UV-VISIBLE AND RESONANCE RAMAN SPECTROSCOPY OF HALOGEN MOLECULES IN CLATHRATE-HYDRATES

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ABSTRACT

Ultraviolet-visible spectra are presented for a polycrystalline sample of chlorine clathrate hydrate and two single crystal samples of bromine clathrate hydrate. The data shows that the UV-visible spectroscopy is a sensitive probe for studying the interactions between the halogen guest molecule and the host water lattice. The spectrum for chlorine hydrate shows a surprisingly strong temperature dependence. The spectra reported for bromine clathrate hydrate single crystals reinforce our previous conclusion that there is a stable cubic type II structure as well as the tetragonal structure. There is also a metastable cubic type I structure. The new results are discussed in the context of previous results, resonance Raman spectroscopy, and how the molecules fit into the host cages.

Keywords: halogen clathrate hydrates, UV-visible, resonance Raman, polymorphism, spectrum shift versus cage size, water, ice

NOMENCLATURE

CS-I: The cubic clathrate hydrate structure, type I CS-II The cubic clathrate hydrate structure, type II HOMO: Highest occupied molecular orbital LUMO: Lowest unoccupied molecular orbital TS-I: The tetragonal structure of bromine hydrate *X*, *B* and *C*: The ground and two valence excited states of bromine that are most important for understanding its UV-visible spectroscopy π and π^* : bonding and antibonding orbitals with π symmetry

 σ and σ^* : bonding and antibonding orbitals with σ symmetry

ω_e: harmonic vibrational frequency

 $\omega_e x_e$: the anharmonicity constant for the vibration

 ω_{max} : the position of the peak intensity of an absorption band $\Delta \omega_{max}$: the shift of the band peak from that of the molecule in the gas phase $5^{x}6^{y}$: cage naming notation. x = number of pentagonal faces, y = number of hexagonal faces

INTRODUCTION

Although the halogen clathrate hydrate solids were first discovered almost two hundred years ago, [1,2], and although they have been extensively studied since then, there is surprisingly little spectroscopic data available to characterize the interaction between the halogen guest molecule and the water host lattice. Prior to the recent work in Irvine[3,4], the only spectroscopy studies for

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halogen clathrates was a Raman study[5] of Cl_2 , Br₂ and BrCl. Here, we report new UV-visible spectra for chlorine and bromine hydrates and compare them to previously reported spectra for bromine and iodine trapped in clathrate cages as well as to the halogen spectra in various solvents. This new work is then discussed in the context of the resonance Raman spectra for the halogens in clathrate hydrate cages. Among the findings revealed by the spectra reported in this paper is a clear confirmation that two stable and one metastable crystal structures exist for bromine clathrate hydrate under specific conditions of temperature and bromine concentration.

Characterization of the halogen hydrates has been complicated and subject to error from the beginning. Chlorine hydrate was synthesized by accident when Davy was trying to liquefy the gas. [1] Seven years later liquid chlorine was finally observed under pressure.[6] The accidental production of chlorine clathrate hydrate by Davy was a preview of one of the reasons that clathratehydrate research regained popularity in the last century: the plugging of natural gas pipelines by clathrate deposits due to residual humidity in the natural gas.

Determining the stoichiometry of clathrates was also difficult. The reason for this was clear after the determination of the crystal structure of chlorine hydrate by x-ray diffraction.[7] In a perfect crystal with complete cage filling the stoichiometry would be fixed. However, in chlorine hydrate the larger $5^{12}6^2$ cages are mostly occupied, but the occupation of the smaller 5^{12} cages depends on the pressure maintained during formation.[8] The variable cage occupancy, and thus variable stoichiometry, of gas clathrate hydrates still presents problems for understanding their stability and thermodynamics in detail.

Determining the structure of bromine hydrate has been especially problematic. A tetragonal unit cell was determined in 1963 by Allen and Jeffrey.[9] However, the variable stoichiometry and crystal shapes persuaded many investigators that several crystalline forms could co-exist.[10] In 1997 Udachin et al.[11] determined that a wide variety of bromine hydrate crystal shapes and stoichiometry all correspond to the Allen and Jeffrey tetragonal unit cell and a cage structure made up of 5^{12} , $5^{12}6^2$, and $5^{12}6^3$ cages in a 10:16:4 ratio. We will refer to this structure as tetragonal structure I, or TS-I. If all of the larger cages are occupied, then the limiting unit cell stoichiometry is $(Br_2)_{20}(H_2O)_{172}$; one bromine molecule for every 8.6 water molecules. Incomplete cage filling could account for H₂O:Br₂ ratios as high as 10.7. [11] Here we report that three structures can readily be observed for bromine hydrate: the TS-I structure, the cubic type-I, CS-I hydrate, and cubic type-II, CS-II, hydrate. The CS-I and CS-II structures are the most common clathrate hydrate forms. CS-I is meta-stable for bromine, but is kinetically preferred under certain formation conditions, while the CS-II structure is the stable form for a range of temperatures and compositions.. We conclude that at least three bromine hydrate crystal structures exist, and that more are possible.[12]

Although it might seem that the halogen hydrates are not so important for understanding the hydrocarbon hydrates that are currently of intense interest, note that the thermodynamics data for hydrates in general are referenced to an early study of bromine hydrate.[13] Since it now appears that this study assumed an incorrect crystal structure, a reexamination of the bromine hydrate data is appropriate. Also, a growing number of studies of the basic interactions of water molecules with the halogens will allow for a more complete analysis of the important host guest interactions in the halogen hydrates than may be possible for other systems.

Since few members of the hydrate research community are familiar with the optical spectroscopy of the halogens, we present a brief review here. Figure 1 shows the UV-visible spectrum of Br_2 and offers a pictorial interpretation. For the ground state, called the *X* state, the orbitals are filled up to the π^* level; often referred to as the highest occupied molecular orbitals or HOMOs. The lowest energy electronic excitation involves the promotion of one electron from the HOMO to the σ^* lowest unoccupied molecular orbital, or LUMO.

Several excited electronic states can result from this electronic excitation, but the absorption spectroscopy of Cl_2 , Br_2 and I_2 are dominated by only two of these states. One, commonly called the *C* state, is repulsive so that the $X \rightarrow C$ absorption spectrum is smooth and continuous, even in the gas phase. The second important excited state, commonly called the **B** state, occurs to slightly lower energy of the **C** state because it contains a bonding well. In the gas phase the $X \rightarrow B$ band contains a structured portion due to transitions to bound states and also a continuum due to transitions to dissociative states. These **B** and **C** states are close in energy and result in overlapping spectra. Formally, the **B** state is a triplet state and the $X \rightarrow B$ transition is only allowed due to spin orbit coupling. Thus, this transition is quite weak for Cl₂, and grows in intensity for Br₂ and I₂. The spectrum for Br₂, shown in Fig. 1, the $X \rightarrow B$ transition forms a shoulder on the low energy side of the stronger $X \rightarrow C$ transition.



Figure 1 Ground and valence excited state potential curves of Br_2 and the two most intense electronic transitions that contribute to the UV-visible spectrum. The inset shows a molecular orbital diagram. See text for more detail.

The peak of the bromine absorption is in the near UV range, resulting in its red color. For Cl₂ the spectra are dominated by the stronger $X \rightarrow C$ transition, mostly in the ultra violet, resulting in the pale yellow color of chlorine gas. For I₂ the two transitions blend together over much of the visible spectral range, resulting in the purple, almost black, color of solid iodine.

EXPERIMENTAL

In our previous studies of the optical spectra of bromine and iodine hydrates we worked with polycrystalline samples. The new data reported here for chlorine hydrate was obtained by similar techniques. Polycrystalline samples of chlorine hydrate were grown from water and gaseous chlorine on a surface of a conventional 10×10 mm quartz cell. The cell used a stopcock to contain the volatile chlorine. The crystallization process was initiated on a cell wall by applying dry ice above the water level. After chlorine and water condensed on the inner surface forming a thin hydrate film of a pale green color, the cell was transferred to a quartz Dewar for spectroscopic measurements. The spectra were recorded at ~200 K and at \sim 77 K.

For bromine hydrate, we have succeeded in recording spectra for single crystal samples. First, a polycrystalline sample was prepared using nanopure water and 99% pure bromine. Upon melting, this sample formed a supersaturated emulsion, which did not phase separate for a considerable time, allowing us to grow crystals from the liquid. The emulsion stayed liquid down to -17 ⁰C, so that crystal growth could be controlled by varying the temperature. Crystal growth and spectroscopy were performed using a 10 µm thick cell that consisted of two windows separated by non-reactive fluorinated grease (Krytox[®]). The top window was a quartz microscope slide. The bottom window was 0.5 mm thick sapphire placed on top of the two Peltier elements (separated by 3 mm to allow the light to pass through the cell), which were, in turn, cooled by a water-cooled copper block. The apparatus enabled us to control the temperature from +20 ^oC to -30 ^oC with a precision of $0.1 \, {}^{0}C.$

After loading the emulsion formed by melting a polycrystalline sample into the cell, it was quickly cooled to -20 0 C to form seed crystals. Upon heating above 0 0 C the ice melted, revealing the small bromine clathrate crystals that were formed. These crystals were stable to +5.8 0 C, the melting point of bromine hydrate in the tetragonal crystalline form, TS-I. Careful cycling of the temperature around the hydrate melting point resulted in a single seed crystal in the optical path. This crystal was then allowed to grow for four days at +4.8 0 C, and formed an optical quality

crystal that filled the 10 μ m space between the windows and had a diameter of ~ 0.5 mm. Under these conditions the crystal is expected to be nearly stoichiometric[14]. The sample was then quickly cooled to -20 $^{\circ}$ C in order to freeze the surrounding water and the spectrum reported in the next section of this paper was recorded.

After obtaining the spectrum of the TS-I bromine hydrate as described in the preceding paragraph, the sample was warmed above 0 0 C to melt the liquid water around the crystal and then the temperature was dropped to $-9 \,^{0}$ C. As previously reported,[12] when the TS-I crystal is exposed to excess water, CS-II crystals grow on the TS-I surfaces at this temperature. After 24 hours, the CS-II hydrate crystals were large enough and were of optical quality. The spectra were recorded at $-9 \,^{0}$ C.

RESULTS

The spectra for chlorine hydrate, the two single crystal samples of bromine hydrate, and iodine in hydrate cages, are shown in Fig. 2. Also shown in Fig. 2 are spectra of halogens in other environments for comparison. Fig. 2a gives the chlorine data. Four curves are shown. The green curve is the gas phase spectrum; the blue curve is the spectrum of chlorine hydrate at 200 K; the gray curve is the hydrate spectrum at 77 K and the red curve is the spectrum in aqueous solution with a small amount of NaCl added to eliminate HOCl from the solution. The possible contamination of aqueous chlorine spectra by HOCl was discussed previously in detail.[15]

The intensity scales, optical density, for the spectra are separately adjusted so that each has the same peak intensity. To the precision of the experiment, the electronic spectrum of chlorine in the clathrate hydrate at 200 K is the same as that of gas phase chlorine, while that of chlorine in aqueous solution is shifted 500 cm⁻¹ to higher energy. When the chlorine hydrate sample temperature was lowered to 77 K, there was a 500 cm⁻¹ shift of the spectrum so that it was much closer to that of the aqueous solution in position but retained the narrow width of the 200 K spectrum. This effect was reproducible and observed with several different samples. As will be discussed below, the width of a spectrum is an important clue to the environment of the chromophore. In this case, the fact that the



Figure 2 Spectra of a) chlorine, b) bromine, and c) iodine in various environments. In each case the green curve is the gas phase spectrum and the red curve is for an aqueous solution. For chlorine, the blue curve was recorded as described above, and is mainly due to chlorine in $5^{12}6^2$ cages at 200 K, the gray curve was recorded at 77K. For bromine, the blue curve is for the TS-I single crystal sample, the magenta curve is for the CS-II crystal, and the dark blue dashed line is the previously recorded spectrum for bromine in $5^{12}6^4$ cages of THF clathrate hydrate. For iodine the blue curve is the previously reported spectrum for iodine substituted into the $5^{12}6^4$ cages of THF clathrate hydrate.

width of the 77 K hydrate spectrum is the same as that of the 200 K sample indicates that the chlorine in each sample is in a clathrate hydrate cage.

The spectra for the two bromine hydrate single crystals show distinct shifts from that of gas phase bromine. The peak of the CS-II spectrum is shifted 440 cm⁻¹ to the blue of the peak of the gas phase spectrum, and the peak of the TS-I spectrum is shifted 880 cm⁻¹ to the blue of the peak of gas phase spectrum. These spectra are similar to, but measurably different than those of the previously reported spectra, as will be discussed below. We note that TS-I and CS-II single crystals were the same thickness, and that the optical density of the TS-I crystal was nearly twice that of the CS-II single crystal was nearly twice that of the CS-II single crystal spectra.

crystal. This reflects the relative stoichiometry of the two crystals, 1:8.6 vs. 1:17, and further supports the assignment of the second crystal to the CS-II structure.

For bromine in aqueous solution, the shift from the gas phase spectrum is 1750 cm⁻¹. The bromine spectra are considerably more sensitive to the specific local environment than are the chlorine spectra. The previously reported shifts for iodine are even more dramatic. The hydrate spectrum is shifted 1440 cm⁻¹ from the gas phase and the aqueous spectrum is shifted 2820 cm⁻¹ from the gas phase.

Also, notice that halogens in aqueous solution exhibit strong UV charge transfer transitions to the blue of the valence bands (mostly off the scale of Fig. 2). In addition, X_3^- (X=Cl, Br, I) bands can also be observed at sufficient halogen concentration midway between the valence and charge transfer bands. Caging the halogen molecule in a clathrate hydrate eliminated the ionic bands and significantly reduces the contribution of the charge transfer bands.

DISCUSSION

In the section above, several new results were presented. For chlorine clathrate hydrate the first UV-visible spectra were reported for polycrystalline samples, and found to have a remarkable temperature dependence. For bromine clathrate hydrate spectra are reported for single crystals of both the TS-I and the CS-II hydrate structures. Although the existence of a stable CS-II crystal structure was reported previously on the basis of Raman spectroscopy, [12] the new data reported here provides an unambiguous, independent confirmation of this result. We will discuss these new results in the context of previous observations and the spectra of halogen molecules in other environments. Results for the shifts of the UV-visible spectra of halogens in various environments are summarized in Table I. Results for the halogen stretching frequencies are summarized in Table II.

Perturbations of halogen by nearby molecules

We start with a general discussion of how halogen molecules interact with other species. A particularly illuminating example is the interaction of bromine with a single argon atom. Most chemists who do not already know the result would be surprised to learn that there are two isomers of the Ar-Br₂ van der Waals molecule. In T-Ar-Br₂ the argon atom attaches to the side of the bromine molecule and interacts equally with each bromine atom via van der Waals forces.[16] In L-Ar-Br₂ the argon atom attaches to the end of the bromine molecule.[17] The linear isomer is stable because the bromine LUMO, a σ^* orbital, is located on the end of the bromine molecule and creates a slight "dimple" in the electron density so that the argon atom can get closer to the bromine atom in this configuration. The net result is that the bond energies of the two isomers are the nearly equal, and that the isomerization barrier between them is surprisingly high.

In addition to having different geometries, the two $Ar-Br_2$ isomers have very different UV-visible spectra. The spectrum of the T-Ar-Br₂ isomer is sharp and very slightly shifted from that of the bromine molecule. This is because the argon atom on the side of the bromine molecule mostly acts as a spectator, hardly interacting with the bromine orbitals. The spectrum of the L-Ar-Br₂ isomer is much broader and is significantly blue shifted from that of the free bromine molecule. This is because the argon atom on the end of the bromine discusse the argon atom on the end of the bromine molecule interacts strongly with the bromine LUMO orbital, stabilizing the ground state and destabilizing the excited state.

Recent calculations show that the analogous result for the H_2O-Br_2 dimer molecule should be even more dramatic.[18] The lone electron pair of the water oxygen atom interacts strongly with the bromine LUMO orbital so that a large blue shift and broadening is predicted by the calculations.

From the above discussion, we note two general observations. To the extent that a second molecule is allowed to interact directly with a halogen LUMO orbital, the valence excitation spectra will tend to be strongly blue shifted and broadened. To the extent that the interacting molecule is a good electron donor, the shift and broadening will be larger. Bonding with water in the linear configuration also results in a considerable lowering of the halogen vibrational frequency.[18]

These effects are apparent in the solution phase spectra summarized in Table I. For instance, the spectrum of bromine in cyclohexane is not blue shifted relative to the gas phase since cyclohexane

| Environment | Chlorine ^a | | Bromine ^b | | | | Iodine ^c | |
|---|---|--|---|---|---|--|---|--|
| | ω_{max}^{d} (cm ⁻¹) | $\Delta \omega_{max}^{e}$ (cm ⁻¹) | ω _{max} (C-X) (cm ⁻¹) | $\Delta \omega_{max}$ (cm ⁻¹) | ω _{max} (B-X) (cm ⁻¹) | $\Delta \omega_{max}$ (cm ⁻¹) | ω _{max} (cm ⁻¹) | $\Delta \omega_{max}$ (cm ⁻¹) |
| Gas phase | 30300 | 0 | 24270 | 0 | 20830 | 0 | 18870 | 0 |
| C ₆ H ₁₂ solution | - | - | 24160 | -120 | 20760 | -70 | 19120 | 250 |
| CCl ₄ solution | 30180 | -120 | 24390 | 120 | 20920 | 90 | 19360 | 490 |
| CH ₂ Cl ₂ solution | 30830 | 530 | 24720 | 450 | 21300 | 470 | 19800 | 930 |
| $5^{12}6^2$ cage | 30300 | 0 | 25150 | 880 | 21720 | 890 | | |
| $5^{12}6^4$ cage (doped THF hydrate) | - | - | 24630 | 360 | 21190 | 360 | 20310 | 1440 |
| 5 ¹² 6 ⁴ cage (single crystal) | - | - | 24710 | 440 | 21270 | 440 | - | - |
| aqueous solution (T=293 K) | 30850 | 550 | 26000 | 1730 | 22590 | 1760 | 21690 | 2820 |
| amorphous ice (T=120 K) | _ | - | 25980 | 1710 | 22670 | 1640 | 21870 | 3000 |

Table I. Band maxima of the valence electronic bands of halogens in different environments compared to the gas phase

a. The chlorine spectrum is dominated by the $X \rightarrow C$ transition.

b. The bromine spectrum has been deconvoluted into the $X \rightarrow C$ and $X \rightarrow B$ transitions. See ref [3] for details.

c. The iodine spectrum is dominated by the $X \rightarrow B$ transition. See ref [4] for details.

d. ω_{max} is the position of the absorption maximum, ± 50 cm⁻¹.

e. $\Delta \omega_{max}$ is the shift of the absorption maximum from the gas phase value.

| Table II. Vibrational frequencies and anharmonicity constants for Chorine, Bromine |
|--|
| and Iodine in clathrate hydrate cages and in aqueous solution. |

| Environment | Chlorine | | Bror | nine | Iodine | |
|------------------|------------------|----------------------|----------------|----------------------|------------------|----------------|
| | $\omega_e{}^b$ | $\omega_e x_e^{\ c}$ | ω_e^{b} | $\omega_e x_e^{\ c}$ | $\omega_e^{\ d}$ | $\omega_e x_e$ |
| Gas phase | 559.7 | 2.67 | 323.3 | 1.06 | 214.5 | 0.61 |
| $5^{12}6^2$ cage | - | - | 321.2 | 0.82 | - | |
| $5^{12}6^4$ cage | - | - | 317.5 | 0.7 | 214 | ≤0.61 |
| Aqueous solution | 538 ^a | - | 306 | - | - | - |

a. Ref. [19]

b. ω_e is the harmonic frequency constant, ± 0.1 cm⁻¹, ³⁵Cl₂ and ^{78,81}Br₂. c. $\omega_e x_e$ is the anharmonicity constant, ± 0.05 cm⁻¹

d. $\pm 1 \text{ cm}^{-1}$.

has no unpaired electrons available to interact with the bromine LUMO orbital. Instead, the shift is slightly toward the red, most likely due to dielectric effects. The blue shift becomes gradually larger going to CCl₄, then to CH₂Cl₂ then to aqueous solution: the order of electron donating propensity. Similar shifts are observed for iodine solutions. The shifts for chlorine are analogous, but substantially less. Also, note that the shifts for halogen molecules frozen into amorphous ice are very similar to those in aqueous solution. Finally, although not reported in Table I, the spectra in both aqueous solution and amorphous ice are considerably broader than those in the gas phase. For more detail, see refs. 3 and 4.

The information above provides a context for discussing the spectra of halogens in the clathrate hydrate cages. First, we note that the widths of the halogen clathrate spectra are very similar to those of the gas phase spectra and considerably less than those of aqueous solutions. From this we infer that the halogen molecules in the cages are not interacting strongly with the lone electron pairs on the surrounding water molecules. To some extent this is not too surprising since the lone electron pairs are all involved in hydrogen bonding. However, the blue shifts for the bromine and iodine clathrate spectra are still substantial, especially when the fit into the cage is relatively tight.

Chlorine clathrate hydrate spectra

Since the chlorine hydrate samples studied here were formed at less than 0.5 atm chlorine pressure, most of the chlorine was located in the larger $5^{12}6^2$ cages of the CS-I crystal structure.[8] At 200 K, the spectrum of the chlorine clathrate hydrate is found to be very similar to that of gas phase chlorine, indicating that the guest host interaction is quite weak at this temperature. The narrow width is further evidence that the spectrum we observe is due to a single cage type. To the extent that the chlorine is in the center of the cage, on average, the chlorine atoms will be 3.45 Å from the surrounding oxygen atoms. This is far enough that even the chlorine excited state may not be perturbed by the cage walls. At a high temperature , 200 K, this assumption might be valid due to the thermal motion, which randomizes the position of the chlorine molecule within the cage. So there is no direct interaction between the cage walls and the chlorine LUMO orbital.

When the spectrum is recorded for chlorine hydrate at 77 K, it shifts nearly as much as for aqueous chlorine solutions, but is narrower than the aqueous spectrum. The narrow width of the spectrum indicates that chlorine is still in the clathrate cage. We speculate that the blue shift at 77 K is due to the chlorine molecules settling into a fixed position near the cage walls so that the excited state. walls perturb the Careful measurements for single crystals as a function of composition and temperature would provide extremely valuable data for to aid the interpretation of the spectra for chlorine hydrate.

Schofield and Jordan performed calculations of the chlorine ground and valance excited states in both the 5^{12} and $5^{12}6^2$ cages.[20] The calculations predict a spectrum shift of 700 cm⁻¹ for a distorted 5^{12} cage. Few details regarding the calculation for the $5^{12}6^2$ cage were presented and they did not test whether the observed spectrum should change with the location of the chlorine molecule within the cage.

Bromine clathrate hydrate spectra

Next, we shift to the interpretation of the bromine clathrate hydrate spectra. Here we report the first spectra measured for halogen clathrate single crystals. The TS-I crystal spectrum is similar, but slightly different from the previously reported bromine clathrate film spectrum; the shift from the gas phase is 880 cm⁻¹. As discussed below, from the differences between the two spectra we conclude that the previously studied bromine hydrate film did not consist of TS-I micro-crystals but rather CS-I micro-crystals.

Similarly, the spectrum reported for the CS-II single crystals is very similar to that reported previously for bromine in substitutional sites in a THF-CS-II sample. Each spectrum exhibits a 400 \pm 40 cm⁻¹ shift from the gas phase. This proves unambiguously that the bromine molecules in the CS-II single crystal are in 5¹²6⁴ cages. These crystals were previous attributed to the CS-II structure on the basis of their morphology and their Raman spectra.[12] The new data reported here confirms that assignment.

The difference between the new spectra for single crystal TS-I and that of the previously reported samples that were thought to be TS-I poly-crystalline films are shown in Fig. 3. Although the

differences between the two spectra are not dramatic, this is because the width of the figure is 8000 cm⁻¹. In each case, the peak of the spectrum is shifted 880 cm⁻¹ compared to that of the gas phase molecule. Upon close inspection the differences between the two spectra are both important and instructive.



Figure 3 Spectra of the TS-I single crystal (3.a) and the previously reported bromine hydrate (3.b). As discussed in the text, we conclude that the TS-I single crystal spectra include contributions from bromine in $5^{12}6^3$ cages, while the previously reported sample does not. We further conclude that the previously reported sample was a CS-I microcrystalline bromine hydrate film.

The single crystal spectrum, Fig. 3.a, shows a less pronounced shoulder and slightly higher intensity on the low frequency side of the peak compared to the polycrystalline sample. We attribute this extra intensity to the contribution of bromine in the $5^{12}6^3$ cages in the single crystal spectrum. If so, why didn't the $5^{12}6^3$ cages contribute to the previously observed spectra? The observations reported here, as well as other observations to be reported in a future paper, convince us that the previously reported poly-crystalline film consisted CS-I microcrystals rather than of TS-I microcrystals. Thus in the previous study only $5^{12}6^2$ cages were occupied. Although the CS-I bromine hydrate crystal structure is thermodynamically unstable with respect to the TS-I structure, the CS-I structure is kinetically favored since its structure is much easier to grow.

Note that the blue shift for bromine in the $5^{12}6^2$ cage is 880 cm⁻¹, while that in the $5^{12}6^4$ cage is only 400 cm⁻¹. Clearly, the blue shift is very

sensitive to cage size. It would be very surprising if bromine in the $5^{12}6^2$ and the $5^{12}6^3$ cages had the same spectrum since the cage sizes are quite different. The longest "free diameter" of the $5^{12}6^2$ cage is 5.9 Å, while that of the $5^{12}6^3$ cage is 6.59 Å, close to the value for the $5^{12}6^4$ cage, 6.56 Å. The fact that the previous microcrystalline film spectrum shows a single, narrow peak is strong evidence that only a single type of cage is occupied.

To follow up the reasoning in the above paragraph, we perform the following simulation of the TS-I single crystal spectrum. First, we assume that the spectrum of bromine in any given cage has a cage independent shape, but a cage dependent shift. Next, we assume that the TS-I single crystal spectrum (Fig. 3.a) contains contributions from both the $5^{12}6^3$ and the $5^{12}6^2$ cages in a 1:4 optical density ratio while the polycrystalline spectrum (Fig. 3.b) is due only to bromine in $5^{12}6^2$ cages. This assumption has built into it a second assumption that the oscillator strength does not vary between cages. This is consistent with the intensities of the TS-I and the CS-II spectra.



Figure 4 The blue curve is the TS-I single crystal spectrum. The dashed black curve is the CS-I spectrum previously obtained from a polycrystalline film and dominated by bromine in $5^{12}6^2$ cages. Its peak intensity is adjusted to be 80% of the TS-I spectrum. The dashed green curve has the same shape as the black curve, but is shifted to the red by 700 cm⁻¹, and adjusted to be 20% as intense as CS-I spectrum. The sum of the black and green curves yields the red curve, which closely fits the observed single crystal spectrum except in the UV wing. The purple curve is the residual of the fit.

Following the above assumptions, the contribution of the $5^{12}6^3$ cages to the TS-I spectrum has the

same shape as the CS-I spectrum, but shifted to the red and only 20% as intense. The contribution of the $5^{12}6^2$ cages is the same as the CS-I spectrum but with the optical density reduced by 20%. This simulation is shown in Fig. 4. The blue line is the TS-I spectrum. The dashed black line is the CS-I spectrum with the intensity reduced by 20%. The green dashed line is the same spectrum, shifted ~700 cm⁻¹ to the red and adjusted to 20% of the peak optical density. The sum of the two dashed lines yields the red line, which is then compared to the TS-I spectrum, the blue line. The residual between the two-component model and the TS-I spectrum is shown as a purple line at the bottom of the figure.

The two-component model yields an excellent fit to the portion of the TS-I spectrum to the red of the peak. There is a slight residual to the blue of the peak that we attribute to surface effects. Since bromine in the $5^{12}6^3$ cages contribute, at most, about 20% of the total intensity, the analysis presented above cannot be taken to be quantitative. We are confident, however, in the conclusion that the polycrystalline sample consisted of CS-I microcrystals.[14]

Comparison of the three halogens:

Table I. summarizes the halogen clathrate spectral shifts from the gas phase observed in this and previous studies. Qualitatively, the shift of chlorine in $5^{12}6^2$ cages is negligible, except at 70 K; that of bromine in $5^{12}6^4$ cages is small, ~ 400 cm⁻¹; that of bromine in $5^{12}6^2$ cages is large, ~ 900 cm^{-1} ; and that of iodine in $5^{12}6^4$ cages is very large, ~ 1400 cm⁻¹. For comparison, the spectral shifts between the gas phase and aqueous solution are 500 cm⁻¹ for chlorine, 1750 cm⁻¹ for bromine and 3000 cm^{-1} for iodine. It is clear that the spectra of halogens are very sensitive to the proximity of water molecules and, once analyzed with a sufficiently detailed model. will reveal considerable insight into the details of the guesthost interaction in halogen clathrates.

Although the valence transition shifts in aqueous solutions are rather large, recent calculations suggest that those of isolated H_2O-X_2 (X = halogen) dimers would be even larger.[18] In the isolated dimers, a rather strong bond is formed between the two molecules: 982 cm⁻¹ for H_2O-Cl_2 and 1273 cm⁻¹ for H_2O-Br_2 . This is due to the propensity of the oxygen atom on water to donate

its non-bonding electrons to the σ^* antibonding orbital of the halogen. Thus the ground state of the H₂O-X₂ dimer is considerably lower in energy that that of the free molecules. Valence electron excitation of the halogen promotes an electron from the π^* HOMO, to the σ^* LUMO. However, in the H₂O-X₂ dimer, the oxygen lone pair electrons are already occupying some of the space of the LUMO and the valence excited states of the dimer at the geometry of the ground state are shifted to higher energy. The lowering of the ground state energy and the raising of the excited state energy account for the large predicted blue shift of the spectrum: 1600 cm⁻¹ for H₂O-Cl₂ and 2000 cm⁻¹ for H₂O-Br₂.

Why is the blue shift for an aqueous solution less than for an isolated H_2O-X_2 dimer? There are probably two important effects. First, the waterwater hydrogen bonding is stronger than the water-halogen bonding and will serve to displace the water molecules away from the ideal geometry for bonding with the halogen molecules. Second, the other water molecules in the liquid environment may serve to stabilize the halogen excited state via dielectric effects.

These caveats are especially true for chlorine, for which the electron-accepting propensity is considerably weaker than for bromine.

Why are the shifts for the halogen clathrates less than those for aqueous solution? To form a clathrate crystal, all of the oxygen atom lone electron pairs must participate in hydrogen bonding. Thus, to a first approximation, the HOMO-LUMO effect is not expected to be important in the clathrate environment. This is as observed for chlorine in $5^{12}6^2$ cages and bromine in $5^{12}6^3$ and $5^{12}6^4$ cages. However, for bromine in $5^{12}6^2$ cages and iodine in $5^{12}6^4$ cages the observed shifts are still substantial. Although this data has yet to be interpreted quantitatively, it seems clear that close proximity to the cage walls will raise the energy of the halogen molecule valence excited states.

Resonance Raman spectroscopy

Another set of data that helps reveal the host guest interactions for halogen hydrates is Raman spectroscopy, the results for which are given in Table II. To date, we have collected stretching vibration frequencies and first anharmonicities for bromine in TS-I and CS-II single crystals, $321.2 \pm 0.1 \text{ cm}^{-1}$, $\omega_e x_e = 0.82 \pm 0.05 \text{ cm}^{-1}$ in the former, $317.5 \pm 0.1 \text{ cm}^{-1} \omega_e x_e = 0.7 \pm 0.05 \text{ cm}^{-1}$ in the later using 532 nm excitation laser source resonant with the X-B transition.[12] These values can be compared to 323.3 cm⁻¹ $\omega_e x_e = 1.06 \text{ cm}^{-1}$ for bromine in the gas phase and 306 cm⁻¹ in aqueous solution. Unlike the UV-visible spectral shifts, the vibrational frequencies are strictly a ground state property. In this case, the larger $5^{12}6^4$ cage produces the larger spectral shift. This is in accord with the trend first noticed by Fleyfel and Devlin:[21] molecules in larger hydrate cages tend to have lower vibrational frequencies.

As for bromine in the $5^{12}6^2$ cage, the stretching vibrational frequency for iodine in the $5^{12}6^4$ cage of THF clathrate is close to the gas phase value. In contrast to the electronic spectra, a tight fitting cage has a smaller effect on the vibrational frequency than a larger cage. At a first glance this is a counterintuitive result. However, the observed trends have a simple explanation when we consider the effect of polarization of the guest molecule by the net electric field of the cage water molecules. The ground electronic state of the polarized molecule would have an admixture of the ion-pair states, which have much lower vibrational frequencies.[22] In a tight cage the guest is closer to the center, where it feels a smaller electric field so that and polarization of the halogen will be smaller. In contrast, when the cage is loose, the guest may fall on a side where electric field causes stronger polarization and thus the vibrational frequency of the guest molecule drops.

Note that the anharmonicity constant for bromine in the $5^{12}6^4$ cage is significantly smaller in the clathrate cages than in the gas phase. This implies that the cage increases the potential energy as the halogen stretches away from its equilibrium bond length. This indicates again that the halogen in the large cage might move to one side and be in closer contact to the cage wall. However, until a quantitative model is developed this remains quite speculative.

The combination of the UV-visible spectrum and the Raman results for liquid water may be especially interesting to simulate. Intermolecular bonding, polarization and thermal effects will all be quite important Calculations on the isolated H_2O -Br₂ dimer predict that the bromine stretching frequency is even lower in the dimer than in aqueous solution.[18]

The resonance Raman spectra of enclathrated bromine are different from those of an aqueous solution in another important respect. Those of the enclathrated bromine exhibit a long progression of vibrational overtones. In aqueous solution, only the fundamental is observed. This difference indicates that electronic dephasing time, which determines formation of the resonance Raman progression, is extremely short in aqueous solution, <5-10fs.[23] Upon electronic excitation of a halogen molecule, vibrational modes of the solvent are directly excited (this is evident in a broadening of the molecular absorption spectrum), leading to a very fast electronic dephasing in the halogen excited state and shortening of the resonance Raman progression.

Pictorial views halogens in the clathrate cages

Although development of a quantitative analysis for the data presented here is yet to come, it is instructive to visualize the cage environments for the halogens in the several cages. To create the following figures, the cages were constructed by taking the oxygen coordinates from X-ray diffraction data and assigning hydrogen positions as described in ref [4]. Bromine molecules were given the correct bond length and their positions with the cage were calculated using the MMFF model[24] in the Spartan program.[25] Although the MMFF potential is not expected to be accurate enough for detailed predictions, it is useful for illustrating the relative sizes of the cages and the relative fits of the halogen molecules.

Figure 5 shows two views of bromine relative to a slice through the $5^{12}6^2$ cage. The bromine is aligned parallel to the hexagonal faces, roughly centered in the cage. The end view, relative to the bromine bond, Fig. 5a, shows that the bromine is in closer contact with the top and bottom of the cage than with the sides perpendicular to the bromine bond. The side view shown in Fig. 5b shows that ends of the bromine molecule are in close contact with the cage walls, but do not align directly with any of the oxygen atoms.

Figure 6 shows analogous views of bromine in the $5^{12}6^3$ cage. For the $5^{12}6^3$ cage the hexagonal faces

form a ring around the bromine bond, giving the cage a prolate shape. This results in a more uniform spacing between the bromine and the cage wall. In particular, the ends of the bromine molecule are well spaced from the cage walls. The special stability of bromine in this cage, resulting in the unique TS-I crystal structure, is probably due to the fact that the prolate shape of the cage allows the van der Waals interaction between the water and bromine molecules to be optimized for a large fraction of the cage walls.



Figure 5. Bromine in the $5^{12}6^2$ cage. The left view (5a) is along the bromine bond, the right view (5b) is from the side of the bromine bond.



Figure 6. Bromine in the $5^{12}6^3$ cage. The left view (6a) is along the bromine bond, the right view (6b) is from the side of the bromine bond.



Figure 7. Bromine in the $5^{12}6^4$ cage. The left view (7a) is along the bromine bond, the right view (7b) is from the side of the bromine bond.

Figure 7 shows views of bromine in the $5^{12}6^4$ cage. In this case the spacing between the bromine and the cage walls is quite large except on the ends of the molecule. It would not be surprising if the bromine is not located in the center of the cage at low temperature.

Prospects for future work

Although a wealth of new data has recently been obtained for the spectroscopy of halogen molecules in clathrate hydrate environments, the analysis of the data has just begun. The first ab *initio* study of chlorine in hydrate cages has been performed.[20] Many more results will be necessary before the spectra can be interpreted. Water-halogen model potentials currently in the literature, such as the MMFF potential used above, do not accurately model the full anisotropy of the intermolecular forces. The success of the electrostatic model in interpreting the iodine spectrum suggests that perhaps a Diatomic-in-Molecule approach might be useful. We hope that the data presented here, along with new data to be collected, will stimulate our theoretical colleagues to investigate these systems in more detail.

Conclusion

The first UV-visible spectra for chlorine clathrate hydrates are reported and the first single crystal spectra for two crystalline forms of bromine clathrate hydrate are reported. The spectrum for chlorine clathrate at 200 K is very similar to the gas phase spectrum, while the spectrum at 77 K is shifted 500 cm⁻¹ to the blue. We speculate that at 200 K the thermally averaged position of the chlorine is in the center of the cage but that at 77 K the lack of thermal motion allows the chlorine to settle into a position near the cage walls. Clearly, more data will be required to test this hypothesis. It will also be valuable to study more highly doped chlorine in the 5¹² cages.

The spectrum of the bromine clathrate CS-II single crystal is quite similar to that previously reported for bromine substituted into some of the $5^{12}6^4$ cages of CS-II THF clathrate. This confirms the previous assignment of the resonance Raman spectra of this crystal to the CS-II structure. The spectrum of the TS-I single crystal shows extra intensity on the red side of the previously recorded polycrystalline spectrum. We conclude that the

previously studied films consisted of metastable CS-I microcrystals.

In general, the more tightly a halogen molecule fits into a clathrate cage, the more blue shifted its UV-visible absorption spectrum. In contrast, the resonance Raman spectra reveal that the halogen vibrational frequencies are shifted less from the gas phase in the tight fitting cavities, while the frequencies are more red shifted in the larger cages. These results will provide a rigorous test for quantitative models, which are under development to better understand the details of the halogenclathrate interactions.

[1] Davy H. The Bakerian Lecture: On Some of the Combinations of Oxymuriatic gas and Oxygen, and on the Chemical relations of These Principles, to Inflammable Bodies. Philosophical Transactions of the Royal Society 1811;101:1-35.

[3] Kerenskaya G, Goldschleger IU, Apkarian VA, Janda KC. *Spectroscopic signatures of halogens in clathrate hydrate cages. 1. Bromine.* Journal of Physical Chemistry A 2006;110:13792-13798.

[4] Kerenskaya G, Goldschleger GI, Apkarian VA, Fleisher E, Janda KC. *Spectroscopic Signatures of Halogens in Cathrate Hydrate Cages.2. Iodine.* Journal of Physical Chemistry A 2007;111(43):10969-10976.

[5] Anthonsen JW. *The Raman Spectra of Some Halogen Gas Hydrates*. Acta Chemica Scandinavia A 1975; 29:175.

[6] Davy H. On the Fallacy of the Experiments in Which Water is Said to Have Been formed by the Decomposition of Chlorine. Philosophical Transactions of the Royal Society 1818;108:169.

[7] Pauling L, Marsh RE. *Structure of the Clorine Hydrate*. Proc. Natl. Acad. Sci. USA 1952;38:112-117.

[8] Cady GH. Composition of Cathrate Gas Hydrates of CHCIF₂, CCI₃F, CI₂, CIO₃F, H₂S, and SF₆. Journal of Physical Chemistry 1981;85:3225-3230.

[9] Allen KW, Jeffrey GA. *On the structure of bromine hydrate.* Journal of Chemical Physics 1963;38:2304.

[10]Dyadin YA, Belosludov VR. *Thermal expansion and lattice distortion of clathrate hydrates of cubic structures I and II.* Comprehensive Supramolecular Chemistry. 1996;6:789.

[11]Udachin KA, Enright GD, Ratcliffe CI, Ripmeester JA. *Polymorphism in Br*₂ *Cathrate Hydrates.* Journal of the American Chemical Society 1997;119:11481.

[12] Goldschleger IU, Kerenskaya G, Janda KC, Apkarian VA. *Polymorphism in Br2 Clathrate Hydrate* Journal of Physical Chemistry A 2008;112(5):787-789.

[13] Platteeuw J. C. van der Waals J. H. *Thermodynamic Properties of gas hydrates*, Advances in Chemical Physics 1957;2:1

[14] Kerenskaya G, Goldschleger I. U., Apkarian V.A., Janda K.C., *Growth and morphology of bromine hydrates*, In preparation.

[15] Zimmerman G, Strong FC. *Equilibria and Spectra of Aqueous Chlorine Solutions*. Journal of the American Chemical Society 1957;79:2063-2066.

[16] Cabrera J, Bieler CR, McKinney N, van der Veer WE, Pio J, Roncero O, Janda KC, *Time and frequency resolved dynamics of ArBr*₂. Journal of Chemical Physics 2007;127:164309.

[17] Pio J, van der Veer WE, Bieler CR, Janda KC. *Product state resolved excitation spectroscopy of He-, Ne- and Ar-Br₂ linear isomers: Experiment and theory.* Journal of Chemical Physics 2008;128:134311.

[18] Hernandez-Lamoneda R, Uc-Rosas VH, Bernal-Uruchurtu MI, Halberstadt N, Janda KC. *Two Dimensional* H_2O - Cl_2 and H_2O - Br_2 potential surfaces: an ab initio study of ground and valence excited electronic states. Journal of Physical Chemistry A 2008;112(1):89-96.

[19] Cherney DP, Duirk SE, Tarr JC, Collette TW. Monitoring the Speciation of Aqueous Free Chlorine from pH 1 to 12 with Raman Spectroscopy to Determine the Identity of the Potent Low-pH Oxidant. Applied Spectroscopy 2006;60(7):764-772.

[20] Schofield DP, Jordan KD. *Theoretical investigation of the electronically excited states of chlorine hydrate.* Journal of Physical Chemistry A 2007;111(32):7690-7694.

[21] Fleyfel F, Devlin JP. *FTIR spectra of 90 K films of simple, mixed and double clathrate hydrates.* Journal of Physical Chemistry 1988;92:631.

[22] Senekerimyan V, Goldschleger I, and Apkarian VA, *Vibronic dynamics of I*₂ *trapped in amorphous ice: Coherent following of cage relaxation.* Journal of Chemical Physics 2007;127:214511.

[23] Ovchinnikov M, Apkarian VA, Voth GA. Semiclassical molecular dynamics computation of spontaneous light emission in the condensed phase: Resonance Raman spectra. Journal of Chemical Physics 2001;114,7130-7143.

[24] Hehre WJ. A Guide to Molecular Mechanics and Quantum Chemical Calculations. Wavefunction, 2001, Irvine, CA.

[25] Spartan '04, Wavefunction Inc., Irvine, CA.

REFERENCES

^[2] Lowig C. *Uber eine Bromverbindungen und uber Brom-Darstellung*. Ann. Chim. Phys. Ser. 1829;42(2):113-119.