

Observation of relaxation of molecular spins in CH₄ and CD₄ crystals in thermal conductivity experiment

Elwira Pisarska, Piotr Stachowiak, and Andrzej Jeżowski

*Institute for Low Temperatures and Structure Research, Polish Academy of Sciences
PN 1410, 50-950 Wrocław, Poland
E-mail: e.pisarska@int.pan.wroc.pl*

Received November 7, 2006.

The paper reports preliminary results on the kinetics of the molecular spin conversion in solid methane (CH₄) and deuterated methane (CD₄), obtained through thermal conductivity measurements in the temperature range 2–10 K.

PACS: **63.20.-e** Phonons in crystal lattices;
66.70.+f Nonelectronic thermal conduction and heat-pulse propagation in solids; thermal waves.

Keywords: organic compounds, nuclear spin conversion rate, thermal conductivity, phonons.

Introduction

Methane (CH₄) is a hydrocarbon molecule that consists of a single carbon atom (placed at the center) bonded to four hydrogen atoms (at the tetrahedron). This simplest hydrocarbon is a solid at 90.66 K at equilibrium vapor pressure, and displays unchanged crystallographic structure down to 20.4 K. In this structure, called phase I, the tetrahedral molecules are orientationally disordered, performing rotations which do not show any long-range correlation. The temperature 20.4 K is the temperature of phase transition to phase II, which structure is illustrated in Fig. 1. There are eight sublattices: six orientationally ordered molecules, occupy sites of dihedral symmetry (D_{2d}) performing collective librations, and two orientationally disordered molecules, rotating almost freely, occupy sites of octahedral symmetry (O_h) where the octupole fields, due to neighboring molecules influence, cancel exactly. Solid CH₄ undergoes one phase transitions, whereas the deuterated methane exhibits one more transition. The deuterated methane solidifies at equilibrium vapor pressure at 89.78 K and exists in the phase identical to phase I of CH₄, down to temperature 27.0 K. Similarly as CH₄, solid deuterated methane exhibits a phase transition to the eight-sublattice partially orientationally ordered state at 27.0 K. Upon further cooling, the crystal undergoes a phase transition, at 22.1 K, to phase III with a complete long-range orientational order.

Methane and deuterated methane molecules in their ground electronic and vibrational state may be classified into three distinct spin species, according to the representation of the tetrahedral group (A, T, or E) to which their orientational wave functions belong. Each spin species is

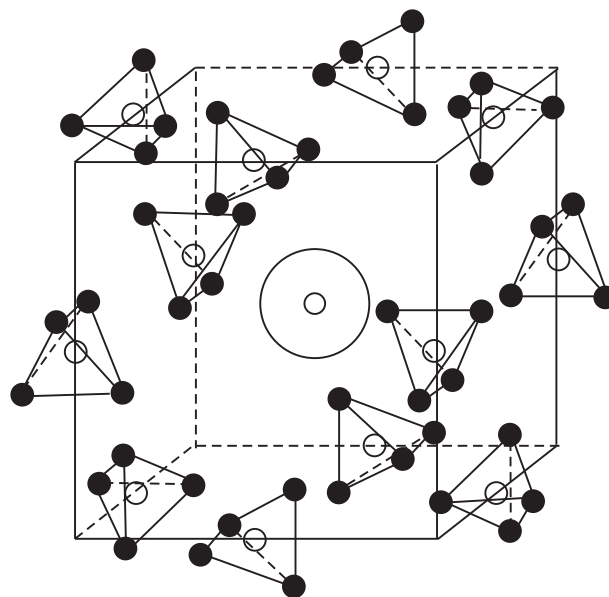


Fig. 1. The structure of CH₄ in phase II. Tetrahedra represent the 75% of molecules which are orientationally ordered in the structure. The circle shows a CH₄ molecule at the site where molecular fields cancel for symmetry reason, which enables almost free rotation of the molecule.

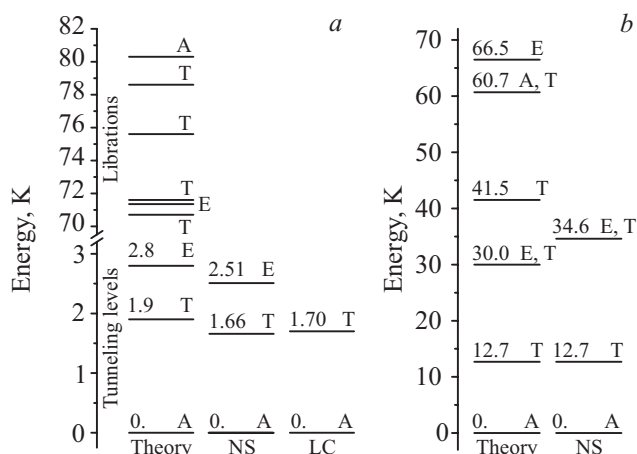


Fig. 2. Low-lying energy levels for different spin modifications of CH₄ molecules: *a* — orientationally ordered molecules, *b* — orientationally disordered molecules. Theory — the theoretical values from [1], NS — obtained from neutron scattering measurements [2], LC — from paramagnetic level-crossing experiment [3].

associated with a unique value of the total nuclear-spin quantum number I (in case of methane: A with $I=2$, T with $I=1$, and E with $I=0$, and in case of deuterated methane: A with $I=4$, T with $I=2$, and E with $I=0$) and has distinct molecule ground-state energy. The energy levels assigned to molecules on the disordered (O_h) and ordered (D_2d) sublattice in phase II of solid CH₄ are shown in Fig. 2.

The occupancy of each state is a function of temperature; after a change of the temperature at slowly reaches its equilibrium value due to the slow process of spin conversion. Several experiments have shown that this conversion occurs between nuclear spin symmetry species in solid methane (CH₄) [4–15]. At the same time, there are few reports where the conversion in solid deuterated methane (CD₄) was observed [17,18]. In these measurements, the nuclear spin conversion was detected in CD₄ molecules embedded in krypton matrix.

In this paper, the results of study of conversion rate in the solid CD₄ and CH₄ at temperatures 2–10 K by using the thermal conductivity technique are presented.

Experimental detail

The crystals were grown from CH₄ and CD₄ of high chemical purity. The concentration of foreign chemical admixtures did not exceed 5 ppm for CH₄, and 10 ppm for CD₄. The O₂ concentration was 0.00007%, for both CH₄ and CD₄. The experiments (crystal growth, thermal treatment and measurement) were performed in a cylindrical glass ampoule with an inner diameter of 4.2 mm and length of 36 mm. The samples were solidified from the

gas phase directly at a rate of 1.5 mm/h. At the beginning of the growth process the ampoule was kept at a temperature just below the triple point (with some temperature gradient applied). Next, the gas was admitted to the ampoule and lowering of the temperature of the bottom of ampoule began. During sample growth the gas pressure was maintained at 10 kPa. After growing, the sample was slowly (at a rate of 1 K/h) cooled down to the desired temperature. The temperature gradient along the crystal and the temperature of the sample were determined by two germanium thermometers separated by 12 mm. The error of measurement of the thermal conductivity was below 1%.

We have measured the conversion rate by observing changes of thermal conductivity in time, in the temperature interval 2–10 K. First, the samples were kept at a constant temperature between 10 and 16 K for a few hours. In the second step, they were further cooled down to the desired final temperature (the temperature of the sample was rapidly lowered after switching off the heater). Then, the thermal conductivity coefficient was recorded every 3 min. The time taken to determine a single thermal conductivity value was 5–10 h and it depended mainly on the final temperature (the lower temperature the longer measurements) and the isotope (the measurement time for CD₄ samples was considerably longer than for CH₄). The time dependence of the thermal conductivity of an exemplary sample is given in Fig. 3. The thermal conductivity (κ) increases continuously, and this change can be approximated by a sum of two exponential terms. The solid line in Fig. 3 is the fit of our data by the function

$$\kappa = \kappa_0 + A_1 \exp[-t/\tau_T] + A_2 \exp[-t/\tau_C], \quad (1)$$

where $\tau_T = 14$ min is the time necessary to achieve the temperature 1.4 K — starting from 10 K — after switching off the heater (this exponent would be observed in any

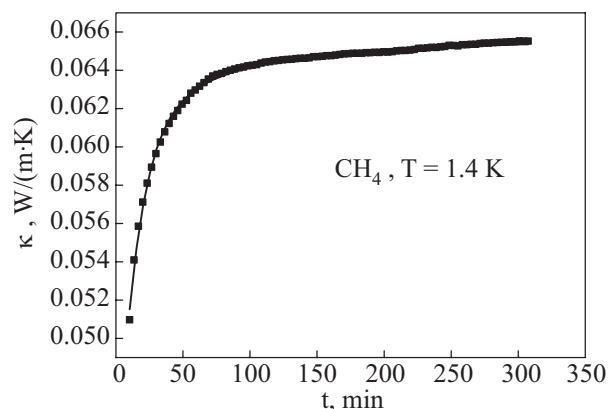


Fig. 3. Dependence of thermal conductivity on time after storing the sample at 10 K and rapid change of the temperature to 1.4 K (CH₄ sample). The solid line approximates the experimental data.

solid), and the thermal conductivity change corresponds to the spin conversion with the characteristic conversion time $\tau_C = 79$ min.

Results and discussion

The observed variations of the thermal conductivity in time is a result of two independent physical phenomena: the energy transfer to the phonon system, which accompanies the change of occupation of spin states, and the change of the influence of symmetry of the molecule wave function (spin state) on interaction with phonons. Both of these effects have the same relaxation time and the data obtained give the resulting conversion rate.

The conversion rate found by times measured for CD_4 and CH_4 crystals is shown in Fig. 4. The points have been obtained by fitting the collected data using Eq. (1). Our conversion measurements are in good agreement with results published earlier for CH_4 samples (see Fig. 4) [4–16]. The CD_4 results we have obtained for the first time.

In Fig. 4 the solid lines show the temperature dependence of the conversion rate α for CH_4 samples, following [4]:

$$\alpha = \frac{1}{\tau_C} = A(1 + 2n_k(E_1)) + B \exp\left(\frac{C}{T}\right),$$

$$n_k = \left[\exp\left(\frac{\omega}{k_\beta T}\right) - 1 \right]^{-1},$$

where the temperature dependence is given by the Bose factor of the phonons. The second term describes a thermally activated process. These two curves describe two characteristic rates: one associated with the conversion of free rotators (the samples were kept at a temperature above 4 K, where the occupation numbers of ordered molecules are near their high-temperature limit so the conversion behavior is dominated by the free rotators) and the other, with the conversion of ordered molecules (the samples were kept at a temperature below 2 K for a few days to let ordered molecules convert, then the samples were heated and the conversion rate measured). In case the conversion behavior is dominated by free rotators, the energy E_1 of the $0 \rightarrow 1$ transition is 12.4 K (see Fig. 2) and $A = (0.91 \pm 0.27) \text{ h}^{-1}$, $B = (42.6 \pm 9.3) \text{ h}^{-1}$, $C = (19.3 \pm 2.7) \text{ K}$. For the ordered molecules $E_1 = 1.7 \text{ K}$, $A = (0.024 \pm 0.003) \text{ h}^{-1}$, $B = (447 \pm 185) \text{ h}^{-1}$, $C = (44 \pm 4) \text{ K}^4$.

All our samples were kept at high temperature and κ was measured after a rapid cool down. Therefore, the temperature dependence of the transition rates of CH_4 similar to the dependence for free rotators was expected. For CD_4 the temperature dependence of the conversion rate is si-

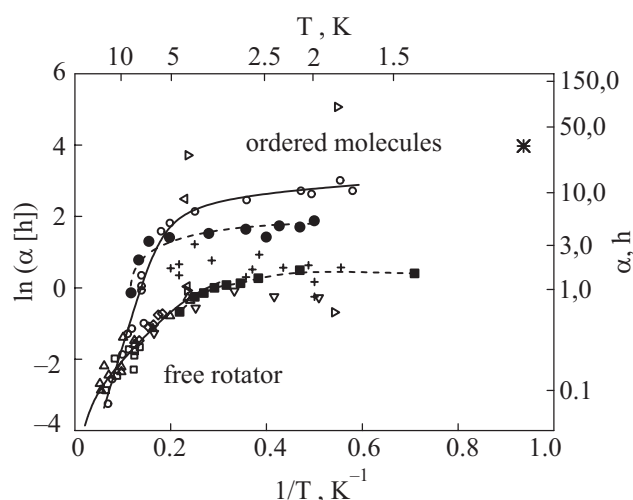


Fig. 4. Comparison between several conversion measurements (our data: CD_4 (●), CD_4 -Kr (3% of Kr) (■), CH_4 (□); data for CH_4 samples from: Grieger et al. [4] (○), Buchman et al. [5] (△), Higinbotham et al. [6] (▷), Lushington et al. [7] (◇), Colwell et al. [8–11] (□), Code et al. [12] (<), Piott et al. [13] (▽), Van Hecke et al. [14] (×), Runolfsson et al. [15] (*), Gorodilov et al. [16] (+)). The dashed lines are a guide to the eye only.

milar to that of the ordered one in the CH_4 . As noticed, CH_4 below 20.4 K in phase II has two sublattices differing in local symmetry. By choosing the initial and final temperatures, the conversion processes of free rotators and ordered molecules can be separated. In our experiment, the data relate to conversion rates of free rotators. In case of CD_4 below 22.1 K the crystal undergoes the phase transition to phase III with complete orientational order. Therefore, regardless of the choice of the initial and final temperatures, our data describe the conversion rate of the ordered molecules of CD_4 .

Concluding, the conversion rate in solidified methane and deuterated methane has been measured by observing changes of the thermal conductivity in time in the temperature range 2–10 K. The CH_4 samples, with regard to the crystallographic phase (phase II) and the measurement procedure, shows temperature dependence of the conversion rate dominated by the «free rotators». In the case of CD_4 samples the temperature dependence of the conversion rate shows that of «ordered molecules». This result is independent of the measurement procedure and is due to the fact that in the crystallographic phase (phase III) only orientationally ordered molecules exist.

The authors are grateful to Dr. A.I. Krivchikov for fruitful discussions. This work was supported by the Polish State Committee for Scientific Research.

1. Y. Kataoka, K. Okada, and T. Yamamoto, *Chem. Phys. Lett.* **19**, 365 (1973).
2. W. Press and A. Kollmar, *Solid State Commun.* **17**, 405 (1975).

3. H.A. Glättli and M. Eisenkremer, *Phys. Rev. Lett.* **28**, 871 (1972).
4. S. Grieger, H. Friedrich, B. Asmussen, K. Guckelsberger, D. Nettling, W. Press, and R. Scherm, *Z. Phys.* **B87**, 203 (1992).
5. S. Buchman, D. Candela, W.T. Vetterling, and R.V. Pound, *Phys. Rev.* **B26**, 1459 (1982).
6. J. Higinbotham, B.M. Wood, and R.F. Code, *Phys. Lett.* **A66**, 237 (1978).
7. K.J. Lushington and J.A. Morrison, *Can. J. Phys.* **55**, 1580 (1977).
8. J.H. Cowell and J.A. Morrison, *J. Chem. Phys.* **36**, 2223 (1962).
9. J.H. Cowell and J.A. Morrison, *J. Chem. Phys.* **39**, 635 (1963).
10. J.H. Cowell and J.A. Morrison, *J. Chem. Phys.* **42**, 3144 (1965).
11. J.H. Cowell, *J. Chem. Phys.* **51**, 3820 (1969).
12. R.F. Code and J. Higinbotham, *Can. J. Phys.* **54**, 1248 (1976).
13. J.E. Piott and W.D. McCormick, *Can. J. Phys.* **54**, 1784 (1976).
14. P. Van Hecke and L. Van Gerven, *Physica* **68**, 359 (1973).
15. Ö. Runolfsson and S. Mango, *Phys. Lett.* **A28**, 254 (1964).
16. B.Ya. Gorodilov, A.I. Krivchikov, and O.A. Korolyuk, *Fiz. Nizk. Temp.* **31**, 1158 (2005) [*Low Temp. Phys.* **31**, 884 (2005)].
17. M.I. Bagatskii, V.G. Manzhelii, D.A. Mashchenko, and V.V. Dudkin, *Fiz. Nizk. Temp.* **29**, 216 (2003) [*Low Temp. Phys.* **29**, 159 (2003)].
18. M.I. Bagatskii, V.G. Manzhelii, D.A. Mashchenko, and V.V. Dudkin, *Fiz. Nizk. Temp.* **29**, 1352 (2003) [*Low Temp. Phys.* **29**, 1028 (2003)].