*Asian Journal of Chemistry* Vol. 7, No. 3 (1995), 604–607

# Molecular Constants of Tricyanomethanide Ion

V. KAMARAJ
*Department of Physics*
*Anna University, Madras-600 025, India*

Coriolis coupling coefficients, centrifugal distortion constants and thermodynamic functions of tricyanomethanide ion $C(CN)_3^-$ have been calculated using the force constants evaluated on the basis of General Valence Force Field.

## INTRODUCTION

The tricyanomethanide ion $C(CN)_3^-$ has been studied in detail by spectroscopic investigations[1-4] and was recognised to have a planar structure of the type $X(YZ)_3$ of symmetry $D_{3h}$, XYZ being linear. The fundamental frequencies of this ion are distributed among five species as $2A_1' + A_2' + 2A_2'' + 4E' + E''$ where the E′ and E″ species are doubly degenerate. Recently, Alix *et al.*[5] have performed the normal coordinate analysis for this ion and evaluated the force constants and the mean amplitudes of vibration. In the present investigation, the other important molecular constants, namely, the Coriolis coupling coefficients, centrifugal distortion constants and thermodynamic functions have been evaluated and presented. The results have been discussed.

The Coriolis forces lead to the coupling between rotation and vibration, when a molecule rotates and vibrates simultaneously. Coriolis coupling constants will be very useful in the normal coordinate treatments. The method suggested by Meal and Polo[6] has been used to calculate the Coriolis coupling coefficients of the ion.

Since the bonds in a molecule are not rigid, the interatomic distances will vary with the speed of rotation giving rise to centrifugal distortion. The theory proposed by Kivelson and Wilson[7] and later modified by Cyvin *et at.*[8] has been made use of to calculate the centrifugal distortion constants. These constants will be very useful in the microwave investigations of the ion. The thermodynamic functions of the ion have been estimated by following reported methods[9,10].

## RSULTS AND DISCUSSION

The molecular parameters and the force constants have been taken from reference 5. The Coriolis coupling coefficients are given in Table-1. According to Jahn's rule[11], the couplings allowed are: $A_1' \times A_2'$, $A_1' \times E''$, $A_1' \times E''$, and

$A_2'' \times E'$. With regard to the values of the coefficients calculated, it is observed that the following square sum rules are satisfied:

TABLE-1
CORIOLIS COUPLING COEFFICIENTS OF $C(CN)_3^-$ ION

| Coupling | $\zeta$ Elements | Values |
|---|---|---|
| $A_1' \times A_2'$ | $\zeta^Z_{1,3}$ | 0.9786 |
| | $\zeta^Z_{2,3}$ | 0.2117 |
| $A_1' \times E''$ | $\zeta^Y_{1,10a} = -\zeta^X_{1,10b}$ | 0.4105 |
| | $\zeta^Y_{2,10a} = -\zeta^X_{2,10b}$ | 0.9063 |
| $A_2' \times E''$ | $\zeta^X_{3,10a}$ | 0.7979 |
| | $\zeta^Y_{3,10b}$ | 0.1960 |
| $A_2'' \times E'$ | $\zeta^X_{4,6a} = -\zeta^Y_{4,6a}$ | 0.0760 |
| | $\zeta^X_{4,7a} = -\zeta^Y_{4,7a}$ | 0 |
| | $\zeta^X_{4,8a} = -\zeta^Y_{4,8a}$ | 0.4409 |
| | $\zeta^X_{4,9a} = -\zeta^Y_{4,9a}$ | 0.9204 |
| | $\zeta^X_{4,6a} = -\zeta^Y_{5,6a}$ | 0.1162 |
| | $\zeta^X_{5,7a} = -\zeta^Y_{5,7a}$ | 0 |
| | $\zeta^X_{5,8a} = -\zeta^Y_{5,8a}$ | 0.8268 |
| | $\zeta^X_{5,9a} = -\zeta^Y_{5,9a}$ | 0.5602 |

$$(\zeta^Z_{1,3})^2 + (\zeta^Z_{2,3})^2 = 1$$

$$(\zeta^Y_{1,10a})^2 + (\zeta^Y_{2,10a})^2 = 1$$

$$(\zeta^X_{1,10b})^2 + (\zeta^X_{2,10b})^2 = 1$$

$$(\zeta^X_{4,6a})^2 + (\zeta^X_{4,8a})^2 + (\zeta^X_{4,9a})^2 = 1$$

$$(\zeta^X_{5,6a})^2 + (\zeta^X_{5,8a})^2 + (\zeta^X_{5,9a})^2 = 1$$

It is observed that the out-of-plane vibrations $\nu_4$ and $\nu_5$ do not have the coupling with the asymmetric degenerate vibration $\nu_7$.

Table-2 contains the centrifugal distortion constants. Since the molecule is an asymmetric rotor all the six coefficients, $D_J$, $D_K$, $D_{JK}$, $R_5$, $R_6$ and $\delta_J$ exist. But the values are rather small excepting those of $D_K$ and $D_{JK}$. This may be mainly attributed to the fact that each of the three stretchings (C—C≡N) of the planar

$C(CN)_3^-$ ion has one single bond C—C of force constant 6.025 md/Å and one triple bond (C≡N) of force constant[5] 17.486 md/Å and that as the triple bond does not contribute much for the centrifugal effect, the resultant centrifugal stretching is mainly due to the elongation of the single bond between the carbon atoms.

TABLE-2
CENTRIFUGAL DISTROTION CONSTANTS OF $C(CN)_3^-$

| Coefficients | Vaue |
|---|---|
| $D_J$ | 4.28 |
| $D_K$ | –54.20 |
| $D_{JK}$ | 49.93 |
| $R_5$ | –3.26 |
| $R_6$ | 2.14 |
| $\delta_J$ | 0.0012 |

The thermodynamic function have been evaluated for the gaseous state of the ion assuming a rigid rotor model and harmonic oscillator approximation under one atmospheric pressure. These values are given in Table-3.

TABLE-3
THERMODYNAMIC FUNCTIONS (cal $deg^{-1}$ $mole^{-1}$) OF $C(CN)_3^-$ ION

| Temp K | Specific heat Capacity | Heat Content | Free Energy | Entropy |
|---|---|---|---|---|
| 100 | 11.062 | 9.041 | 47.437 | 56.478 |
| 200 | 16.534 | 11.375 | 54.381 | 65.756 |
| 273.2 | 20.197 | 13.309 | 58.251 | 71.560 |
| 300 | 21.230 | 13.944 | 59.593 | 73.537 |
| 400 | 24.366 | 16.161 | 63.802 | 79.963 |
| 500 | 26.609 | 18.039 | 67.626 | 85.665 |
| 600 | 28.441 | 19.732 | 71.136 | 90.868 |
| 700 | 29.853 | 20.980 | 74.135 | 95.115 |
| 800 | 31.043 | 22.188 | 77.077 | 99.265 |
| 900 | 31.992 | 23.203 | 79.672 | 102.875 |
| 1000 | 32.887 | 24.144 | 82.256 | 106.400 |

## REFERENCES

1. D.A. Long, R.A.G. Carrington and R.B. Gravenor, *Nature*, **196,** 371 (1962).
2. F.A. Miller and W.K. Baer, *Spectrochim. Acta*, **19A,** 73 (1963).
3. J. Kenneri and D. Britton, *Inorg. Chem.*, **5,** 1193 (1966).
4. A. Kolbe and H. Kochler, *Z. Anorg. Allg. Chem.*, **428,** 113 (1977).
5. A.J.P. Alix, C. Kappenstein, B.N. Cyvin and S.J. Cyvin, *Spectr. Letters*, **12,** 387 (1979).
6. J.H. Meal and S.R. Polo, *J. Chem. Phys.*, **24,** 119, 1126 (1956).
7. D. Kivelson and E.B. Wilson (Jr.), *J. Chem. Phys.*, **20,** 1575 (1952); **21**, 1229 (1953).
8. S.J. Cyvin, B.N. Cyvin and G. Hagen., *Z. Naturforsch.*, **23(a),** 1649 (1968).
9. H.J. Taylor and S. Glasstone, A Treatise on Physical Chemistry, D. Van Nostrand Co., New York (1942).
10. K.S. Pitzer, Quantum Chemistry, Prentice-Hall Inc. (1954).
11. H.A. Jahn, *Phys. Rev.*, **56,** 680 (1939).

(*Received*: 15 September 1994; *Accepted*: 9 January 1995) AJC-918