Title	Cartesian Displacements of Normal Vibrations of 1, 2, 4, 5-Tetracyanobenzene and 1, 2, 4, 5-Tetracyanobenzene-d $_2$ Molecules
Author(s)	Umemura, Junzo; Takenaka, Tohru
Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1973), 51(4): 206-219
Issue Date	1973-11-26
URL	http://hdl.handle.net/2433/76496
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 51, No. 4

Cartesian Displacements of Normal Vibrations of 1, 2, 4, 5-Tetracyanobenzene and 1, 2, 4, 5-Tetracyanobenzene-d_2 Molecules

Junzo UMEMURA and Tohru TAKENAKA*

Received August 1, 1973

Displacements of the intramolecular normal vibrations of the TCNB and TCNB-d_2 molecules were calculated in terms of the Cartesian coordinates, and graphically represented in a diagram. The results were compared with the numerical representation of the normal vibrations by means of the potential energy distribution.

INTRODUCTION

It is well known that fully conjugated cyano-compounds such as tetracyanoethylene (TCNE), 7, 7, 8, 8-tetracyanoquinodimethane (TCNQ), and 1, 2, 4, 5-tetracyanobenzene (TCNB) are strong electron acceptors in charge-transfer complexes. In a series of studies on molecular vibrations of these compounds, we have recently carried out the normal coordinate analysis of the TCNB and TCNB-d_2 molecules, using a modified Urey-Bradley force field for the in-plane vibrations and a valence force field for the out-of-plane vibrations.1) In that study, the assignments of the fundamental vibrations have been made on the basis of the potential energy distribution among the internal symmetry coordinates. It was found, however, that descriptions of the precise vibrational modes of some fundamentals were very difficult because of the wide distribution of their potential energies among many internal symmetry coordinates. The same difficulties have also been found for the fundamental vibrations of planar ring molecules, such as benzene2) and halogenated benzenes.3)

In the present paper, the atomic displacements of the fundamental vibrations of the TCNB and TCNB-d_2 molecules were calculated in terms of the Cartesian displacement coordinates and the precise vibrational modes were schematically drawn in diagrams. The representation of the fundamental vibrations by this method was of satisfactory for the purpose of visualization of the precise vibrational modes.

PROCEDURE OF CALCULATION

In the normal coordinate analysis by Wilson's ***GF*** matrix method,4) it is possible to obtain useful informations about the fundamental vibrational modes from the ***L*** matrix whose columns are the characteristic vectors of the ***GF*** matrix. The ***L***

---

* 梅村純三, 竹中 亨 : Laboratory of Surface and Colloid Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

matrix is given by the internal symmetry coordinate matrix $\boldsymbol{R}$ and the normal coordinate matrix $\boldsymbol{Q}$ as

$$\boldsymbol{R} = \boldsymbol{LQ} \tag{1}$$

However, the potential energy distribution P_{ij} defined by

$$P_{ij} = L_{ji}^2 \, F_{jj}/\lambda_i \tag{2}$$

is usually utilized for the quantitative evaluation of the potential energy distribution of the i-th fundamental vibration into the j-th internal symmetry coordinate R_j. Here λ_i is the frequency parameter of the i-th fundamental vibration, *i.e.* the i-th characteristic value of the $\boldsymbol{GF}$ matrix, L_{ji} is the j-th element of the i-th characteristic vector, and F_{jj} the j-th diagonal element of the potential energy matrix $\boldsymbol{F}$. Among all the terms of P_{ij}'s with a fixed value of i, usually only one or two terms become so large that the fundamental vibration can easily be assigned to the corresponding internal symmetry coordinates. When, however, many terms of P_{ij}'s have fairly large values, in other words, when the potential energy is widely distributed among many internal symmetry coordinates, the assignment is difficult in terms of the internal symmetry coordinate. In this case, the calculation of the $\boldsymbol{L_X}$ matrix defined by

$$\boldsymbol{X}=\boldsymbol{L_X Q} \tag{3}$$

is useful, because the $\boldsymbol{L_X}$ matrix permits us a graphical representation of the normal vibrations. Here, $\boldsymbol{X}$ is the column matrix whose elements are the Cartesian coordinates in unit of Å. Equation (3) means that the $\boldsymbol{L_X}$ matrix represents the atomic displacements in terms of the Cartesian coordinate when the normal coordinate makes a unit change. The $\boldsymbol{L_X}$ matrix is also given by[5,6]

$$\boldsymbol{L_X} = \boldsymbol{M}^{-1} \tilde{\boldsymbol{B}} \boldsymbol{G}^{-1} \boldsymbol{L}, \tag{4}$$

where $\boldsymbol{M}^{-1}$ is the diagonal matrix whose elements are the inverses of the atomic masses, $\tilde{\boldsymbol{B}}$ the transpose matrix of the $\boldsymbol{B}$ matrix which is defined by $\boldsymbol{R}=\boldsymbol{BX}$, and $\boldsymbol{G}^{-1}$ the inverse matrix of the kinetic energy matrix $\boldsymbol{G}$ presented in terms of the internal symmetry coordinate. Equation (4) can be modified to[7]

$$\boldsymbol{L_X} = \boldsymbol{M}^{-1} \tilde{\boldsymbol{B}} \boldsymbol{L_G}^{\circ} \boldsymbol{\Lambda_G}^{-1} \boldsymbol{L_c} \tag{5}$$

which is the useful form for calculation of the $\boldsymbol{L_X}$ matrix. Here, $\boldsymbol{\Lambda_G}^{-1}$ is the inverse matrix of the $\boldsymbol{\Lambda_G}$ matrix whose elements are characteristic values of the $\boldsymbol{G}$ matrix, $\boldsymbol{L_G}^{\circ}$ the product of $\boldsymbol{\Lambda_G}^{1/2}$ and the $\boldsymbol{L_G}$ matrix whose columns are characteristic vectors of the $\boldsymbol{G}$ matrix, and $\boldsymbol{L_c}$ the matrix whose columns are characteristic vectors of $\tilde{\boldsymbol{L}}_{\boldsymbol{G}}{}^{\circ}\boldsymbol{F}\boldsymbol{L_G}^{\circ}$.

In the present study, the $\boldsymbol{L_X}$ matrix was calculated by the use of Eq. (5) with the aid of the previous results of the normal coordinate analysis of the TCNB and TCNB-d_2 molecules.[1] All computations were carried out with a Facom 230–60 computer at Data Processing Center, Kyoto University, and the displacements obtained were directly drawn in a diagram by a Calcomp model 770/763 off-line XY plotter. The molecular-fixed axes of TCNB were chosen as shown in Fig. 1.

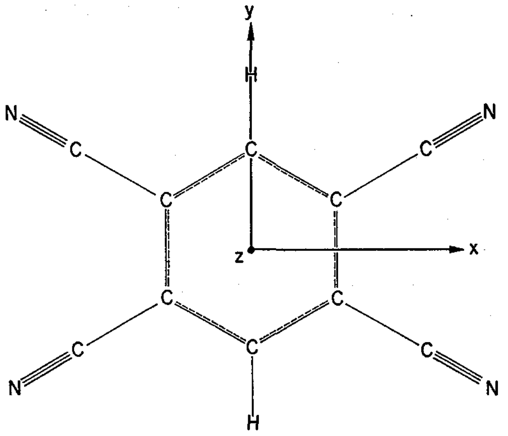


Fig. 1. Molecular-fixed axes of TCNB.

RESULTS AND DISCUSSIONS

The Cartesian displacements of the twenty-nine in-plane normal vibrations of the TCNB molecule (the point group is $D_{2h} \equiv V_h$), eight of which belong to the A_g species, seven to the B_{1g} species, seven to the B_{2u} species, and seven to the B_{3u} species, are shown by arrows in Fig. 2A, together with their calculated frequencies$^{1)}$ in cm^{-1}. The displacements of the thirteen out-of-plane normal vibrations of the TCNB molecule, two of which belong to the B_{2g} species, four to the B_{3g} species, three to the A_u species, and four to the B_{1u} species, are also shown in Fig. 2B, where the positive displacements with respect to the molecular-fixed z-axis are given by upward arrows and the negative ones by downward arrows. The arrows were drawn with a magnification of 3.5 times as compared with the molecular scale.

It is apparent from Fig. 2 that the graphical representation of the normal vibrations has some advantages over the numerical representation by the potential energy distribution, especially when the potential energy are widely distributed among many internal symmetry coordinates. The previous paper$^{1)}$ has reported that the potential energy of the ν_5 vibration (730 cm^{-1}) belonging to the A_g species is distributed among the internal symmetry coordinates S_3 (the C-CN stretching) by 12%, S_4 (the CCN-CCN ring stretching) by 30%, S_5 (the CCN-CH ring stretching) by 7%, S_6 (the C-CH-C ring bending) by 36%, and S_7 (the C-C-CH ring bending) by 12%. Furthermore, it has been reported$^{1)}$ that the potential energy of the ν_7 vibration (406 cm^{-1}) belonging to the A_g species is distributed among S_3 by 29%, S_5 by 20%, S_6 by 34%, and S_7 by 11%. In these cases, the precise descriptions of these vibrations are very difficult as far as only the results of the potential energy distribution are used. But the Cartesian displacements of these vibrations apparently show that the ν_5 and ν_7 vibrations are the elongation modes of the benzene ring along the y- and x-axes, respectively.

From Fig. 2A, the ν_4 vibration (1261 cm^{-1}) of the A_g species is easily found to have a character of the so-called "breathing" mode which generally gives a large intensity in Raman spectra. In fact, the Raman spectrum of this molecule gives the strong peak at 1262 cm^{-1}.$^{1)}$

The results of the normal coordinate analysis[1)] that the Kekulé interaction force constant contributes mainly to the ν_{25} vibration (1276 cm^{-1}) of the B_{3u} species is well understood by a glance at the displacement of this vibration drawn in Fig. 2A, because this is a pure "Kekulé deformation" mode of the benzene ring.

It has been indicated by the normal coordinate analysis that the C—C≡N bending mode and the C-C-CN bending mode are often coupled with each other.[1)] This is clearly seen in the Cartesian displacements of many vibrations such as the ν_6 vibration (557 cm^{-1}) of the A_g species, the ν_{13} vibration (701 cm^{-1}) of the B_{1g} species, the ν_{21} vibration (466 cm^{-1}) of the B_{2u} species, and the ν_{28} vibration (499 cm^{-1}) of the B_{3u} species. The similar coupling between the C≡N and C-C stretching modes are found in the ν_2 vibration (2251 cm^{-1}) of the A_g species, the ν_9 vibration (2249 cm^{-1}) of the B_{1g} species, the ν_{17} vibration (2249 cm^{-1}) of the B_{2u} species, and the ν_{23} vibration (2250 cm^{-1}) of the B_{3u} species.

It is also apparent from Fig. 2 that the displacements of the hydrogen atoms are very large as compared with those of the carbon and nitrogen atoms, especially in the C-H stretching vibrations (the ν_1 vibration of the A_g species and the ν_{16} vibration of the B_{2u} species). This fact suggests that the anharmonisity must be taken into account in the theoretical analysis of such vibrations.

In the case of the out-of-plane skeletal deformation vibrations, the advantages of the graphical representation of the normal vibrations over the description by the potential energy distribution are much more remarkable, because of the difficulty of a visual grasp of the atomic movements represented by the tortional symmetry coordinates and of the wide distribution of the potential energies among many internal symmetry coordinates. Figure 2B apparently shows that the ν_{40} vibration (522 cm^{-1}) of the B_{1u} species and the ν_{32} vibration (888 cm^{-1}) of the B_{3g} species, have the characters of the so-called "butterfly" and "chair form deformation" modes, respectively, with respect to the benzene ring, although they can not be imagined from the numerical representation by the potential energy distribution.

The Cartesian displacements of the normal vibrations of the TCNB-d$_2$ molecule are almost the same as those of the corresponding vibrations of the TCNB molecule, except for six in-plane vibrations as well as six out-of-plane vibrations which are given in Figs. 3A and 3B, respectively. In these vibrations, the amplitudes of the displacements of the deuterium atoms in the TCNB-d$_2$ molecule are much smaller than those of the hydrogen atoms in the TCNB molecule, as is expected from the difference of their atomic masses.

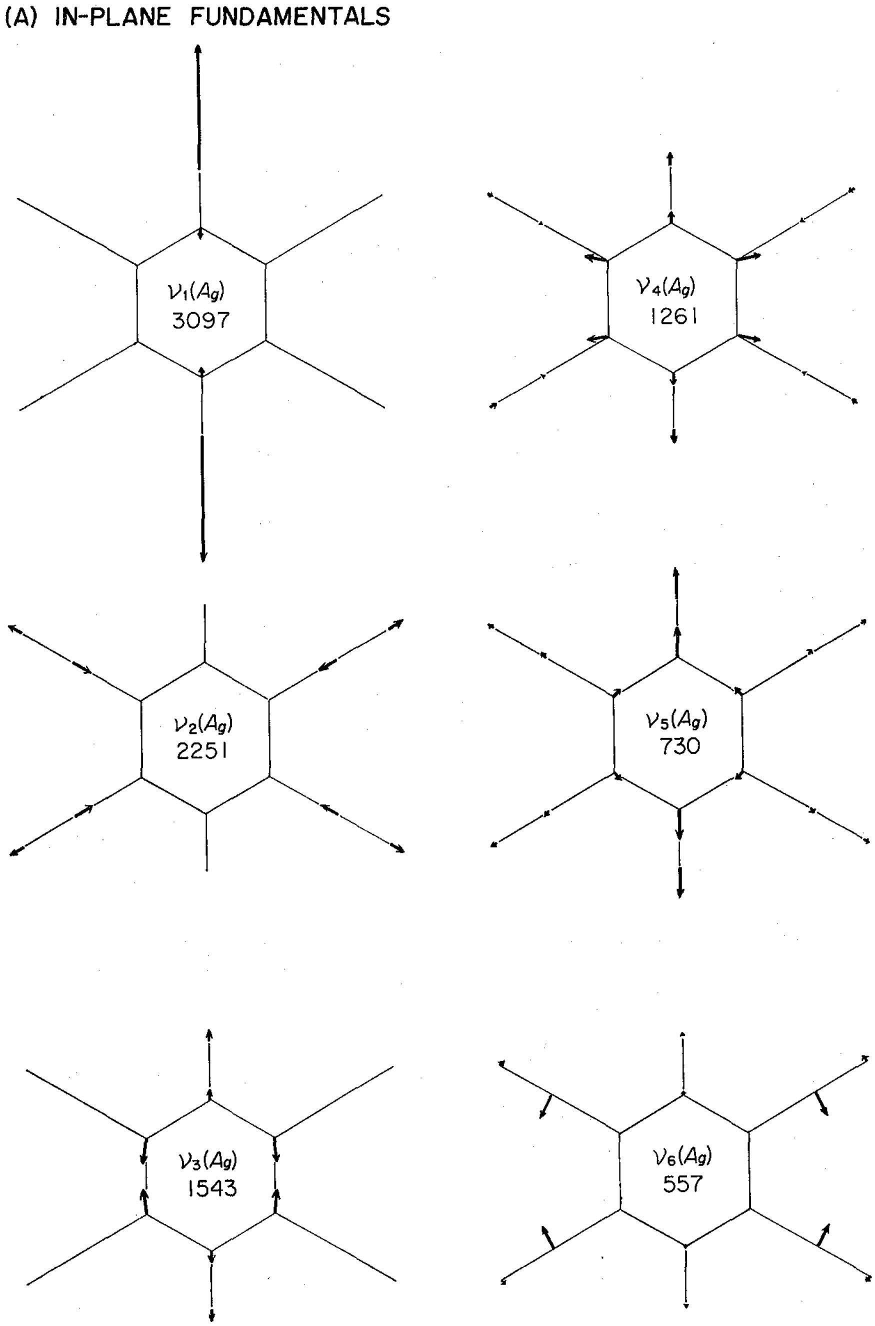


Fig. 2. Cartesian displacements of the normal vibrations of TCNB.
The displacements are magnified by 3.5 times as compared with the molecular size.

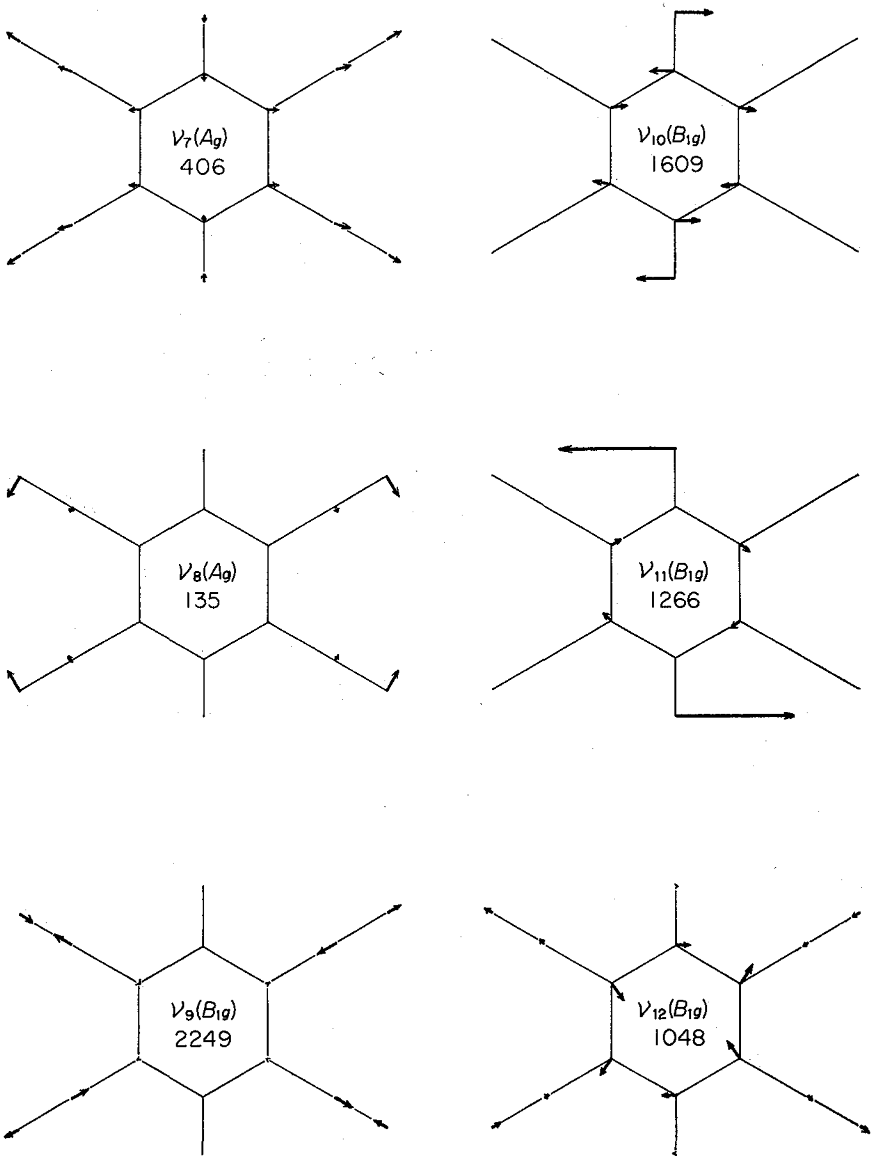


Fig. 2. Continued.

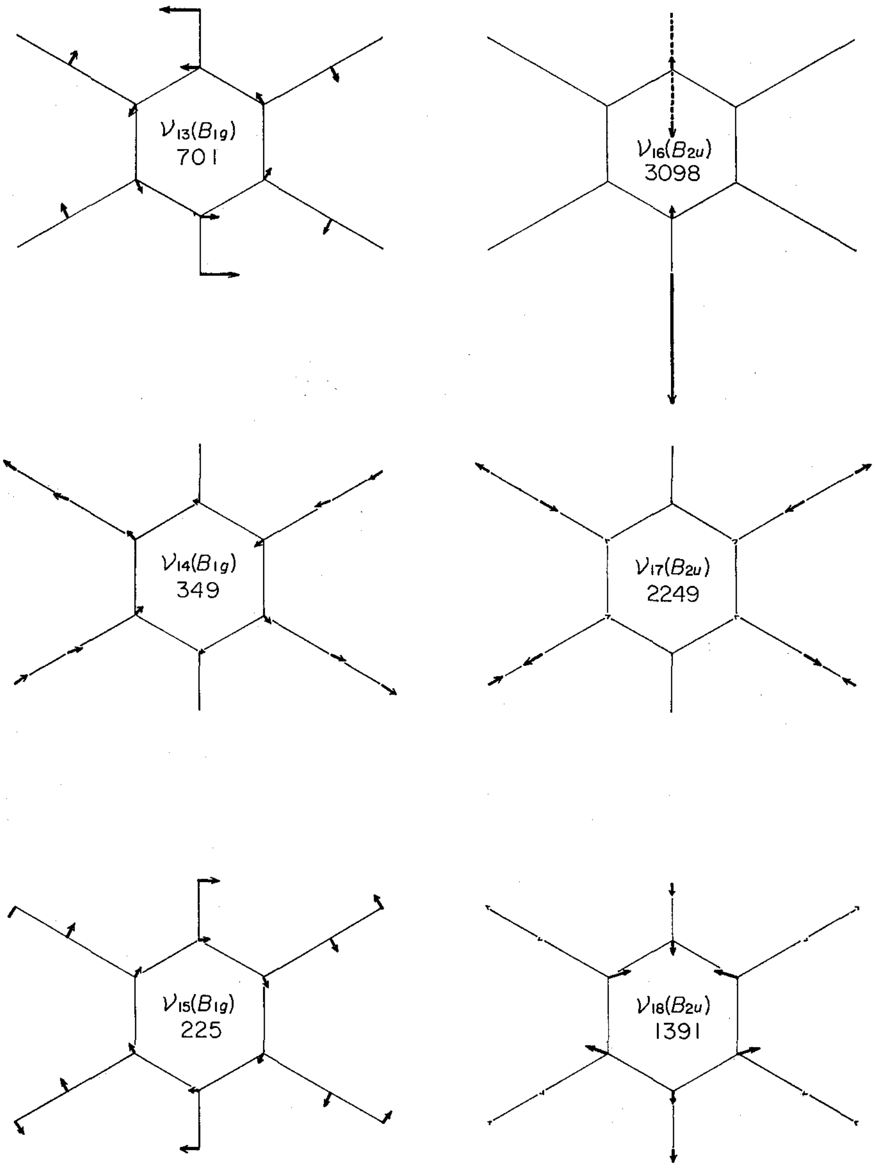


Fig. 2. Continued.

Cartesian Displacements of Normal Vibrations of TCNB and TCNB-d_2

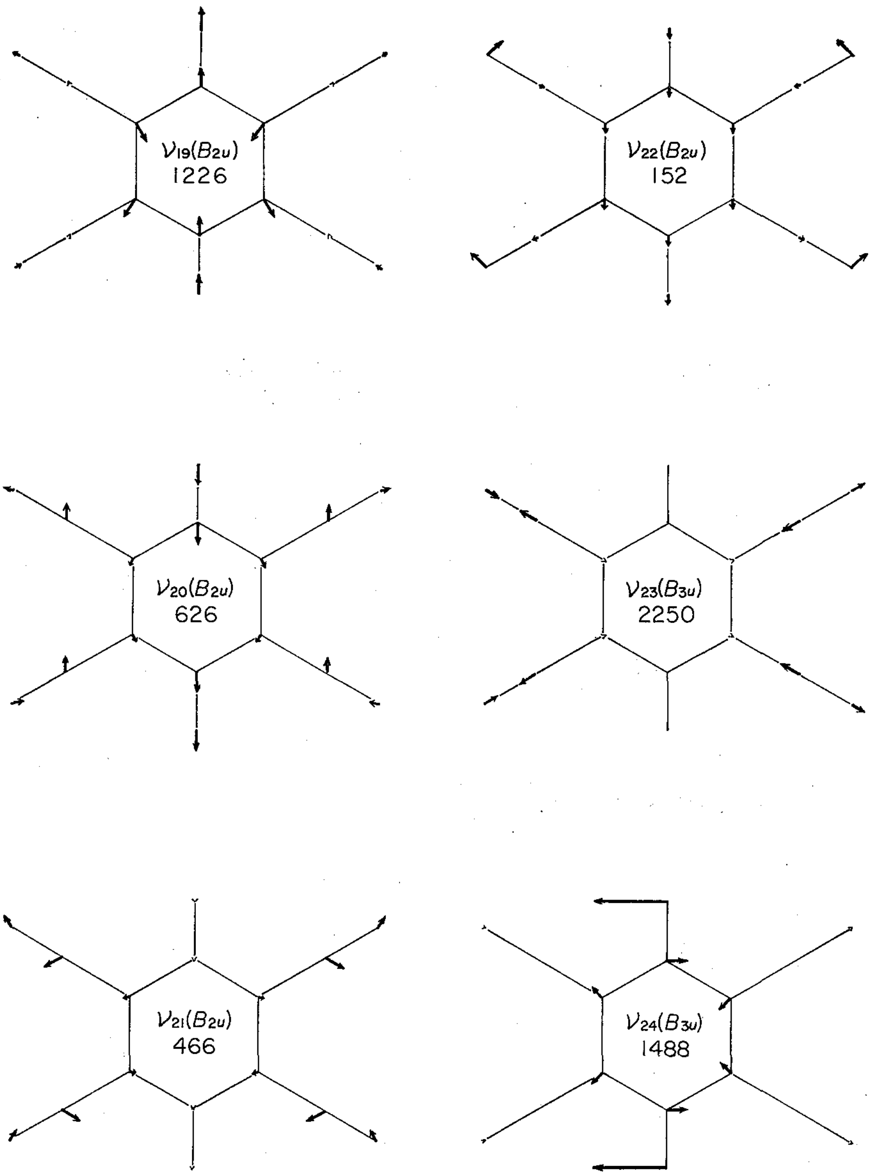
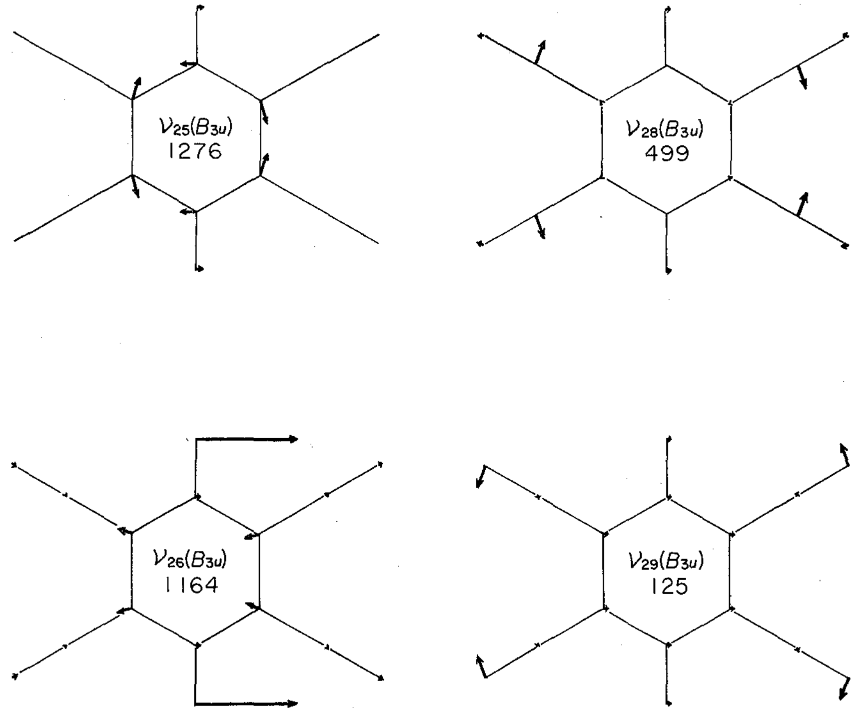
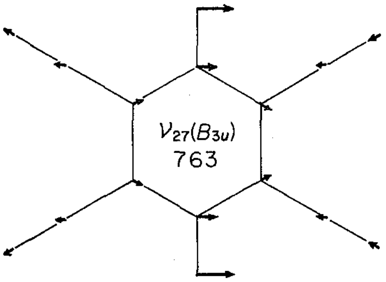


Fig. 2. Continued.





(B) OUT-OF-PLANE FUNDAMENTALS

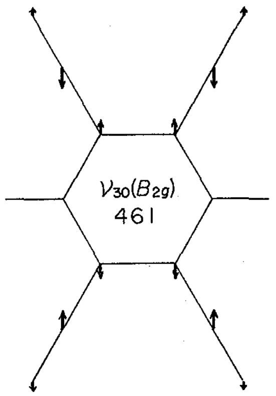


Fig. 2. Continued.

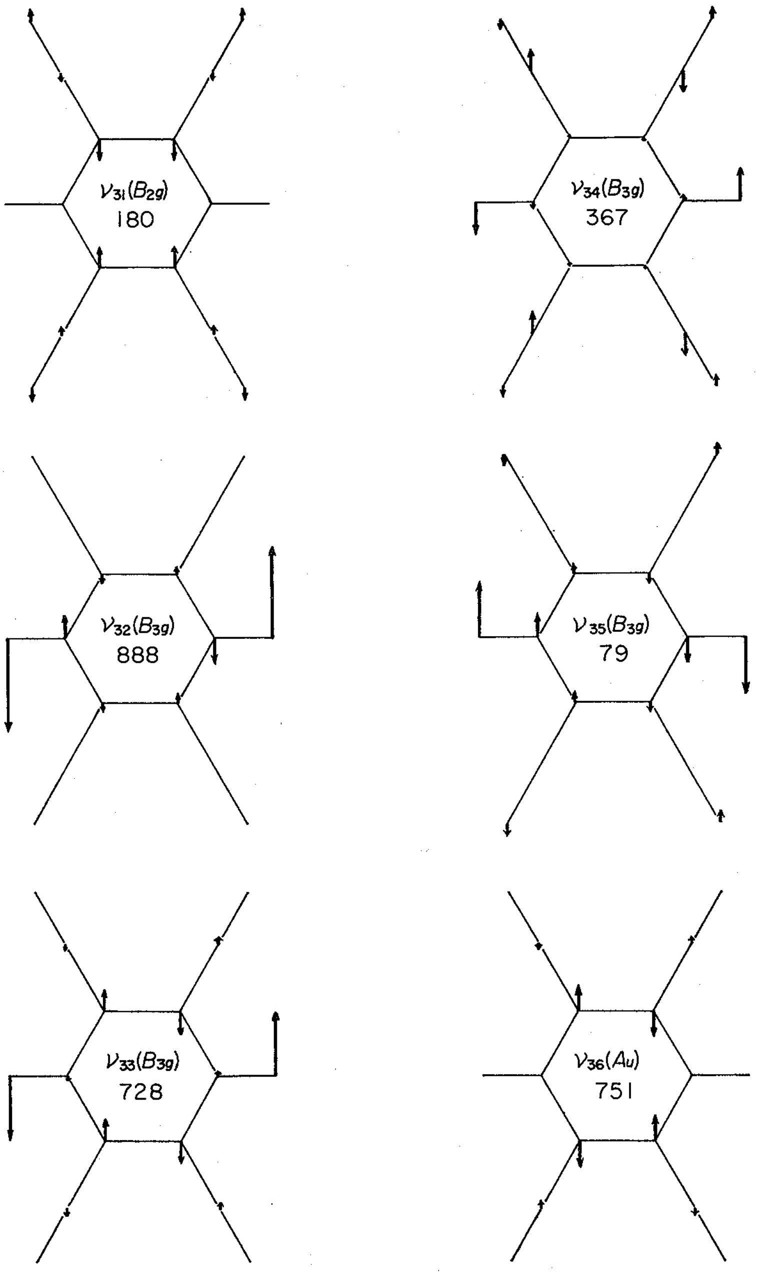


Fig. 2. Continued.

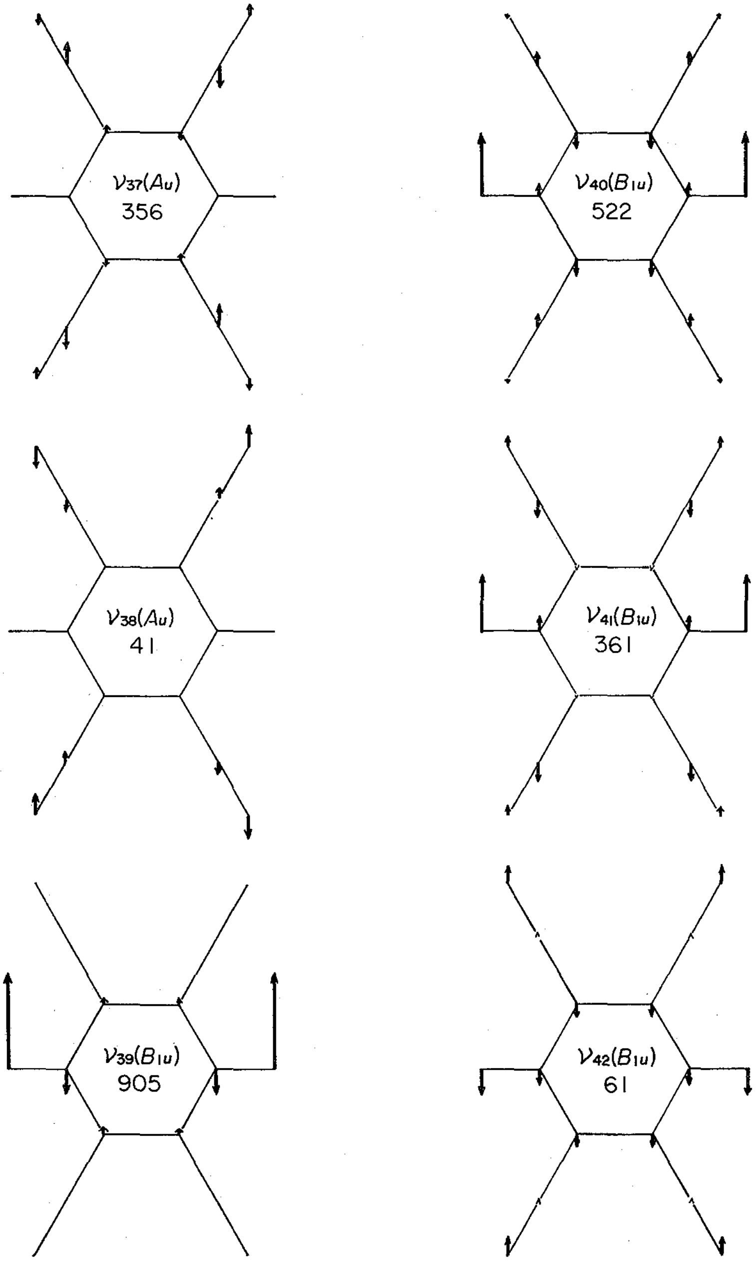


Fig. 2. Continued.

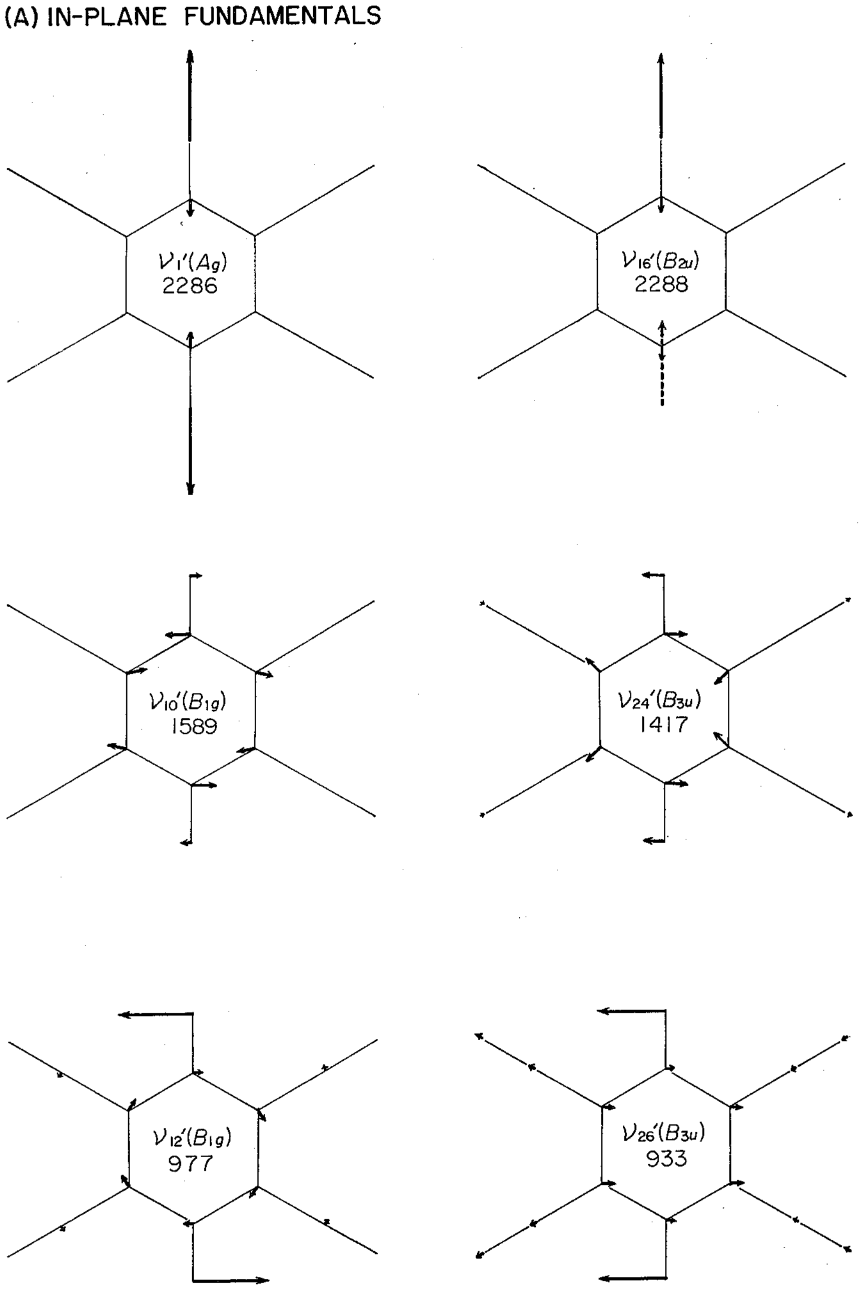


Fig. 3. Cartesian displacements of the normal vibrations of TCNB-d_2.
The displacements are scaled as in Fig. 2.

(B) OUT-OF-PLANE FUNDAMENTALS

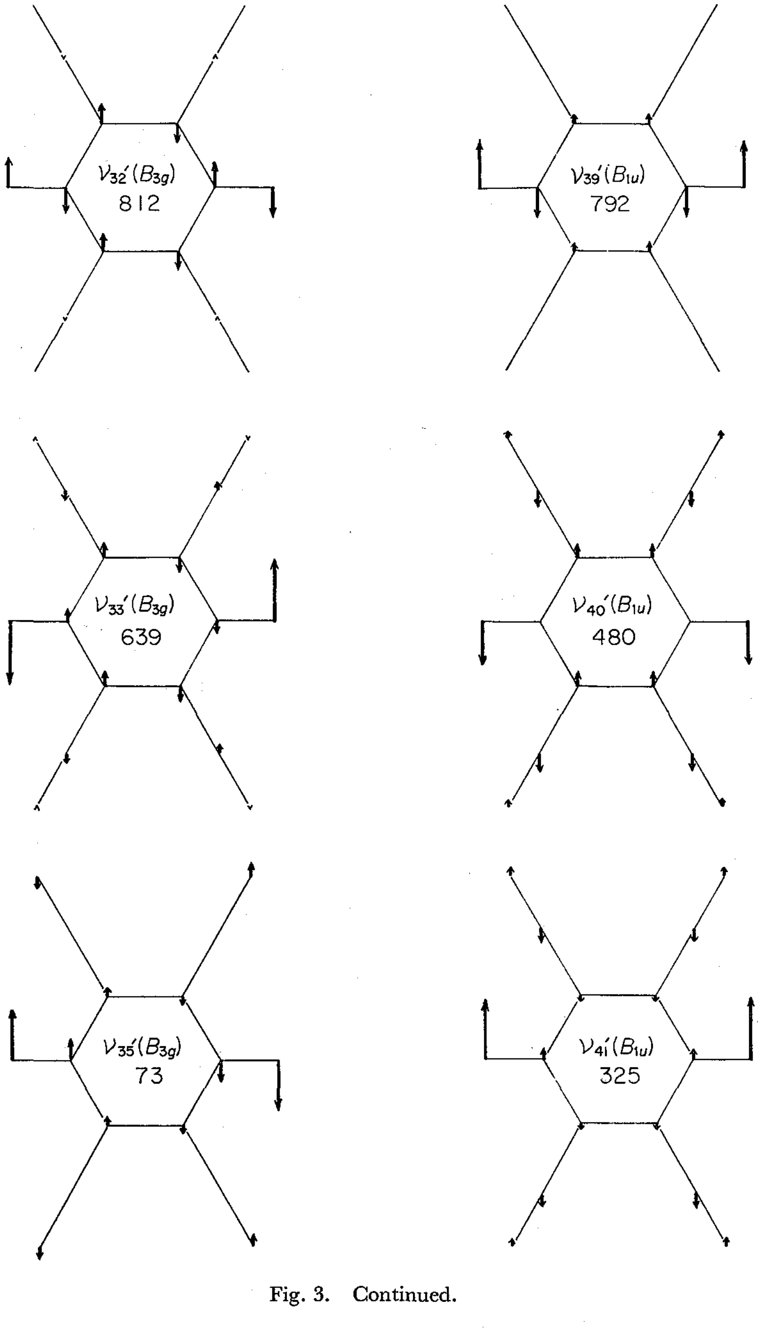


Fig. 3. Continued.

REFERENCES

(1) T. Takenaka, J. Umemura, S. Tadokoro, and S. Oka, *Spectrochim. Acta,* to be published.

(2) D. H. Whiffen, *Phil. Trans. Roy. Soc.* (*London*), **A 248**, 131 (1955).

(3) N. A. Narasimham and Ch. V. S. Ramachandrarao, *J. Mol. Spectrosc.,* **30**, 192 (1969).

(4) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, 1955.

(5) B. L. Crawford, Jr. and W. H. Fletcher, *J. Chem. Phys.,* **19**, 141 (1951).

(6) D. A. Long, *Proc. Roy. Soc.* (*London*), **A 217**, 203 (1953).

(7) H. Takahashi, "Zikken Kagaku Koza (Zoku)", Edited by the Chemical Society of Japan, Vol. 10, p. 491, Maruzen, Tokyo, 1964.