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Internal Rotation in Liquid 1Fluoro1,1,2,2Tetrachloroethane J. Chem. Phys. **47**, 3130 (1967); 10.1063/1.1712364

Erratum: Infrared and Raman Spectra of Fluorinated Ethanes XII. 1,1,2,2Tetrafluoroethane J. Chem. Phys. **33**, 617 (1960); 10.1063/1.1731205

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## The Molecular Structure of 1,1,2,2-Tetrafluorodichloroethane

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NDER superatmospheric pressures, CF<sub>2</sub>Cl-CF<sub>2</sub>Cl was obtained by the fluorination of C<sub>2</sub>Cl<sub>6</sub> with SbF<sub>3</sub> in the presence of an SbCl<sub>5</sub> catalyst. The product was distilled at 4°C. The purity of this sample was tested by an infrared absorption spectrum.1

The molecular structure of gaseous CF2Cl-CF2Cl was investigated with the electron diffraction method. The diffraction camera<sup>2</sup> used had a rotating sector, the aperture of which was proportional to S2. The diffraction pattern was measured up to S=22 by a recording microphotometer. A procedure similar to that employed by Karle<sup>3</sup> was used for deriving the radial distribution curve from a microphotometer record. The radial distribution curve thus obtained from the experimental intensity curve is shown in Fig. 1. The bond distances and bond angles determined from this are as follows:

C - F = 1.33A,	$\angle CCF = 108^{\circ}$
C - Cl = 1.74A,	$\angle FCF = 108^{\circ}$
C - C = 1.45A (assumed),	$\angle$ ClCF = 110°30′.

The C-C single bond distance was assumed to be 1.45A, appreciably smaller than the normal value 1.54A. Unless this short distance is assumed, one cannot give reasonable interpretation of the radial distribution curve. It is because the positions of a peak at 2.15A and those lying between 3A and 4.5A show values smaller than those expected for a model having a normal C-C bond distance; the former peak corresponds to the nonbonded C ··· F distance, while the latter to the long inter-halogen distances.

This shortening of the C-C bond distance has already been found in some fluorinated hydrocarbons, viz., CHF2-CHF2, CH<sub>3</sub>CF<sub>2</sub>CH<sub>3</sub>, CF<sub>3</sub>CF<sub>2</sub>CF<sub>3</sub>, and CF<sub>3</sub>CH<sub>2</sub>Cl.<sup>4</sup> Other bond distances and bond angles have reasonable values compared with the structures of similar fluorinated hydrocarbons.4

Two rotational isomers, trans and gauche, are expected in this molecule as in related halogenated ethanes. In fact, the peak at 4.24A corresponds to trans-(Cl···Cl) distance characteristic of



FIG. 1. The radial distribution curve of 1 1,2,2-tetrafluorodichloroethane.

the trans-form, and the peak at 3.84A to trans- $(F \cdots Cl)$  distance characteristic of the gauche-form. These two peaks show evidently the existence of the two rotational isomers. From the ratio of the heights of these two peaks, one can roughly estimate the abundance ratio of the two isomers. Hence, this molecule can be considered to be a nearly equimolecular mixture of the trans- and gauche-forms. From Raman<sup>5</sup> and infrared<sup>6</sup> spectroscopic data, the existence of rotational isomers has already been confirmed.

The abscissa of the vertical lines shown in Fig. 1 are the interatomic distances calculated from the results mentioned above while the heights are drawn proportional to  $Z_i Z_j / r_{ij}$ . The agreement with the peaks in radial distribution curve is very good in regard to the positions and the heights.

This experiment was carried out using an apparatus in Nagoya University. We would like to express our gratitude to Professor M. Kubo and Dr. M. Kimura for giving us facilities to use the apparatus. Thanks are also due Mr. S. Saheki for his measurement on the infrared absorption spectrum.

<sup>1</sup>An infrared absorption spectrum was obtained on a Perkin-Elmer Model 12C spectrometer in the Government Chemical Industrial Research Institute, Tokyo. <sup>2</sup> Annual Meeting of the Chemical Society of Japan held in April, 1953. Morino, Kimura, and Iwasaki, "Construction of an electron diffraction camera with a rotating sector." This apparatus has recently been set up in the Chemical Department, Faculty of Science, Nagoya University, Nagoya Japan

 <sup>8</sup> J. L. Karle and J. Karle, J. Chem. Phys. 17, 1052 (1949); 18, 957 (1950).
 <sup>9</sup> J. H. Simones, *Fluorine Chemistry* (Academic Press Inc., New York, <sup>8</sup> I. L. Karle and J. Karle, J. Chem. Phys. 17, 1052 (1949); 16, 937 (1950).
 <sup>4</sup> J. H. Simones, Fluorine Chemistry (Academic Press Inc., New York, 1950), Vol. 1, p. 348.
 <sup>5</sup> G. Glockier and C. Sage, J. Chem. Phys. 8, 291 (1940).
 <sup>6</sup> D. Simpson and E. K. Plyler, J. Research Natl. Bur. Standards 50, 223 (1953).

### Equivalence of Chang's and Nakamura's Theories of Hindered Rotation in Molecular Crystals

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AND

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HEORIES of "rotational" transitions in crystals have been developed by Chang<sup>1</sup> and by Nakamura,<sup>2</sup> both following the general ideas of Bethe's<sup>3</sup> treatment of order-disorder transitions in alloys. The two formulations of the theory are rather dissimilar in appearance, Nakamura's being the more elegant, and Chang's following more closely the pattern of Bethe's original work. When applied to identical crystal models, consisting of molecules with next-neighbor coupling energy proportional to  $\cos\theta_{ij}$ , they obtain the same values for the transition temperature, but different values for the discontinuity in  $C_v$  at the transition point. In discussing this discrepancy, Nakamura has suggested that Chang's theory is not correctly modeled after Bethe's approximation. We wish to point out that Chang's theory and Nakamura's are in fact equivalent, and that the discrepancy in values of  $\Delta C_v$  is due to a numerical error in Chang's work.

The basic function in Nakamura's theory is  $g_a(\omega_i)$ , which gives the distribution of orientations  $\omega_i$  for molecule *i* on an *a* site in the lattice. This is determined by the consistency condition

where

$$\int K(\omega,\omega') [g_b(\omega')]^{(z-1)/z} d\omega' = \lambda [g_a(\omega)]^{1/z},$$
(1)

$$K(\omega,\omega') = \frac{1}{4\pi} \exp\left[-\frac{J}{2kT}\cos(\omega,\omega')\right],$$
(2)

and  $g_b(\omega')$  is the distribution of orientations of a molecule on a b site, this function being identical with  $g_a$  if J < 0, and differing by a reflection in the xy plane if J > 0. As usual, z is the number of b sites surrounding an a site.

Nakamura formulates his theory by considering only a pair of next-neighbor molecules, but Chang considers a central molecule and all its next neighbors, which form the "outer shell." The basic function of Chang's theory is  $g(\omega_i)$ , which is not itself a distribution function, but a weight function that represents the weight given to orientation  $\omega_i$  of an outer-shell molecule by its interaction with its z-1 next neighbors that lie outside the outer shell; the effect of coupling to the central molecule in determining the orientational distribution of this outer-shell molecule is considered separately. Nakamura's criticism of Chang's theory seems to be based on identification of Chang's  $g(\omega)$  with his own  $g_a(\omega)$ . Actually, since  $g_a(\omega)$  represents the orienting effect of interaction with z neighbors,  $g(\omega)$  the effect of interaction with only z-1neighbors, one must expect  $g(\omega)$  to be proportional to  $[g_a(\omega)]^{(z-1)/z}$ . Since  $g_a(\omega)$  and  $g(\omega)$  both integrate to  $4\pi$ , in the respective theories, the precise relation between them is

$$g(\omega) = 4\pi [g_a(\omega)]^{(z-1)/z} / \int [g_a(\omega)]^{(z-1)/z} d\omega.$$
(3)

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In terms of Chang's function  $g(\omega)$ , Nakamura's consistency condition becomes, for J < 0,

$$\int K(\omega,\omega')g(\omega')d\omega' = \lambda' [g(\omega)]^{1/(s-1)}.$$
(4)

Chang's consistency relation is expressible as

$$\int d\omega' K(\omega,\omega')g(\omega) \left[ \int d\omega'' K(\omega',\omega'')g(\omega'') \right]^{z-1} = \int \left[ d\omega' K(\omega,\omega')g(\omega') \right]^{z}.$$
 (5)

It is easily seen that Eq. (5) follows from Eq. (4), but it is not evident that the converse is true. Thus every solution obtained in Nakamura's formulation will be a solution in Chang's formulation, but we cannot exclude the possibility that Chang's approach might lead to other solutions without physical significance. Our own work on transitions in systems with a more general type of molecular interaction<sup>4</sup> is based on a consistency condition that leads to Eq. (4) with an appropriately generalized form of  $K(\omega,\omega')$  [see Eq. (8.11) of reference 4]; it is thus equivalent to Nakamura's condition.

Nakamura writes

$$g_a(\omega) = 1 + \sum_{\tau=1}^{\infty} c_{\tau} P_{\tau}(\cos\theta), \qquad (6)$$

converts Eq. (4) to a set of conditions on the  $c_{\tau}$ , and solves these assuming  $c_{\tau} = O(c_1^{\tau})$ . Chang writes

$$g(\omega) = 1 + \sum_{\tau=1}^{\infty} a_{\tau} P_{\tau}(\cos\theta), \qquad (7)$$

converts Eq. (5) to a set of conditions on the  $a_{\tau}$ , and solves these assuming  $a_{\tau} = O(a_1^{\tau})$ . We have verified by direct comparison that these solutions are entirely equivalent,<sup>5</sup> and that Chang's expression for  $\Delta C_v$  is equivalent to Nakamura's; our numerical calculations check those of Nakamura, rather than those of Chang.

- T. S. Chang, Proc. Cambridge Phil. Soc. 33, 524 (1937).
   T. Nakamura, J. Phys. Soc. Japan 7, 264 (1952).
   H. A. Bethe, Proc. Roy. Soc. (London) A150, 552 (1935).
   H. M. James and T. J. Krieger, J. Chem. Phys. 22, 796 (1954).
   The following misprints in Nakamura's paper should be noted:

Eq. (29) and (30); replace  $\lambda t$  by  $(-1)^{j}\lambda t$ Eq. (33); replace  $[z/(z-2)]^{2}$  by  $[z/(z-1)]^{2}$ .

### Erratum : Magnetic Susceptibilities of Np<sup>+6</sup>, Np<sup>+5</sup>, and Np<sup>+4</sup>

[J. Chem. Phys. 22, 386-393 (1954)]

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OOTNOTE number 11 should be replaced by the following:

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#### Announcement

I N accordance with the By-Laws, By-Law III, Sections 6c and 6d, the Nominating Committee has informed me of nominations for the new officers of the Division of Chemical Physics, and I have cast a ballot whereby they are elected. These new officers, accordingly, are J. G. Kirkwood as Vice-Chairman, and C. H. Townes as Executive Committee member.

The complete new list of officers, with the year in which they will cease from their offices, is as follows.

E. H. Nielsen	Chairman (1955)
J. G. Kirkwood	Vice-Chairman (1955)

Bryce Crawford, Ir. Secretary (1955) F. G. Brickwedde Treasurer (1955) C. H. Townes A. A. Frost K. S. Pitzer D. F. Hornig J. O. Hirschfelder

Executive Committee (1957) Executive Committee (1956) Executive Committee (1956) Executive Committee (1955) Executive Committee (1955)

> BRYCE CRAWFORD, JR. Secretary