January, 1990] © *1990 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***63***, *21—25 (1990)*

Molecular Rotational Potentials in Solid Halogenated Benzenes: C_6Cl_6, *sym*-$C_6Cl_3F_3$, and C_6F_6

Nobuo Nakamura* and Hiroshi Yoshino
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka 560

(Received July 8, 1989)

In a previous paper which examined the molecular rotation in *sym*-$C_6Cl_3F_3$ crystal by the ^{35}Cl NQR an unrealistically long activation parameter, τ_0, for the molecular rotation was obtained by assuming the three-fold molecular uniaxial reorientation. In order to examine the reason for such unacceptable result the relaxation time (T_1) data were reanalyzed with the help of the computer experiment which calculates the rotational potential function for each molecule in the crystal lattice. The computation was carried out using the 6-exponential type interatomic pair potential functions. It was found that the potential for the plane molecular rotation in the hexagonal unit cell is non-sinusoidal and has, in addition to the most stable orientation, an extra minimum where the molecules can stay for a finite time at moderately high temperatures. The rotational potential thus obtained was used successfully to reanalyze our previous T_1 data for this material. ^{35}Cl NQR T_1's were measured for C_6Cl_6 crystal and analyzed using anisotropic rotational potentials. The analysis predicted possible disordered structure of this material. In the case of C_6F_6 it was confirmed that the in-plane rotation of two crystallographically inequivalent molecules can be excited with different activation energies from each other, being consistent with the previous fluorine NMR work.

Organic molecules crystallize usually into an anisotropic unit cell and, since the shapes of molecules themselves are usually anisotropic, they execute in general a complex motion. The procedure to deduce information about the dynamical characteristics of the crystals from NMR, NQR, or other spectral data is thus very complicated, and we are often led to wrong assignment of the molecular motion as has been pointed out for molecular rotation or reorientation of *t*-butyl groups[1) and tetramethylammonium ions.[2)

Previously we measured the ^{35}Cl spin-lattice relaxation time in *sym*-$C_6Cl_3F_3$ and observed a sharp decrease in the T_1 which is due obviously to an excitation of a large amplitude motion of the molecules.[3) As this substance crystallizes into a hexagonal $P6_3/m$ structure in which the C_3 axes of nearly planar molecules are aligned parallel to the crystalline c axis[4) and our ^{19}F high-resolution NMR spectra indicated that a motional averaging of the shielding tensor components in the molecular plane occurs,[5) we assigned that ^{35}Cl relaxation and ^{19}F line narrowing are due to molecular three-fold reorientation. However, the quantitative analyses of the relaxation data with the three-fold reorientation led to an activation energy of 18.2 kJ mol^{-1} and the corresponding preexponential factor, $\tau_0=3.42\times10^{-7}$ s, the latter being unbelievably long.[3) Therefore, we have tried to reexamine the relaxation data with the aid of computer calculation of the rotational potentials for the molecules. The analyses of the relaxation data 'combined' with the computer works are also carried out on crystalline C_6Cl_6 and C_6F_6. This paper presents new results of reanalysis of experimental data.

Experimental and Computational Procedures

The measurements of the spin-lattice relaxation times were conducted for the three ^{35}Cl NQR lines in solid C_6Cl_6 using MATEC pulsed NQR apparatus between 77 and 250 K by the 90°-τ-90° and the saturation-τ-90° methods. The experimental uncertainty was estimated to be within ±10% throughout the measurement. The specimen was of commercial source and purified by recrystallization twice from benzene solution, then followed by vacuum sublimation.

sym-$C_6Cl_3F_3$ (Alfa Products) was purified by vacuum sublimation and sealed in an ampule with He gas (ca. 2000 Pa) for the heat exchange. The spin-lattice relaxation time of the ^{19}F in *sym*-$C_6Cl_3F_3$ was carried out using a home-built pulsed NMR equipment at 10 MHz between 228 and 334 K with the experimental accuracy of ±30%.

The computational works were done with the Buckingham 6-exp interatomic pair potential functions; the parameters presented originally by Williams[6) and evaluated by Gavezzotti and Simonetta[7) were used. The computation was simply to take the lattice sum for individual atom pairs within the cut off distance of 1.2—1.4 nm using a FORTRAN program which is a modification of PACK2 coded by Williams[8) so as to compute the molecular rotational potentials. The static lattice energy and the rotational potential about the molecular C_3 axis were calculated for C_6Cl_6, *sym*-$C_6Cl_3F_3$, and C_6F_6 using the crystal structural data.[4,9,10) The error introduced by cutting off the lattice sum was estimated to be less than 0.7%.

Results and Discussion

Table 1 summarizes the activation parameters obtained from the present and the former[3) NQR and NMR experiments, and the computed results of static lattice energies and rotational potential barriers for the three compounds together with the reported heats of sublimation for C_6Cl_6 and C_6F_6. The values of the activation parameters for C_6F_6 were taken from a previous work.[11)

The static lattice energy of C_6Cl_6 is slightly larger than the experimental heat of sublimation but the difference is considered to be insignificant. In the case

Table 1. The Calculated Lattice Energy E_L, Rotational Potential Barrier V_0, and the Experimental Results of Heat of Sublimation ΔH_s, and Activation Parameters in Halobenzenes

Substance	Space group	E_L	ΔH_s	V_0	E_a	τ_0
		kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	s
C_6Cl_6	$P2_1/n$	89.3	91.79$^{a)}$	63.0	61.9±0.9 (ν_1)	3.7×10^{-16}
					59.8±1.7 (ν_2)	1.1×10^{-15}
					64.1±2.4 (ν_3)	1.4×10^{-17}
sym-$C_6Cl_3F_3$ (LTP)	$P6_3/m$				18.2±0.5$^{c)}$	$3.42 \times 10^{-7\,c)}$
		71.6		42.0	19.7±0.8	4.97×10^{-11}
(HTP)					35 ±3	
C_6H_6	$P2_1/n$	54.8	46.62$^{b)}$	27.6 (c)	31.2$^{d)}$	$2.3 \times 10^{-15\,d)}$
				15.3 (e)	12.6$^{d)}$	$1.1 \times 10^{-13\,d)}$

a) G. W. Seas and E. R. Hopke, *J. Am. Chem. Soc.*, **71**, 1632 (1949). b) J. F. Messerly and H. L. Finke, *J. Chem. Thermodyn.*, **2**, 867 (1970). c) Ref. 3. d) Ref. 11.

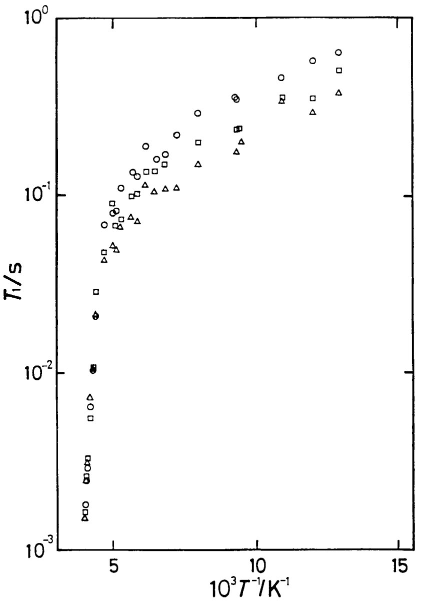

Fig. 1. ^{35}Cl spin-lattice relaxation times for three NQR lines; ○: ν_1, □: ν_2, △: ν_3 of C_6Cl_6.

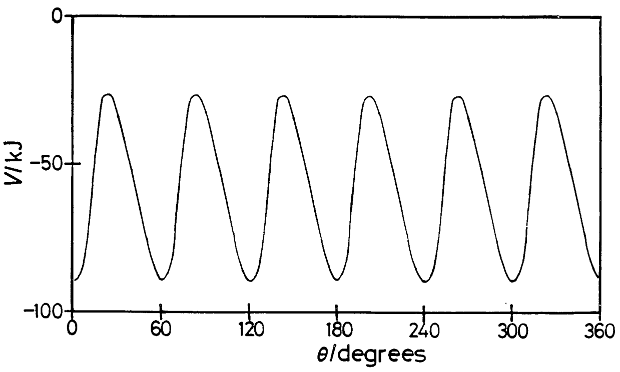

Fig. 2. Potential energy for the molecular rotation about the molecular 6-fold axis in C_6Cl_6 crystal.

of C_6F_6 agreement is very good provided that the zero-point lattice vibration contributes to some extent to the heat of sublimation. Thus we can say that the lattice sums based on the Williams' potential parameters can be used to evaluate the static energetics of crystal lattices of the halogenated benzenes in almost a quantitative manner.

C_6Cl_6. C_6Cl_6 crystal contains four crystallographically equivalent molecules in a monoclinic unit cell.[9] Each molecule has three inequivalent chlorines and the corresponding ^{35}Cl NQR frequencies were ν_1=38.390, ν_2=38.465, and ν_3=38.504 MHz at liquid nitrogen temperature. The spin-lattice relaxation times, T_1, for these three chlorines are shown in Fig. 1. The plot of T_1 vs. T^2 gave straight lines for each transition below about 200 K, indicating that the quadrupolar relaxation is governed by the lattice vibrations at low temperatures. The drastic shortening of the T_1 above 200 K is obviously brought about by some molecular reorientation. In the course of the present work we found that an NQR experiment on C_6Cl_6 above 77 K was done by Danilov and Izmest'ev.[12] Our experimental T_1's for each of the three inequivalent chlorines agree well with their result. Our average activation energy, 61.6 kJ mol^{-1}, is slightly higher than theirs, 59.0 kJ mol^{-1}. However, the preexponential factors, τ_0, in our measurements (Table 1) are significantly short compared with their values, 5×10^{-13}—1.3×10^{-14} s due probably to the difference in the evaluation of the contribution of the lattice vibrations to the relaxation rate below about 200 K.

The rotational potential energies were calculated by rotating the molecules about their figure axes in the crystal lattice; the simultaneous rotation of all the molecules led, however, to an unrealistically low potential barrier and so we rotated molecules which are located at the next nearest neighbor sites while fixing the nearest neighbors at their original orientations. The rotational potential function thus obtained is shown in Fig. 2 and the values of the potential barrier is 63.0 kJ mol^{-1}.

The rotational potential satisfies the six-fold symmetry but the individual potential wells are asymmetric because the molecular site symmetry is low in the crystalline unit cell. The potential barrier to the molecular 6-fold reorientation, 63 kJ mol^{-1},[13] agrees

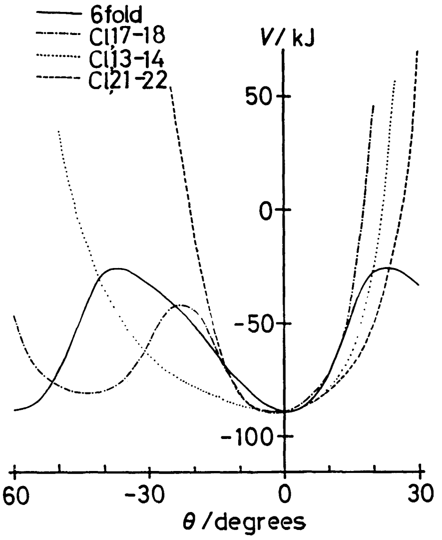

Fig. 3. Rotational potential energies about the 6-fold axis and three two-fold axes in C_6Cl_6 crystal; the notation is referred to in Ref. 9.

excellently, when the zero-point vibrational effect is taken into account, with the average value of the experimental activation energies, indicating that the 6-fold reorientation is responsible for the ^{35}Cl relaxation.

Reynolds pointed out the existence of some orientational disorder or defects in C_6Cl_6 crystal at room temperature.[14] In order to examine the possibility of such disorder we attempted again the computation of the rotational potential function by rotating the molecules about other molecular axes: The results are shown in Fig. 3. We see in this figure a metastable orientation which can be reached by rotating the molecule about the axis through Cl_{17} and Cl_{18} (the notation in Ref. 9) by 45° and has the potential energy of 8.4 kJ mol^{-1} measured from the equilibrium orientation. This metastable state is located close to the position of misorientation indicated by Reynolds and so our model calculation supports his assertion. He estimated the misorientation energy to be 2—3 kJ mol^{-1} so that 3 to 4 percent of molecules can be at the disordered orientation at room temperature; such a disorder can induce the disturbance of the electric field gradient at nearby sites of chlorines, causing the broadening and fade-out of the ^{35}Cl NQR signals which has been recognized above room temperature.[15]

Molecular jumps between these two orientations may cause the quadrupole relaxation as in the case of *sym*-$C_6Cl_3F_3$ (see in Section C below). However, we could not distinguish this relaxation process from the 6-fold reorientation due probably to relatively small difference in the potential barriers for the two-site jump (estimated as 46.2 kJ mol^{-1}) and for the 6-fold reorientation. A ^{35}Cl relaxation experiment with greater precision will discern such different relaxation processes.

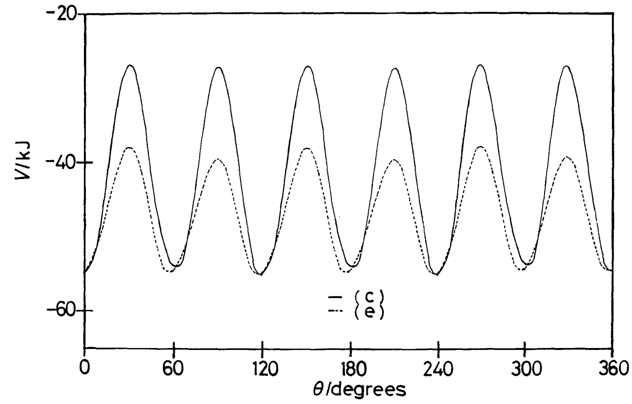

Fig. 4. Rotational potential energies about the molecular 6-fold axes for two inequivalent molecules in C_6F_6 crystal. Solid line: c-site, broken line e-site, the notation is referred to in Refs. 10 and 11.

C_6F_6. Two different rotational potential functions were obtained for C_6F_6 crystal corresponding to the two crystallographically inequivalent molecular sites (e- and c-sites)[10] as shown in Fig. 4. The shapes of these two potential functions are slightly asymmetric because we rotated slightly asymmetric molecules as rigid bodies. The heights of the rotational barriers, 15.3 (for the e-site) and 27.6 kJ mol^{-1} (c-site), can be compared with the experimental activation energies, 12.6 and 31.2 kJ mol^{-1}, which were assigned to the 6-fold reorientations for the e- and the c-site molecules, respectively.[11]

***sym*-$C_6Cl_3F_3$.** The relaxation of the ^{19}F in *sym*-$C_6Cl_3F_3$ above its phase transition point, 296 K, was represented by a single relaxation process up to the melting point (335.0 K); the T_1 assumes the value, (4.0±0.7) s, at 296 K and decreases monotonously on heating, giving rise to an activation energy of (35±4) kJ mol^{-1}. This activation energy above the phase transition point is about twice as large as that deduced previously from the T_1 of ^{35}Cl in the low temperature phase.[3] This fact suggests that different molecular motional modes are responsible for the relaxation in the low and high temperature phases of this compound.

Figure 5 shows the rotational potential functions for a rigid molecule located in the unit cell of the low temperature form at room temperature and at 4.2 K, respectively. It can be seen that the contraction of the unit cell by only about 0.01 and 0.023 nm along the crystallographic a- and c-axes, respectively, leads to the stabilization of the equilibrium structure and a significant increase in the rotational barrier. The potential function possesses, between the equilibrium molecular orientations (S of Fig. 5) at the rotational angles $\theta=0$ and 120°, two extra minima at 60° (M_U) and 95° (M_L), the heights of which measured from the

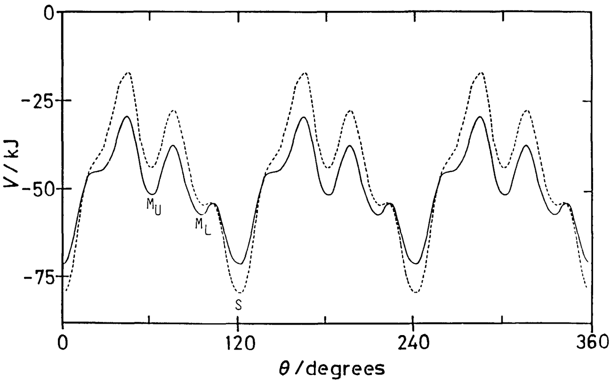

Fig. 5. Potential energy for the molecular rotation about the molecular figure axis in *sym*-$C_6Cl_3F_3$ crystal. Solid line: at room temperature; broken line: at 4.2 K.

equilibrium orientation are 19.8 and 14.3 kJ mol^{-1}, respectively, at room temperature. The heights of the potential barriers for reaching the metastable orientations M_L and M_U amount to 17.4 and 33.9 kJ mol^{-1}, respectively, and that for the 3-fold reorientation is 42.0 kJ mol^{-1}.

The value of the potential barrier for the 3-fold reorientation, 42 kJ mol^{-1} is higher than the activation energy, 35 kJ mol^{-1}, obtained from ^{19}F NMR in the high temperature phase; however, taking account of the thermal expansion and possible structural change due to the phase transition, one can expect that the potential barrier is reduced to some extent at high temperatures. Therefore, the above value of the activation energy can be reasonably assigned to the molecular 3-fold reorientation which is excited only in the high temperature phase.

The potential energy needed to excite the molecule to the metastable orientation M_L, 17.4 kJ mol^{-1}, can be compared with the value of the experimental activation energy, 18.2 kJ mol^{-1}, evaluated previously from the analysis of the T_1 of ^{35}Cl and attributed then to the 3-fold reorientation. It is now obvious that the misled assignment of the experimental activation energy led to an unreasonable value of the preexponential factor τ_0 as we pointed out above. Here we will reanalyze the chlorine T_1 data on the basis of the molecular jump mechanism between the equilibrium and the lower metastable orientations M_L by applying the strong collision theory for the quadrupole relaxation.[16,17]

When a molecule jumps stochastically between two sites, the stable α and a metastable α', separated by an angle $\theta_{\alpha\alpha'}$ with a potential energy difference ΔE, the rate equation for the polarization P^α at the α site is represented by

$$\mathrm{d}(P^\alpha(t) - <P^\alpha>)/\mathrm{d}t = \textstyle\sum_{\alpha'} P(w_{\alpha\alpha'}P^{\alpha'} - w_{\alpha'\alpha}P^\alpha) - \textstyle\sum_{\alpha'} w_{\alpha'\alpha}Q(P^\alpha - <P^\alpha>), \quad (1)$$

where

$$P = (3\cos^2\theta_{\alpha\alpha'} - 1)/2, \quad Q = 3\sin^2\theta_{\alpha\alpha'}/2, \quad (2)$$

and $w_{\alpha\alpha'}$ is the transition probability from the site α' to the α, and the following relation between $w_{\alpha\alpha'}$ and $w_{\alpha'\alpha}$ holds:

$$w_{\alpha\alpha'} = w_{\alpha'\alpha}\exp(\Delta E/RT). \quad (3)$$

The general solution of the rate equation with an initial condition that $P^\alpha(0)=0$, i.e. just after the 90° pulse, is given by

$$[P^\alpha(t) - <P^\alpha>]/<P^\alpha> = A_1\exp(-t/T_1^{\mathrm{I}}) + A_2\exp(-t/T_1^{\mathrm{II}}), \quad (4)$$

where

$$(1/T_1^{\mathrm{I,II}}) = (1/2)[(w_{\alpha'\alpha} + w_{\alpha\alpha'})(P + Q) \pm \{(w_{\alpha'\alpha})^2(P + Q)^2 + 4(Q^2 + 2PQ)w_{\alpha'\alpha}w_{\alpha\alpha'}\}^{1/2}], \quad (5)$$

$$A_1 = (1/T_1^{\mathrm{II}} - w_{\alpha'\alpha}Q)/(1/T_1^{\mathrm{I}} - 1/T_1^{\mathrm{II}}), \quad (6)$$

where the plus sign is taken for T_1^{I} and the minus sign for T_1^{II}, and

$$A_2 = (1/T_1^{\mathrm{I}} - w_{\alpha'\alpha}Q)/(1/T_1^{\mathrm{II}} - 1/T_1^{\mathrm{I}}). \quad (7)$$

Calculation of the A_1 and A_2 with $\theta_{\alpha\alpha'}=25°$ and $\Delta E=14.3$ kJ mol^{-1} gives $A_1\approx 0$. Hence the relaxation process can be described by a single relaxation time T_1^{II}. By insertion of the experimental T_1 of ^{35}Cl into the above equations, the transition probabilities, $w_{\alpha\alpha'}$ and $w_{\alpha'\alpha}$ can be obtained and, defining the correlation time τ_c by $\tau_c=1/w_{\alpha'\alpha}$, the value of the τ_c at each temperature is derived as is shown in Fig. 6. The fitting of the τ_c's to the Arrhenius activation process,

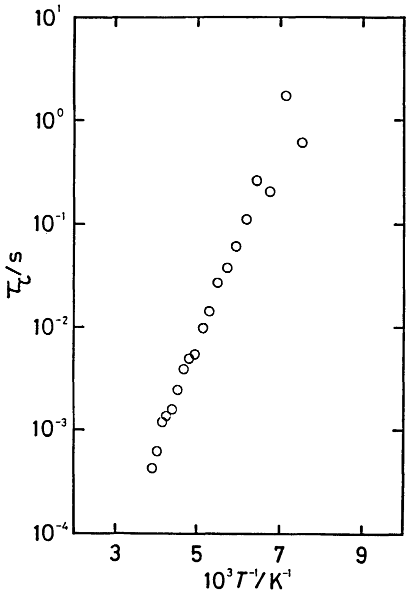

Fig. 6. The correlation time for the two-site jump process in *sym*-$C_6Cl_3F_3$ crystal.

$$\tau_c = \tau_0 \exp(E_a/RT), \qquad (8)$$

leads to a new set of activation parameters, E_a=19.7 kJ mol^{-1} and τ_0=4.97×10^{-11} s, for the molecular jump between the S and M_L orientations.

This value of the E_a is slightly higher than the potential barrier, 17.4 kJ mol^{-1} between the S and M_L orientations, and the corresponding τ_0 seems to be still very long compared with those in C_6Cl_6 and C_6F_6.[11,18] However, it is obvious that the molecular motion which governs the ^{35}Cl quadrupole relaxation is the orientational jump between the stable and a metastable site, though the possibility that small fraction of the molecules can overcome the higher potential barrier to realize the 3-fold reorientation at moderately high temperatures can not be ruled out.

We see in the above examples that the model calculation of the potential energy functions can be used to distinguish various molecular motional modes and so it helps greatly to endorse the analyses of the magnetic relaxation data and also perhaps of other spectral data in complex molecular crystals.

Although the above calculation of the crystal properties gives almost quantitative interpretation to the experimental findings, we will need further refinement of the potential parameters for performing more reliable computational works. Very recent work on the lattice dynamics in *sym*-$C_6Cl_3F_3$ states, for example, shows that a new set of the pair potential parameters is superior to the widely accepted Williams parameters in reproducing the experimental phonon dispersion relations.[19] Molecular dynamics approach will also be very useful for understanding of both the static and dynamic structures of these and other more complex molecular crystals in which large amplitude molecular motion and some kind of molecular misalignment are closely concerned with the crystal stability.

We are grateful to Professor Hideaki Chihara for many helpful and stimulating discussions. We are also grateful to Professor G. Wulfsberg (Middle Tennessee State University) for valuable comments.

References

1) J. C. Frost, A. J. Leadbetter, R. C. Ward, and R. M. Richardson, *J. Chem. Soc., Faraday Trans. 2*, **78**, 1009 (1982); T. Hasebe and J. H. Strange, *ibid.*, **81**, 735 (1985).

2) C. I. Ratcliffe and J. A. Ripmeester, *Can. J. Chem.*, **64**, 1348 (1986).

3) Y. Yoshioka, N. Nakamura, and H. Chihara, *J. Mol. Struct.*, **111**, 195 (1983).

4) S. L. Chaplot, G. J. McIntyre, A. Mierzejewski, and G. S. Pawley, *Acta Crystallogr., Sect. B*, **37**, 1896 (1981).

5) Y. Yoshioka, N. Nakamura, and H. Chihara, *Z. Naturforsch.*, **40a**, 137 (1985).

6) D. E. Williams, *J. Chem. Phys.*, **45**, 3770 (1966).

7) A. Gavezzotti and M. Simonetta, *Acta Crystallogr., Sect. A*, **31**, 645 (1975).

8) D. E. Williams, U. S. AER Report, IS-1042 (1964).

9) G. M. Brown and O. A. W. Strydom, *Acta Crystallogr., Sect. B*, **30**, 801 (1974).

10) N. Boden, P. P. Davis, C. H. Stam, and G. A. Wesselink, *Mol. Phys.*, **25**, 81 (1973).

11) N. Boden, P. P. Davis, C. H. Stam, and G. A. Wesselink, *Mol. Phys.*, **25**, 87 (1973).

12) A. V. Danilov, I. V. Izmest'ev, Radiospektroskopiya, Perm, No. 15, 136 (1983).

13) The static lattice energy and rotational potential function were calculated in Ref. 7. The former value is lower than ours by about 10% and their rotational potential barrier seems to be too high, the reason for which is not clear.

14) P. A. Reynolds, *Acta Crystallogr., Sect. A*, **31**, 386 (1975).

15) T. Eguchi, K. Mano, and N. Nakamura, *Z. Naturforsch.*, **44a**, 15 (1989).

16) S. Alexander and A. Tzalmona, *Phys. Rev. A*, **138**, 845 (1965).

17) N. E. Ainbinder, I. A. Kyuntsel', V. A. Mokeeva, and G. B. Soifer, *Soviet Phys. Solid State*, **21**, 1441 (1979).

18) S. Albert, H. S. Gutowsky, and J. A. Ripmeester, *J. Chem. Phys.*, **56**, 2844 (1972).

19) M. T. Dove, B. M. Powell, G. S. Pawley, S. L. Chaplot, and A. Mierzejewski, *J. Chem. Phys.*, **90**, 1918 (1989).