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Intermolecular Potential for Carbon Tetrafluoride

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An attempt has been made to give a more realistic molecular potential for carbon tetrafluoride by using published X-ray diffraction data for α-CF_4. It was found that an addition of anisotropic Lennard-Jones potentials between nonbonded atoms is preferable for molecular interactions in crystal. The values of the potential parameters are evaluated and give a reasonable interpretation of the temperature dependence of the lattice parameters.

INTRODUCTION

In a previous paper[1] we examined a molecular potential for silicon tetrafluoride (SiF_4), which may be treated as a standard substance in tetrahedral molecular crystals from the point of view of molecular interactions. In the present paper we treat carbon tetrafluoride (CF_4) which undergoes an orientationally disordering transition below its melting point.

According to the X-ray diffraction study by Bol'shutkin *et al.*,[2] the crystal structure of α-CF_4 is monoclinic and belongs to the space group $C_{2h}^5 - P2_1/c$. A unit cell consists of four molecules. The structural model is shown in Figure 1.

A large amount of work has been done on the potential for CF_4 by using the Lennard-Jones or the Kihara potential and electrostatic octopole–octopole interactions. However, a realistic intermolecular potential for solid-CF_4 has not been known accurately. In the present work the model of the molecular interaction potential is the same as that used in the previous study of SiF_4.[1] The values of the potential parameters are evaluated by using the X-ray diffraction data at 10 K, which is the lowest temperature among the measurements,[2] and are discussed using the temperature dependence of the lattice parameters.

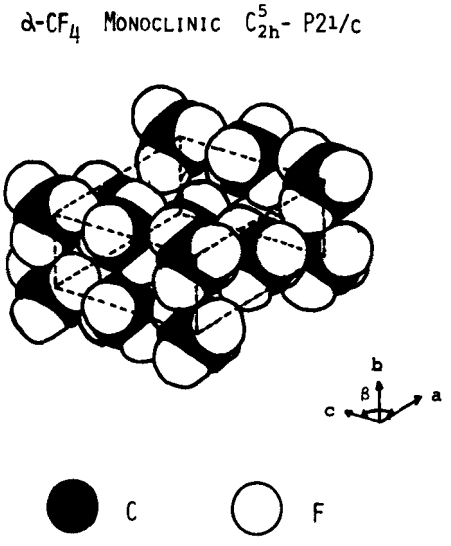

FIGURE 1 Structural model of α-CF_4, taken from Figure 2 of Ref. 2.

ESTIMATION OF POTENTIAL PARAMETERS

The model of the interaction potential for the pair of molecules was the same as that used in the study of SiF_4[1] as follows:

$$\begin{aligned}\phi(\text{pair}) = {} & 4\varepsilon[(\sigma/R)^{12} - (\sigma/R)^6]f \\ & - e^2(a_1\nabla)(a_2\nabla)(a_3\nabla)(a'_1\nabla)(a'_2\nabla)(a'_3\nabla)(1/R) \\ & + \varepsilon' \sum_{n(\text{F-F})} [(\sigma'/r_n)^{12} - (\sigma'/r_n)^6] \\ & + \varepsilon'' \sum_{m(\text{C-F})} [(\sigma''/r_m)^{12} - (\sigma''/r_m)^6]. \end{aligned} \tag{1}$$

Here the first term is the contribution of the central Lennard-Jones potential, the second is from the electrostatic octopole–octopole interaction and the third and fourth are from the nonbonded F atom–F atom potential and the C atom–F atom potential of the molecules.

There is the fact that the transport properties are much less sensitive to long-range intermolecular forces than the second virial coefficient. Therefore, the assumption that the presence of molecular octopole moments may be neglected in the computation, is more reasonable for the viscosity coefficient than for the second virial coefficient. The values of the central Lennard-Jones[3] were obtained from the analysis of viscosity data. The value of

octopole moment for CF_4 molecules was estimated $\sum_i e_i x_i y_i z_i = 4.44 \times 10^{-34}$ e.s.u. by using the second virial coefficient data previously.[3] Literature values are 3.4–7.9 $\times 10^{-34}$ e.s.u. and the origin of these discrepancies remains unexplained.

Sataty *et al.*[4] measured the far-infrared spectrum of crystalline CF_4 and reinterpreted the X-ray diffraction data in terms of a unit cell with space group $C2/c$. However, the number of observed lattice modes is generally smaller than expected by means of group analysis. Since the atomic positions of CF_4 are unchanged whether the space group may be $P2_1/c$ or $C2/c$, we adopted the result of the X-ray diffraction.

In order to estimate the values of the parameters ε', σ' (between F and F), ε'', σ'' (between C and F) and the central Lennard-Jones potential factor f, an attempt was made to fit the equilibrium conditions such that the values of the lattice parameters a, b, c, and β and molecular orientation at 10 K give the minimum in the intermolecular potential energy (E). As a result it was seen that they are not independent functions for E and a, c and β are probably related in terms of more dominant condition than equilibrium one. If molecules are understood as the three-dimensional rotators with the Euler angles (θ, ϕ, ψ), $(\delta E/\delta\theta)$ is to be zero at $\theta = 0°$, and $(\delta E/\delta\phi)$ is equal to $(\delta E/\delta\psi)$. Then, we employed the conditions that a, c and β on an average give the minimum in E, i.e.

$$[(\delta E)/(\delta a) + (\delta E)/(\delta c)][1 + \sin(\beta) - \cos(\beta)] + [(\delta E)/(\delta\beta)][\sin(\beta) + \cos(\beta)][(1/a) + (1/c)] = 0, \quad (2)$$

since the relations among a, c and β are unknown. In order to supply one more relation, the value of the static lattice energy for solid-CF_4 at 10 K was adopted. E is related to the heat of sublimation (ΔH) and the zero point energy (E_z) as follows:

$$-E = \Delta H + E_z. \quad (3)$$

The value of ΔH at 10 K was calculated from experimental data on thermodynamic properties,[3,5] and frequencies of intramolecular vibrations,[6] and the result is summarized in Table I. The value of E_z was estimated to be 422.5 cal mol^{-1} by assuming 6 N degrees of vibrational freedom of the Debye model (where N is Avogadro's number and θ_D (10 K) = 94.5 K[3]).

RESULTS

The intermolecular interactions were taken over neighboring molecules which connect to a center molecule for each kind of energies above 1 cal mol^{-1} ($R \leqq 10$ A, $r_n \leqq 11.9$ A and $r_m \leqq 10.2$ A).

TABLE I

Calculation of heat of sublimation at 10 K (in units of cal mol^{-1})

$\int_{10\,K}^{76.221\,K} C_p(\text{solid})\,dT$	697.7
Heat of transition (at 76.221 K)	349.5
$\int_{76.221\,K}^{89.529\,K} C_p(\text{solid})\,dT$	216.4 ± 1.5
Heat of fusion (at m. p.)	169.6
$\int_{89.529\,K}^{145.12\,K} C_p(\text{liquid})\,dT$	1039.4 ± 4.5
Heat of vaporization (at 145.12 K, 1 atm)	2823.6
$\int_{145.12\,K}^{10\,K} C_p(\text{gas})\,dT$	−1118.5
Correction for gas imperfection	25.4
Heat of sublimation at 10 K, ΔH	4203.1 ± 6.0

The results give $0.039625 < f < 0.058817$, since the potential parameters ε', $\varepsilon''\sigma'$ and σ'' must be all positive. We calculated by using its middle value ($f = 0.04922$), and the assigned uncertainty in f is no more than an error of E within 5 cal mol^{-1}. Results of the calculations are summarized in Table II.

DISCUSSION

The calculated value of the static lattice energy for solid CF_4 in terms of the potential form neglecting the third and fourth terms in Eq. (1) is no more than about a half of the heat of sublimation at 10 K. This is an important difference from that in SiF_4,[1] and suggests that the effect of the anisotropic

TABLE II

Results of calculations of the potential parameters and static lattice energy at 10 K for CF_4

	(1)	(2)
$\varepsilon' \times 10^{14}$ (erg)	—	0.6218
σ' (A)	—	3.235
$\varepsilon'' \times 10^{14}$ (erg)	—	1.415
σ'' (A)	—	3.357
f	1	0.04922
Spherical L-J	606.8	37.8
Nonspherical L-J ($\varepsilon'\sigma'$)	—	−286.1
Nonspherical L-J ($\varepsilon''\sigma''$)	—	−1518.9
Octopole interaction	−2858.4	−2858.4
Static lattice energy	−2251.6	−4625.6

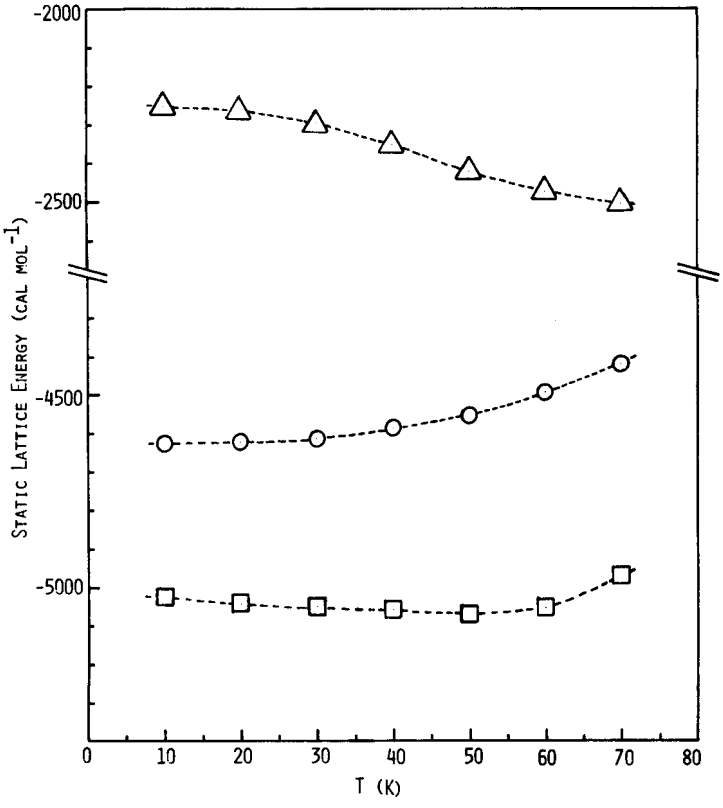

FIGURE 2 Temperature dependence of the calculated values of the static lattice energy for α-CF_4. ○: present work (Eq. (1)) △ : spherical L-J □ : Kihara potential

potential brings about the low-symmetry of the crystal and the phase transition in contrast with the octopole interaction. The small value of f means to change into nonspherical from spherical for the Lennard-Jones potential.

We have attempted to calculate the temperature dependence of the static lattice energy by employing the obtained value of the potential parameters and the X-ray diffraction data of lattice parameters.[2] For purposes of comparison the value of the static lattice energy was also estimated by using the Kihara potential[7] with the spherical core of radius a, i.e.

$$W(R > 2a) = 4\varepsilon[\{(\sigma - 2a)/(R - 2a)\}^{12} - \{(\sigma - 2a)/(R - 2a)\}^{6}]; \quad W(R < 2a) = \infty, \tag{4}$$

where $\sigma = 4.319$ A, $a = 0.72$ A and $\varepsilon/k = 289.7$ K. The results are shown in Figure 2.

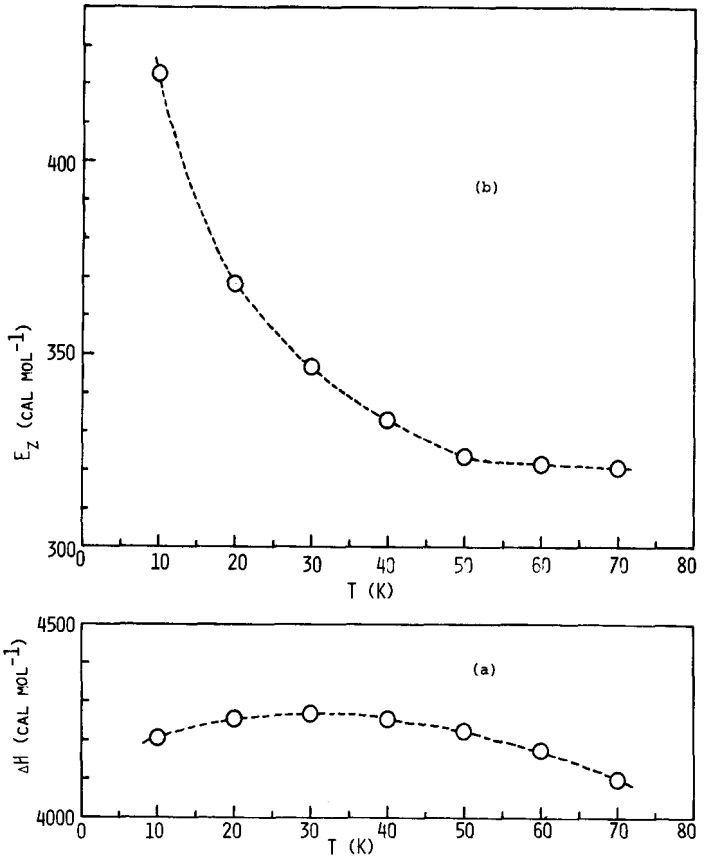

FIGURE 3 Plots of the heat of sublimation (ΔH) (a) and the zero point energy (E_z) (b) against temperature.

Until now it has been said that the Kihara potential is the most appropriate one in order to describe various properties of polyatomic molecules. As seen from Figure 2, however, the result using the Kihara potential gives an unreasonable temperature dependence which has its minimum point at 50 K. It is needless to say that the spherical L-J potential is unreasonable, and the calculated values by using Eq. (1) give a reasonable temperature dependence. We also investigated the temperature dependence of the zero point energy in terms of the potential obtained in the present work by estimating the heat of sublimation at each temperature from thermodynamic data.[3,5] The result is plotted in Figure 3 and is not unreasonable.

The orientations of the molecules in the unit cell are considered in the X-ray diffraction report[2] that $\theta = 0°$ over the whole temperature range of

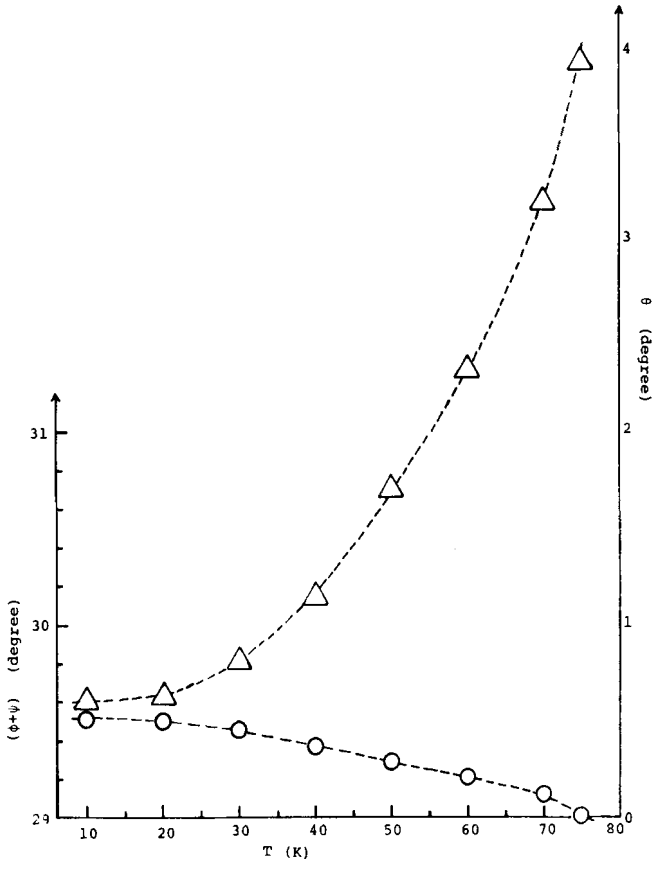

FIGURE 4 Calculated temperature dependence of $(\phi + \psi)$ and θ. ○: $(\phi + \psi)$ △ : θ

α-CF_4. However, a slight temperature dependence of θ is seen from a temperature dependence of the lattice parameters, and causes an arbitrary calculation of the static lattice energy (Figure 2) and the zero point energy (Figure 3). We estimated the temperature dependences of θ, ϕ, and ψ so as to fit the temperature dependence of the lattice parameters by assuming r(C-F) $= \sqrt{3} \times 0.1765 \times 4.320$ A, and the result is shown in Figure 4. It seems more realistic for α-CF_4 to consider a temperature dependence of θ than to be zero degree.

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