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INFRARED SPECTRA, VIBRATIONAL ASSIGNMENT, NORMAL COORDINATE ANALYSIS AND THERMODYNAMIC FUNCTIONS OF TETRACYANOMETHANE

D. J. GARDINER
Department of Chemistry, University of York, Heslington, York (England)

E. MAYER
Institut für Anorganische und Analytische Chemie, Universität Innsbruck, Innsbruck (Austria)
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ABSTRACT

The infrared spectrum of tetracyanomethane in acetonitrile solution has been recorded and the full set of fundamental frequencies assigned. A normal coordinate analysis has been carried out and the values of the calculated force constants are compared with those of related molecules. Some thermodynamic functions have also been computed.

INTRODUCTION

The preparation of tetracyanomethane was first reported[1] in 1969. Some vibrational spectroscopic studies were carried out and infrared frequencies of the solid and vapour and Raman frequencies of solid and solution have been reported[2]. The structural parameters for tetracyanomethane in the gas phase have recently been determined by electron diffraction measurements[3]. We have carried out normal coordinate calculations on tetracyanomethane and have determined a set of force constants. During these calculations the presence of two infrared active fundamentals was suggested in the region 400–600 cm^{-1} which had not previously been recognised. Spectra are presented here which confirm this suggestion.

EXPERIMENTAL

Tetracyanomethane was prepared by treating cyanogen chloride with silver tricyanomethanide [$ClCN + AgC(CN)_3 = C(CN)_4 + AgCl$] as reported earlier[1]. Acetonitrile (S.L.R.) was dried over a 4 Å molecular sieve before use as a solvent and a nitrogen filled glove bag was used for handling the solutions. $C(CN)_4$ is only sparingly soluble in CH_3CN necessitating the use of a 1 mm path length infrared cell which was compensated in the reference beam to obtain the spectrum. A conventional infrared liquid cell was assembled using AgCl plates which are not attacked by $C(CN)_4$. Infrared spectra were measured on a Perkin–Elmer 621 spectrophotometer which was calibrated with CO_2; band positions are reported accurate to ± 2 cm^{-1}.

RESULTS

The infrared spectrum of $C(CN)_4$ in CH_3CN solution was examined following indications from the normal coordinate analysis that two infrared active bands should appear in the 400–600 cm^{-1} region. As the CH_3CN spectrum is conveniently void of infrared bands in this region it proved to be a suitable solvent. The infrared spectrum is presented in Fig. 1. The fundamental frequencies are

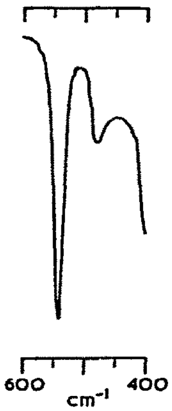

Fig. 1. Infrared spectrum of $C(CN)_4$ in CH_3CN solution in the region 600–400 cm^{-1}.

TABLE 1

OBSERVED INFRARED AND RAMAN FREQUENCIES FOR TETRACYANOMETHANE

Observed frequency[a] (*cm^{-1}*)	*Method*
2288	Raman, solution
560	Raman, solution
573	Raman, solid
115	Raman, solid
2273	Infrared, gas
1061	Infrared, gas
540 (this work)	Infrared, solution
478 (this work)	Infrared, solution

[a] Frequency data from ref. 2.

listed in Table 1 and include Raman frequencies of CH_3CN solutions and the solid, and infrared frequencies of the gas from an earlier work[2].

NORMAL COORDINATE ANALYSIS AND DISCUSSION

Tetracyanomethane is tetrahedral in the gas phase[3], and is depicted in Fig. 2. The structural parameters are: C–C bond length = 1.484 Å, C–N bond length = 1.161 Å. The molecule belongs to the point group T_d and gives rise to the following vibrational representation

$$\Gamma_{\text{vib}} = 2A_1(\text{R})+2E(\text{R})+F_1(\text{inactive})+4F_2(\text{IR, R})$$

where the infrared and Raman activities are shown in parentheses. Ideally gas phase frequencies would be used to calculate force constants; however, in this case these were not available for all the fundamentals. It has been shown[2] that there is close agreement between the observed gas phase frequencies and solution and solid state frequencies and therefore we feel justified in using the frequencies as listed in Table 1.

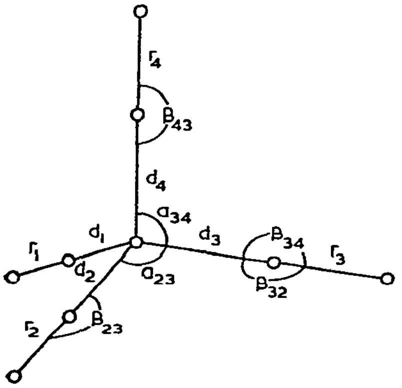

Fig. 2. Internal coordinates of $C(CN)_4$ (several have been omitted for the sake of clarity).

The normal coordinate calculations were carried out using a version of Schachtschneider's[4] computer programs. These refined a set of valence force constants to give a least squares fit to the observed frequencies using the Wilson *FG* method[5]. *G* matrices were computed by the Wilson *S* vector method[5]. The *UGU'* and *UFU'* transformations were performed by the computer to assist in solution of the secular equations. The *U* matrix given by Pistorius[6] for $Ni(CO)_4$ was used. There are 21 vibrational degrees of freedom for $C(CN)_4$ and by using the full symmetry of the molecule we define 26 internal coordinates, thus causing 5 redundancies. The internal coordinates, shown in Fig. 2 are: $4d_i$ the C–C bond stretch, $4r_i$ the C–N bond stretch, $6\alpha_{ij}$ the C–C–C angle deformation, and $12\beta_{ij}$, the C–C–N angle deformation. There are three β_{ij} coordinates associated with each C–C–N angle which define bending in each of the σ planes of the molecule. The redundancies are one of the α_{ij} and one β_{ij} from each of the 4 sets of β_{ij} associated with each C–C–N angle. It is possible to remove the redundancies in the β_{ij} as shown by Murata and Kawai[7]. This would remove the reported difficulty[8] in interpreting the meanings of force constants associated with the β_{ij}. We chose, however, to take advantage of the full symmetry and retain the redundancies which gave rise to zero frequencies in the calculation.

As we have no isotopic frequency data it was necessary to restrict the number of force constants entered into the iterative procedure. The following force constants were used in the analysis:

f_d	stretching of C–C
f_r	stretching of C–N
f_α	bending of C–C–C
f_β	bending of C–C–N
f_{dd}	interaction of C–C with C–C (d_i with d_j)
f_{rr}	interaction of C–N with C–N (r_i with r_j)
f_{dr}	interaction of C–C with C–N (d_i with r_i)
$f_{\alpha\alpha}$	interaction of C–C–C with C–C–C (α_{ij} with α_{kj})
$f_{\beta\beta}$	interaction of C–C–N with C–C–N (β_{ij} with β_{ik})
$f'_{\beta\beta}$	interaction of C–C–N with C–C–N (β_{ij} with β_{ji})

The remaining force constants required to define the full general valence force field have been listed by Pistorius[6] and were fixed at zero in our calculations. These interaction force constants are believed to be negligibly small. Similar approximations have been made in a detailed analysis[9] of $Ni(CO)_4$.

As an initial set of force constants we used the values listed by Herzberg[12] for the aliphatic nitriles. A simple diagonal force field could not be refined to give a satisfactory fit to the observed frequencies. By including f_{dd} and $f_{\beta\beta}$ in the calculation an acceptable solution was obtained. Further refinements of the force field by entering one at a time the remaining interaction force constants listed above did not improve the fit of observed to calculated frequencies. These constants therefore were assumed to be negligibly small and were accordingly fixed at zero. We also attempted to refine the set of force constants using different frequency assignments but only the assignment given here resulted in a viable solution.

Table 2 lists the values of the refined force constants and in Table 3 are listed the calculated frequencies and percentage potential energy distributions. These

TABLE 2

CALCULATED VALENCE FORCE CONSTANTS FOR TETRACYANOMETHANE

$f_d = 4.12 \pm 0.04$ m dyne Å^{-1}
$f_r = 18.31 \pm 0.04$ m dyne Å^{-1}
$f_\alpha = 0.38 \pm 0.02$ erg rad^{-2}
$f_\beta = 0.52 \pm 0.01$ erg rad^{-2}
$f_{dd} = 0.37 \pm 0.02$ m dyne Å^{-1}
$f_{\beta\beta} = 0.10 \pm 0.01$ erg rad^{-2}

TABLE 3

CALCULATED FREQUENCIES, SYMMETRY ASSIGNMENTS AND POTENTIAL ENERGY DISTRIBUTIONS FOR THE VIBRATIONAL MODES OF $C(CN)_4$

Frequency (cm^{-1})		*Symmetry*	*Percentage P.E.D.*						*Approx.*
Observed	*Calculated*		f_d	f_r	f_α	f_β	f_{dd}	$f_{\beta\beta}$	*normal mode*
2288	2288.4	$\nu_1(A_1)$	6.8	91.4	0.0	0.0	1.8	0.0	(C–N)ν
560	559.9	$\nu_2(A_1)$	72.1	8.6	0.0	0.0	19.3	0.0	(C–C)ν
573	575.3	$\nu_3(E)$	0.0	0.0	19.0	100.0	0.0	−19.0	(C–C–N)δ
115	112.7	$\nu_4(E)$	0.0	0.0	81.0	23.5	0.0	−4.5	(C–C–C)δ
inactive	136.2	$\nu_5(F_1)$	2.9	0.2	78.7	21.5	−0.3	−3.0	(C–C–C)δ
2273	2272.6	$\nu_6(F_2)$	9.2	91.6	0.0	0.0	−0.8	0.0	(C–N)ν
1061	1061.6	$\nu_7(F_2)$	72.4	6.7	12.2	18.0	−6.5	−2.8	(C–C)ν
540	537.0	$\nu_8(F_2)$	23.3	1.4	7.7	85.7	−2.1	−16.0	(C–C–N)δ
478	478.0	$\nu_9(F_2)$	2.0	0.1	1.4	98.2	−0.2	−1.5	(C–C–N)δ

potential energy distributions reveal that there is no extensive normal mode mixing in $C(CN)_4$ and allow the approximate descriptions of the normal modes, included in Table 3, to be made. In Table 4 are listed the diagonal force constants of $C(CN)_4$ and some related molecules. In $C(CN)_4$ the C–N force constant is seen to be slightly larger and the C–C force constant slightly smaller than in CH_3CN and $CH_2(CN)_2$. The opposite is found for these force constants in $CF_2(CN)_2$. The C–C force constant for $C(CN)_4$ is very close to that of C–Cl in CCl_4 and it has earlier been suggested[2] that $C(CN)_4$ may be considered as a pseudo carbon tetrahalide. The more noticeable difference in the force constants of Table 4 is that of f_α, the C–C–C bending force constant, which appears to be markedly lower in $C(CN)_4$ than in $CH_2(CN)_2$ suggesting that the C–C–C tetrahedral angle in $C(CN)_4$ may be more

TABLE 4

COMPARISON OF $C(CN)_4$ DIAGONAL FORCE CONSTANTS WITH THOSE OF RELATED MOLECULES

Molecule	f_d	f_r	f_α	f_β
$C(CN)_4$	4.12	18.31	0.38	0.52
CH_3CN (ref. 13)	5.26	17.73	—	0.30
$CH_2(CN)_2$ (ref. 13)	5.20	17.85	1.13	0.32
$CF_2(CN)_2$ (ref. 10)	3.79	19.18	—	0.54
CCl_4 (ref. 12)	4.38	—	1.04	—

easily distorted. This is in keeping with the suggestion made by Hoffmann[11] that for $C(CN)_4$ a low lying electronic state with planar geometry exists.

THERMODYNAMIC FUNCTIONS

Our normal coordinate calculations allowed us to determine the frequency of the inactive F_1 mode of $C(CN)_4$, and thus we have been able to use the full set of fundamental frequencies to calculate thermodynamic functions using the harmonic oscillator–rigid rotator, approximation[12]. The functions which were calculated over a range of temperatures from 273 K to 500 K are presented in Table 5.

TABLE 5

CALCULATED THERMODYNAMIC FUNCTIONS (J mol^{-1} K^{-1}) FOR $C(CN)_4$

Temperature (K)	$-(G^0-H_0^0)/T$	$(H^0-H_0^0)/T$	$(H^0-H_0^0)$	S^0	C_p^0
273.15	266.93	76.77	20.97	343.70	116.98
298.15	273.81	80.37	23.96	354.18	122.23
300.00	274.31	80.63	24.19	354.93	122.60
350.00	287.24	87.28	30.55	374.53	131.53
400.00	299.30	93.29	37.31	392.58	138.88
450.00	310.60	98.71	44.42	409.31	145.06
500.00	321.26	103.61	51.81	424.87	150.38

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REFERENCES

1 E. Mayer, *Monatsh.*, 100 (1969) 462.
2 R. E. Hester, K. M. Lee and E. Mayer, *J. Phys. Chem.*, 74 (1970) 3373.
3 H. Oberhammer, *Z. Naturforsch.*, 26A (1971) 2043.
4 J. H. Schachtschneider, Shell Development Company, Technical Reports No. 231-64 and 57-65 (1964).
5 E. B. Wilson Jr, J. C. Decius and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1955.
6 C. W. F. T. Pistorius, *Spectrochim. Acta*, 9 (1959) 717.
7 H. Murata and K. Kawai, *J. Chem. Phys.*, 26 (1957) 1355.
8 L. H. Jones, *J. Mol. Spectrosc.*, 5 (1960) 133.
9 L. H. Jones, R. S. McDowell and M. Goldblatt, *J. Chem. Phys.*, 48 (1968) 2663.
10 H. O. Desseyn, B. J. van der Veken, L. van Haverbeke and M. A. Herman, *J. Mol. Structure*, 13 (1972) 227.
11 R. Hoffmann, R. W. Alder and C. F. Wilcox Jr, *J. Amer. Chem. Soc.*, 92 (1970) 4992.
12 G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, Princeton, N.J., 1945.
13 R. Yamadera and S. Krimm, *Spectrochim. Acta*, 24A (1968) 1677.