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EXPERIMENTAL AND COMPUTATIONAL ^{13}C NMR STUDIES OF GUEST MOLECULE CONFORMATIONS IN LARGE CAGES OF STRUCTURE H CLATHRATE HYDRATES

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ABSTRACT

Binary structure H clathrate hydrates of large alkane molecules with methane help gas have been synthesized and their lattice structure verified by powder X-ray diffraction measurements. The chemical shifts of the carbon atoms of the guest molecules in the solid-state ^{13}C NMR spectra in the hydrate phase show significant up-field shifts compared to the pure liquid guest species. Quantum chemistry chemical shift calculations of different conformers of the guest molecules have been performed and compared with the experimental pure guest and guest in hydrate ^{13}C NMR spectra. These comparisons allow us to determine the relative contributions of conformation changes of the guests in the cages and the guest-host dipolar coupling to the changes in ^{13}C NMR chemical shift upon enclathration. The guests studied in this work include 2-methylbutane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, n-pentane, n-hexane, methylcyclopentane and methylcyclohexane.

Keywords: Clathrate hydrates, NMR spectroscopy, X-ray diffraction, conformation change, hydrocarbons

INTRODUCTION

Hydrocarbon gas hydrates mostly form in the three canonical structure I (sI), structure II (sII) and structure H (sH) forms.[1] To determine the properties of these hydrates, knowledge of both their molecular scale properties (such as percent cage occupancy by the guests and macroscopic properties (such as temperature, pressure, or macroscopic guest-water stoichiometry) are important. Molecular-scale characterization of gas hydrates is performed by a variety of techniques such as solid-state nuclear magnetic resonance

(NMR), Raman spectroscopy,[2] powder X-ray diffraction (XRD), neutron diffraction,[3] and molecular simulation, each of which has its own advantages and limitations.

The first application of NMR to determine cage occupancies in hydrocarbon hydrates was that of Ripmeester and Ratcliffe.[4] They reported cage occupancies from ^{13}C NMR and its relation to the hydrate structure for CH_4 in sI and sII hydrates. Since then, the technique has become one of the most powerful qualitative and quantitative methods for hydrate characterization.[5,6] A

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general trend observed was that the isotropic chemical shift scales with cage size, with guests in the smallest cages showing the largest shift difference from the gas phase because of deshielding by collisions of the guest with the cage wall.[7]

The larger cage size allows more hydrocarbons to become guests in sH hydrates than for sI or sII forms. Many of these larger guests can have conformational freedom, which can change their structure in the hydrate cage as compared with the pure bulk phase. In addition to the encapsulation, ^{13}C chemical shifts may also provide information on conformation structures of the guest in the cage. It is valuable to have a systematic study of ^{13}C chemical shifts of more complex sH guest molecules to note chemical shifts differences between the encaged guests and the bulk and to try and explain the differences in terms of the effects noted above. Here, the ^{13}C NMR spectra of the hydrate samples obtained are compared with those of the hydrocarbons in the bulk. Structures of the hydrates were confirmed by powder XRD measurements and the unit cell parameters were determined. The ^{13}C chemical shifts were calculated with electronic structure methods for different conformers of the guest molecules to assess the importance of conformational changes for the observed chemical shift differences.

EXPERIMENTAL AND COMPUTATIONAL METHODS

High purity hydrocarbon liquids and methane were used without further treatment. The hydrate samples were prepared by loading 5.0 g of finely ground powder ice into a high-pressure cell and adding 1.0 mL of the hydrate formers. The high-pressure cell and the hydrate formers were cooled in a freezer at 253.15 K before use. The high-pressure cell was then moved to a water bath, cooled to a constant temperature of 271.15 K, then, CH_4 helper gas was slowly introduced to a pressure up to 30.0 bar so as not to form pure CH_4 hydrate (sI) due to the reaction between ice and CH_4 gas. When the pressure drop due to hydrate formation was observed after 1 day, the temperature was increased to 274.15 K to promote the conversion of water into hydrate. To convert additional water into hydrate, this thermal cycling was used twice. After the pressure drop reached a steady state, the cell was cooled with liquid nitrogen before releasing pressure and taking out the samples.

Structural identification of the prepared samples was carried out on a Rigaku powder X-ray diffractometer equipped with an Anton Paar low-temperature controller. During the diffraction measurements, the experimental temperature was kept at about 85 K with liquid nitrogen.

^{13}C NMR spectra were obtained at 200 K by packing the hydrate samples in a 7-mm diameter Zirconium rotor, which was loaded into the variable temperature (VT) probe of a Bruker DSX400 solid-state NMR spectrometer. All spectra were recorded at a Larmor frequency of 100.6 MHz with magic angle spinning (MAS) at 2.0 kHz with cross-polarization (CP) or from single-pulse free induction decays with 1H decoupling. The ^{13}C NMR resonance peaks of adamantane, with assigned chemical shifts of $\delta = 38.56$ and 29.50 ppm at 298 K were used as the external chemical shift reference.

The ^{13}C chemical shielding of the carbon atoms for guest molecules were calculated using the gauge invariant atomic orbital (GAIO) method [8] in the Gaussian 98 suite of programs.[9] Optimized structures of each molecule in conformations with different dihedral angles with respect to the carbon backbones were determined with density functional theory at the B3LYP/6-311++G(*d,p*) level and the ^{13}C NMR isotropic chemical shielding was calculated at the MP2/6-311+G(2*d,p*) for each structure. For guest molecules with a maximum four carbon chain (i.e. 2-methylbutane, 2,2-dimethylbutane, and 2,3-dimethylbutane), relaxed potential energy surface scans at 10° dihedral angle intervals were performed along with GIAO calculations to determine the chemical shifts of the carbons at each dihedral angle.

RESULTS AND DISCUSSION

Binary structure H hydrates of hydrocarbons 2-methylbutane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, n-pentane, n-hexane, methylcyclopentane and methylcyclohexane with methane were synthesized.

The a and c lattice parameters from powder X-ray diffraction (PXRD) for the alkane guests vary within the range of 0.1 and 0.013 Å, respectively and the unit cell volumes range between 1289.85 and 1311.75 Å³. [10] The variation of the lattice parameters are consistent with those of other sH hydrates with nonalkane guests determined by PXRD. [11]

The ¹³C NMR spectra of the hydrate samples were compared with those of the pure liquid hydrocarbon guests to examine changes in chemical shifts after hydrate formation. The isotropic chemical shifts of the pure hydrocarbons at 273 K and in the hydrate phases are given in Table 1. The carbon designations will be used in the discussion that follow.

The ¹³C NMR chemical shifts of the spectral lines for most hydrocarbon samples decrease (shielding effect) after hydrate formation with changes in chemical shifts ranging from +0.4 ppm to roughly -4.1 ppm for different guests atoms. Figure 1 shows ¹³C NMR spectra of 2-methylbutane, 2,2-dimethylpentane and 2,3-dimethylpentane. The possible conformers for these molecules are also shown in this figure. The spectra for the other guests are given in Ref. [10].

Below, we will discuss the spectra of two guest species. Analyses of the shieldings of other guests are given in Ref. [10]. For 2,2-dimethylbutane, the changes in the chemical shifts are mainly observed for the terminal -C_αH₃ and central -C_γ- atoms, while the other terminal -C_δH₃ atoms are also affected. All the carbon atoms except for -C_βH₂- show an upfield shift. For 2,3-dimethylbutane, the terminal -C_αH₃ shows significant shielding, while the internal -C_βH- atom is also slightly affected.

The calculated chemical shifts for all conformers are given in Table 2. Calculated chemical shifts are for guests in the isolated gas phase but experimental values are for the guests in neat liquid form.

The relative energies of the conformers, their Boltzmann probabilities, and the longest C...C lengths as a measure of the effective conformer diameter are calculated and can be used to determine the stability of different conformers in the cages, see Ref. [10].

Hydrate formers		δ _{pure,expt.} / ppm	δ _{hydrate} / ppm
2-methylbutane (C _δ H ₃) ₂ C _γ H- C _β H ₂ C _α H ₃	C _α	12.84	11.56
	C _δ	22.88 (10.04)	22.39 (10.8)
	C _γ	30.67 (17.83)	30.67 (19.1)
	C _β	32.33 (19.49)	32.43 (20.9)
2-methylpentane (C _ε H ₃) ₂ C _δ HC _γ H ₂ - C _β H ₂ C _α H ₃	C _α	15.18	12.93
	C _β	21.71 (6.53)	19.36 (6.43)
	C _ε	23.27 (8.09)	22.92 (9.99)
	C _δ	28.92 (13.74)	25.10 (12.17)
3-methylpentane C _α H ₃ C _β H ₂ C _γ H- (C _δ H ₃) C _β H ₂ C _α H ₃	C _α	11.87	11.77
	C _δ	18.88 (7.01)	17.62 (5.85)
	C _β	29.79 (17.92)	30.18 (18.41)
	C _γ	36.81 (24.94)	36.90 (25.13)
2,2-dimethyl butane (C _δ H ₃) ₃ C _γ - C _β H ₂ C _α H ₃	C _α	9.63	8.53
	C _δ	29.50 (19.87)	29.21 (20.7)
	C _γ	31.06 (21.43)	30.18 (21.6)
	C _β	36.90 (27.27)	36.90 (28.4)
2,3-dimethyl butane (C _α H ₃) ₂ C _β H- C _β H(C _α H ₃) ₂	C _α	20.05	19.08
	C _β	34.37 (14.32)	34.00 (14.92)
n-pentane C _α H ₃ C _β H ₂ C _γ H ₂ - C _β H ₂ C _α H ₃	C _α	14.89	13.72
	C _β	23.95 (9.06)	21.61 (7.89)
	C _γ	35.54 (20.65)	34.47 (20.75)
n-hexane C _α H ₃ C _β H ₂ C _γ H ₂ - C _γ H ₂ C _β H ₂ C _α H ₃	C _α	14.11	13.24
	C _β	23.22 (9.11)	20.83 (7.59)
	C _γ	32.28 (18.17)	28.14 (14.90)
methyl cyclopentane C _α H ₃ - (C _β H(C _γ H ₂ C _δ H ₂) ₂)	C _α	20.93	20.25
	C _δ	25.80 (4.87)	25.61 (5.36)
	C _β	35.44 (14.51)	35.44 (15.19)
	C _γ	35.93 (15.00)	35.93 (15.68)
methyl cyclohexane C _α H ₃ (C _β H- (C _γ H ₂ C _δ H ₂) ₂ C _ε H ₂)	C _α	23.95	23.65
	C _ε	27.36 (3.41)	26.97 (3.32)
	C _δ	27.36 (3.41)	26.97 (3.32)
	C _β	33.69 (9.74)	33.71 (10.06)
	C _γ	36.12 (12.17)	36.10 (12.45)

Table 1. Experimental ¹³C chemical shifts of hydrate formers in their pure form and hydrate phases. The differences between the chemical shift of the α-carbon and other carbons in each molecule are given in parentheses.

Figure 1. The experimental ^{13}C NMR spectra of (a) 2,2-dimethylbutane and (b) 2,3-dimethylbutane in the pure liquid form (\circ) and clathrate hydrate (\bullet). The possible conformations of the two hydrocarbons are shown for each case.

To compare the calculated chemical shifts with the experimental liquid-state chemical shifts, Boltzmann averaged chemical shifts of all calculated conformers should be determined. Calculated chemical shifts are systematically lower than experimental values which are partly related to the known systematic deviations in computed chemical shifts when using the TMS reference. Experimental chemical shifts for the liquid hydrocarbons arise from mixtures of conformers of the hydrocarbons and we have not applied a regression to optimize the agreement between experimental and calculated chemical shifts which represent fixed conformations. To better compare experimental and calculated chemical shifts within each molecule in the liquid state, the differences between the ^{13}C chemical shifts of the α -carbons and the other carbons, $\Delta\delta = \delta(x\text{-carbon}) - \delta(\alpha\text{-carbon})$, with $x = \beta, \gamma, \delta$, or ϵ are given in Tables 1 and 2. The calculated difference values, $\Delta\delta_{\text{calc.}}$, are easier to compare with the experimental values, $\Delta\delta_{\text{expt.}}$, and are used for analysis. In most cases, the relative order of calculated chemical shifts for the different carbons for each hydrocarbon are in qualitative agreement with the experimental shifts for the pure liquids.

For 2,3-dimethylbutane, the changes in chemical shift of the α - and β -carbons with the 1-4 dihedral angle are shown in Figure 2. Dihedral angles within 30° of the anti conformation will be energetically accessible and the chemical shift

Hydrate		Conformer 1	Conformer 2	Conformer 3
2MB	C_α	9.7	4.3	NA
	C_δ	18.2 (8.4)	16.0 (11.8)	
	C_γ	25.4 (15.2)	23.5 (19.2)	
	C_β	27.1 (17.4)	25.3 (21.0)	
2MP	C_α	12.3	12.2	9.5
	C_β	18.9 (6.6)	12.7 (0.5)	16.2 (6.7)
	C_ϵ	18.5 (6.3)	16.6 (4.4)	17.9 (8.4)
	C_δ	25.2 (12.9)	23.5 (11.2)	20.2 (10.7)
	C_γ	35.6 (23.3)	33.5 (21.3)	33.3 (23.8)
3MP	C_α	9.9	9.9	6.69
	C_δ	12.1 (2.1)	16.5 (6.6)	16.51 (9.82)
	C_β	27.5 (17.6)	24.8 (14.9)	21.10 (14.41)
	C_γ	31.6 (21.6)	31.5 (21.6)	28.74 (22.06)
22DMB	C_α	6.6	NA	NA
	C_δ	23.7 (17.1)		
	C_γ	24.9 (18.4)		
	C_β	31.3 (24.7)		
22DMB	C_α	17.5	14.6	-
	C_β	30.2 (12.7)	28.5 (13.9)	
n-P	C_α	8.6	7.4	4.8
	C_β	20.0 (11.4)	17.5 (10.1)	12.8 (8.0)
	C_γ	31.0 (22.4)	28.6 (21.2)	25.9 (21.0)
n-H	C_α	12.2	11.2	10.7
	C_β	21.4 (9.2)	20.6 (9.4)	16.9 (6.2)
	C_γ	29.4 (17.2)	26.9 (15.7)	24.4 (13.8)
MCP	C_α	12.7	12.3	NA
	C_δ	18.8 (6.1)	16.4 (4.1)	
	C_β	33.7 (21.0)	31.9 (19.6)	
	C_γ	31.0 (18.4)	28.6 (4.1)	
MCH	C_α	19.4	14.14	NA
	C_ϵ	22.1 (2.7)	22.50	
	C_δ	22.5 (3.1)	17.26	
	C_β	27.5 (8.1)	23.70	
	C_γ	29.7 (10.3)	26.59	

Table 2. Calculated ^{13}C chemical shifts of different hydrocarbon conformers. The description of the guest atom labels are similar to Table 1.

variation in this range is ~ 0.2 and ~ 2.5 ppm for the α - and β -carbons, respectively. The changes in experimental chemical shift upon enclathration for the α - and β -carbons are 0.97 and 0.37 ppm, respectively, which are incompatible with both the small changes in the dihedral angle about the anti conformation (discussed above) and the gauche 2,3-dimethylbutane conformation chemical shifts given in Table 2. We can conclude that the change in chemical shifts is due primarily to the dipolar coupling of the 2,3-dimethylbutane guest carbon atoms which, as expected, is greater in magnitude for the outermost α -carbons.

For 2,2-dimethylbutane guest, the changes in chemical shift as a function of the 1-4 dihedral angle are shown in Figure 2. Dihedral angle

variations up to $\sim 35^\circ$ may be accessed at 273 K. Within this range of dihedral angle, the chemical shifts of the α -, β -, γ -, and δ - carbons change by approximately 0.9, 1.9, 0.9, and 0.7 ppm. This molecule has no gauche conformation. Given the pattern of the changes in experimental chemical shifts upon enclathration for the α -, β -, γ -, and δ -carbons, which from Table 2 are 1.10, 0.29, 0.84, 0.00 ppm, respectively, we conclude that the changes in chemical shifts between the pure liquid and hydrate phase are incompatible with only small changes in the dihedral angle about the anti conformation and that changes in chemical shifts are primarily due to the dipolar coupling of the 2,2-dimethylbutane guest α - and γ -carbon atoms with the cage waters.

X-ray structural analysis has shown that in the sII large cages, *n*-butane guests have gauche conformations and tetrahydropyran molecules have the boat conformation and in the sH hydrate the 2,2-dimethylpentane guests in the large cages are closer to the anti conformation with some deviation from ideal 180° angles.[12] The structural optimization at the B3LYP/6-311++G(*d,p*) level shows that the energy difference between the anti and gauche conformers of 2,2-dimethyl pentane is high (10.65 kJ·mol⁻¹) and this may lead to unfavorable gauche conformations for this guest. The other alkane guests in this work have much lower minimum dihedral rotation barriers (between 3.5 to 4.1 kJ·mol⁻¹, see Ref.[10]) and gauche conformations may be accessible to the enclathrated molecules. The long axis of the 2,2-dimethylpentane molecule lies parallel the *c*-axis of the sH unit cell and the long axis of the sH large cage.[12]

To explicitly calculate the effect of the cage on the ¹³C chemical shifts, we would need to calculate the chemical shielding of the guests in positions in the cage determined by X-ray crystal structure analysis. Computational optimization of the guest positions in clathrate hydrates are difficult to perform. The present calculations thus do not unambiguously determine the relative

contributions of conformational changes and cage wall-guest dipolar coupling in changing the guest ¹³C NMR chemical shifts. However, they can contribute to separating these two effects and until such time as the positions of the molecules in the cages are crystallographically determined, this analysis can be helpful in determining guest shapes and strengths of coupling in the cages.

The hydrate cage water molecules change the ¹³C chemical shift of methane from -7 ppm in the gas phase to -2.73 ppm for methane in the small sII small cages.[5] This change in chemical shift is the result of dipolar coupling between methane and the cage water molecules and is consistent with the magnitude of changes between the chemical shifts of the free guests and encapsulated guests in the sH hydrate.

CONCLUSIONS

Binary sH hydrates of methane and well-known hydrate formers of 2-methylbutane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, *n*-pentane, *n*-hexane, methylcyclopentane and methylcyclohexane were synthesized. These samples were characterized by means of ¹³C NMR spectroscopic methods, powder X-ray diffraction, and computation. In case of the NMR spectra, chemical shifts of the hydrate formers show different peak positions in the hydrate phase from those in the pure chemical states. Computational analysis of the different conformers of the guest molecules allows us to understand possible changes in the guest conformations upon hydrate formation and to estimate the effect of dipolar coupling with the cage water molecules on the chemical shifts of the guests. The experimental and computational results obtained in this study give fundamental information on molecular behaviors of structure H guests during hydrate formation.

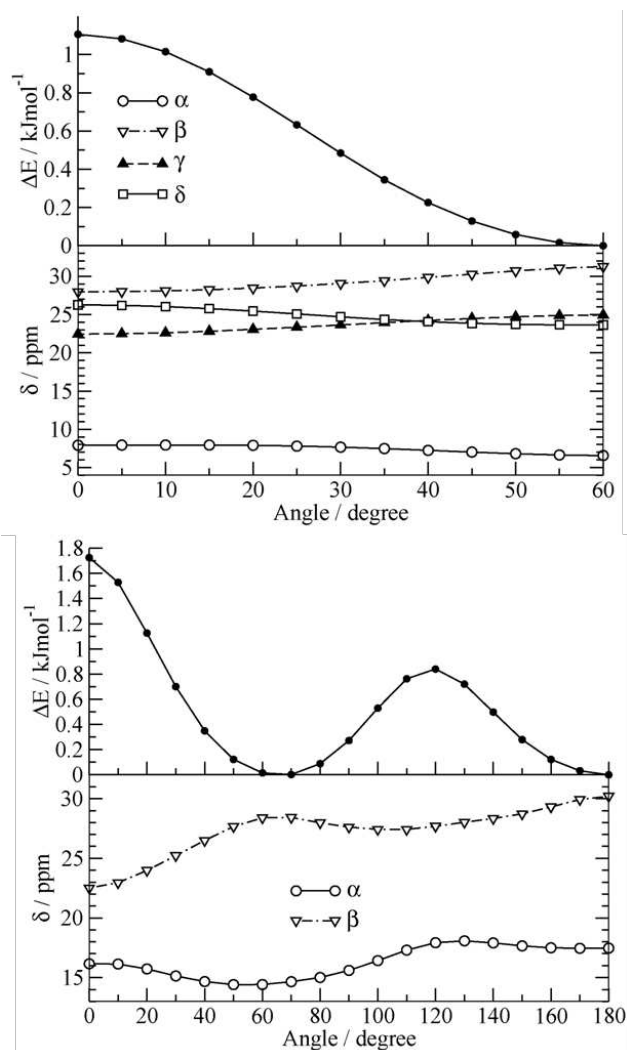


Figure 2. Changes in the chemical shifts of the carbon atoms in 2,2-dimethylbutane (top) and 2,3-dimethylbutane (bottom) and the relative energies with rotation about the 1-4 dihedral angle.

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