Collective excitations of the quantum rotation motion of methane molecules in the solid state

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Abstract. The present study is aimed at elucidating of specific quantum mechanical properties of solid methane suggesting contribution of collective effects to the rotational motion of molecules. Analysis of NMR and EPR low temperature experiments of pure and doped solid methanes gives strong evidence of the hindered quantum rotation of CH4 and CD4 molecules even at liquid helium temperatures.

1. Introduction

In the beginning of the present century, it was commonly believed that the solid methane was studied as thoroughly as possible both experimentally and theoretically. It is worth noting, however, that until the end of the previous decade [1], the methane thermodynamics researches were mostly concentrated on the free molecules, i.e. the methane gas phase. The present article is aimed at elucidating hints in the methane physical properties which are specific of the quantum solid.

2. Peculiar properties of the solid methane and their analysis

The first experimental investigations of the solid methane were performed in the low temperature range – particularly, in the vicinity of the α-β phase transition at 20.48 K. These studies yielded certain peculiarities of the methane characteristics originated from its quantum properties. More specifically, the plasticity was found to increase drastically with temperature decreasing even in the range below 9 K where no thermal fluctuations occur [2] (figure 1).

In the EPR investigations [3, 4] of radicals matrix isolated in solid methanes, CH4 and CD4, at low temperatures when the host molecules are partially or fully ordered, the tunneling reorientation of the impurity molecules was discovered. With methyl, CH3, and formyl, HCO, radicals the reorientation motion was shown to be fast enough to average appreciably the hyperfine coupling tensor and g-tensor anisotropies. A numerical estimation gave the tunneling frequency of about 40 MHz even at the liquid helium temperature, 4.2 K [4]. The orientation tunneling was found to be temperature-assisted with frequency rising as the sample temperature was increased. It seems obvious that, in the closely-packed matrix with the orientation-ordered host molecules, the substitutionally trapped impurity molecules are able to rotate only if the methane molecules themselves perform correlated low temperature rotation. In such a case, the effective inertia of the radical, I, is expected to increase with the consequence of decreasing rotation constant. Indeed [4], in the solid deuterated methane, the constant B of the methyl
radical, CH$_{3}$, is decreased by 53% compared to the free molecule value, $B_{\text{free}} = 6.76$ K. Approximately the same reduction in $B_{\text{free}}$ is found for CH$_{3}$ in light methane, CH$_{4}$, matrix. Our analysis of the experimental data reveals that the methyl rotation constant is reduced for the radical in solid methanes to much more extent than in any other solid gas matrix.

Figure 1. Temperature dependence of the stationary creep rate for the solid methane and classical (without accounting for the quantum contributions) solid argon in the range 4 – 9 K [2].

Thus, the dynamics of the impurity methyl radical proves tunneling rotation of methane molecules in solid CH$_{4}$ and CD$_{4}$. It is reasonable assuming that seemingly to the methyl the matrix molecules would have exceptionally large effective inertias at low temperatures about 4.2 K.

In recent years, disparate studies have been published at a time showing that at high temperatures above 0.5$T_{\text{melt}}$ the methane crystal behaves abnormally. Concerning this staff, the reader is referred to publications by Tomita [5], Leont’eva [6], Prokhorov [7], Kirichek [8]. Such anomalies turned out to emerge in a number of experiments by other authors while received no explanation [9]. Interestingly, the working temperatures of the newly found methane abnormal physical properties in thermodynamics, spectroscopy, mechanics (plasticity, elasticity) and some others fall into the same range from 60 to 70 K [10]. In our studies, the quantum contributions to the methane properties were shown to last right to these high temperatures. An explanation is based on an assumption made for the first time in [11, 12] that due to the intermolecular coupling in the solid methane the rotation motion of particles should be considered to occur through excitations of the collective rotational degrees of freedom but not as the rotation of isolated molecules like in the gas phase. Such an approach is an accordance with results by Pauling [13] and is attributable to the solid methane between 20.48 K, the temperature of the orientation order-disorder transition, and the melting temperature. Pauling was first to bring attention to the potentialities of the model of collective rotational excitations in solid molecular methane.

The first experimental evidence of the molecular rotation in solid methane was obtained by Tomita [5] in nuclear magnetic resonance studies. The author discovered [5] that, in an unexpectedly narrow temperature range 60 – 65 K, the methane molecule reorientation changed from the hindered to the almost free rotation characteristic of the liquid state, figure 2.
Figure 2. Half-width of the NMR absorption resonance line, $\Delta H_{1/2}$, in solid methane. The figure evidences the line narrowing which is due to the dynamically averaged out local fields of the rotating molecules; according to Tomita [5]. The experimental curve shows a clear step at 60 K.

Later on, in the investigation of low frequency internal friction (LFIF) in solid methane [6], the experimental temperature curve showed a surprisingly intense peak in the same temperature range, Figure 3, which was far in excess of peaks observed in other cryocrystals had been studied before.

Figure 3. Solid methane. Temperature dependences of the low frequency internal friction $Q^{-1}$, red open circles, and squared frequency of the torsion oscillations $f^2$, blue solid triangles. The later parameter is proportional to the dynamical shear modulus $G$.

This work was referred to the publication by Kirichek and coauthors [8] on solid methane adhesion on different materials. The measurements showed similar temperature behavior for all probes under study with maxima around 60 K, figure 4.
Figure 4. Temperature dependencies [8] of shear stresses corresponding to the breaking point of the bond between solid methane and samples of different materials: black solid rhombs, aluminum alloy 7075; red solid squares, stainless steel; green solid triangles, polytetrafluoroethylene (PTFE).

Solid methane used as a hot neutron moderator shows [14] complicated defect recombination after being exposed to the ionizing irradiation: it happens in two different temperature ranges. The low-temperature one has a maximum around 20 K, while the high-temperature process takes place between 50 and 60 K. The same features, figure 5, shows thermally stimulated echo-electron emission of solid methane pre-irradiated with fast electrons [15]. Such a temperature behavior of the defect mobility may be explained in the model of the collective rotational degrees of freedom of the methane molecules in the solid phase [11].

Figure 5. Temperature dependencies of thermally stimulated echo-electron emission TSEE, red solid line, and post-desorption of solid methane or products of radiolysis, black solid line [15].
Temperature peculiarities in some other solid methane properties, including longitudinal and transverse sound velocity, molar volume, thermal expansion, heat capacity, were overviewed quite recently [10]. The new model of collective rotational excitations received a theoretical verification through analysis of the rotational heat capacity of the solid methane [11], figure 6. Here, the rotational temperature defined by the effective moment of inertia of an elementary excitation, $T_r = \frac{\hbar^2}{2I}$, is taken as the only parameter characterizing the rotational degrees of freedom of solid methane. This elementary excitation of collective rotational degrees of freedom of methane molecules was named “topon”. A temperature point $T_0$, figure 6, corresponding to the curve maximum may be considered as a boundary between the predominantly quantum and classical behavior of topons. To compare, classical solids show no maximum of the heat capacity dependence.

![Figure 6](image-url)  
Figure 6. Theoretical specific heat capacity (in relative units) of topons, C, plotted against the dimensionless temperature, $T/T_r$. When calculating the partition function, one hundred terms were saved [11].

3. Conclusion
Various physical properties of the solid methane were found to show abnormal temperature dependencies with specific features occupying the same temperature range of 60 - 65 K. Quantum effects markedly contribute to the methane properties in the whole temperature range of its solid state occurrence. Based on the analyzed peculiarities, a model of the collective rotational excitations of methane molecules was presented. The host molecules were proved to rotate in solid methane even at liquid helium temperatures.

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