Determination of Gaseous and Solid Methane Heat Capacity of the Rotational Properties

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Abstract

Rotational characteristics of methane molecules at various temperatures are the subject of this study. When it comes to the collective rotation of CH4 molecules, we previously proposed using a topon quasiparticle to capture the motion. The rotational heat capacity of methane in both gaseous and solid form is compensated for the effects of quantum physics. There are abnormalities between 60 and 70 K in the collective rotation of methane molecules, which is proven to be essentially quantum in nature. The high-temperature anomalies are studied in more depth than the low-temperature anomalies.

Keywords: *Solid methane, Anomalies, Gaseous, Temperature, Heat.*

I. INTRODUCTION

The lightest molecular crystal (hydrocarbon) is solid methane, which is produced by tetrahedral molecules of the CX4 type (symmetry 4-3m). Molecular methane is spherical in shape. Using NMR in 1953, scientists discovered that at 60 K, the rotation of solid methane molecules from the hindered to the more free, as they approached the liquid state, is dramatically different. The most significant finding in this study is that molecules in solid methane do not have the expected freezing of their rotational degrees of freedom.

Generally speaking, a specific temperature must be reached before the quantum essence of matter can be observed to show itself for each degree of freedom. It is the Debye temperature for phonons (vibrational degrees of freedom) in a crystal.

The rotating heat capacity has a distinctive maximum at temperature, but the vibrational heat capacity is a monotonic function of temperature. This is a significant qualitative difference. The rotational temperature of methane should be around 7.5 K if we start with the known value of the molecule's moment of inertia. According to methane spectroscopic evidence from the gas giants of the solar system, rotating temperatures of around 100 K are possible.

II. RESULTS

At a temperature of roughly 65 K, Tomita's groundbreaking experiment revealed a dramatic shift in the nature of the rotations of solid methane molecules. This is a startling revelation. As a first surprise, the existence of molecular rotations in the solid phase of methane despite the "ears" inhibiting molecular rotations is remarkable The sole property of the rotational component of heat capacity whose temperature dependence is non-monotonic, if we start with the idea that anomalies are linked with the rotation of molecules, is that it is. At a certain temperature, the maximum heat capacity is reached.

$$T_{rot} = \frac{\hbar^2}{2kT} \tag{1}$$

Where k is the Boltzmann constant

The rotational temperature T_{rot} is first calculated from the methane molecule's known properties using the formula (1). The relationship between the spherical top's moment of inertia and its radius

$$I = ma^2 = \frac{8}{3}ml^2 \tag{2}$$

Proton mass (m), distance (a) between methane molecules (h), and length (l) of carbon-hydrogen bond ($l = 1.093\ 10^{-10}$ m) are all included in this equation. Because of this, we are able to determine the methane molecule's moment of inertia

$$I = 5.324 \cdot 10^{-47}\ \text{kg} \cdot \text{m}^2. \tag{3}$$

Methane's moment of inertia has been measured experimentally to be 5.1710-47 kg m2. The rotational temperature of methane may be determined by replacing (3) with (1).

$$T_{\text{rot}} = 7.57\ K. \tag{4}$$

The rotational temperature is the temperature at which quantum effects begin to exhibit themselves clearly in the rotational degrees of freedom of methane molecules.

It is important to note that Tomita's effect occurs at temperatures that are an order of magnitude above the rotational temperature of gaseous methane. As a result, the rotational degrees of freedom of the methane molecules appear to follow classical statistics at a temperature of T=60 K. As a result, it was initially impossible to anticipate the appearance of quantum effects in rotational degrees of freedom at this temperature range.

It has been hypothesized that the characteristic seen by Tomita is connected to the quantum nature of methane molecules' crystalline rotating degrees of freedom. Molecular rotation in solids is made feasible by the tunnel effect; hence the effective moment of inertia of elementary excitations corresponding to the collectivization of rotational degrees of freedom of methane molecules should be entered into formula (1) instead of the molecule's moment. Due to the fact that elementary excitations (topons) have a significantly less inertia than the methane molecule, they are more likely to be stable.

Topon quasiparticle model is used to represent the rotating component of thermodynamic functions for solid methane in this example. It was in the late 1920s that the thermodynamics of an ideal quantum gas with molecular rotational degrees of freedom were developed. Tops in an ideal gas have a spindle-like heat capacity that depends on the temperature in a dimensionless way.

$$C_{\text{rot}} = f(\tau), \quad \tau = \frac{T}{T_{\text{rot}}}. \tag{5}$$

To determine how methane's rotational heat capacity changes with temperature, one must first identify the associated partition function.

$$Z=\sum_{n=0}^{\infty} g_n e^{-\frac{n(n+1)}{\tau}}, \qquad (6)$$

A dimensionless temperature,, is determined by the connection between n g and the multiplicity of degeneracy of nth state of the top (5).

Because the degeneracy multiplicity of a top depends on its state number, the thermodynamics of a given ideal quantum gas is unique in terms of dimensionless temperature. When compared to other degrees of freedom, the rotational heat capacity has a non-monotonic relationship with temperature, increasing until a specific maximum value is reached at $T=T_0$ before descending to zero at T0. Even at its classical maximum of very high temperatures, the rotational heat capacity has a bigger value than its classical value. To begin with, it should be emphasized that the occurrence of this maximum is a strong indication that this subject matter is quantum.

We'll review the present status of the theory of ideal methane gas before looking at the thermodynamic features of crystalline methane in the topon model. The theoretical estimations of the rotating component of the heat capacity of methane, considerably differ from one another.. The results of these computations may be found in the monographs and teaching materials that have been published thus far.

The spherical top's internal degrees of freedom dictate the symmetry type, which in turn determines the sort of link between the degeneracy multiplicity and the top's state number.

The formula may be used to determine the number of degenerate polyatomic molecules with big spins of identical nuclei.

$$g_n=(2n+1)^2. \qquad (7)$$

Two kinds of degeneracy exist here, both with multiplicity g = 2n+1. The first is related to the angular momentum of the molecule, whereas the second is related to the angular momentum of the molecule in space.

Methane, on the other hand, contains tiny spins of identical nuclei and is shaped like a spherical top due to its symmetry. According to the rotational partition function, the three spin-modifications that make up methane are $5A_2$, 1E, and $3F_1$. There isn't a straightforward formula of type (7) for figuring out degeneracy multiplicities. All three spin-modifications are taken into account in the low-temperature expansion of the statistical total of methane, although only the first few terms are considered. The probability of a transition between two spin-modifications is so minimal that the actual mixes of modifications are almost never in equilibrium when they exist.

An extension of the partition function involving methane with all three spin changes yields the first few terms in this expansion.

$$Z=5+9e^{-\left(\frac{2}{\tau}\right)}+25e^{-\left(\frac{6}{\tau}\right)}+77e^{-\left(\frac{12}{\tau}\right)}+117e^{-\left(\frac{20}{\tau}\right)}+\cdots. \qquad (8)$$

Up to n=4, all of the words are included in this expansion. When T T0, this phrase can be used. When TT0, the missing components do not decline as quickly as the stored ones do outside of the low-temperature zone, thus they can be included in a rough approximation (7), but this is only valid for big n. This leads us to the following formula for partitioning functions:

$$Z=\left[5+9e^{-\left(\frac{2}{\tau}\right)}+25e^{-\left(\frac{6}{\tau}\right)}+77e^{-\left(\frac{12}{\tau}\right)}+117e^{-\left(\frac{20}{\tau}\right)}\right]+\sum_{n=5}^{\infty}(2n+1)^2 e^{-\frac{n(n+1)}{\tau}}. \qquad (9)$$

Methane's thermal conductivity may be determined using the following equation:

$$\tilde{N}=\beta^2\frac{\partial^2(\ln Z)}{\partial\beta^2}, \qquad \beta=\frac{1}{\tau}. \qquad (10)$$

Figures 1 and 2 shows the numerical results of calculations on the temperature dependency of the rotational component of methane's heat capacity

T_0 is sensitive to the type of dependency of the degeneracy multiplicity on n in all computations, but a distinctive maximum of specific heat capacity is seen. In particular, increasing T_0=0.59 by three, or almost five times, by substituting equation (8) for (7) at the same rotational temperature of the ball top has the same effect. The sole explanation for this is that the symmetry qualities of these two peaks differ.

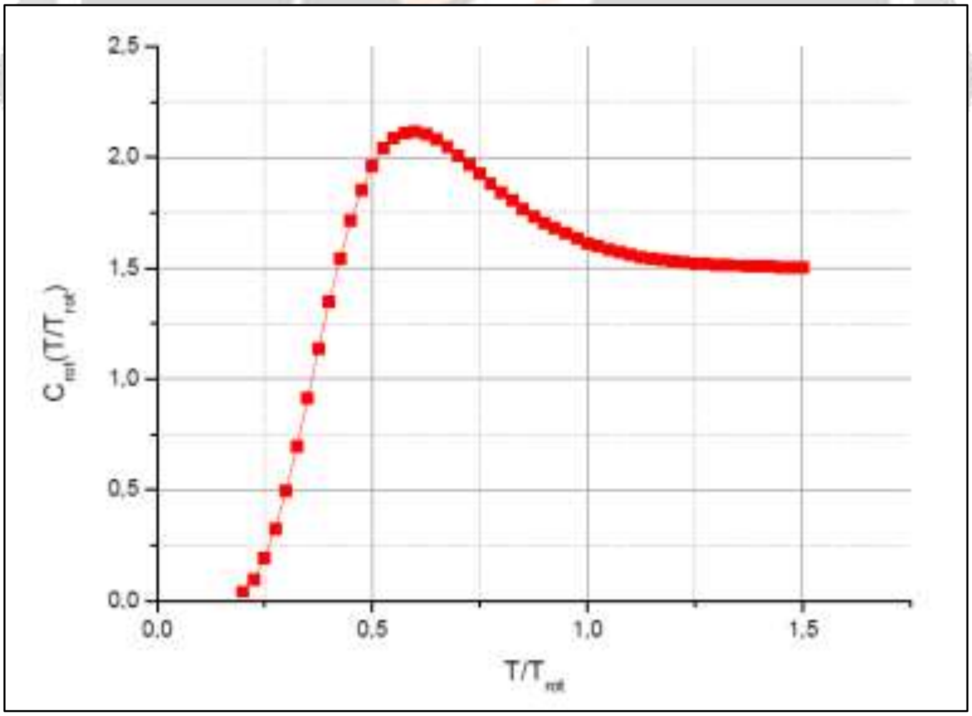

Figure 1: The rotational heat capacity of a spherical top with degeneracy multiplicity gn = (2n+1).

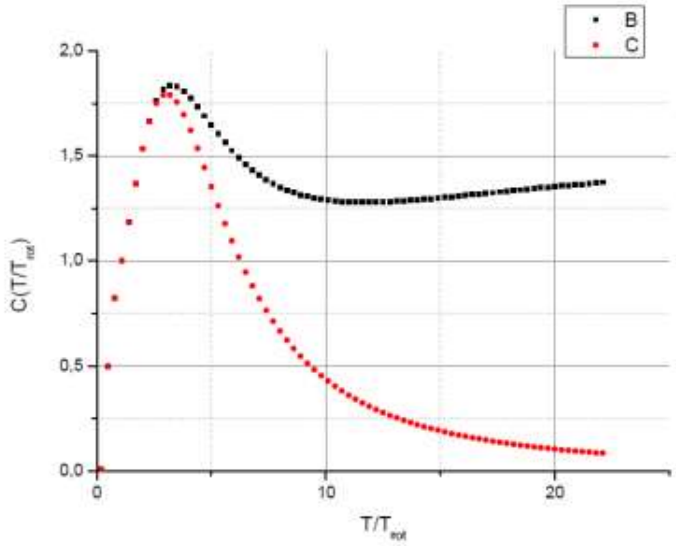

Figure 2: The rotational heat capacity of methane with only the first five terms of the low-temperature expansion (8) of the partition function (curve C) taken into account, and with compensation of the discarded terms in approximation (7) (curve B).

Spherical top distortion causes the gas's partition function to abruptly alter when its symmetry is violated, as is well-known. For example, if the configuration of a methane molecule is distorted into an asymmetric top with point symmetry D2h, the initial terms of the low-temperature expansion of the rotational partition function have the form.

$$Z = 7 + 27e^{-\left(\frac{2}{\tau}\right)} + 115e^{-\left(\frac{6}{\tau}\right)} + 175e^{-\left(\frac{12}{\tau}\right)} + 351e^{-\left(\frac{20}{\tau}\right)} + \cdots. \tag{11}$$

By replacing (8) in (9) with this formula, we can determine the heat capacity's temperature dependency. Figure 3 depicts the outcome of our numerical analysis.

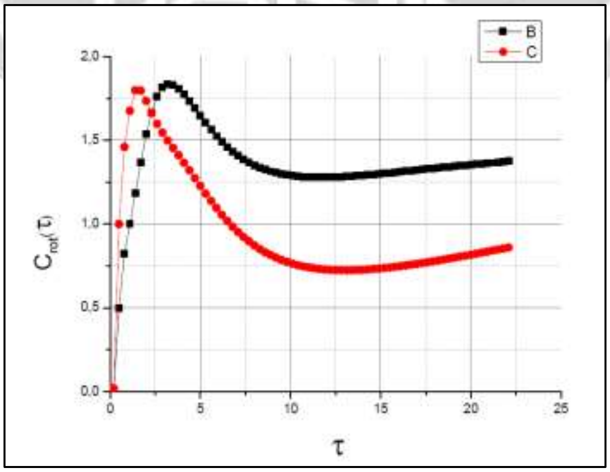

Figure 3: Teat capacity versus temperature for two variants of the low-temperature part of the expansion of the partition function: curve (B) corresponds to formula (8), curve (C) - to formula (11).

As a result, the maximum point of the heat capacity of an ideal gas made up of spherical-top type molecules varies greatly on the kind of symmetry of the top with respect to the dimensionless temperature.

III. DISCUSSION

There are a couple of factors that complicate the process of determining the maximal rotational heat capacity of actual gaseous methane in an experiment.

i A combination of spin modifications of methane takes a long time to reach thermodynamic equilibrium because the transition probabilities between these modifications are so tiny.

ii The division function can suddenly change even if the spherical top is just slightly distorted. Many factors contribute to the distortion, from intermolecular interactions to electromagnetic radiation in the environment.

In light of this, an experimental examination of the low-temperature heat capacity of methane in the gaseous form is unlikely to be reproducible. In the literature of recent years, including Landau's publications, this key conclusion has been completely lacking.

The thermodynamics of crystallized methane are next on the agenda. Solid methane molecules rotate at 60-65 K with an abrupt change in character, which Tomita ascribed to a 20-fold increase in the height of the barrier that rotating molecules must overcome. The spinning of methane molecules in the solid phase is supported by both experimental and theoretical evidence. In some molecular crystals (such as CH4, N2, and O2), the vibrational degrees of freedom of molecules can be changed into rotating degrees of freedom with a rise in temperature up to the melting point. Solids, in particular, expand due to their thermal expansion.

For example, it was hypothesized that in solid methane, rather than individual molecules rotating independently, collective excitations should be considered because of intermolecular interactions. These findings are in accordance with Pauling's discoveries and apply between the transition point (about 20 K) from the low-temperature cubic phase to a disordered phase along hydrogen atoms of the fcc phase, and to melting point (about 500 K).

The effective moment of inertia of the matching quasiparticle (topon) is all that is needed to describe it. Unlike the methane molecule, which is round due to symmetry, the topon molecule has a spherical top, and the number of degenerate rotational levels it has is defined by the formula (7). As a result, the temperature-dependent heat capacity graph looks like the one depicted in Fig. 1. Assuming that the maximum heat capacity of methane is equal to Tomita's temperature measurement, we arrive at a rough estimate of the rotational temperature of topon Trot 100 K, which means that the rotating temperature of topons is roughly 13 times higher than that of methane molecules in the gas phase. Solid methane is therefore a quantum cryocrystal over the whole range of temperatures that it may reside in. A variety of physical parameters of crystalline methane in the 60-65 K temperature range indicate abnormalities in solid methane: Temperature dependency of the molar volume; the coefficient of thermal expansion; ultrasonic velocity; low-frequency friction; adhesion; radiolysis of defects at a neutron source and other factors are examples of changes in the rotational character of the molecules. In the solid phase, methane molecules' collective rotational degrees of freedom provide for an explanation of these abnormalities.

IV. CONCLUSION

The heat capacity of methane in the gas phase is determined and refined. Methane's quantum heat capacity is demonstrated to surpass its rotational temperature by an order of magnitude due of the symmetry features of the molecule. Solid methane is proved to be a quantum cryocrystal across the whole temperature range of existence.

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