Phase III of CD4: Reconciliation of inelastic neutron scattering and heat capacity measurements of rotational tunneling levels

M. A. White

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Phase III of CD_4: Reconciliation of inelastic neutron scattering and heat capacity measurements of rotational tunneling levels

M. A. White

Department of Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1 Canada
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Recent inelastic neutron scattering measurements of CD_4 in phase III, the lowest temperature phase, show[1,2] low-lying rotational tunneling energy levels. In principle, the information derived from such a study should complement that obtained from measurements of a Schottky heat capacity anomaly in the temperature range of thermal depopulation of the tunneling levels.[3] However, calculations of C_p of CD_4 based on several different assignments of the neutron scattering tunneling spectrum all give[2] very poor agreement with the experiment. A similar discrepancy exists in the case of CH_3NO_2 where the neutron spectrum shows[4,5] a transition at 35 μeV, yet the heat capacity measurements[6] place an upper limit of 2 μeV on the tunneling transitions.

The key to the reconciliation of C_p and neutron scattering measurements of tunneling levels is that while the two methods are complementary, they measure different properties: heat capacity measurements reflect transitions between levels that depopulate as the temperature is lowered, while neutron scattering measures those transitions that are allowed by the neutron scattering selection rules.

In the case of CD_4, the rotational and nuclear spin functions combine to produce one A, one E, and three T nuclear spin symmetry species. The symmetry of the molecular field determines the configuration of the T states, which may be degenerate or split.

In inelastic neutron scattering from CD_4, selection rules that originate from the symmetry of the neutron scattering operator forbid transitions between A and E states, and also between some of the T states for special site symmetries.[7,8] Therefore, the observed[1,2] inelastic neutron scattering spectrum in CD_4 is due to A-T, T-E, and possibly some T-T transitions.

On the other hand, C_p measurements depend on the thermal depopulation of tunneling levels, and this depends on whether or not conversion between nuclear spin symmetry species takes place. If so, the observed[3] Schottky anomaly is due to A-T, A-E, T-E and possibly T-T transitions. If conversion does not occur, only T-T transitions can give rise to a Schottky anomaly.

Analysis of the Schottky tail in CD_4 has shown that the responsible tunnel splitting has an energy gap of ≈ 0.04 K (4 μeV). While the exact value of the splitting depends on the degeneracies of levels that are depopulated, an upper bound of about 5 μeV can be placed on the splitting of thermally accessible transitions.

However, the neutron scattering experiments[2] show the existence of a tunneling spectrum out to about 8 μeV, and we can therefore conclude that the higher energy neutron scattering transitions cannot be due to transitions that are thermally accessible, and therefore some transitions must be thermally inaccessible. In other words, complete nuclear spin species conversion does not occur in CD_4.

As an aside concerning conversion, it should be noted that, on the basis of heat capacity data alone, conversion was thought to be a possible explanation for the relatively long thermal relaxation times in CD_4 for $T<0.25$ K.[3] In light of the above argument, we can take this as a caveat concerning conclusions about conversion based solely on thermal relaxation times. (The longer relaxation could have been due to increased C_p for $T<0.25$ K.)

We can now use the experimental C_p data to compare the various models proposed[2] for the tunneling spectrum of CD_4 in phase III. The difference between the present and previous[2] calculations of C_p is that only T-T contributions are included here, under the simplifying assumption that conversion does not occur at all. (It should be noted here that the possibility of partial conversion cannot be ruled out at this point, but complete conversion can be.) The calculated and experimental values of C_p are illustrated in Fig. 1, where the model numbers refer to those of Ref. 2, as described in Table I. The level assignments of models 2 and 4 most accurately reproduce the observed C_p, whereas models 1 and 3 give C_p values that are outside the range of experimental error ($5\times10^{-4}R$).

In conclusion, concurrent analyses of the heat capacity and neutron scattering results for CD_4 indicate that

TABLE I. The table describes various models for CD_4 in phase III, as proposed in Ref. 2 based on the best fit of the tunneling spectrum. C_p calculated for each of the models is illustrated in Fig. 1.

Model no.	Number of sites	Multiplicities	Site symmetry
1	5	1/4	3(m)
		1/4	2
		1/4	3(m)
		1/8	$\bar{4}$
		1/8	$\bar{4}$
2	2	1/2	m
		1/2	m
3	3	1/2	3(1)
		1/4	2
		1/4	3(m)
4	2	1/2	m
		1/2	m

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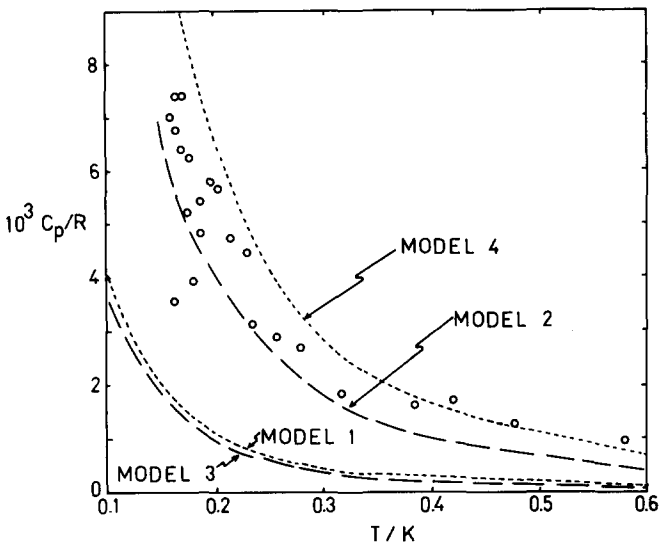

FIG. 1. Heat capacity of CD_4 as a function of temperature. (o) Experimental values of the Schottky contribution to C_p, based on the measurements of Ref. 3 corrected for 0.2% CHD_3 impurity with the lattice contribution represented by $\theta = 126$ K. Models 1–4 refer to calculated values of C_p based on $T-T$ transitions only according to the level assignments proposed in Ref. 2, as described in Table I.

complete nuclear spin species conversion does not occur, and, if conversion is totally absent, thermally depopulated transitions must be between T states only. By arguments parallel to those presented here, the apparent discrepancy between C_p[6] and neutron scattering[4,5] measurements of the tunneling levels in CH_3NO_2 must mean that conversion is also absent in that compound, as has been concluded recently.[5]

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[1]W. Press, M. Prager, and A. Heidemann, J. Chem. Phys. 72, 5924 (1980).
[2]M. Prager, W. Press, and A. Heidemann, J. Chem. Phys. 75, 1442 (1981).
[3]M. A. White and J. A. Morrison, J. Chem. Phys. 72, 5927 (1980).
[4]S. F. Trevino, J. Chem. Phys. 71, 1973 (1979).
[5]B. Alefeld, I. S. Anderson, A. Heidemann, A. Magerl, and S. F. Trevino, J. Chem. Phys. 76, 2758 (1982).
[6]K. J. Lushington and J. A. Morrison, J. Chem. Phys. 73, 2015 (1980).
[7]W. Press, *Springer Tracts of Modern Physics* (Springer, Berlin, 1981), Vol. 92.
[8]A. Hüller and W. Press, Phys. Rev. B 24, 17 (1981).

Scaling relations and analytic solution for the Thomas–Fermi metal–dielectric surface

D. Dahl

School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455 and Physics Department, St. Olaf College, Northfield, Minnesota 55057

J. W. Halley

School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455
(Received 4 February 1982; accepted 12 April 1982)

A correct treatment of metal–insulator and electrochemical interface problems requires an understanding of the dependence of the form of the depletion layer on the dielectric constant of the insulator in contact with a semi-infinite metal. Taking the simplest available model, we consider the Thomas–Fermi approximation for semi-infinite jellium in contact with a dielectric insulator with dielectric constant ϵ. The problem has previously been solved numerically.[1] Here we exhibit an explicit solution and scaling behavior which permits the solution for all ϵ to be obtained from two universal functions.

The Thomas–Fermi model for $\epsilon = 1$ is described by the equations

$$\tilde{n}(\tilde{x}) = [\tilde{\phi}(\tilde{x})]^{3/2} , \tag{1}$$

$$\tilde{\phi}''(\tilde{x}) = [\tilde{\phi}(\tilde{x})]^{3/2} - \Theta(-\tilde{x}) , \tag{2}$$

all distances being scaled by the Thomas–Fermi length in a.u.

$$\lambda = (3\pi a_0/8k_F)^{1/2} = 0.783 r_S^{1/2} .$$

Here $r_S = (3/4\pi n_S)^{1/3}$, where n_S is the bulk electron density in a.u.. In Eqs. (1) and (2), $\tilde{n}$ and $\tilde{\phi}$ are the electron density and electrostatic potentials divided by their values at $x \to -\infty$ (i.e., deep in the metal). Equations (1) and (2) possess the explicit solution

$$\tilde{\phi}(\tilde{x}) = 400/(\tilde{x}+a)^4 , \quad \tilde{x} > 0 , \tag{3}$$

where $a = 2/3(15)^{3/4} = 5.08$ and

$$\tilde{x} = -(10)^{1/2} \int_{(3/5)^{1/2}}^{(\tilde{\phi})^{1/2}} \frac{v\,dv}{(1-v)(2v^3+4v^2+6v+3)^{1/2}} , \quad \tilde{x} \le 0 . \tag{4}$$

For $\tilde{x} \le 0$, the equation for $\tilde{x}$ must be inverted to give $\tilde{\phi}(\tilde{x})$. We note that, for all densities $\tilde{\phi}(0) = 3/5$ and

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