J. J.; Devlin, J. P. *J. Chem. Phys.* **1973**, *58*, 4750.

(5) Mayer, E.; Gardiner, D. J.; Hester, R. E. *J. Mol. Struct.* **1974**, *20*, 127.

(6) Miller, F. A.; Baer, W. K. *Spectrochim. Acta* **1963**, *19*, 73.

(7) Long, D. A.; Carrington, R. A.; Gravenor, R. B. *Nature* **1962**, *196*, 371.

(8) Kireeva, I. K.; Kharitnov, Y. Y.; Knyazeva, N. A.; Keller, K. *Russ. J. Inorg. Chem.* **1978**, *23*, 653.

(9) Pentin, Y. A.; Makhon'kov, D. I.; D'yachkova, L. Y.; Baburina, I. I.; Zefirov, N. S. *Zh. Obshch. Khim.* **1978**, *48*, 1850.

(10) Mazur, U.; Hipps, K. W. *J. Phys. Chem.* **1982**, *86*, 2854.

(11) Hipps, K. W.; Keder, J. W. *J. Phys. Chem.* **1983**, *87*, 3186.

(12) Mazur, U.; Hipps, K. W. *J. Phys. Chem.* **1983**, *87*, 4641.

(13) Hipps, K. W.; Geiser, U.; Mazur, U.; Willett, R. E. *J. Phys. Chem.* **1984**, *88*, 2498.

(14) Early, R.; Mazur, U.; Hipps, K. W., in preparation.

(15) Bekoe, D. A.; Gantzel, P. K.; Trueblood, K. N. *Acta Crystallogr.* **1967**, *22*, 657.

(16) Sakanoue, S.; Yasuoka, N.; Kasai, N.; Kakudo, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1.

(17) Schmidtmann, H. *Ber.* **1896**, *29*, 1171.

(18) Trofimenko, S.; Little, E. L.; Mower, H. F. *J. Org. Chem.* **1962**, *27*, 433.

(19) Anderson, P.; Klewe, B.; Erling, T. *Acta Chem. Scand.* **1967**, *21*, 1530.

(20) Witt, J. R.; Britton, D. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1835.

Experimental Section

Synthesis. TCM was made by the method of Trofimenko et al.[18] by using reagents purchased from Aldrich Chemical Co. The crude product was multiply purified by treatment with activated charcoal in acetone solution. KTCM was precipitated from solution by the addition of anhydrous ether. After about 10 such treatments, the KTCM was doubly recrystallized from water to remove most of the residual organic solvents. The above procedure gave a very white crystalline solid having no fluorescence background in the Raman spectrum when excited by 5145-Å radiation. Isotopic samples were prepared by using >95% enriched $K^{13}CN$ or $KC^{15}N$ and were purified as above. Trofimenko's method[18] allows the insertion of one and only one isotopic cyanide without racemization.

$Mn(TCM)_2 \cdot ^1/_4H_2O$ and $Co(TCM)_2 \cdot ^1/_2H_2O$ were synthesized by methods reported in the literature by using our highly purified KTCM as starting material.[21] No recrystallizations were performed.

Raman Spectra. Raman spectra were obtained with an Instruments S.A. double 1-m spectrometer having matched holographic gratings. The 5145 argon ion line was used to excite KTCM and $Mn(TCM)_2$, but produced rapid decomposition of the Co complex. The 6471 Kr ion line was used to excite the $Co(TCM)_2$ Raman spectra. In either case, the laser radiation was passed through a prism monochromator and a narrow pass filter before being used for excitation. The signal was detected by a cooled Hamamatsu R666 photomultiplier and counted by a Spex DPC2 photon counter. The spectrometer and photon counter were under the control of a Cromemco microcomputer. The spectra reported here are generally the sum of a number of repetitive scans.

Polarization data were obtained with solutions having about 0.1 g of KTCM dissolved in 0.4 g of water. A rectangular strain-free quartz cell was used to hold the sample. A 90-deg excitation geometry was used and the plane of polarization of the laser radiation was modified by a polarization rotator supplied by Lexel Corp. A depolarizer is permanently mounted within the spectrometer.

IR. Infrared spectra were obtained on either a Perkin-Elmer 283B dispersive IR or a Nicolet 60SX Fourier Transform IR. KBr pellets were used to support the samples in the mid-IR region of the spectrum, and spectra showing expanded segments of the spectrum are reported with the KBr reference spectrum subtracted. In the far-IR, KTCM was pressed on clear tape and run with a matching piece of tape as reference.

Tunneling Data. Tunneling spectra were obtained by adsorbing TCM from a solution having 8 mg of KTCM in 1 mL of water on the alumina barrier of an $Al-Al_2O_3-Pb$ tunnel junction. This high concentration immediately indicates to the experienced tunneling spectroscopist that TCM adsorbs weakly on alumina (from water). Thus, as will be shown later, even exceedingly small amounts of residual organic solvents in the KTCM will lead to CH modes being seen in the tunneling spectrum. The spectrometer used in these studies has been described previously.[22]

Tunneling spectra were obtained at 4 K by using modulation voltages of 1.2 and 2.0 mV (rms) for medium and low resolution spectra, respectively. In general, each spectrum reported is the sum of multiple scans. While the line widths reported are relatively broad, this is strictly an artifact of the experimental conditions. Line widths of less than half those reported here would be obtained if the measurements were performed at 1.4 K with 0.5-mV modulation.

Theory

Group Theory. As will be shown below, TCM is best treated as a D_{3h} symmetry ion. The decomposition of the vibrational displacements into irreducible representations of D_{3h} gives the following count of the various symmetry types.

$$2a_1' + a_2' + 4e' + 2a_2'' + e''$$

(21) Enemark, J. H.; Holm, R. H. *Inorg. Chem.* **1964**, *3*, 1516.
(22) Hipps, K. W.; Mazur, U. *J. Phys. Chem.* **1980**, *84*, 3162.

TABLE I: Structural Parameters for the $C(CN)_3^-$ Ion

coordinate	SCF[a]	NaTCM[b]	KTCM[c]
r_{CC}	1.401	1.408 (0.003)	1.39 (0.002)
r_{CN}	1.153	1.15 (0.01)	1.17 (0.01)
$\angle CCC$	120.0	120 (0.8)	120 (0.2)
$\angle CCN$	180.0	179.5 (0.4)	178 (0.5)

[a] This work. [b] Reference 19. [c] Reference 20. Values in parentheses represent approximate variation in values.

Of these, only the e′ modes are both Raman and IR active. The a_1' and e″ modes are Raman active only, while the a_2'' modes are IR active only. The single a_2' mode is silent in both the IR and Raman.

A general quadratic potential for this ion will be completely specified by 18 potential constants, 14 in plane and 4 out of plane. Thus, if all nine Raman or IR active modes are correctly assigned, less than half the potential constants can be determined with precision. In order to partially compensate for this, two isotopomers were synthesized. The ^{13}C isotopic species had a single noncentral carbon isotopically labeled. The ^{15}N istopomer had a single labeled nitrogen. Both isotopic species, therefore, were of symmetry C_{2v}. To facilitate vibrational force constant calculations, all three isotopomers were assumed to have C_{2v} symmetry normal coordinates.

The vibrational bands of all three isotopomers were simultaneously fit (vide infra) to a quadratic potential. To avoid confusion, we report many of our results using the irreducible representations of the group of the free normal isotopic ion, D_{3h}; but, calculations were carried out in the true group of the labeled ions, C_{2v}. In C_{2v}, the normal modes transform as one of four irreducible representations:

$$6a_1 + 5b_2 + a_2 + 3b_1$$

The a_1' and one component (component a, say) of the e′ modes of D_{3h} transform as a_1 in C_{2v}. The second component of the e′ modes (component b, say) and the a_2' mode transform as b_2. The a component of e″ transforms as a_2 and the b component and the two a_2'' modes transform as b_1.

SCF. A linear combination of atomic orbitals self-consistent field (LCAO-SCF) method utilizing a single electronic configuration was used to determine the equilibrium geometry and several vibrational potential constants of the tricyanomethanide ion. This method has been described in a series of papers by Pople et al.,[23,24] and is implemented by the program GAUSSIAN-76.[25] The internal 4-31G basis set was used and calculations were performed on an Amdahl V-8 computer.

We optimized the geometry by varying one internal coordinate (IC) at a time in a cyclic fashion. Each IC (in each cycle) was varied over a uniform grid and the equilibrium IC was determined by assuming a parabolic dependence of the potential. The initial pass utilized a 0.05-Å or 5-deg grid. Both the penultimate and the final pass used 0.01-Å or 1-deg displacements. The ion was found to be planar and to have D_{3h} symmetry. Table I gives our results for bond lengths and angles, and contrasts them with those obtained by X-ray crystallography in the Na and K salt cases. We consider the agreement to be very good.

The desired in-plane potential constants were computed subsequent to geometry optimization. Bond stretch displacements of 0.015 Å and $\angle CCC$ displacements of 1° were used. A larger value, 2°, was used for the $\angle CCN$ and out-of-plane bending displacements. This method of force constant determination is inelegant and slow, but it should give results equivalent to more sophisticated methods. The potential evaluated by this method is given as eq 1, where the redundant coordinate involving the third

(23) Newtin, M. D.; Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1970**, *52*, 4064.
(24) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.
(25) QCPE program 391; Department of Chemistry, Indiana University.

$$2V = K_{CC}(\Delta r_1^2 + \Delta r_2^2 + \Delta r_3^2) + K_{CN}(\Delta r_4^2 + \Delta r_5^2 +$$
$$\Delta r_6^2) + H_{CCC}(\Delta\phi_1^2 + \Delta\phi_2^2 + \Delta\phi_1\Delta\phi_2) + H_{CCN}(\Delta\phi_3^2 +$$
$$\Delta\phi_4^2 + \Delta\phi_5^2) + H'_{CCN}(\Delta\beta_1^2 + \Delta\beta_2^2 + \Delta\beta_3^2) + H'_{CCC}\Delta\beta_4^2 +$$
$$2G_{CCC,CCN}(\Delta\phi_1\Delta\phi_3 + 2\Delta\phi_1\Delta\phi_4 + \Delta\phi_1\Delta\phi_5 - \Delta\phi_2\Delta\phi_3 +$$
$$\Delta\phi_2\Delta\phi_4 + 2\Delta\phi_2\Delta\phi_5) + 2G'_{CCC,CCN}\Delta\beta_4(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3) +$$
$$2F_{CC,CC}(\Delta r_1\Delta r_2 + \Delta r_1\Delta r_3 + \Delta r_2\Delta r_3) + 2F_{CC,CN}(\Delta r_1\Delta r_4 +$$
$$\Delta r_2\Delta r_5 + \Delta r_3\Delta r_6) + 2F_{CC,CCC}(\Delta r_1(\Delta\phi_1 + \Delta\phi_2) - \Delta r_2\Delta\phi_2 -$$
$$\Delta r_3\Delta\phi_1) + 2F_{CN,CN}(\Delta r_4\Delta r_5 + \Delta r_4\Delta r_6 + \Delta r_5\Delta r_6) \quad (1)$$

∠CCC bend has been removed by assigning a constant value (360°) to the sum of all CCC in-plane angles. The prime constants refer to out-of-plane motion and the coordinates are as displayed in Figure 1. Note that all diagonal and nearest-neighbor force constants were calculated. Unfortunately, the calculated value of $G'_{CCC,CCN}$ was too small (<0.01) to be reliable. The results of this calculation are given in Table II.

The development of this potential, and the handling of the redundancy conditions, is similar to Appendix VI in ref 36. Further, Supplement 1 gives the transformation from these force constants to the general quadratic potential constants (see supplementary material).

Vibrational Analysis. The method used here to perform nonlinear least-squares fitting of a potential, such as given in eq 1, to observed frequencies has been discussed extensively.[13,26] Two kinds of parameterizations of the potential will be used in the present work. The empirical method simply uses the potential constants themselves as parameters. Thus, there is one parameter per force constant determined.

The semiempirical method was pioneered by Blom and Altona,[27,28] and has been further advanced by Pullay and Boggs,[29] and by Swanson and co-workers.[30-32] In this case, one chooses a small number of scaling factors, generally associated with classes of bonds, and uses these to scale the more extensive set of SCF calculated force constants. These scaling factors are then optimized by the least-squares fitting of calculated to observed frequencies. Thus, the number of fitting parameters is less than the number of force constants obtained. This method works exceedingly well for many types of aromatic compounds,[27-29] and performs reasonably by cyanocarbanions.[13,26]

Results

Figure 2 displays the primary features of the polarized solution-phase Raman and solid-state IR data obtained from KTCM. The two intense bands in the isotropic (or symmetric) part of the solution Raman spectrum (a) can be due only to the two totally symmetric a_1' modes. The anisotropic part (b) can contain both symmetric and asymmetric contributions, but the e' CN stretch (2173 cm^{-1}) and e' CCN in-plane bend (159 cm^{-1}) carry most of the anisotropic intensity. In the mid-IR, the e' CN stretch is about 3 times more intense than any other feature. The e' CCN bend is also seen in the far-IR, but the different method of sample preparation makes it difficult to assign intensities relative to mid-IR bands. The scale shown in Figure 1 was chosen for graphic convenience only. Note that a number of overtone and combination bands can be observed in the IR spectrum (c).

Figure 3a shows the low-resolution tunneling spectrum of TCM. The bands marked by * are due to a very small amount of organic solvent still present in the potassium salt. The very broad feature near 1000 cm^{-1} is due to Al–O motions of the oxide support, and
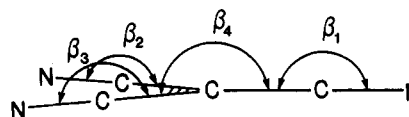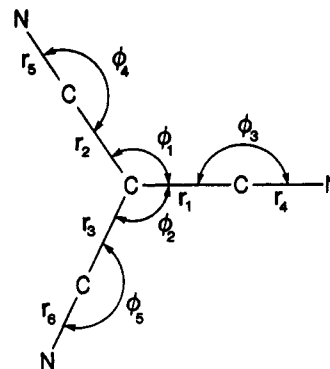

Figure 1. Coordinates used in the vibrational analysis of tricyanomethanide ion.
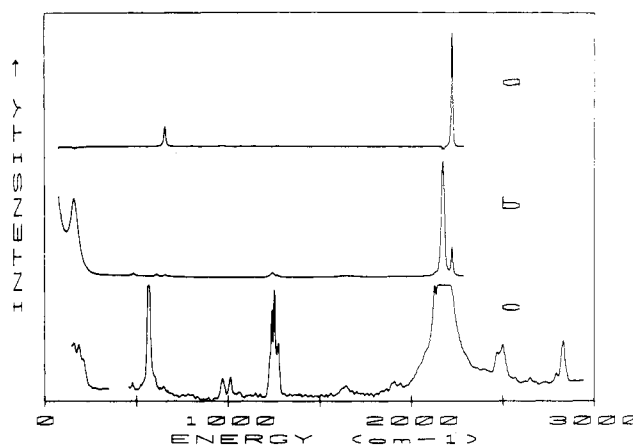

Figure 2. Vibrational spectra of tricyanomethanide. Parts a and b are, respectively, the isotropic (or symmetric) and anisotropic parts of the solution-phase Raman spectrum. Part c is medium-resolution mid- and far-IR data obtained from the potassium salt. Note that the far-IR data is not displayed on the same scale as the mid-IR data.

**TABLE II: Force Constants for the $C(CN)_3^-$ Ion^a**

constant	SCF	scaled SCF		empirical	
K_{CC}	7.18	6.44	(0.01)	5.02	(0.004)
K_{CN}	21.30	16.42	(0.04)	17.36	(0.004)
H_{CCC}	1.78	1.33	(0.01)	2.16	(0.004)
H_{CCN}	0.50	0.36	(0.002)	0.36	(0.002)
H'_{CCC}	0.21	0.14	(0.001)	0.14	(0.001)
H'_{CCN}	0.66	0.52	(0.002)	0.52	(0.001)
$G_{CCC,CCN}$	−0.065	−0.054	(0.003)	−0.063	(0.001)
$G'_{CCC,CCN}$		0.053	(0.001)	0.053	(0.001)
$F_{CC,CC}$	0.43	0.35	(0.002)	1.09	(0.003)
$F_{CC,CN}$	0.58	0.48	(0.002)	0.70	(0.003)
$F_{CC,CCC}$	0.55	0.46	(0.002)	−0.01	(0.0004)
$F_{CN,CN}$	0.20	0.17	(0.001)		

^{a} Values in parentheses are the standard deviations of parameters.

the smaller broad band near 300 cm^{-1} is due to Al–Al motions in the metal layer. The remaining bands are due to TCM. Figure 3 also displays the medium-resolution solid-state Raman (b) and IR (c) of KTCM. As in Figure 2, the relative intensities of the far and mid-IR regions are not known. Note that the band near 180 cm^{-1} is present as a strong band in all three types of spectra (this band shifts to 159 cm^{-1} in solution).

Figure 4 displays the medium resolution tunneling, Raman, and IR spectra obtained from KTCM in the 300–800-cm^{-1} region.

(26) Hipps, K. W.; Poshusta, R. D. *J. Phys. Chem.* **1982**, *86*, 4112.
(27) Blom, C. E.; Altona, C. *Mol. Phys.* **1976**, *31*, 1377.
(28) Blom, C. E.; Altona, C. *Mol. Phys.* **1977**, *33*, 875.
(29) (a) Pullay, P.; Forgarasi, G.; Boggs, J. E. *J. Chem. Phys.* **1981**, *74*, 3999. (b) Carlowitz, S.; Zeil, W.; Pulay, R.; Boggs, J. E. *J. Mol. Struct.*, **1982**, *87*, 113.
(30) Swanson, B. I.; Arnolds, T. H.; Yamagouchi, Y. *J. Mol. Struct.* **1979**, *75*, 363.
(31) Arnold, T. H.; Swanson, B. I.; Yamagouchi, Y.; Nelson, D. J. *J. Mol. Struct.* **1979**, *78*, 267.
(32) Swanson, B. I.; Arnold, T. H.; Dewar, M. J. S.; Rafalko, J. J.; Rzepa, H. S.; Yamagouchi, Y. *J. Am. Chem. Soc.* **1978**, *100*, 771.
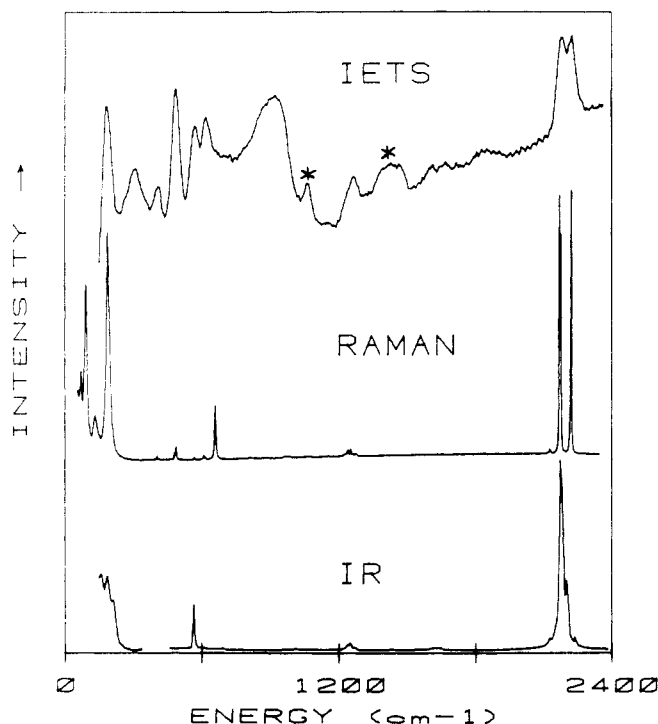
Figure 3. Vibrational spectra of potassium tricyanomethanide. A low-resolution tunneling spectrum (a), a medium-resolution solid-state Raman spectrum (b), and a medium-resolution IR spectrum (c) are shown.
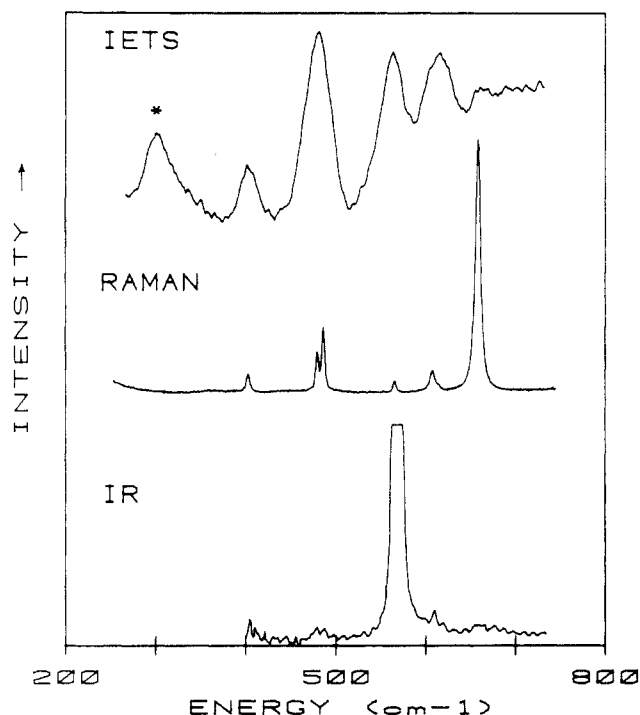

Figure 4. Tunneling (IETS), Raman, and IR spectra obtained from solid KTCM in the region from 300 to 700 cm⁻¹.

The band marked * in the tunneling spectrum is due to Al–Al motions in the aluminum metal layer. For later reference, several points about this figure should be noted. The weak band at 402 cm⁻¹ in the solid Raman is not present in the solution-phase Raman spectrum or in the IR. It is a significant band in the tunneling (or IET) spectrum. The weak doublet near 484 cm⁻¹ in the Raman spectrum is the second strongest single band in the IET spectrum, and is barely discernible in the IR. The intense IR band at 568 cm⁻¹ is barely seen in the Raman and is a significant band in the tunneling spectrum. The very weak band near 610 cm⁻¹ in both the IR and Raman appears as a strong band in the tunneling spectrum. The a_1'' band at 658 cm⁻¹ is reasonably intense in the
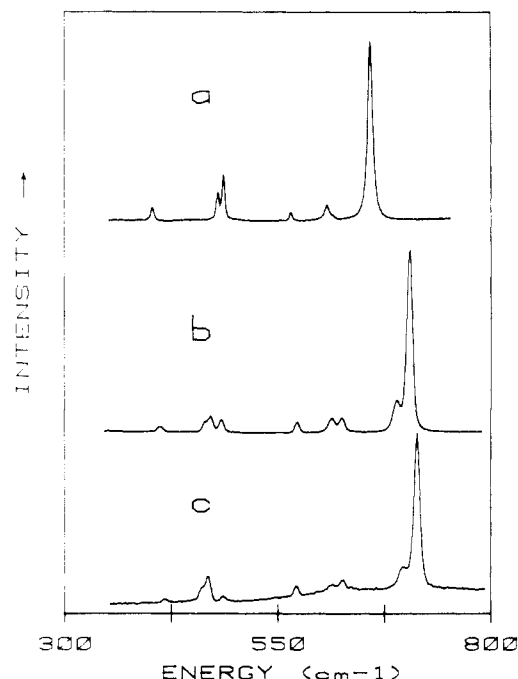
Figure 5. Solid-state Raman spectra obtained from TCM salts: (a) potassium, (b) manganese, and (c) cobalt salts of TCM.
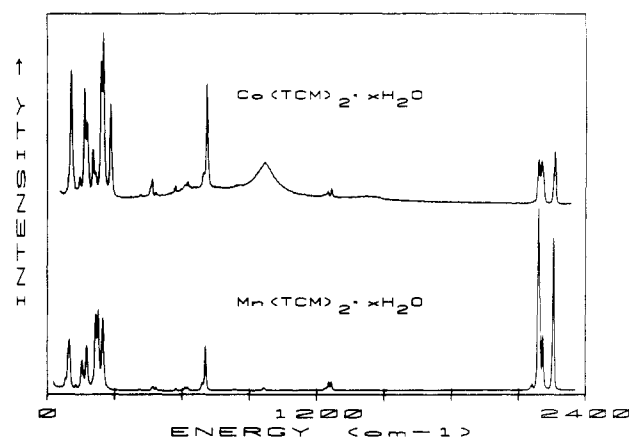
Figure 6. Raman spectra obtained from solid samples of cobalt and manganese complexes of tricyanomethanide.

Raman spectrum but essentially nonexistent in the IR or tunneling spectra.

Figure 5 contrasts solid-state Raman spectra obtained from potassium (a), manganese (b), and cobalt (c) salts of TCM in the 300–700-cm⁻¹ region. Two points are of special significance. First, the band near 402 cm⁻¹ in the K salt is present, though somewhat shifted, in the Mn and Co salts. Second, the single band near 610 cm⁻¹ in the K salt spectrum splits into two bands in the spectra obtained from the Mn and Co salts.

Figure 6 shows the full Raman spectra obtained from Co-(TCM)₂·¹/₂H₂O and Mn(TCM)₂·¹/₄H₂O solids. They are given here for completeness. Enemark and Holm[21] reported their IR spectra, but no previous Raman spectra have been published.

Discussion

Assignments. Using the isotropic part of the Raman spectrum (Figure 2a), the symmetric CN and CC stretching motions can be instantly assigned at 2224 and 658 cm⁻¹. The e′ motions are assigned as follows. The bands near 2173, 1243, 610, and 160 cm⁻¹ are all present in both the IR and Raman spectra. All but the 610-cm⁻¹ band are reasonably intense and easily assigned. The 610-cm⁻¹ band is so weak in both Raman and IR (see Figure 4), that further confirmation was desired. The 610-cm⁻¹ band is quite strong in the tunneling spectrum indicating that it is probably a fundamental. This band is also split into a doublet in the Raman

TABLE III: Observed and Calculated Normal Mode Energies (cm⁻¹) Using an 11-Parameter Empirical Potential[a]

type D_{3h}	C_{2v}	obsd	calcd	obsd(C)	calcd(C)	obsd(N)	calcd(N)
a_1'	a_1	2224	2225	13	10	9	7
a_1'	a_1	658	657	3	3	4	5
e_a'	a_1	2173	2170	44	41	22	22
e_a'	a_1	1243	1243	5	1	3	3
e_a'	a_1	610	609	0	2	2	2
e_a'	a_1	159	157	3	0	2	0
a_2'	b_2	402	404	4	4	1	1
e_b'	b_2	2173	2170	2	0	2	0
e_b'	b_2	1243	1243	4	3	3	0
e_b'	b_2	610	609	10	11	2	0
e_b'	b_2	159	157	3	0	2	3
e_a''	a_2	484	484	4	0	1	0
a_2''	b_1	568	568	3	3	1	1
a_2''	b_1	176	177	0	1	0	1
e_b''	b_1	484	484	9	10	1	2

[a] Obsd(X) and calcd(X) values are the negatives of the observed and calculated isotopic shift due to substitution of a single noncentral atom X. Standard deviation = 1.75 cm⁻¹. Mean percentage error = 0.3%.

spectrum of the Co and Mn salts, indicating that it is either an e type mode or that we are seeing factor group splitting. We next noted the presence of a three strong bands and a shoulder (rather than the expected two bands) in the solid-state Raman and IR feature near 1273 cm⁻¹. This extra band is very near 658 (a_1') + 610 cm⁻¹. Since its intensity strongly suggests that Fermi resonance is present, the 1273-cm⁻¹ feature must be due to an e' symmetry motion. Therefore, the 610-cm⁻¹ band is an e' type motion.

The out-of-plane motions are assigned as follows. The doublet near 484 cm⁻¹ in the Raman of solid KTCM is present as a single band in the solution spectrum and is exceedingly weak in the solid-state IR spectrum. It is the second strongest band in the tunneling spectrum. Thus, it is an e type fundamental. Further, since it has significant Raman intensity, it is the e'' mode. The strong band at 568 cm⁻¹ in the IR is not present in the solution Raman spectrum and must be one of the a_2'' modes. The second a_2'' band is assigned at 176 cm⁻¹ in accord with the arguments given by Mayer.[5]

At this point we have assigned all of the strong bands in the tunneling spectrum of TCM, except one. The 402-cm⁻¹ band is as intense as the bands due to several other fundamentals in the tunneling spectrum. This band is not present in the IR or solution Raman, but is a universal feature in the Raman spectrum of all three solid salts of TCM; thus, it is highly unlikely that it is due to counterion motion. Finally, we note that there is a weak band in the symmetric part of the solution-phase Raman spectrum at 805 cm⁻¹. Thus, the 402-cm⁻¹ band is the inactive a_2' mode. It is interesting to note that this is not the first evidence that IR and Raman forbidden modes can be seen with good intensity in the tunneling spectrum.[22,33,34]

The above assignments and the observed isotopic shifts are collected in Table III. It is important for the reader to note that not all the frequencies given in Table III are from the same phase of material. While many of the bands could be observed in solution, a significant number of them were only observed in the solid state. Further, some of the bands were very broad in solution and isotopic shifts could not be accurately determined in the liquid phase. The values in Table III, therefore, are a mix of solution and KTCM solid data. While this is not ideal, we believe it is probably acceptable in this case because the bands above 300 cm⁻¹ (the region in question) shift very little with a change in phase.

Empirical Potential. An 11-parameter empirical potential of the form given in eq 1, with all the force constants of eq 1 except for the CN–CN interaction term, was fit to the observed fun-

(33) Hipps, K. W.; Williams, S. D.; Mazur, U. *Inorg. Chem.* **1984**, *23*, 3500.
(34) Kirtley, J.; Hansma, P. K. *Surf. Sci.* **1977**, *66*, 125.

TABLE IV: Scaling Parameters Used and Values Obtained[a]

parameter	value	
$S(CC)$	0.897	(0.002)
$S(CN)$	0.771	(0.002)
$S(\angle CCC$ in-plane)	0.748	(0.005)
$S(\angle CCN$ in-plane)	0.733	(0.004)
$S(\angle CCC$ out-of-plane)	0.686	(0.006)
$S(\angle CCN$ out-of-plane)	0.791	(0.003)
S(off-diagonal in-plane)	0.833	(0.005)

[a] Values in parentheses are standard deviation of parameters.

TABLE V: Observed and Calculated Normal Mode Energies (cm⁻¹) Using an 8-Parameter Semiempirical Potential[a]

type D_{3h}	C_{2v}	obsd	calcd	obsd(C)	calcd(C)	obsd(N)	calcd(N)
a_1'	a_1	2224	2204	13	6	9	5
a_1'	a_1	658	650	3	3	4	5
e_a'	a_1	2173	2181	44	48	22	21
e_a'	a_1	1243	1242	5	1	3	6
e_a'	a_1	610	617	0	1	2	2
e_a'	a_1	159	141	3	0	2	0
a_2'	b_2	402	403	4	4	1	1
e_b'	b_2	2173	2181	2	0	2	0
e_b'	b_2	1243	1242	4	1	3	0
e_b'	b_2	610	617	10	12	2	1
e_b'	b_2	159	141	3	0	2	2
e_a''	a_2	484	483	4	0	1	0
a_2''	b_1	568	568	3	3	1	1
a_2''	b_1	176	176	0	1	0	1
e_b''	b_1	484	483	9	10	1	2

[a] Obsd(X) and calcd(X) values are the negatives of the observed and calculated isotopic shift due to substitution of a single noncentral atom X. Standard deviation = 7.9 cm⁻¹. Mean percentage error = 1.8%.

damentals for all three isotopomers. The observed and calculated frequencies in cm⁻¹ are given in Table III. The standard deviation of this fit is exceptionally good, 1.74 cm⁻¹. The force constants determined by this procedure are reported in the last column of Table II. The potential energy distribution is available as supplementary material.

Semiempirical Fit. Seven bond oriented scaling factors and the out-of-plane $\angle CCC$–$\angle CCN$ interaction term were used as fitting parameters. The scaling factors fell into one of three classes. We used two bond stretching, four angle bending, and one nondiagonal factor to scale the ab initio values of the force constants reported in the first column of Table II. These factors and their value as determined by fitting the observed vibrational spectrum are given in Table IV. Note that all the values are close to 0.8; that is, the 4-31G SCF values are about 25% too large to give a reasonable fit to the data. The best fit of this 8-parameter potential to the experimental data is shown in Table V. The resulting scaled force constants are reported in Table II. The potential energy distribution is available as supplementary material.

Considering that (a) the calculations were performed for the free ion and the data was obtained from condensed phases, (b) observed frequencies rather than harmonic frequencies were used, and (c) the data come from both solution and solid phases, the results of the semiempirical fitting procedure are quite good. The only really obvious flaw in the scaled SCF potential is that it underestimates the energy of the lowest e' mode, a CCN in-plane bending motion.

General. At this stage one has an excellent empirical fit to the data and a very good semiempirical fit. Unfortunately, the two potentials are not identical (see Table II). All of the K, H, and G terms are in reasonable agreement considering the very different methods by which they were obtained. The F terms, however, are very different. The 11-parameter empirical potential gives values that differ by at least a factor of 2, and in one case by sign, from the values obtained by the SCF scaling method. This is to be expected in the case of $F_{CC,CN}$ since the $F_{CN,CN}$ term is present in the semiempirical fit and not in the purely empirical one. The

large differences in $F_{CC,CC}$ and $F_{CC,CCC}$ are not so easily explained.

Our preferred explanation for the differences in results for the two fitting schemes is that in neither case did we use the full quadratic potential. Since the potential has been truncated to 11 or 12 terms, and the full potential requires 18, the least-squares refinement tends to weight the small interaction terms differently. the obvious solution is to increase the number of potential constants fit to the data, or, to calculate the remaining quadratic potential constants. We were unable to do either to our satisfaction. Increasing the number of parameters in the empirical fit led to slow and nonsingular convergence, thus indicating that insufficient independent data were available to justify more parameters. Calculations of a few of the "missing" quadratic terms yielded results smaller than our precision in calculating them, and were judged unreliable. The smallness of these terms does not make them insignificant, however, as is well demonstrated by the importance of the $G'_{CCC,CCN}$ term in defining the energies of the out-of-plane motions. In order to obtain the true quadratic potential for this ion, either more isotopic data or more accurate calculations are required.

The size of K_{CC} and K_{CN} are of interest in understanding the bonding in this ion. K_{CC} is about the same size here as it is in the prototypical resonance case, benzene.[35] Further, the CC bonds are much shorter than aliphatic CC bonds. These data clearly show that there is significant electronic delocalization over the ion and sizable resonance stabilization. The values of K_{CN} and r_{CN} are very similar to those of TCNE.[26] In this context, it is interesting to note that the SCF calculation indicates that the nitrogen atoms are all negatively charged, and that the central carbon is positively charged. The noncentral carbons are almost neutral.

Conclusion

Raman, IR, and tunneling spectroscopy have been used to directly measure all of the fundamentals of the TCM ion. Tunneling spectroscopy was especially useful for locating the IR and Raman silent a_2' mode. Frequency shifts with ^{13}C and ^{15}N substitution were given. Raman spectra of the manganese and cobalt complexes of TCM were also reported. These data were used to completely assign the vibrational spectrum of the non-radical cyanocarbanion, tricyanomethanide (TCM).

Ab initio SCF calculations at the 4-31G level were used to determine the geometry and several force constants of TCM. The calculated geometry agrees very well with experimental data, but the force constants are generally too large. Semiempirical and empirical quadratic potentials were fit to the experimental data to obtain force constants for the ion. While the diagonal terms resulting from these different fitting methods are similar, some of the off-diagonal terms are quite different. This is attributed to the use of incomplete potentials. Further improvement in the force field will require either more isotopomeric data or more accurate quantum mechanical calculations.

The structure of the ion and the force constants obtained indicate that there is significant resonance stabilization of the ion. The CC bonds are similar to those in benzene. The CN bond is quite similar to those found in tetracyanoethylene (TCNE). The ion is planar in solution with symmetry D_{3h}.

Registry No. $C(CN)_3^-$, 17997-24-9; $C(CN)_2(^{13}CN)^-$, 98800-28-3; $C(CN)_2(C^{15}N)^-$, 98800-29-4; $C(CN)_2(^{13}CN)^-$·potassium, 98800-32-9; $C(CN)_2(C^{15}N)^-$·potassium, 98800-33-0; $C(CN)_3^-\cdot^1/_2$cobalt, 98800-31-8; $C(CN)_3^-$·potassium, 34171-69-2; $C(CN)_3^-\cdot^1/_2$manganese, 98800-30-7.

Supplementary Material Available: Transformation to general quadratic potential constants and potential energy distributions (4 pages). Ordering information is given on any current masthead page.

(35) Califano, S.; Crawford, B. L. *Spectrochim. Acta* **1960**, *16*, 889. Steger, E.; Weber, K.; *Z. Phys. Chem.* **1983**, *264*, 37. Painter, P. C.; Koenig, J. L. *Spectrochim. Acta, Part A* **1977**, *33A*, 1019.

(36) Jones, L. H. "Inorganic Vibrational Spectroscopy"; Marcel Dekker: New York, 1971.