# NMR study of rotational tunneling in the partially deuterated methanes

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We have observed the deuteron NMR absorption line at 46 MHz in phase III of the partially deuterated methanes in the temperature range 40 mK to 4 K. For CHD<sub>3</sub> the line shape depends strongly on the temperature up to 700 mK. A model is developed for the tunneling states of CHD<sub>3</sub> which reproduces both the derivative NMR line shape and the temperature dependence of the line area. We find that the line shape is determined by the interaction of the deuteron quadrupole moment with the gradient of the electric field of the molecular carbon-deuteron bond. The coupling constant for this interaction,  $e^2qQ/h$ , is measured to be 158±8 kHz, and the broadening of the NMR line is found to be consistent with the strength of the intramolecular dipole-dipole interactions. The data imply an absence of spin-species conversion in  $CHD<sub>3</sub>$  on a time scale of 10 h. Our tunneling-level model for CHD<sub>3</sub> is also compared with thermodynamic measurements. For CH<sub>2</sub>D<sub>2</sub> in the temperature range 40 to 60 mK, the NMR line is compared with the predictions of an energy-level scheme deduced from neutron scattering and thermodynamic measurements. We conclude that the tunneling of the deuterons around the  $C_3$  symmetry axis in CHD<sub>3</sub>, and around the  $C_2$  symmetry axis in  $CH<sub>2</sub>D<sub>2</sub>$ , proceeds at a rate fast compared with  $e<sup>2</sup>qQ/\hslash$ . No absorption lines of satisfactory signalto-noise ratio were observed for  $CH<sub>3</sub>D$ .

# I. INTRODUCTION

Deuterated methanes undergo two phase transitions at around 20 K, the phases being labeled I, II, and III in order of decreasing temperature. Phase I is the hightemperature phase of the solid, having an fcc lattice structure. In this phase the molecules are virtually free rotors. Phase II retains the fcc lattice structure and  $\frac{1}{4}$  of the molecules remain free rotors. The rest of the molecules are strongly hindered in their rotations by the molecular field.<sup>1,2</sup> Phase III exhibits a slight tetragonal distortion of the lattice. $3$  The number of nonequivalent molecular sites and their energy-level structure remain the subjects of ongoing research. Inelastic neutron scattering,  $4-6$ calorimetric,<sup>5-8</sup> and NMR<sup>9-11</sup> methods have been used to determine the structure of phase III in deuterated methanes. Phase III also has been studied in CH4, which has a transition to this phase at  $0.2 \text{ kbar.}^{12-14}$ 

We refer to rotational states that are localized in a single minimum of the orientational potential as "pocket states." Owing to the tunneling probability among the pocket states, the correct eigenstates of the Hamiltonian are linear combinations of pocket states, which are called "tunneling states."<sup>15</sup> Characteristically, the energies of the tunneling states are of the order of 2 K for CH<sub>4</sub> and 70 mK for  $CD_4$ <sup>4,16</sup> The partially deuterated methanes have splittings which increase with the number of protons and lie between those of CH<sub>4</sub> and CD<sub>4</sub>.<sup>1</sup>

Neutron scattering studies can provide a large amount of information in the form of the energies and intensities of the lines in the tunneling spectra. Prager et al. fitted neutron scattering data for  $CD_4$  using tunneling-level schemes with two to five nonequivalent sites.<sup>4</sup> Increasing the number of sites did not substantially improve the agreement with the data.

Calorimetric measurements pose fewer restrictions on tunneling models. These studies provide the temperature dependence of the specific heat, but a detailed energy-level scheme cannot be extracted. On the basis of residual entropy measurements, an attempt was recently made to find a unified model for all the partially deuterated methanes.

The quenching of the intramolecular quadrupolar and dipolar interactions limited the amount of information provided by an NMR study<sup>9</sup> in  $CD<sub>4</sub>$  to the temperature dependence of the NMR line area and of the intermolecular dipolar broadening. The situation is much more favorable in the partially deuterated methanes. In this case the lower symmetry of the molecules prevents the quenching of the intramolecular interactions. The NMR absorption spectra are rich in detail and pose stringent constraints on tunneling-level models. The resonance of the deuterons has the additional advantage of being sensitive to quadrupolar interactions, which are large in deuterated methanes. The nuclear-spin symmetry requirements in symmetric molecules give rise to long-lived nuclear-spin species.<sup>18</sup> Different tunneling levels will be associated with different spin species and conversion among these species will, in general, be forbidden. The departure of the area of the NMR absorption line from the Curie law is a measure of the amount of spin conversion. 'the amount of spin conversion.<sup>9,10</sup> Spin-species conversion<br>has been observed in CH<sub>4</sub>, CH<sub>3</sub>D, and CD<sub>4</sub>,<sup>5,9,19</sup> while has been observed in CH<sub>4</sub>, CH<sub>3</sub>D, and CD<sub>4</sub>,<sup>5,9,19</sup> while none has been observed in  $CH<sub>2</sub>D<sub>2</sub>$  and  $CHD<sub>3</sub>$ .

In this paper we report an NMR study of partially deuterated methanes. We present measurements of  $CHD<sub>3</sub>$  in the temperature range 40 mK-4.2 K, and of  $CH_2D_2$  in the temperature range <sup>40</sup>—<sup>60</sup> mK. The NMR line shape is determined by the interaction of the nuclear quadrupolar moment of the deuterons with the gradient of the electric field of the carbon —deuteron bond, which we will refer to as the quadrupolar interaction. This interaction is dependent on the angle the <sup>C</sup>—D bond makes with the external static magnetic field. For different tunneling states the deuterons occupy different positions in the molecule, and consequently the NMR line shape will depend on the tunneling-level structure. In Sec. II we show the re-

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lationship between NMR data and the tunneling-level structure. Section III is a brief description of the experimental procedures employed. In Secs. IV and V we discuss our results and conclusions.

#### II. THEORETICAL OVERVIEW

# A. Tunneling states and nuclear-spin symmetry

 $CH<sub>3</sub>D$  and  $CHD<sub>3</sub>$  are symmetrical top molecules, and belong to the point group  $C_3$  under the exchange of identical nuclei.<sup>18</sup> The irreducible representations of  $C_3$  are usually named  $A$  and  $E$ .  $A$  is a one-dimensional representation with equal amplitudes and phases for all three possible orientations, while  $E$  is a two-dimensional representation for which the amplitudes are equal and the phases differ by  $2\pi/3$ . The overall wave function must transform similar to the totally symmetric  $\Lambda$  representation of  $C_3$ , meaning that for a given molecule the nuclear-spin symmetry must be the same as the rotational symmetry. The nuclear-spin states associated with the  $A$ and  $E$  representations are for  $CH<sub>3</sub>D$ ,

$$
A: I_{\mathbf{H}} = \frac{3}{2}(1), E: I_{\mathbf{H}} = \frac{1}{2}(2)
$$

for CHD<sub>3</sub>,

 $A: I_D = 3(1), 1(1), 0(1), E: I_D = 2(2), 1(2)$ .

The numbers in parentheses give the multiplicity of the respective nuclear-spin value, and the subscripts H and D stand for protons and deuterons, respectively. The degeneracy of the tunneling states for  $CH<sub>3</sub>D$  will contain a factor of 3 due to the degeneracy of the nuclear spin of the deuteron. For  $CHD<sub>3</sub>$ , the proton will contribute a factor of 2 to the degeneracy of the tunneling levels. An additional degeneracy is introduced by the four positions this nucleus can occupy in the molecule.

 $CH<sub>2</sub>D<sub>2</sub>$  is an asymmetric-top molecule belonging to the point group  $C_2$ .<sup>18</sup> The irreducible representations of this group are labeled A and B, with A a one-dimensional symmetric representation, and  $B$  a one-dimensional antisymmetric representation. The overall wave function must be completely antisymmetric, implying that rotational  $A$ states will be associated with an antisymmetric nuclearspin function, and  $B$  states with a symmetric one. The nuclear-spin states in  $CH<sub>2</sub>D<sub>2</sub>$  are for A,

$$
I_{\rm H}
$$
 = 1(3),0(6),  $I_{\rm D}$  = 2(1),1(3),0(1)

for B,

$$
I_{\rm H}
$$
 = 1(6),0(3),  $I_{\rm D}$  = 2(3),1(1),0(3).

There are six different ways of placing two protons and two deuterons at the corners of a tetrahedron, leading to an additional degeneracy.

Figure <sup>1</sup> presents tunneling levels for the partially deuterated methanes, inferred from neutron scattering and thermodynamic measurements.<sup>5-7</sup> Earlier theoretical studies have derived level schemes which are somewhat different: Maki, Kataoka, and Yamamoto<sup>20</sup> computed tunneling-level schemes for  $CH_3D$  and  $CH_2D_2$  from the extended James and Keenan model.<sup>2</sup> Nagamiya<sup>21</sup> determined level splittings for  $CD_4$  and  $CH_3D$  in fields of various symmetries, and Hopkins et  $aL^{22}$  have extended his model to all of the deuterated methanes.



FIG. 1. Typical tunneling-level schemes for  $CH<sub>3</sub>D$  (Ref. 5),  $CH<sub>2</sub>D<sub>2</sub>$  (Ref. 6), and CHD<sub>3</sub> (Ref. 7). The labels  $A, E, B$  refer to spin species, while the numbers in parentheses give the degeneracy of each level.

### B. Nuclear magnetic susceptibility

The area of the NMR absorption line is proportional to the expectation value of the nuclear spin  $\langle I(I+1) \rangle$ , averaged over the relevant nuclear-spin states. The area is also inversely proportional to the temperature (Curie law) at temperatures high compared to the Zeeman splitting. In the high-temperature limit the areas of the deuteron NMR lines for CH<sub>3</sub>D, CH<sub>2</sub>D<sub>2</sub>, and CHD<sub>3</sub> will be in a 1:2:3 ratio. The same will be true at low temperatures, if the spinconversion time is longer than the time for which the sample is cooled. The average deuteron  $\langle I(I+1)\rangle$  for the different spin species is for  $CH<sub>3</sub>D$ ,

$$
\langle I(I+1)\rangle_A = 2, \ \langle I(I+1)\rangle_E = 2
$$

for  $CH<sub>2</sub>D<sub>2</sub>$ ,

$$
\langle I(I+1)\rangle_A = 3.20, \ \langle I(I+1)\rangle_B = 4.57
$$

for  $CHD<sub>3</sub>$ ,

$$
\langle I(I+1)\rangle_A = 8.18, \ \langle I(I+1)\rangle_E = 4.5
$$

where the subscripts identify the spin species. The totally symmetric <sup>A</sup> representation is generally the lowest-energy state. Therefore, the departure from Curie law expected in the case of spin-species conversion at low temperatures is an increase in the NMR absorption line area for both  $CH<sub>2</sub>D<sub>2</sub>$  and CHD<sub>3</sub>.

## C. Quadrupolar interaction

The inhomogeneous broadening due to the quadrupolar interaction of the deuterons is the largest perturbation to the Zeeman Hamiltonian in a strong magnetic field, and as such will determine the major features of the NMR line. The quadrupolar shift in resonant frequency  $\Delta v_Q$  is given by<sup>23</sup>

$$
\Delta v_Q = \pm \frac{3}{8} e^2 q Q (3 \cos^2 \theta - 1 + \eta \sin^2 \theta \cos 2\phi) , \qquad (1)
$$

where  $eQ$  is the deuteron quadrupole moment, and  $eq$  and  $\eta$  are defined as follows in terms of the principal values  $V_{XX}$ ,  $V_{YY}$ ,  $V_{ZZ}$  of the field-gradient tensor:

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$$
eq = V_{ZZ}, \ \ \eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}, \ \ |V_{ZZ}| \ge |V_{XX}| \ge |V_{YY}| \ .
$$
 (2)

 $\theta$  and  $\phi$  are the polar angles made by the external magnetic field with respect to the principal axes  $(X, Y, Z)$ . It has been estimated from molecular-beam measurements<sup>24</sup> and from spin-lattice relaxation time measurements<sup>25</sup> that  $130 \le e^2 qQ /h \le 200 \text{ kHz}.$ 

The NMR line shape  $g(v)$  in a powder sample as computed from Eq.  $(1)$  is given by  $2<sup>6</sup>$ 

$$
g(v) = \frac{CK(m)}{\pi[\eta(1-x)]^{1/2}},
$$
  
where  $m = S(x)$  for  $0 \le S(x) \le 1$ ,  

$$
CK(m')
$$

$$
g(\nu) = \frac{CK(m')}{\pi [(2x+1+\eta)(3-\eta)]^{1/2}} , \qquad (3)
$$

where  $m' = 1/S(x)$  for  $S(x) > 1$ ,

$$
g(v)=0,
$$

$$
g(v) = 0,
$$
  
\nfor  $S(x) < 0$ . Here  $C$ ,  $x$ , and  $S(x)$  are defined as  
\n
$$
C \equiv \frac{8}{3V_{ZZ}eQ}, \quad x \equiv Cv, \quad S(x) \equiv \frac{1}{4} \frac{(2x+1+\eta)(3-\eta)}{\eta(1-x)}.
$$
  
\n
$$
G = \frac{8}{3V_{ZZ}eQ}, \quad x \equiv Cv, \quad S(x) \equiv \frac{1}{4} \frac{(2x+1+\eta)(3-\eta)}{\eta(1-x)}.
$$
  
\n
$$
G = \frac{8}{3V_{ZZ}eQ}, \quad x \equiv Cv, \quad S(x) \equiv \frac{1}{4} \frac{(2x+1+\eta)(3-\eta)}{\eta(1-x)}.
$$
  
\n
$$
G = \frac{8}{3V_{ZZ}eQ}, \quad x \equiv Cv, \quad S(x) \equiv \frac{1}{4} \frac{(2x+1+\eta)(3-\eta)}{\eta(1-x)}.
$$

 $K(m)$  is the complete elliptic integral as defined in Ref. 27.

For  $\eta = 0$ , the line reduces to a Pake doublet,<sup>28</sup> while for  $\eta=1$ , a line with a central logarithmic divergence is obtained. Figure 2 shows derivative line shapes for  $\eta=0$ , 0.5, and 1. The lines were convoluted with a Gaussian the width of which was 5% of the total linewidth, correspond-



FIG. 2. Computed powder-averaged derivative lines for the quadrupolar interaction.  $\eta$  is the asymmetry parameter. The lines are convoluted with a Gaussian of width 5% of the total linewidth.

ing to the homogeneous dipolar broadening of the NMR line in  $CHD<sub>3</sub>$ .

For the case in which the deuterons can tunnel between different positions in the methane molecule at a rate fast compared with  $e^2qQ/\hslash$ , the effective quadrupolar tensor  $V'_{ii}$  will be given by

$$
V' = \frac{eq}{2} \begin{bmatrix} 0 & a & b \\ a & 0 & c \\ b & c & 0 \end{bmatrix}
$$
 (4)

where

$$
a = P_1 - P_2 - P_3 + P_4,
$$
  
\n
$$
b = P_1 - P_2 + P_3 - P_4,
$$
  
\n
$$
c = P_1 + P_2 - P_3 - P_4.
$$

Here  $P_i$  is the probability for the deuteron to occupy corner i of the tetrahedron. We use a coordinate system in which the four hydrogen atoms in the methane molecule are placed symmetrically in alternating octants.<sup>24</sup>

From Eq. (4) we find  $V'_{ZZ}$  and  $\eta'$ :

$$
V'_{zz} = D \cos \alpha, \quad \eta' = \sqrt{3} \tan \alpha \tag{5}
$$

where  $D$  and  $\alpha$  are defined as

$$
V'_{zz} = D \cos \alpha, \quad \eta' = \sqrt{3} \tan \alpha,
$$
  
where *D* and  $\alpha$  are defined as  

$$
D = \left[ \frac{a^2 + b^2 + c^2}{3} \right]^{1/2}, \quad \alpha \equiv \frac{1}{3} \cos^{-1} \left[ \frac{|abc|}{D^3} \right].
$$

For CD4 tunneling makes every deuteron have equal probability to be in any of the four possible positions, thereby quenching the quadrupolar interaction ( $\eta = 0$ ,  $V_{ZZ}$  =0). A deuteron in a fixed position will produce a Pake doublet of maximum width  $3e^2qQ/2h$  or about 200 kHz.

### D. Dipolar interactions

The dominant internuclear dipole-dipole interaction will be the intramolecular one. In partially deuterated methanes it will consist of the like-spin interaction among the deuterons and of the unlike-spin interaction of the protons with the deuterons. First-order perturbation theory gives for the energy shifts due to the intramolecular dipolar interactions,<sup>23</sup>

$$
\Delta E_{\rm DH} = \sum_{i,j} \frac{\hbar \gamma_{\rm D} \gamma_{\rm H}}{r^3} (1 - 3 \cos^2 \theta_{ij}) \langle S_{Zi} I_{Zj} \rangle \;, \tag{6}
$$

$$
\Delta E_{\rm DD} = \sum_{i < j} \frac{\hbar \gamma_{\rm D}^2}{2r^3} (1 - 3 \cos^2 \theta_{ij}) \langle 3I_{Zi} I_{Zj} - \vec{1}_i \cdot \vec{1}_j \rangle \tag{6'}
$$

The subscripts DH and DD refer to the deuteron-proton and deuteron-deuteron interactions, respectively. In Eq. (6) the sum is over all proton-deuteron pairs, and in Eq. 6') over all the deuteron pairs.  $\theta_{ij}$  is the angle made by the external magnetic field with the pair bond. S and I stand for the nuclear spins of the protons and deuterons. In methane the distance  $r$  between hydrogen nuclei is 1.786 A.

The proton-deuteron dipolar interaction leaves  $I_z$  a

good quantum number for each deuteron and lifts the degeneracy due to the nuclear spin of the proton. In the simplest case, where the orientation of the C-H bond is fixed, its effect will be to split the deuteron Pake doublet into two doublets with a difference in widths of about 3 kHz. The splitting will depend on the spin species of the molecule. In more complicated cases the net effect of the proton-deuteron dipolar interaction will be a more complex splitting of the resonance line, which we will approximate by a Gaussian broadening.

The deuteron-deuteron interaction is more difficult to compute, due to the fact that  $I_z$  for individual deuterons, which commutes with the Zeeman and the quadrupolar terms in the Hamiltonian, is no longer a good quantum number. Computations of the dipolar interaction for systems of two and three spins<sup>29,30</sup> show a rather complex line shape, becoming somewhat simpler if tunneling is allowed. The maximum splitting due to deuteron-deuteron interactions in partially deuterated methanes is of the order of 1.5 kHz, and will contribute to the broadening of the line.

The intermolecular dipolar interaction produces a homogeneous broadening with an approximately Gaussian form. The broadening is determined from the second moment of the absorption line.<sup>9,13</sup> A computation for CHD<sub>3</sub>, assuming no spin conversion at low temperatures, and taking all the spins as located at the center of the molecule, gives a Gaussian broadening of 0.5 kHz width.

We conclude that the dipolar internuclear interactions in deuterated methanes are a small perturbation of the quadrupolar interaction, and effectively produce a homogeneous broadening of the deuteron NMR line. The main contribution to this broadening is due to the intramolecular dipolar interactions, and in particular to the protondeuteron part of the interaction. The magnitude of the broadening is about 3 kHz for each proton in the molecule.

## III. EXPERIMENTAL PROCEDURE

The NMR spectrometer, sample chamber, and condensation procedure were described in a previous paper.<sup>9</sup> Deuterated methane samples were supplied by Merck, Sharp, and Dohme (Montreal). The isotopic purity for all three gases is given by the supplier as 98%. The sample size was typically 300-cm<sup>3</sup> STP, limited by the size of the homogeneous region of the magnet. The 7-T superconducting magnet had an inhomogeneity of less than three parts in 10<sup>6</sup>.

The primary temperature reference was a carbon thermometer soldered to the sample chamber. In addition, we checked the temperature using Curie-law thermometry in the copper wires which provided thermal contact to the sample and in a separate deuterium sample. Details of the procedure used for Curie-law thermometry can be found in Ref. 31. The departure of the temperature of the deuterium sample from the temperature of the empty cavity was consistent with the heat of ortho-para conversion of deuterium in the presence of the Kapitza thermal resistance of the copper-deuterium boundary. After correcting for the heat of spin-species conversion in deuterium, the three temperature scales agreed, and provided a temperature calibration with an error of about 3%.

# IV. RESULTS AND DISCUSSION

# A. CHD<sub>3</sub>

The derivative of the deuteron NMR absorption line was measured at 4.2 K, and at 20 logarithmically equidistant temperatures in the range 40-700 mK. The line shape is strongly temperature dependent over the entire range 40-700 mK, and narrows to about 4 kHz at 4.2 K where it exhibits complete rotational quenching of the quadrupolar interaction. Figure 3 presents a sequence of



FIG. 3. NMR derivative line shapes in CHD<sub>3</sub> (closed circles), and the line shapes computed from model 1 (solid line).

derivative NMR absorption lines. The temperature dependence of the line shape suggests that the first tunneling level above the ground state has an energy not larger than about 60 mK, and that the highest-lying tunneling level has an energy not larger than about 2 K. The line shape and area showed no dependence on whether the temperature at which they were measured was reached from above or from below. The line area did not change over a period of 10 h at 40 mK, and over 3h at 150 mK. These observations alone do not rule out spin conversion. Such conversion may be masked by a tunneling-level scheme in which A and  $E$  spin-species levels alternate closely.

The NMR lines at five logarithmically equidistant temperatures were fitted simultaneously to a model of the tunneling levels of CHD<sub>3</sub>, using a least-squares-fitting routine. The parameters of the fit were the tunneling levels of three nonequivalent sites, the percentage of molecules in each of these sites, the quadrupolar coupling constant, the width of the Gaussian broadening of the line, and an overall scaling constant. The Curie-law variation of the line area was incorporated into the fitting routine. The computation of the NMR absorption line shape was done along the following lines.

(i) The 40-kHz splitting between derivative peaks at low temperatures indicates that tunneling occurs between the three deuterons around the  $C_3$  symmetry axis, and that the tunneling rate is fast compared with  $e^2qQ/\hbar$ . The electric-field-gradient tensor is therefore averaged over three corners of the tetrahedron. With the use of Eq. (4) it is apparent that this situation is equivalent to one in which the deuterons were fixed, but had  $e^2qQ$  reduced by a factor of 3. (It is this threefold tunneling which gives rise to the  $A$  and  $E$  spin species.)

(ii) The fast tunneling of the deuteron around the  $C_3$ axis cannot account for the variation of the line shape with temperature, and therefore we have to consider tunneling of the proton between the four positions in the tetrahedron. We approximate the four energy levels associated with the proton tunneling by its four pocket states. This approximation implies that the splitting among the  $A$ (or  $E$ ) states is due to the differences in the energies of the different proton orientations, and that the mixing of these states due to tunneling can be neglected.

(iii) The complete narrowing of the line at high temperatures precludes the possibility that each of the energy levels contributes a line independent of all other energy levels. We therefore assume that tunneling occurs between the pocket states at a rate fast compared with  $e^2qQ/\hbar$ .

(iv) Each nonequivalent site will give two separate contributions to the total NMR line; one due to the  $A$  molecules, and one to the  $E$  molecules. In view of the typical spin-conversion times in methanes, we dismiss the possibility that conversion may occur at rates faster than  $e^2qQ/\hbar$ . For each of these lines the quadrupolar tensor is computed from Eq.  $(4)$ ,  $P_i$  being given by the Boltzmann probabilities. The line shape is computed from Eq. (5).

(v) The effect of the internuclear dipolar interactions is approximated by a homogeneous Gaussian broadening of the NMR line. The variation of this broadening with temperature and its dependence on spin species is ignored.

(vi) No a priori assumption was made about the occurrence of spin conversion. Two versions of the fitting program were used, one allowing it and one forbidding it.



FIG. 4. Tunneling-level models for  $CHD<sub>3</sub>$  derived from the temperature dependence of the NMR line shape.

(vii) We neglect the possible temperature dependence of the energy levels.<sup>2</sup>

No satisfactory fit was found when spin-species conversion was allowed. Figure 4 presents the energy-level schemes for the best fits for tunneling models with two (model 2) and three (model 1) nonequivalent sites, under the assumption that spin-species conversion is forbidden. The two models differ only with respect to the number of nonequivalent sites. The proportions of molecules at the various nonequivalent sites were free parameters in the fitting program. However, the fitted values for these fractions were generally close to simple fractions, as might be expected from physical considerations. For our models <sup>1</sup> and 2, the fitting procedure was repeated after fixing these proportions to multiples of  $\frac{1}{4}$ . The level schemes with the fixed contributions from the different sites were not substantially different from the previous ones, and  $\chi^2$  did not increase more than 3%. For model 1,  $\chi^2$  was 5% higher than for model 2. The errors in the tunneling-level energies, as determined by the fitting routine, are around 10% for the levels below <sup>1</sup> K, and around 20% for those of higher energy. It was determined that  $e^2qQ/h = 158\pm 8$ kHz. The best fit was obtained with a Gaussian broadening of  $2.8 \pm 0.5$  kHz. This may be interpreted as an estimate of the strength of the intramolecular dipolar interactions. Figure 3 shows derivative lines calculated from model 1, as compared with the experimental results. The



FIG. 5. Temperature dependence of the specific heat of CHD<sub>3</sub> computed from model 1 (solid line), model 2 (dashed line), and determined from calorimetric measurements in Ref. 7 (closed circles).

two-site model 2 reproduces the lines in the range 200-300 mK better than model 1, but the agreement with the low-temperature data is significantly worse. The departures of our models from the data can be attributed to the approximation of the energy levels as pocket states, and to the neglect of their temperature dependence. The overall agreement with experiment is good, considering the sensitivity of the derivative to small variations in the absorption line shape. The fit could be improved by allowing the broadening to decrease with increasing temperature, but as an approximation we used a temperatureindependent value.

The values for the residual entropy  $S_0$  computed from our models are  $S_0/R = 4.15$  for model 1, and  $S_0/R = 4.30$ for model 2. This is in good agreement with the value  $S_0/R = 4.23 \pm 0.10$  obtained from thermodynamic measurements.<sup>7</sup> Figure 5 shows the heat capacity computed from models 1 and 2 as compared with the measurements of White and Morrison.<sup>7</sup> The large discrepancy is due to the low-lying tunneling levels of our models. The  $C_p$  data implies a lowest-energy state above ground state at 290  $mK$ , which is incompatible with changes in the NMR line shape at 40 mK.

## $B. CH<sub>2</sub>D<sub>2</sub>$

Under similar experimental conditions, the amplitude of the NMR line for  $CH<sub>2</sub>D<sub>2</sub>$  is significantly smaller than that for CHD<sub>3</sub>. The difference is due to the smaller number of deuterons and to the increased width of the resonance in  $CH_2D_2$ . We measured  $CH_2D_2$  NMR lines with good signal-to-noise ratio in the temperature range  $40-60$  mK. The shape and width of the line are consistent with free



FIG. 6. NMR derivative line shapes in  $CH<sub>2</sub>D<sub>2</sub>$  (closed circles), and the line shapes computed using the tunneling-level model of Ref. 6 (solid line).

tunneling around the  $C_2$  symmetry axis. Figure 6 presents two derivative absorption lines. No change is visible in the line shape, indicating that the first tunneling levels above the ground state must have energies above about 150 mK. The amount of information contained in the one line shape is too small for the determination of a tunneling-level model. We use a model derived by White et al. from neutron scattering and thermodynamic measurements<sup>6</sup> to check our determination of the  $e^2qQ$ , and the assumption of fast tunneling among the deuterons. Spin conversion is forbidden in this model. The  $CH<sub>2</sub>D<sub>2</sub>$ line shapes were generated using the computational procedure described earlier in connection with CHD<sub>3</sub>. In  $CH<sub>2</sub>D<sub>2</sub>$  the pocket states are probably not as good an approximation to the eigenstates as in CHD<sub>3</sub>. This is because the tunneling matrix elements for  $C_3$  rotations, which interchange protons and deuterons, cannot be assumed to be smaller than the  $C_2$  tunneling matrix elements. In the computation of the quadrupolar tensor, the matrix elements  $a, b$ , and  $c$  in (4) must be replaced by

$$
a = P_1 - P_2 ,\nb = P_3 - P_4 ,\nc = P_5 - P_6 .
$$
\n(4')

 $P_i$  are the Boltzmann probabilities corresponding to the

six tunneling levels of the  $A$  or  $B$  molecules. The pocket states to which the pairs of probabilities in the definitions of  $a, b$ , and  $c$  correspond, are chosen in such a way as to make the two pairs of deuterons occupy all four corners of the tetrahedron. Figure 6 shows the NMR line shape computed with the tunneling levels of Ref. 13 as fixed parameters. The fitting routine gives  $e^2qQ/h = 160 \pm 15$ kHz, in good agreement with the value determined from CHD3. The dipolar broadening needed for a good fit is around 18 kHz, larger by a factor of 3 than the value estimated from Eqs. (6) and (6'). A possible cause for this discrepancy is the approximation of the tunneling levels by the pocket states. Correct tunneling levels, which are combinations of different pocket states, would produce a line shape with less prominent features and avoid the artificial need for a large broadening. In the case of  $CH<sub>3</sub>D$ one expects full quadrupolar broadening at low temperatures. We did not obtain NMR lines with satisfactory signal-to-noise ratio with the sample of  $CH<sub>3</sub>D$ .

### V. CONCLUSIONS

The NMR of the deuterons proved to be a very good method for studying the properties of partially deuterated methanes at low temperatures, and, in particular, for determining their tunneling-level structure and their spinspecies conversion rates. In CHD<sub>3</sub>, the deuterons have a fast tunneling rate around the  $C_3$  symmetry axis, and also tunnel freely among the states corresponding to the four different orientations of the proton. The tunneling-level models developed from our NMR data show energy splittings smaller than those for  $CH_2D_2$ , and larger than the splittings for  $CD_4$ , consistent with theoretical predictions. $17$  Evidence was found that spin-species conversion does not occur in CHD<sub>3</sub>, at least over the course of 10 h. The quadrupolar coupling constant  $e^2qQ$  was measured to a much better accuracy than previously achieved. The estimates of the strength of the internuclear dipolar interactions are confirmed.

In  $CH<sub>2</sub>D<sub>2</sub>$  the deuterons tunnel freely around the  $C<sub>2</sub>$ symmetry axis. The quadrupolar coupling constant deduced from  $CH<sub>2</sub>D<sub>2</sub>$  agrees with the measurement made in  $CHD<sub>3</sub>$ . At 4.2 K, the highest temperature probed, the NMR lines of  $CH<sub>3</sub>D$  and  $CH<sub>2</sub>D<sub>2</sub>$  were not observable, suggesting that complete motional narrowing does not occur at this temperature. This is consistent with tunneling levels lying at 2 K or above.<sup>5,6</sup>

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