

# Molecular Dynamics of the Phase Transition in Deuteroammonium Chloride

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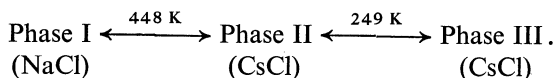
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## Abstract

Computer simulation studies have been made to investigate the phase transition in  $\text{ND}_4\text{Cl}$  at low temperature. Two different types of potential have been used to represent the interaction between  $\text{ND}_4^+$  and  $\text{Cl}^-$ : (i) the Lennard Jones potential and (ii) the twelfth inverse power or  $r^{-12}$  repulsive potential. The present study reveals the occurrence of a phase transition in  $\text{ND}_4\text{Cl}$  in a well-defined region. The Lennard Jones potential appears to be more appropriate in depicting the two well-defined phases known as II and III in the literature. The energy pattern curves obtained in this study give us the nature of the rotational behaviour of  $\text{ND}_4^+$  before and after the transition at 249 K. The libration frequency of the  $\text{ND}_4^+$  ion is estimated to be of the order of  $130\text{ cm}^{-1}$ .

## 1. Introduction

Deuteroammonium chloride is known to occur in three phases, namely



Recently Garland and Baloga (1977) have observed the  $\lambda$ -type transition of the specific heat in  $\text{ND}_4\text{Cl}$  at one atmosphere pressure, corresponding to  $249.6\text{ K}$ , using the high resolution a.c. calorimeter technique. Other measurements of, for example, the dielectric constant, the coefficient of expansion and piezoelectric effects have also been found to exhibit discontinuities in other ammonium halides. Experimentally it has generally proved difficult to decide whether the transitions in ammonium halides at low temperature are of first or second order.

To explain the nature of the specific heat anomaly, two different points of view have been suggested. In one of these, due to Pauling (1930), the tetrahedral ammonium ion is believed to be executing torsional oscillations at low temperatures in the potential well created by the halogen ions. With a rise in temperature the amplitude of these oscillations is supposed to increase until the ions acquire sufficient energy to overcome the potential barrier and go into free rotation. According to Frenkel (1935), the anomaly in the specific heat could be explained in terms of the transition from the state in which the  $\text{NH}_4^+$  ions are ordered, with one of the two possible orientations, to a state in which the ions are disordered (i.e. distributed randomly). Frenkel's suggestion has been further supported by NMR studies as well as by considerations of thermodynamics.

However, studies of the neutron spectra in ammonium halides by Woods *et al.* (1961), Venkataraman *et al.* (1963) and Bajorek *et al.* (1965) suggested the idea of hindered and free rotation of the ammonium ion at low and high temperatures respectively. At low temperatures sharp peaks in the spectra are obtained, some of which might be interpreted as being caused by torsional vibration, whereas at higher temperatures the broad distribution of scattered neutrons in the spectra suggests the possibility of free rotations of the ammonium ions.

In the present paper an attempt is made to explain the phase II  $\leftrightarrow$  phase III transition at 249 K in terms of the change in rotational behaviour of the  $\text{ND}_4^+$  ion by using a computer simulation technique. Although Pauling's (1930) view concerning the explanation of the specific heat anomaly is discarded from considerations of the entropy change, computer simulation studies here are nevertheless quite in agreement with his hypothesis. Earlier, Trikha and Jain (1975) reported work on the phase transition in  $\text{NH}_4\text{Cl}$  using this approach.

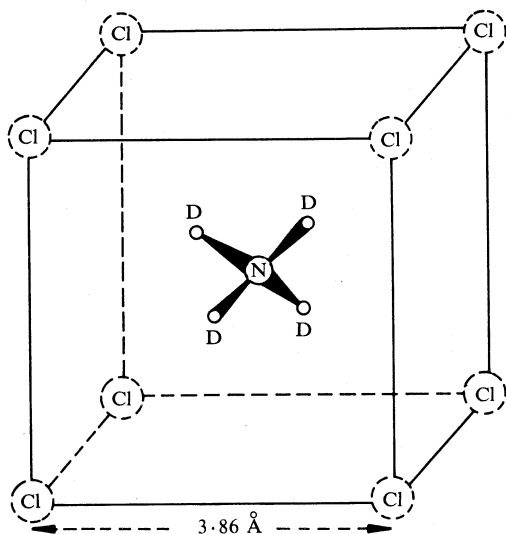


Fig. 1. Unit cell of  $\text{ND}_4\text{Cl}$  having the CsCl type structure.

The crystal structure of  $\text{ND}_4\text{Cl}$  is known from the neutron diffraction study by Goldschmidt and Hurst (1951). In Fig. 1 we show the unit cell of deuterioammonium chloride; the four deuterium atoms are arranged tetrahedrally about the nitrogen atom (at the origin) in positions  $xxx$ ,  $x\bar{x}\bar{x}$ ,  $\bar{x}\bar{x}x$  and  $\bar{x}x\bar{x}$ , with  $x$  equal to  $r/(3a_0)^{\frac{1}{3}}$ , where  $r = 1.03 \text{ \AA}$  is known as the bond length and  $a_0 = 3.86 \text{ \AA}$  is the side of the unit cell ( $1 \text{ \AA} \equiv 10^{-10} \text{ m}$ ). The moment of inertia of  $\text{ND}_4^+$  is  $14.2 \times 10^{-40} \text{ g cm}^2$ . The nearest neighbours are the eight chlorine atoms situated at the vertices of the unit cell.

## 2. Rotating Model and the Interacting Potential

The precise nature of the molecular rotation of  $\text{ND}_4^+$  corresponding to the phase II  $\leftrightarrow$  phase III transition is not yet clear and is still the subject of detailed study, both experimentally as well as theoretically. In the present study, in order to avoid excessive computational work, we confine ourselves to a single unit cell and the nearest neighbour interaction. In reality one must consider all possible inter-

actions between ND<sub>4</sub><sup>+</sup> ions situated at different unit cells, which would involve considerable computational time. However, we feel that the rotational behaviour of ND<sub>4</sub><sup>+</sup> in a single unit cell is a fairly true representation of the whole ND<sub>4</sub>Cl system. We propose a model in which, for simplicity, ND<sub>4</sub><sup>+</sup> is assumed to be rotating about the vertical axis, an assumption based on the results of neutron scattering experiments on the rotational dynamics of molecules. The rotational motion of the ND<sub>4</sub><sup>+</sup> ion is governed by a proper algorithm equation, as well as by the interatomic forces of its nearest neighbours, and the rotational kinetic energy of the system is calculated for different values of the angular momenta.

The potential energy of the dynamical system is computed by considering the interaction between ND<sub>4</sub><sup>+</sup> and Cl<sup>-</sup>, which can be represented by the well-known Lennard Jones potential

$$\Phi(r) = 4\epsilon\{(\sigma/r)^{12} - (\sigma/r)^6\}, \quad (1)$$

where  $\sigma$  represents the distance of closest approach ( $=3.5 \text{ \AA}$ ). For the second case we drop the attractive term  $(\sigma/r)^6$  in the interatomic potential. The electrostatic interaction has not been taken into consideration.

### 3. Algorithm for the Rotational Motion

Let  $I_1(t)$ ,  $I_2(t)$  and  $I_3(t)$  be the directions of the principal axes of the ND<sub>4</sub><sup>+</sup> ion at time  $t$  and  $I_1$ ,  $I_2$  and  $I_3$  be the principal moments of inertia. The angular velocity  $W$  and angular momentum  $\Omega$  of ND<sub>4</sub><sup>+</sup> are written

$$W(t) = \omega_1(t)I_1(t) + \omega_2(t)I_2(t) + \omega_3(t)I_3(t), \quad (2)$$

$$\Omega(t) = I_1\omega_1(t)I_1(t) + I_2\omega_2(t)I_2(t) + I_3\omega_3(t)I_3(t), \quad (3)$$

where  $\omega_1(t)$ ,  $\omega_2(t)$  and  $\omega_3(t)$  are the components of the angular velocity  $W(t)$ .

The equations of motion to be solved are

$$\dot{I}_\alpha(t) = W(t) \times I_\alpha(t), \quad (4)$$

$$\dot{\Omega}(t) = \tau(t), \quad (5)$$

where  $\tau$  is the torque exerted on each molecule by its environment and  $\alpha$  ( $=1, 2, 3$ ) refers to the direction of the principal axes.

In the present case we use an algorithm which is very similar to that in conventional studies of molecular dynamics in liquids. The rotational motion of ND<sub>4</sub><sup>+</sup> is governed by the algorithm equations

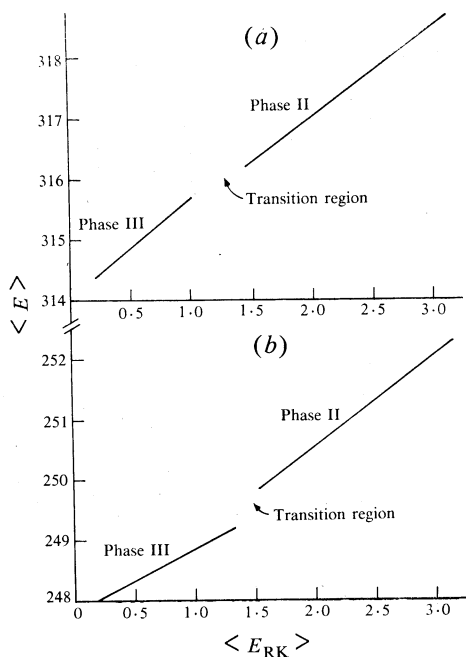
$$I_\alpha(t+\Delta t) = I_\alpha(t) + \dot{I}_\alpha(t)\Delta t + \frac{1}{6}\{4\ddot{I}_\alpha(t) - \ddot{I}_\alpha(t-\Delta t)\}\Delta t^2, \quad (6)$$

$$\Omega(t+\Delta t) = \Omega(t) + \frac{1}{6}\{2\tau(t+\Delta t) + 5\tau(t) - \tau(t-\Delta t)\}\Delta t, \quad (7)$$

where  $\dot{I}_\alpha(t)$  and  $\ddot{I}_\alpha(t)$  are the first and second time derivatives of the direction cosines respectively. The only complication in the present case is that we have the additional constraint that  $I_\alpha(t)$  are orthogonal unit vectors. Further, we write

$$W(t) = I^{-1} \cdot \Omega(t), \quad (8)$$

where  $\mathbf{I}$  denotes the inertia tensor. The algorithm given by equations (6) and (7) has been found to give both excellent stability and energy conservation over long periods of time, which are the necessary conditions for this type of computation.



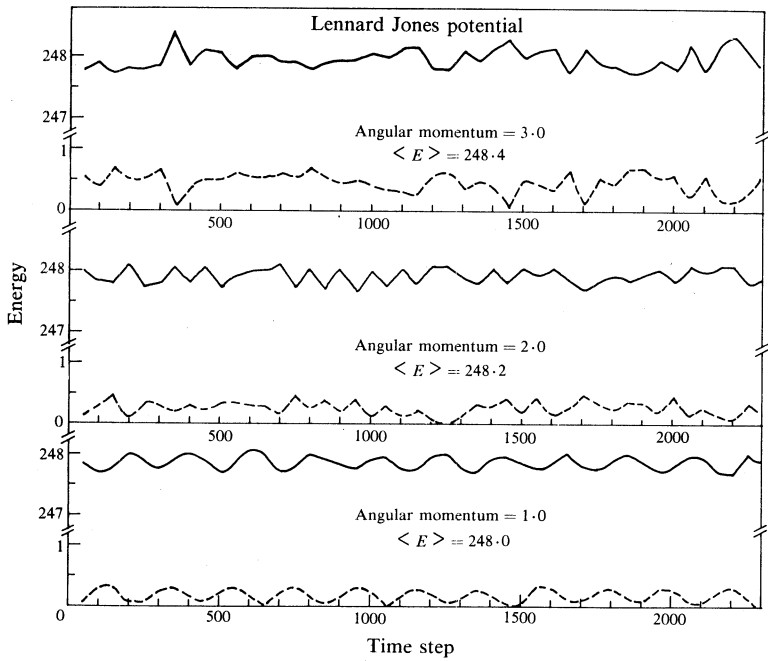
**Fig. 2.** Average total energy as a function of the rotational kinetic energy (in reduced units) for the  $\text{ND}_4^+$  ion under the influence of (a) the  $r^{-12}$  repulsive potential and (b) the Lennard Jones potential.

#### 4. Results and Discussion

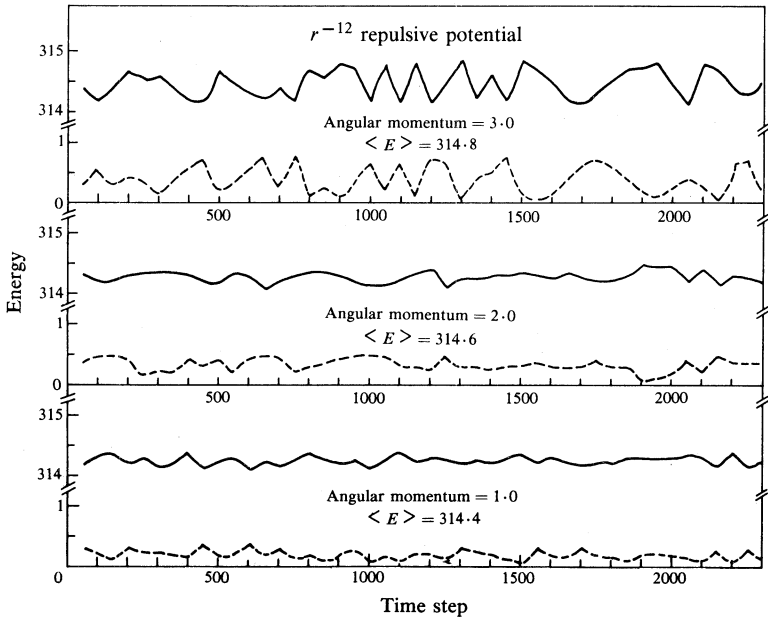
In the present analysis the angular momentum of the  $\text{ND}_4^+$  ion is gradually increased to study its rotational motion in the field of eight chlorine atoms. The rotational kinetic energy of the system is computed for different values of angular momentum in the range 1.0 to 10.0 (in reduced units).

In Fig. 2 the variation of the average total energy  $\langle E \rangle$  is shown as a function of the average rotational kinetic energy  $\langle E_{\text{RK}} \rangle$  of the system for 5000 time steps with  $\Delta t = 0.05$ , corresponding to (a) the  $r^{-12}$  repulsive potential and (b) the Lennard Jones potential. In each case, the two solid lines of different slopes correspond to the two phases II and III in  $\text{ND}_4\text{Cl}$ . These phases are well separated by a transition region. Here phase III corresponds to lower values of  $\langle E \rangle$  and  $\langle E_{\text{RK}} \rangle$  before the transition, and phase II to higher values of  $\langle E \rangle$  and  $\langle E_{\text{RK}} \rangle$  after the transition. A comparison of the two potentials indicates that the Lennard Jones force is more appropriate in depicting the two well-defined phases.

In Fig. 3 we plot the potential energy (solid curves) and the rotational kinetic energy (dashed curves) as a function of time for the angular momenta indicated (in reduced units) for the Lennard Jones potential. In each case the potential energy is found to dominate the rotational kinetic energy. It is observed that the variation of the two energies with respect to time is more or less of the same type indicating the ordered motion of the  $\text{ND}_4^+$  ion under the influence of its neighbours. This system corresponds to the phase III shown in Fig. 2b.



**Fig. 3.** Potential energy (solid curves) and rotational kinetic energy (dashed curves) as a function of time for the ND<sub>4</sub><sup>+</sup> ion having angular momenta 1.0, 2.0 and 3.0 (in reduced units) with the Lennard Jones potential. The average energy in each case is indicated.



**Fig. 4.** As for Fig. 3, but for the  $r^{-12}$  repulsive potential.

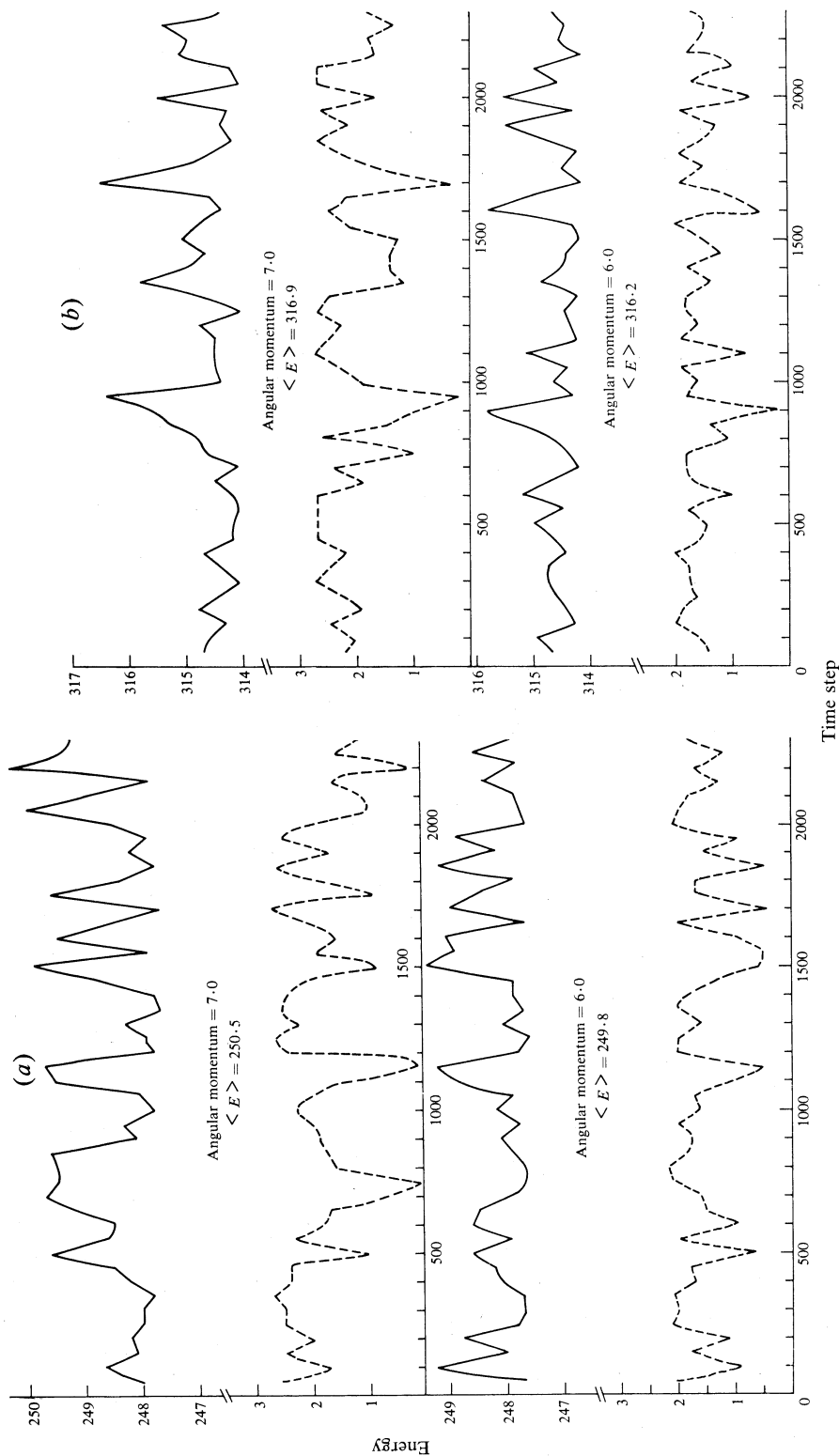


Fig. 5. Potential energy (solid curves) and rotational kinetic energy (dashed curves) as a function of time for the  $\text{ND}_4^+$  ion having angular momenta 7.0 and 6.0 (in reduced units) for (a) the Lennard Jones potential and (b) the  $r^{-12}$  repulsive potential. The average energy in each case is indicated.

In Fig. 4 we plot energy as a function of time for the  $r^{-12}$  repulsive potential. In this case the energy pattern curves are again more or less similar indicating again the ordered motion of the  $\text{ND}_4^+$  ion. The magnitude of the potential energy is increased here compared with the Lennard Jones potential because the attractive  $r^{-6}$  term has been omitted. This system corresponds to the phase III shown in Fig. 2a.

In Fig. 5 we show the energy pattern curves corresponding to angular momenta 7.0 and 6.0 for (a) the Lennard Jones potential and (b) the  $r^{-12}$  repulsive potential. Since all these energy pattern curves are different for different angular momentum imparted to the  $\text{ND}_4^+$  ion about the z-axis, this situation therefore corresponds to phase II. The motion of  $\text{ND}_4^+$  becomes quite complex, consistent with it having free motion.

## 5. Conclusions

We draw the following conclusions from this work:

- (1) The present rotating model of  $\text{ND}_4^+$  supports the hypothesis of Pauling (1930) for the explanation of the specific heat anomaly at 249 K.
- (2) The computed libration frequency of  $\text{ND}_4^+$  comes out to be  $\sim 130 \text{ cm}^{-1}$  which is nearly half the value of  $280 \text{ cm}^{-1}$  quoted by Hüller and Kane (1974). The discrepancy can be attributed to the fact that in the present model  $\text{ND}_4^+$  rotates through  $360^\circ$  even in phase III which has some type of hindered rotation whereas, in reality,  $\text{ND}_4^+$  undergoes torsional oscillation where the angle of rotation may be much less than  $45^\circ$ . In phase II,  $\text{ND}_4^+$  undergoes some kind of free rotation through  $360^\circ$  and, therefore, the present model of  $\text{ND}_4^+$  is quite close to reality.
- (3) From the energy pattern curves we notice that with an increase of temperature the  $\text{ND}_4^+$  ion is also subject to vibrational motion. The tumbling motion is the combined effect of rotational as well as vibrational motion at higher temperatures.
- (4) The Lennard Jones potential appears to be much more effective in predicting phases II and III than the  $r^{-12}$  repulsive potential.
- (5) Since we have assumed the structure of  $\text{ND}_4\text{Cl}$  to be of CsCl type in our computational work, the discontinuity in the  $\langle E \rangle$  versus  $\langle E_{\text{RK}} \rangle$  curve therefore corresponds to phases II and III of  $\text{ND}_4\text{Cl}$ .

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