

The Three Phases of Solid Deuterated Methane

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Abstract

By using a computer simulation technique, the three phases of solid deuterated methane have been interpreted in terms of the changes in dynamical behaviour of the CD_4 molecule located at the centre of a tetragonal unit cell having dimensions $a = b = 5.872 \text{ \AA}$ and $c = 5.95 \text{ \AA}$. The central molecule is influenced by twelve nearest neighbour molecules situated at the mid-points of the sides of the unit cell. The rotational motion of the tetrahedral molecule is described by the appropriate algorithm equations, as well as by the well-known Lennard-Jones potential. The present calculations reveal two transition regions separating three distinct phases, which can be attributed to the two λ -type transitions depicted by Clusius *et al.* (1937). Making use of the (dimensionless) average rotational kinetic energy corresponding to the lower transition region, $\langle E_{\text{RK}} \rangle_{\text{critical}} = 4.8$, and the experimental libration frequency 6700 m^{-1} reported by Savoie and Fournier (1970), the transition temperature turns out to be 21.2 K , close to the experimentally observed value.

1. Introduction

Clusius *et al.* (1937) carried out specific heat measurements in solid deuterated methane at low temperatures and observed two anomalies in the specific heat data at around 22 and 27 K . Later work by Colwell *et al.* (1963) confirmed the occurrence of these two λ -type transitions while studying the thermodynamic properties of CD_4 . Consequently, one can correlate these anomalies with the existence of three phases which are usually designated I, II and III in order of decreasing temperature. In other words, the deuterated methane crystal is said to undergo the following transformations:



James and Keenan (1959) developed a theory to account for the existence of three phases in terms of the various symmetries by considering interactions between CD_4 molecules in the classical molecular field approximation. Press (1972) studied these phase transitions in deuterated methane by means of coherent neutron scattering and noticed a drop in the neutron intensity at 27 K corresponding to reflection (531) and also at 22.1 K for reflection (321). This type of study also supports the existence of three phases.

It is a well established fact that optical birefringence is a very useful technique for obtaining information on small distortions from symmetrical structures. Clusius

and Popp (1940) showed heavy methane (CD_4) to be weakly birefringent for the low temperature phase III. Later Ballik *et al.* (1973) carried out experiments on optical birefringence in solid CD_4 using a more advanced experimental arrangement and observed a birefringence of magnitude $\approx 4 \times 10^{-4}$. Surprisingly, light methane (CH_4) does not show any birefringence. The above experimental observations corresponding to a temperature less than 22 K show the deuterated methane crystal to be anisotropic and devoid of cubic symmetry.

An infrared spectroscopic study of solid deuterated methane by Savitsky and Hornig (1962) indicated that the spectral characteristics of phase III correspond to a complex, rather than simple, structure. A later study of the infrared spectra by Chapados and Cabana (1970) also indicated a structure of CD_4 with lower symmetry and with the absence of a three-fold axis of symmetry.

An X-ray diffraction study by Bol'shutkin *et al.* (1971) pointed to the occurrence of a small tetragonal distortion for a temperature less than 22.2 K in solid deuterated methane. However, the deviation from a cubic lattice was only slight and the ratio of two sides c/a came out to be 1.013 at 10 K.

In our earlier work on deuterated methane (Kansal and Trikha 1993b) we assumed that a small distortion from cubic symmetry in CD_4 would not affect the dynamics of the central molecule and the calculations were carried out by considering the structure suggested by Press *et al.* (1970). Since we could not get three phases as desired, we were therefore tempted to incorporate the small distortion in the cubic unit cell in the hope that it would shed light on the splitting of λ -type transitions. We proposed a tetragonal unit cell for deuterated methane to carry out the calculation.

In the present work, we find three phases of solid deuterated methane which are based upon calculations performed with great precision. A detailed analysis of direction cosine data for the rotating central molecule reveals a distinct dynamical behaviour pertaining to different phases. The mathematical formalism and method of solution used were reported in our previous studies.

2. Discussion and Results

In the present model we consider a tetragonal unit cell of solid deuterated methane having a ratio $c/a = 1.013$, as reported in the X-ray structural investigation by Bol'shutkin *et al.* (1971). We assume the dimensions of the unit cell to be $a = b = 5.872 \text{ \AA}$ along the x and y axes and $c = 5.95 \text{ \AA}$ along the z axis. Consequently, the nearest neighbour distance in the xz and yz planes turns out to be $4.207 \text{ \AA}$. The central CD_4 molecule is not located symmetrically with respect to all 12 neighbours situated at the mid-points of the sides of the tetragonal unit cell. For details of the structure see our earlier work (Kansal and Trikha 1993a). The well known Lennard-Jones potential has been used to represent the molecular interaction. The angular momentum imparted to the central molecule along the z axis varies from 1.0 to 20.0 (in reduced units of $10^{-34} \text{ kg m}^2 \text{ s}^{-1}$). The calculations are performed for 10 000 time steps having a value $\Delta t = 0.001$ (in reduced units of 10^{-13} s). The moment of inertia of CD_4 is taken to be $15.88 \times 10^{-47} \text{ kg m}^2$.

In Fig. 1 the variation of the average total energy $\langle E \rangle$ (the sum of the rotational kinetic and potential energy) is shown against the average rotational kinetic energy $\langle E_{\text{RK}} \rangle$ corresponding to the tetragonal structure of CD_4 . Unlike our

earlier study with the cubic structure, we note three distinct lines with different slopes. The calculations were repeated with an increased number of time steps from 10 000 to 50 000 to verify the existence of these three distinct lines. The values of $\langle E \rangle$ and $\langle E_{RK} \rangle$ averaged over 50 000 time steps turn out to be nearly same, so the energy conservation condition of the system is not violated. Here we refer to the phases I, II and III in order of decreasing temperature. Phase I corresponds to higher values of angular momentum ≥ 17.0 , whereas phases II and III are obtained by imparting angular momentum in the ranges 12.0 – 16.0 and 1.0 – 11.0 respectively. The calculations show two transition regions corresponding to different values of critical rotational kinetic energy. One can correlate these discontinuities with the two λ -type transitions in the specific heat data obtained by Clusius *et al.*

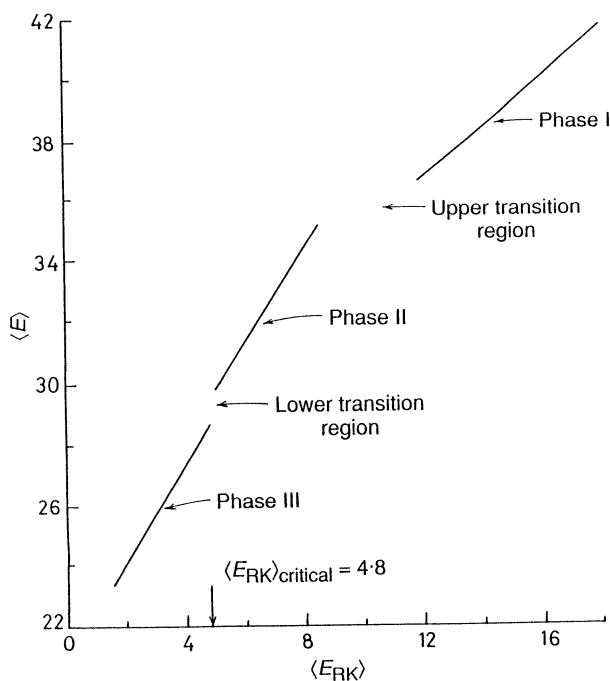


Fig. 1. Average total energy $\langle E \rangle$ versus average rotational kinetic energy $\langle E_{RK} \rangle$ (in reduced units) for the central CD_4 molecule subject to the Lennard-Jones potential.

To investigate the effect of structural change on the dynamics of the central CD_4 molecule at low temperatures, we have made use of the direction cosine data recorded at each time-step to calculate the various angles θ_x , θ_y and θ_z (between the fixed and the moving frame of reference). In Fig. 2 we show the variation of these angles against time for angular momentum 4.0 (phase III), corresponding to the tetragonal as well as cubic structure. The angles shown for the cubic structure are taken from our earlier work (Kansal and Trikha 1993*b*). We observe that the path followed by the central molecule is different in the two cases while undergoing hindered torsional oscillations. This may be due to the

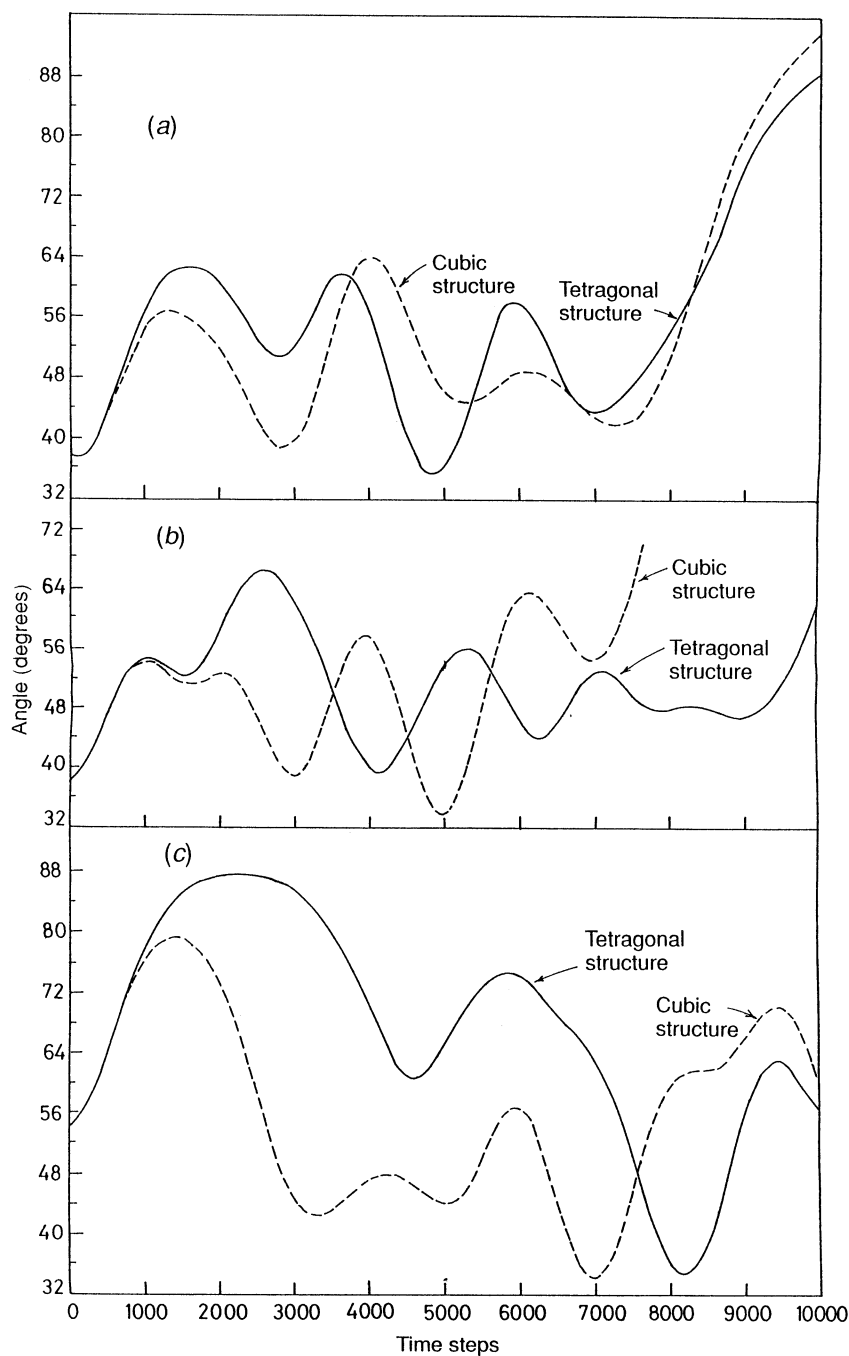


Fig. 2. Variation of angles (a) θ_x (between fixed x and moving x' axes), (b) θ_y (between fixed y and moving y' axes) and (c) θ_z (between fixed z and moving z' axes) as a function of time for the tetragonal and the cubic structures corresponding to angular momentum 4.0.

asymmetry of the central molecule with respect to its neighbours resulting from the tetragonal structure.

In Fig. 3 the variation of θ_z against time is shown for phases I, II and III, corresponding to the tetragonal structure. The angle varies from 47° to 64° for phase I, from 40° to 165° for phase II and from 33° to 67° for phase III.

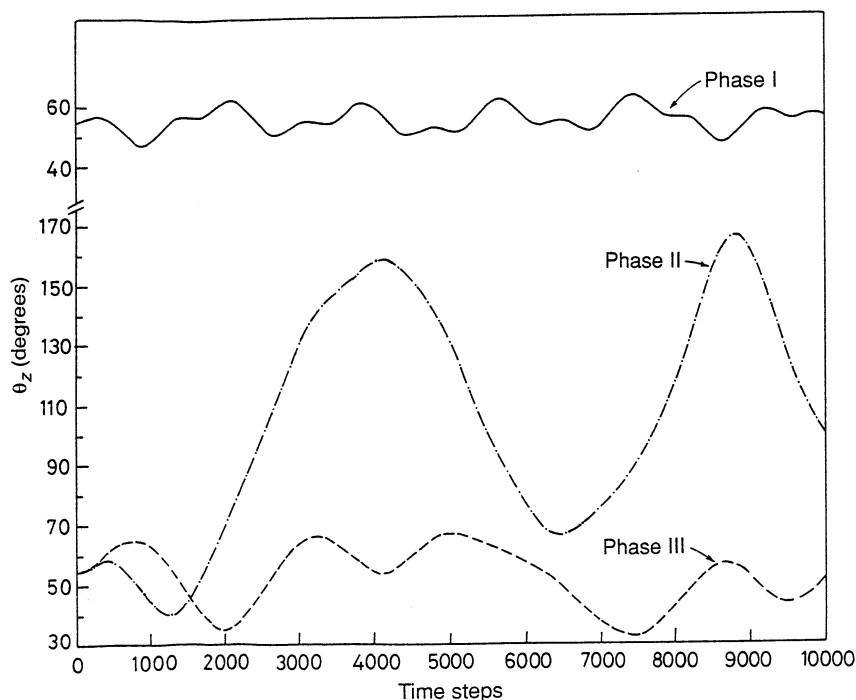


Fig. 3. Variation of θ_z between the fixed z axis and moving z' axis associated with the rotating central CD_4 molecule, as a function of time for angular momenta of 8.0, 15.0 and 20.0 (corresponding to phases III, II and I respectively), subject to the Lennard-Jones potential.

Using the libration frequency of 6700 m^{-1} , as reported by Savoie and Fournier (1970) on the basis of their far infrared spectroscopic study, and the computed value of $\langle E_{\text{RK}} \rangle_{\text{critical}} = 4.8$ pertaining to the lower transition region, the transition temperature of the deuterated methane system turns out to be 21.2 K , which is in good agreement with the experimental value.

3. Dynamics of the Three Phases

The dynamics of the central molecule corresponding to the three phases can be understood by analysing the direction cosine data recorded at each time step:

- (i) In phase III, the central molecule performs hindered torsional oscillations accompanied by relatively large nutational motion. As a result, the period of oscillation is not well defined and we have to make use of the experimental libration frequency.
- (ii) In phase II, the central molecule experiences maximum nutational motion as indicated by the maximum variation of θ_z shown in Fig. 3 (middle

curve). A change in the plane of oscillation also occurs. We note that this phase resembles the stepwise transition region depicted in Fig. 1a of our earlier work on the cubic structure (Kansal and Trikha 1993b).

- (iii) In phase I, the amplitude of nutational motion is nearly 17° , about the same as for the cubic structure. This indicates that, when the central molecule acquires enough energy to overcome the potential barrier, it is irrelevant whether the neighbour molecules are situated at the mid-points of the sides of a cubic or tetragonal unit cell.

4. Conclusions

The molecular dynamics calculation on the deuterated methane system with tetragonal structure leads us to conclude that a small distortion in the cubic unit cell is responsible for the splitting of λ -type transitions. However, no plausible theoretical explanation seems to have been put forward.

It may be mentioned that a similar situation exists in the case of the ammonium bromide system where the distortion from the cubic structure is very small, $\approx 0.4\%$. Two anomalous λ -type peaks in the specific heat data at 108 and 235 K were observed by Sorai *et al.* (1965). Though the peaks are widely separated, it would be worth while performing a similar calculation taking into account the distortion from cubic structure to account for the different phases.

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