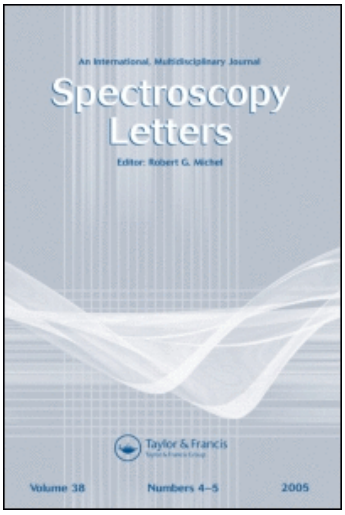

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MOLECULAR VIBRATION ANALYSIS OF TETRACYANOMETHANE

Keywords: Molecular vibrations, Mean amplitudes, Shrinkage effects, Tetracyanomethane

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ABSTRACT

The experimental vibrational frequencies for $C(CN)_4$ from literature were re-assigned with the aid of approximate force field calculations. Refined force fields were deduced on the basis of (I) the original experimental assignment and (II) the present re-assignment. Calculated mean amplitudes of vibration and Bastiansen-Morino shrinkage effects strongly support the re-assignment (II) when comparing with gas electron diffraction results.

INTRODUCTION

The tetrahedral model of $C(CN)_4$ is especially well suited for combined vibrational spectroscopic and electron diffraction studies. The symmetric structure of normal modes of vibration is

$$2A_1 + 2E + F_1 + 4F_2$$

Here the totally symmetric species (A_1) contains only the stretching modes and no bendings. Hence the Bastiansen-Morino shrinkage effects,[1] in addition to the mean amplitudes,[1] may readily be computed from a harmonic vibration analysis. In the present work these quantities have been calculated from different harmonic force fields for the molecule. It was found necessary to change the experimental assignment of vibrational frequencies from literature in order to obtain results compatible with the available electron diffraction measurements.

SYMMETRY COORDINATES

The symmetry coordinates were constructed as the appropriate linear combinations of: (Species A_1) C≡N and C-C stretchings, (E) CCC and CCN bendings, (F_1) CCN bendings, and (F_2) C≡N and C-C stretchings, CCC and CCN bendings. CCN are linear bendings. The bending coordinates (both linear and nonlinear) were scaled with factors of the dimension of length in the usual way.

APPROXIMATE FORCE FIELD

In the initial calculations the force constant f(C≡N) was taken as 18.12 mdyne/Å, which is supposed to be a reliable estimate guided by previous analyses of CH_3CN.[2,3] For the C_4 framework the following force constants were applied in the appropriate part of the F matrix; all values in mdyne/Å:

(A_1)	5.5	(E)	0.490	(F_2)	5.0
					0.214 0.459

The bending and interaction force constants were transferred from CH_4 calculations.[4] Apart from this interaction force constant all the others were neglected. Finally the value of 0.336 mdyne/Å was adopted for CCN linear bendings in all species (E, F_1 and F_2). The calculated frequencies with this approximate force field are found in Table 1.

TABLE 1

Calculated Vibrational Frequencies (cm^{-1}) and Potential Energy Distribution

	Approximate	Refinements (I)[b]	Refinements (II)[c]	PED[a] (II)[c]
A_1	2282	2288	2288	$90S_1$
	572	562	562	$91S_2$
E	739	190	573	$91S_1 + 56S_2$
	172	115	190	$56S_2 + 21S_1$
F_1	606	(271.6)[d]	(413.6)[d]	$100S$
F_2	2292	2270	2270	$87S_1$
	1227	1061	1061	$81S_2 + 35S_3$
	664	178	550	$45S_3 + 32S_4$
	207	156	178	$62S_4 + 28S_3$

[a] $100 \cdot F_{ii}L_{ik}^2/\lambda_k$; terms below 15 are omitted. The sequence of symmetry coordinates is consistent with the description in text.

[b] Assignment from Hester et al.[5]

[c] Present re-assignment.

[d] Unobserved frequencies in parentheses.

REFINED FORCE FIELDS

The following refinements were made starting from the initial approximate force field. (I) The symmetry force constants were adjusted to fit accurately the experimental assignment of Hester et al.[5] (II) The same type of calculation using a re-assignment of the experimental frequencies[5] produced with the aid of the initially calculated frequencies. In both cases the force constant of the F_1 species, for which the frequency is unobserved, was taken as the average value of $F_{22}(E)$ and $F_{44}(F_2)$. The vibrational frequencies from both refinements (I) and (II) are given in Table 1. Table 2 shows the symmetry force field corresponding to refinement (II), which is considered here as the final result.

TABLE 2

Symmetry Force Constants (mdyne/Å) Corresponding to Refinement (II) of Table 1

(A_1)	18.14			(E)	0.720			
	-0.12	5.32			0.121	0.187		
(F_1)	0.156	(F_2)	17.61					
			-0.19	4.71				
			0.12	0.40	0.531			
			0.01	0.02	-0.026	0.126		

The terms of potential energy distribution from this final force field are included in Table 1.

MEAN AMPLITUDES AND SHRINKAGE EFFECTS

Table 3 shows the calculated mean amplitudes and shrinkage effects at 398 K, which is the reported nozzle temperature of the gas electron diffraction experiment due to Oberhammer.[6] On comparing the calculated results corresponding to the assignments (I) and (II) (cf. Table 1) with the observed values many interesting details are found. As to the mean amplitudes (u values in Table 3) the value for the nonbonded CC distance (C···C) from (II) shows clearly better agreement with the electron diffraction value than (I). Most of the other calculated mean amplitudes from (I) and (II) tend to fall on each side of the observed values, but still so that the agreement is best for (II) in most of the cases (N···N is an exception). For the shrinkage effects the situation is more dramatic. The calculated values from (I) are seen to deviate substantially from the observed values, while those from (II) display a remarkably good agreement. In conclusion is believed that the electron diffraction results in this case really are an efficient tool to distinguish between the two trends in the assignment of vibrational frequencies.

TABLE 3

Mean Amplitudes of Vibration (u, Å) and Bastiansen-Morino Shrinkage Effects (δ, Å) at the Absolute Temperature 398 K

	Distance	Calculated (I)	Calculated (II)	Observed[6]
u	C≡N	0.035	0.034	0.039(1)
u	C-C	0.059	0.049	0.054(2)
u	C•••C	0.156	0.071	0.069(3)
u	C•••N(linear)	0.066	0.053	0.058(3)
u	C•••N(non-lin.)	0.158	0.095	0.120(3)
u	N•••N	0.189	0.143	0.179(12)
δ	C•••C	0.010	0.003	0.003
δ	C•••N(linear)	0.038	0.011	0.015
δ	C•••N(non-lin.)	0.044	0.015	0.013
δ	N•••N	0.074	0.027	0.028

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REFERENCES

1 S.J. Cyvin, Molecular Vibrations and Mean Square Amplitudes, Universitetsforlaget, Oslo / Elsevier, Amsterdam 1968.

2 J.L. Duncan, Spectrochim. Acta 20, 1197 (1964).

3 S.J. Cyvin and V. Devarajan, J. Mol. Struct. 10, 393 (1971).

4 S.J. Cyvin, J. Brunvoll, B.N. Cyvin, L.A. Kristiansen and E. Meisingseth, J. Chem. Phys. 40, 96 (1964).

5 R.E. Hester, K.M.Lee and E.Mayer, J.Phys. Chem. 74, 3373 (1970).

6 H. Oberhammer, Z. Naturforsch. 26a, 2043 (1971).

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