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## Probing Transient Hydrate Structures with Hyperpolarized $^{129}$Xe NMR Spectroscopy: A Metastable Structure II Hydrate of Xe

Igor L. Moudrakovski, Christopher I. Ratcliffe, and John A. Ripmeester*

The formation of gas hydrates involves the reaction of water or ice with small hydrophobic atoms or molecules in the size range of about 4.0 (Ar) to about 8.0 Å (methylcyclohexane).[1] Several hydrate structural families are known, and these are designated as structure I, II, and H (Str. I, Str. II and Str. H), the structure usually being determined by the largest guest in the hydrate.[1] Many questions remain about the nucleation of hydrates, their growth, and inhibition.[2] Such issues are of importance in a number of areas, as hydrates exist both in nature and in industrial environments.[2] To learn to control hydrate formation and decomposition is of continuing interest, especially to solve hydrate control problems in the hydrocarbon resource industry.[2]

Methods capable of monitoring hydrate formation processes are relatively few, especially if molecular-scale information is desired. Vibrational and NMR spectroscopies do have such capabilities.[3, 4] For the latter, the chemical shift tensors or isotropic shifts of molecules in different guest sites can be observed, and in this way provide a signature that is characteristic of the structural type.[4] $^{129}$Xe was the first guest to be used this way;[5] however, as the time required to record Xe NMR spectra is significant because of long spin-lattice relaxation times, it is not a suitable probe for studying processes. Advances in the development of optical pumping techniques for producing highly polarized Xe (HP Xe)[6] have solved this problem, and it has already been demonstrated that kinetic studies of hydrate formation can be carried out on a subsecond time scale.[7, 8] Herein we draw attention to the HP Xe approach as a powerful way of observing transient behavior and thereby yielding structural information in a time-resolved fashion. We show that unusual phenomena observed when HP Xe is placed in contact with a Str. II hydrate of tetrahydrofuran give new insights into hydrate formation reactions at the molecular level.

The experiment in which we were interested involved the exposure of a Str. II hydrate with empty small cages to a Str. I guest. In the case of THF hydrate, THF occupies the large cages in Str. II hydrate which has a crystal structure with a unit cell that can be formulated as $16\,M_s \cdot 8\,M_l \cdot 136\,H_2O$, where $M_s$ and $M_l$ are the small ($5^{12}$) and large cages ($5^{12}6^4$), respectively (where $5^{12}$ corresponds to a cage with twelve five-sided faces). In Str. II hydrate the small cages may be empty or they may be occupied by small molecules such as Ar, Kr, Xe, $N_2$, $O_2$, and $CH_4$. On the other hand, Xe on its own forms a Str. I hydrate, with a structural designation of $2\,M_s \cdot 6\,M_l \cdot 46\,H_20$, where $M_s$ is a $5^{12}$ cage and $M_l$ is the $5^{12}6^2$cage.

Experiments were carried out on a Bruker AMX-300 NMR spectrometer (magnetic field 7.05 T, $^{129}$Xe resonance frequency 83.03 MHz) by exposing powdered Str. II THF hydrate samples to HP Xe gas, which was prepared by optical pumping[6] directly in the NMR probe.[9, 10]

The time development of the Xe spectrum is shown in Figure 1. For closer scrutiny, selected spectra, along with those obtained for a control sample of powdered ice, are shown in

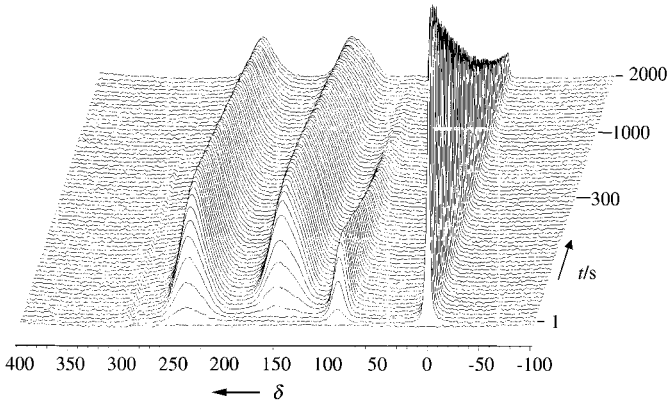


Figure 1. Time development of the $^{129}$Xe NMR spectrum after exposure of a powdered THF sample to hyperpolarized Xe. The line at $\delta \approx 0$ can be assigned to the gas, the lines at $\delta \approx 90$, 150, and 240 to Xe in the large cage of Str. II, the large cage of Str. I, and the two small cages in the Str. I and Str. II, respectively. Experimental conditions: temperature 223 K; starting pressure of Xe 530 mbar. Before adsorption of HP xenon, the sample was evacuated for 30 – 40 min at $10^{-5}$ mbar to minimize the presence of adsorbed oxygen.

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Figure 2. For the control reaction, the spectral lines characteristic of Xe in the Str. I large ($\delta = 150$) and small cages ($\delta = 242$) appear after a characteristic induction time, and the reaction finishes after a layer of thickness of about 1000 Å has formed, as estimated from the pressure drop and the surface area of the samples. The decay of the signals is due to spin-lattice relaxation.

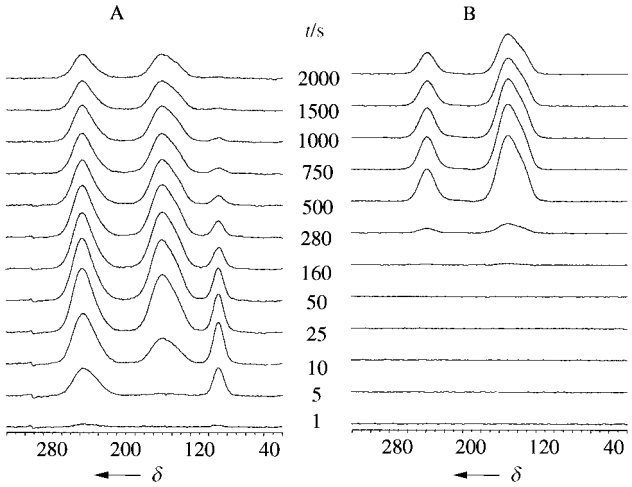


Figure 2. Selected spectra taken from Figure 1 (A), along with spectra obtained for a control sample of powdered ice (B), also at 223 K and with a starting Xe pressure of 580 mbar. In the latter case, formation of only Str. I hydrate is observed. Note the difference in the times when hydrates first appear.

When powdered THF hydrate is exposed to HP Xe, several surprising features become apparent. Almost immediately upon exposure of the Str. II hydrate sample to xenon, signals can be seen at $\delta \approx 230$ and 90. This indicates that Xe does not only occupy the small cage of Str. II, but the second signal indicates that Xe also occupies the large cage in Str. II, and to quite a high degree of occupancy. This is not a stable situation, and from the disappearance of the peak at $\delta \approx 90$ it is clear that on a somewhat longer time scale ($\sim 1000$ s) this Str. II signature is transient. We also note that after a short delay, signals appear at $\delta \approx 242$ and 150, indicating that Str. I Xe hydrate has appeared and that the amount grows with time. The delay can be attributed to the need for Str. I hydrate to nucleate as a separate phase. Whether Str. I results from the decomposition of the Str. II Xe hydrate is not immediately apparent, although it is unlikely that it forms from ice. From the stoichiometry used for the THF hydrate there should not have been excess ice in the system. Also, direct nucleation from ice would require a much longer induction time, as seen in Figure 2B.

Although it is not immediately apparent from the spectra in Figure 1 and 2, one may guess that some Xe remains in the small cage of Str. II upon conversion of the metastable Xe hydrate to a double hydrate. One indication of this is the very low ratio of integral intensities of the lines from xenon occupying large and small cages. If only Str. I hydrate were present, the expected ratio would be between 3:1 and 4:1,[5] however, the observed ratio is only 1.2:1 – 1.3:1. The residence of Xe in the small cage of Str. II is confirmed by examining the spectra upon decomposition (Figure 3). In this case a vacuum was applied to pump away Xe after the Xe – THF hydrate reaction had progressed for some time. The Str. I large cage line disappears quickly, along with some of the signal at $\delta \approx 240$. However, a residual signal at $\delta = 230$ remains for quite a

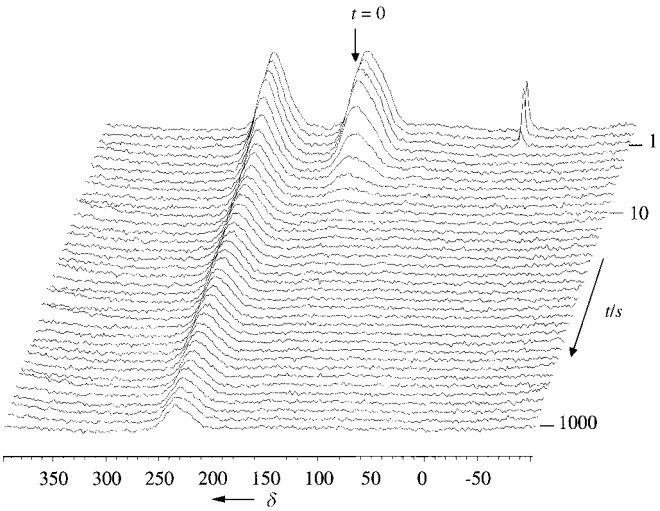


Figure 3. Time dependence of the Xe NMR spectrum of a sample of THF hydrate after its initial reaction with HP Xe and following the application of a vacuum (at time $t = 0$) to desorb Xe from the sample. Note the rapid decay of the gas line and the Str. I hydrate signals.

long time. This must be attributed to Xe in the small cage of the double hydrate of Xe and THF. Its lineshape also shows anisotropy of the chemical shift which is characteristic of Xe in the small cages of Str. II but not of those in Str. I.

Based on the discussion above, the reactions given in Equations (1) – (3) are suggested by the spectra.

$$\text{Str. II (THF)} + \text{Xe} \longrightarrow \text{Str II (Xe)} + \text{THF} \quad (1)$$

$$\text{Str. II (Xe)} \longrightarrow \text{Str. I (Xe)} \quad (2)$$

$$\text{Str. II (Xe)} + \text{THF} \longrightarrow \text{Str. II (Xe, THF)} \quad (3)$$

The first step [Eq. (1)] is the formation of a metastable Str. II hydrate of Xe that most likely exists as an epitaxial layer on Str. II THF hydrate.[11] The metastable Xe hydrate decomposes by either converting to Str. I Xe hydrate [Eq. (2)] or by reacting with THF that is liberated as shown in Equation (1) to form a double hydrate with Xe in the small cages [Eq. (3)]. On the time scale of the experiment, Str. I Xe hydrate and the double hydrate of Xe and THF continue to coexist. On a longer time scale, at true equilibrium, a single phase would be expected, that being a Str. II hydrate with partial occupancy of the small cages by Xe.[12] Reactions similar to the one reported here might well occur in natural or industrial environments if the composition of gases in contact with a hydrate changes suddenly. The complex processes observed, which lead to unexpected hydrate structures, should also be taken into account if the design of structure-specific hydrate inhibitors is contemplated.

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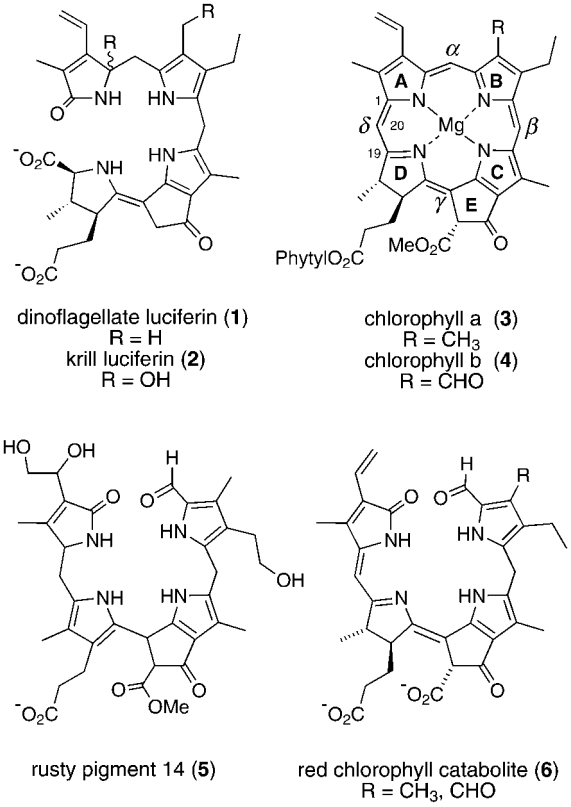
[11] We note here the FTIR observation of $CO_2$, normally a structure I hydrate guest, as occupying the large cage in Str. II hydrate in epitaxially grown hydrate thin films at low temperature: F. Fleyfel, J. P. Devlin, *J. Phys. Chem.* **1991**, *95*, 3811 – 3815.

[12] This will also explain the persistence of the signal of Xe in the small cages of str. II hydrate on application of a vacuum. If Str. I is formed strictly from the decomposition of the metastable str. II hydrate it will always be on the surface and decompose readily. However, Xe atoms can migrate deep into the str. II hydrate to fill the small cages as it is the stable phase and the dynamic properties of the THF hydrate water lattice are favorable for easy transport.


# Chlorophyll Catabolism Leading to the Skeleton of Dinoflagellate and Krill Luciferins: Hypothesis and Model Studies**

George Topalov and Yoshito Kishi*

In the late 1980s, we reported the structures of dinoflagellate luciferin (**1**) and krill luciferin (**2**) (Scheme 1).[1] Recognizing their structural similarity with chlorophylls a and b (**3** and **4**, respectively), we speculate that dinoflagellate luciferin




Scheme 1. Structure of dinoflagellate and krill luciferins and representative chlorophyll catabolites.

(**1**) and krill luciferin (**2**) are derived through an oxidative ring cleavage at the C1–C20 bond of chlorophylls with retention of the C20 carbon atom as a carboxylate at ring D. Shortly after the structures of **1** and **2** were disclosed, chlorophyll catabolites from barley and *Chlorella protothecoides* were isolated and characterized (**5** and **6**, respectively; Scheme 1).[2, 3] It is evident that, unlike dinoflagellate and krill luciferins, these catabolites are formed through cleavage of the C4–C5 bond of chlorophylls with retention of the C5 carbon atom as a

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