

$^2\text{H}$  and  $^{13}\text{C}$  NMR study of guest molecule orientation  
in clathrate hydrates\*

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Abstract. At relatively high temperatures (200–270K), clathrate hydrate cages achieve their full crystallographic symmetry because of time averaging of different cage configurations which exist because of disorder in the water molecule orientations. The average orientation of guest molecules in the cages can be obtained from the NMR spectrum, in case of spin  $\frac{1}{2}$  nuclei from the nuclear shielding tensor, in case of spin 1 nuclei from the quadrupole coupling tensor. Guest molecules studied include carbon dioxide, carbonyl sulphide, methyl- $\text{d}_3$  fluoride, methyl- $\text{d}_3$  chloride, methyl- $\text{d}_3$  bromide, ethane- $\text{d}_6$ , acetylene- $\text{d}_2$  in the structure I hydrates, and methyl- $\text{d}_3$  iodide in the structure II hydrate.

For the slightly flattened large cage of structure I hydrate, the guest molecules rotate so that the plane which contains the long axis of the molecule is confined to be nearer to the equatorial plane of the cage than the axial regions.

Since the structure II large cage has tetrahedral symmetry on time average, it exerts no orienting effect on guest molecules.

## 1. INTRODUCTION

The study of molecular motion of guest molecules in clathrate hydrate cages is a complex problem, with most previous dielectric and NMR work emphasizing the low temperature behaviour (1,2). Even when guest motions are rapid, non-spherical clathrate hydrate cages should exert an orienting effect on enclathrated guest molecules. However, the water molecules which form the hydrate framework are disordered (3,4), as they are in ice  $\text{I}_h$ , so that many different low symmetry configurations exist for the clathrate cages. Only at sufficiently high temperatures does water molecule reorientation cause time averaging of different cage configurations (5,6,7) so that the individual cages attain the high space-average symmetries found in diffraction studies (see, e.g. ref. 2), and in any one clathrate hydrate sample all

guest molecules in each type of cage should experience the same orienting effect.

In the past, this has been studied semi-quantitatively by means of  $^1\text{H}$  NMR second moments and  $^2\text{H}$  NMR quadrupole echoes (5,6,7). Here we show that at high temperatures ( $\sim 270\text{K}$ )  $^2\text{H}$  and  $^{13}\text{C}$  NMR lineshapes can be obtained with sharp, well-defined features, so that quadrupole coupling or nuclear shielding (chemical shift) tensor components can be measured directly to yield information on guest molecule orientation in the clathrate hydrate cages.

Guest molecules such as  $^{13}\text{CO}_2$ ,  $^{13}\text{COS}$ ,  $\text{C}_2\text{D}_6$ ,  $\text{CD}_3\text{F}$ ,  $\text{CD}_3\text{Cl}$ ,  $\text{CD}_3\text{Br}$  and  $\text{C}_2\text{D}_2$  in the nearly axially symmetric structure I hydrate large cage (oblate spheroid) should show a marked orientational preference, whereas  $\text{CD}_3\text{I}$  in the tetrahedral structure II large cage should show no such preference.

## 2. THEORY

In powdered clathrate hydrates, the order parameter  $S$  can be obtained with respect to a cage-fixed axis by expressing  $\theta$  (see fig. 1), the angle between the principal component of the molecule-fixed

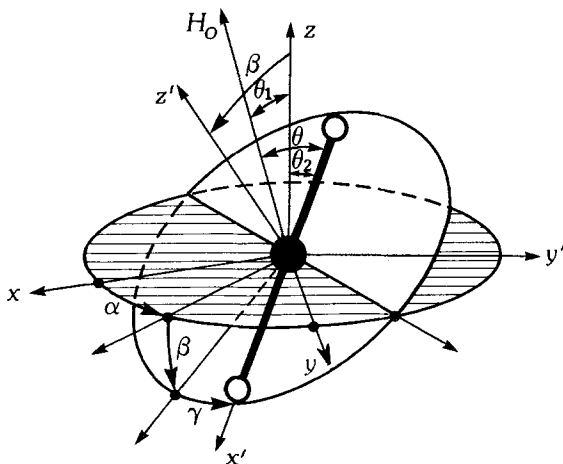


Fig. 1 Coordinate systems used in the motional model calculations.

quadrupole coupling or nuclear shielding tensor and the magnetic field direction, in terms of  $\theta_1$ , the angle between the magnetic field direction and the cage symmetry axis, and  $\theta_2$ , the angle between the tensor principal component and the cage symmetry axis, and performing a powder average over  $\theta_1$ . Then,

$$S = \frac{1}{2} \langle 3 \cos^2\theta_2 - 1 \rangle$$

where the angular brackets indicate a motional average.

For  $^{13}\text{CO}_2$ ,  $^{13}\text{COS}$ , and  $\text{C}_2\text{D}_2$ , the unique principal component of the axially symmetric shielding ( $^{13}\text{C}$ ) or quadrupole coupling ( $^2\text{H}$ ) tensor lies along the long molecular axis. In the case of the  $\text{CD}_3$  group containing molecules, rapid  $\text{CD}_3$  group rotation again causes the unique principal component of the quadrupole coupling tensor to lie along the long molecular axis.

The coordinate systems in Fig. 1 were used to calculate order parameters for a number of motional models. The xyz coordinate system is fixed to the cage, with the z along the cage symmetry axis. The guest molecule lies along the x' axis, where the primed and unprimed coordinate systems are related by the Euler rotation angles  $\alpha$ ,  $\beta$  and  $\gamma$ . Tensor components in the primed and unprimed coordinate systems are related by the Euler angle rotation matrix (8). The effect of molecular rotation is then obtained by integrating over the angles  $\alpha$  or  $\gamma$ , or both these angles, leaving  $\beta$ , the angle between the molecular axis and the equatorial plane of the cage as the only variable which depends on the guest molecule.

#### Model 1

The guest molecule rotates about the cage symmetry axis with the long molecular axis inclined to the equatorial plane of the cage at an angle  $\beta$ .

$$(\gamma = 0, \alpha = 0 \rightarrow 2\pi)$$

$$S = 0.5 (2 - 3 \cos^2\beta)$$

#### Model 2

As model 1, except that  $\beta$  can vary between 0 and  $\beta_{\text{max}}$ .

$$S = 0.5 (1 - \cos\beta_{\text{max}} - \cos^2\beta_{\text{max}})$$

#### Model 3

As model 1, except that the guest molecule rotates in its own plane as well.

$$(\gamma = 0 \rightarrow 2\pi, \alpha = 0 \rightarrow 2\pi)$$

$$S = 0.25 (1 - 3 \cos^2\beta)$$

Model 4

As model 3, except that  $\beta$  can vary between 0 and  $\beta_{\max}$ .

$$S = -0.25 (\cos\beta_{\max} + \cos^2\beta_{\max})$$

Figure 2 shows the order parameter  $S$  as a function of  $\beta$  or  $\beta_{\max}$  for the four motional models.

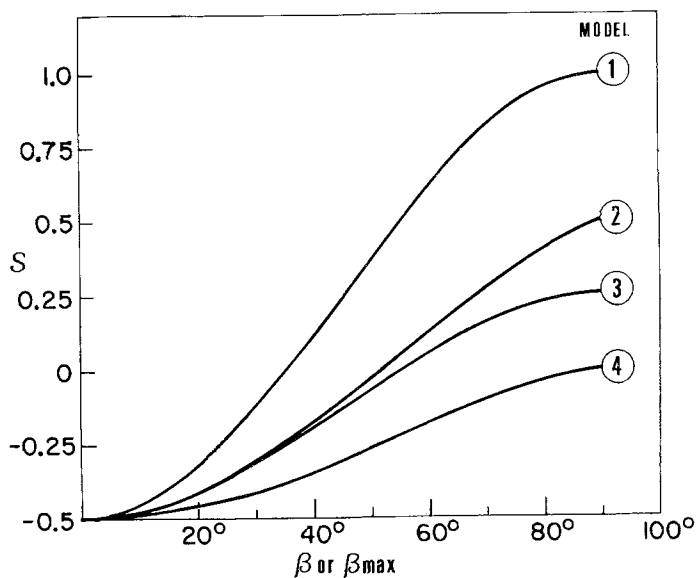


Fig. 2 Order parameters calculated for different motional models as a function of the angle  $\beta$  or  $\beta_{\max}$ .

### 3. EXPERIMENTAL SECTION

Deuterated and  $^{13}\text{C}$  labeled chemicals were obtained from MSD Isotopes and Prochem. Hydrates were prepared according to previously published techniques (9).  $^{13}\text{C}$  and  $^2\text{H}$  lineshapes were measured on a Bruker CXP-180 NMR spectrometer at frequencies of 45.28 and 27.63 MHz respectively. In the case of  $^{13}\text{C}$  lineshapes, the powder patterns were recorded using the pulse sequence proposed by Rance and Byrd (11). For the hydrates, high power  $^1\text{H}$  decoupling was employed as well.  $^2\text{H}$  powder patterns were recorded using the phase alternated quadrupole echo sequence (10).

### 4. RESULTS AND DISCUSSION

$^2\text{H}$  and  $^{13}\text{C}$  NMR lineshapes for selected enclathrated guest molecules, as well as reference lineshapes for the pure solid materials are shown in Figs. 3 and 4. The lineshapes for guest molecules in the

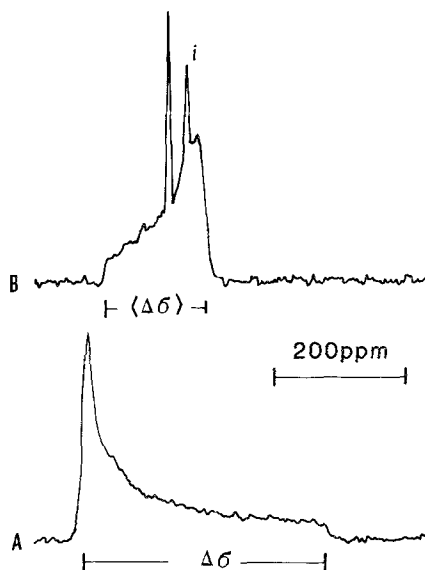


Fig. 3  $^{13}\text{C}$  NMR lineshapes of  
 a) a 20% solid solution of  $^{13}\text{COS}$  in  $\text{CS}_2$  at 77K.  
 b)  $^{13}\text{COS}$  in the structure I clathrate hydrate cage at 250K.  
 i marks  $\text{CO}_2$  impurity.

structure I cages indicate axial symmetry. The absence of doublet structure in the lineshape of  $\text{CD}_3\text{I}$  in the structure II large cage (Fig. 4c) shows that indeed the tetrahedral cage does not orient guest molecules.

Experimentally determined order parameters  $S$  are found from

$$\langle \Delta\sigma \rangle = \Delta\sigma S \text{ and}$$

$$\langle e^2qQ/h \rangle = (e^2qQ/h) S$$

where  $\Delta\sigma$  and  $e^2qQ/h$  are the nuclear shielding anisotropy and quadrupole coupling constant for pure guest materials at 77K, the values in angular brackets are those found for enclathrated guests.

It should be noted that for spin  $\frac{1}{2}$  nuclei, both the sign and magnitude of the order parameter may be determined; for spin 1 nuclei, only the magnitude.

Results are tabulated in Tables I and II.

Table II lists van der Waals' lengths and dipole moments of the guest molecules, as well as order parameters of these molecules enclathrated in the structure I large cage. The presence of a molecular dipole does not appear to be important in defining guest molecule motions. The order parameters do correlate roughly with the

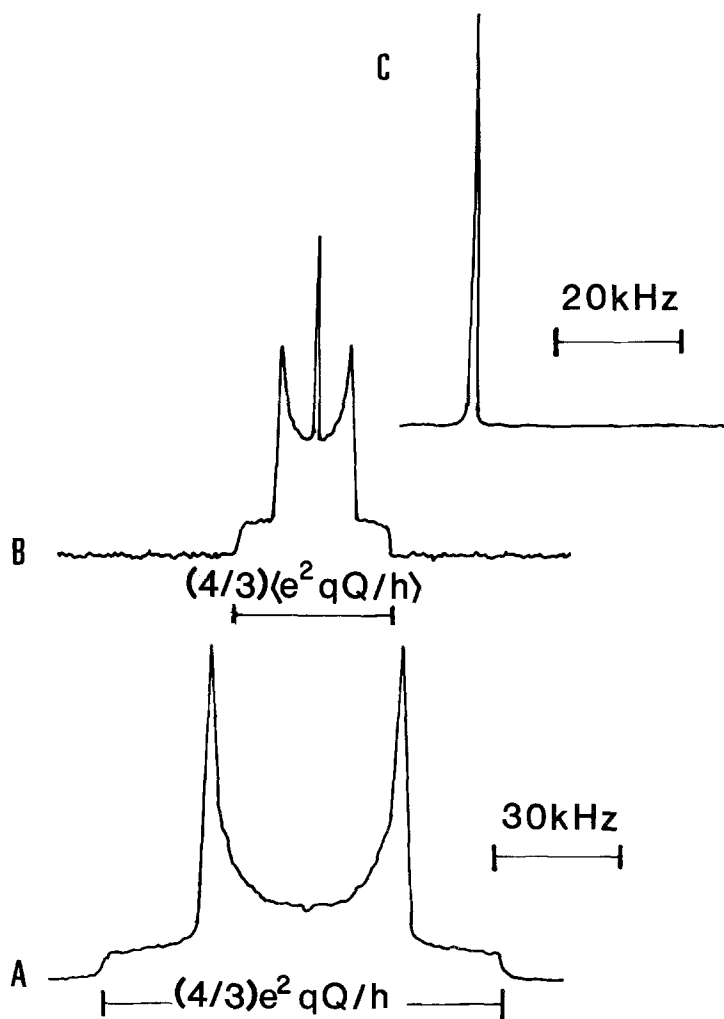


Fig. 4  $^2\text{H}$  NMR lineshapes of  
 a) solid  $\text{CD}_3\text{Br}$  at 77K.  
 b)  $\text{CD}_3\text{Br}$  in the structure I clathrate hydrate at 260K.  
 c)  $\text{CD}_3\text{I}$  in the structure II clathrate hydrate at 268K.

van der Waals' lengths of the molecules, i.e. the longer the molecule the larger the order parameter, although ethane, and especially acetylene do not conform to this trend.

In terms of the motional models considered before, this means that larger molecules are confined to be nearer to the equatorial plane of the cage than shorter molecules, as witnessed by the angles  $\beta$  in Table III. Ethane, and especially acetylene, are less strongly oriented than expected for molecules of that length. A possibility is that the terminal protons in these two guest molecules can penetrate the pentagonal rings of the hydrate cage, or even the fluctuating hydrogen bonds which make up the edges of the pentagonal rings.

The  $^2\text{H}$  or  $^{13}\text{C}$  experiments cannot be used to distinguish among the four motional models considered here.

When the structure I hydrate cage geometry is considered, perhaps model 2 is the most satisfactory. The barrier constraining molecules to be near to the equatorial plane of the cage has its origin in repulsive interactions between guests and the water oxygens which are part of the hexagonal rings at either end of the cage, and this barrier

Table I. Nuclear Shielding Anisotropies and Quadrupole Coupling Constants of Enclathrated Guest Molecules and Pure Solid Guest Materials

Guest Molecule	$\Delta\sigma$ /ppm (pure solid)	$\langle\Delta\sigma\rangle$ /ppm (guest)
$^{13}\text{CO}_2$	334 <sup>d</sup>	-101
$^{13}\text{CO}_2$	365 <sup>d</sup>	-148
Guest Molecule	$e^2qQ/h$ /kHz (pure solid)	$\langle e^2qQ/h \rangle$ /kHz (guest)
$\text{CD}_3\text{F}$	50 <sup>b,g</sup>	5.3 <sup>a</sup>
$\text{CD}_3\text{CD}_3$	53.7 <sup>b,d</sup>	12.3 <sup>a</sup>
$\text{CD}_3\text{Cl}$	60.3 <sup>b,d</sup>	19.1 <sup>a</sup>
$\text{CD}_3\text{Br}$	63.6 <sup>b,d</sup>	21.3 <sup>a</sup>
$\text{C}_2\text{D}_2$	183.0 <sup>e</sup>	35.3 <sup>a</sup>
$\text{CD}_3\text{I}$	56.0 <sup>b,f</sup>	0 <sup>c</sup>

<sup>a</sup>Guest in structure I large cage

<sup>b</sup> $\text{CD}_3$  groups rotating

<sup>c</sup>Guest in structure II large cage

<sup>d</sup>This work

<sup>e</sup>Ref. 12

<sup>f</sup>Ref. 13

<sup>g</sup>Estimate

**Table II.** Lengths, Dipole Moments and Order Parameters for Guest Molecules in the Structure I Hydrate Large Cage

Guest Molecule	Length/Å	Dipole Moment/D	Order Parameter S
$^{13}\text{COS}$	5.97	0.67	-0.405
$\text{C}_2\text{D}_2$	5.72	0	$\pm 0.193$
$\text{CD}_3\text{Br}$	5.64	1.80	$\pm 0.335$
$\text{CD}_3\text{CD}_3$	5.47	0	$\pm 0.229$
$\text{CD}_3\text{Cl}$	5.36	1.87	$\pm 0.316$
$^{13}\text{CO}_2$	5.12	0	-0.302
$\text{CD}_3\text{F}^2$	4.56	1.81	$\pm 0.11$

**Table III.** Angles  $\beta$ , or  $\beta_{\text{max}}$  for Different Motional Models

Guest Molecule	Model 1	Model 2	Model 3	Model 4
$^{13}\text{COS}$	14.7°	20.8°	20.8°	30.0°
$\text{C}_2\text{D}_2^a$	27.0°	38.8°	39.8°	59.6°
$\text{CD}_3\text{Br}^a$	19.3°	27.8°	28.4°	40.4°
$\text{CD}_3\text{CD}_3^a$	25.2°	36.2°	37.2°	54.8°
$\text{CD}_3\text{Cl}^a$	20.5°	29.4°	30.0°	43.3°
$^{13}\text{CO}_2$	21.7°	30.8°	31.8°	45.7°
$\text{CD}_3\text{F}^a$	31°	45°	47°	71°

<sup>a</sup>Order parameters were assumed to be negative.

should have a maximum near  $\beta \sim 45^\circ$ . Therefore models where all angles  $\beta$  are less than  $\sim 45^\circ$  would seem to be acceptable (i.e. models 1-3).

Other models, for instance with the angle  $\beta$  weighted according to an appropriate scheme, might be equally satisfactory. However, one of the main conclusions remains that the molecular motion of non-spherical guests in non-spherical cages cannot be regarded as isotropic, or even pseudo-isotropic.



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