The Raman Spectra of Some Halogen Gas Hydrates

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The Raman spectra of Br_2 , Cl_2 , and BrCl gas hydrates have been recorded at -196°C in the range $\sim 20 - 600\text{ cm}^{-1}$. The spectra indicate remarkably little interaction between the "guest" and "host" molecules in bromine and chlorine gas hydrates and a little more pronounced interaction in bromine chloride gas hydrate. The isotope effect observed in the spectra is in fair agreement with the expected. Bands observed below 200 cm^{-1} are tentatively assigned to translational vibrations of the host molecules.

A clathrate compound may be described as a group of molecules called "guest" molecules, which are enclosed in the cavities in a crystal lattice called the "host" lattice. In the cases where water forms the lattice and where the guest molecules have a diameter less than approximately $5.9\text{ \AA}$, the compound is designated a "gas hydrate".

The first known gas hydrate was that of chlorine, which was discovered by Davy¹ in 1811. The number of guest molecule species, which take part in the formation of gas hydrates, has since turned out to be large.²⁻⁵

Though it is difficult exactly to predict which molecular species are able to form gas hydrates, the following conditions must in general be fulfilled:⁵ The molecule must have a size, which fits in the cavities of the lattice; it must not form hydrogen bonds to the solvent (low solubility in water) and the van der Waals forces in the given molecular species must not be too large (b.p. $< \sim 60^\circ\text{C}$).

The structures of these compounds have been described by several authors.²⁻⁵ According to these investigations all such compounds crystallize in one of two cubic structures called type I and type II. The guest molecules are trapped in the cavities formed by a network of hydrogen bonded water molecules. The number and size

of these cavities are different in the two structures. As all compounds described in the present investigation belong to type I, type II will not be further discussed.

The unit cell in structure I contains 46 water molecules which form two smaller and six larger cavities. The smaller cavities are very nearly spherical and have a free diameter of approximately $5.2\text{ \AA}$. The larger cavities are slightly oblate with a free diameter of approximately $5.9\text{ \AA}$.

The "empty" host lattice itself is thermodynamically unstable, but becomes stabilized by inclusion of guest molecules.

The difference in chemical potentials $\Delta\mu$ between the stable phase (ice) and the empty type I hydrate has been calculated by van der Waals and Platteeuw⁹ at 0°C to be 167 cal/mol . Though the difference is small, it may explain why the "open ice" host lattice has never been prepared in absence of guest molecules to stabilize it.

The compositions of the compounds investigated here has been determined to be $\text{Cl}_2 \cdot 7.27\text{H}_2\text{O}$,¹⁰ $\text{Br}_2 \cdot 8.47\text{H}_2\text{O}$,¹¹ and $\text{BrCl} \cdot 4\text{H}_2\text{O}$.¹²

It is believed that the enclosed guest molecules interact only weakly with the surrounding host molecules. By comparing the wavenumbers of the vibrations of a given molecular species enclosed in the cavities of the lattice with the wavenumbers observed in other phases, it is possible to form an impression of the sizes of these forces.

Chassonneau *et al.*¹³ have reported an NMR investigation on some type II hydrates. Until now no spectroscopic investigation on type I gas hydrates have been reported.

EXPERIMENTAL

Chlorine gas hydrate has been prepared by bubbling chlorine gas through a 5 % aqueous CaCl_2 solution at 0°C . The "feathery" crystals, which separated, were filtered off in a cold room at 0°C . The compound was greenish yellow.

Bromine chlorine gas hydrate was prepared according to the method reported by Anwar-Ullah.¹² Chlorine was bubbled into a layer of bromine under water at 0°C until a large crop of crystals had separated. The water and crystals were decanted from the bromine and warmed until all crystals were dissolved. The solution was then cooled and inoculated with a few crystals, which had been kept. The crystals, which then precipitated out of solution, were orange-red. The compound were filtered off in a cold room at 0°C .

In order to prepare bromine gas hydrate, liquid bromine was purified as described by D'Ans and Höfer.¹⁴ The purified bromine was added to distilled water and the mixture then kept agitated for four days at 0°C in a cold room. The compound was brought to crystallize out of solution by cooling under vigorous stirring. The crystals were filtered off in a cold room at 0°C . The red gas hydrate was recrystallized once from water.

Instrumental

The Raman spectra were recorded with a spectrometer equipped with a Jarrell-Ash model 25-101 double grating monochromator. The exciting lines used were $6471\text{ \AA}$ and $6764\text{ \AA}$ obtained from a Spectra-Physics model 165-01 Krypton-ion laser.

The spectra were recorded at -196°C in the range from the exciting line up to 600 cm^{-1} .

The spectral resolution in any scan is better than 3 cm^{-1} . The spectrometer was calibrated using standard Krypton lines and the wave-

numbers are believed to be accurate to within $\pm 1\text{ cm}^{-1}$.

The compounds were placed at the bottom of a little dewar vessel and cooled directly from the top with liquid nitrogen.

RESULTS

The spectra above 200 cm^{-1}

(i) *Cl_2 gas hydrate*. Above 200 cm^{-1} three bands have been observed in this compound at 538 , 545 , and 554 cm^{-1} , with a relative intensity ratio at about 1:6:9, respectively. These bands are assigned to the stretching vibration in $^{37}\text{Cl}^{37}\text{Cl}$, $^{37}\text{Cl}^{35}\text{Cl}$ and $^{35}\text{Cl}^{35}\text{Cl}$, respectively. The isotope shift between $^{35}\text{Cl}^{35}\text{Cl}$ and $^{37}\text{Cl}^{37}\text{Cl}$ has been calculated to about 8 cm^{-1} and between $^{35}\text{Cl}^{35}\text{Cl}$ and $^{37}\text{Cl}^{37}\text{Cl}$ to about 15 cm^{-1} . The relative intensity ratio $^{37}\text{Cl}^{37}\text{Cl}:^{37}\text{Cl}^{35}\text{Cl}:^{35}\text{Cl}^{35}\text{Cl}$ has been calculated to about 1:6:9. Both the observed isotope shift and relative intensity ratio are in very good agreement with the calculated values. The wavenumbers are given in Table 1 and for comparison the wavenumbers of the fundamental in other phases are also given.

(ii) *BrCl gas hydrate*. In this range three bands at 317 , 414 , and 424 cm^{-1} are observed in the Raman spectrum. The two latter, which have a relative intensity ratio at about 1:3.5, are assigned to the stretching vibration in bromine chloride. The isotope shift between $^{79}\text{Br}^{35}\text{Cl}$ and $^{81}\text{Br}^{35}\text{Cl}$ is small (calculated to $\sim 2\text{ cm}^{-1}$) and the band at 424 cm^{-1} is assigned to the fundamental in these two isotropic species. The isotope shift between $^{79}\text{Br}^{37}\text{Cl}$ and $^{81}\text{Br}^{37}\text{Cl}$ is

Table 1. Wavenumbers of the stretching vibrations in diatomic halogens (cm^{-1}).

Species	Phase gas hydrate	gas	liquid	solid	matrix	Ref.
$^{35}\text{Cl}^{35}\text{Cl}$	554	554	548	540	546	16,19,15,20
$^{35}\text{Cl}^{37}\text{Cl}$	545	547	541	532	539	16,19,15,20
$^{37}\text{Cl}^{37}\text{Cl}$	538	~ 540	533	524	—	16,19,15,20
$^{79}\text{Br}^{35}\text{Cl}$	424	440	—	—	—	16
$^{81}\text{Br}^{35}\text{Cl}$	424	440	—	—	—	16
$^{79}\text{Br}^{37}\text{Cl}$	414	432	—	—	—	16
$^{81}\text{Br}^{37}\text{Cl}$	414	432	—	—	—	16
$^{79}\text{Br}^{79}\text{Br}$	318	318	306	~ 300	305	16,17,15,18
$^{79}\text{Br}^{81}\text{Br}$	318	318	306	~ 300	305	16,17,15,18
$^{81}\text{Br}^{81}\text{Br}$	318	318	306	~ 300	305	16,17,15,18

small as well (calculated to $\sim 1 \text{ cm}^{-1}$) and the band at 414 cm^{-1} is assigned to the fundamental of these two isotopic species. The isotope shift between these two pairs is calculated to be approximately 8 cm^{-1} and the relative intensity ratio to be about 1:3. Although the observed isotope shift is larger than expected, the calculated data are in fair agreement with the observed values. The wavenumbers are given in Table 1 together with the wavenumbers in other phases.

The band at 317 cm^{-1} is assigned to the fundamental in bromine, as it is very likely that the bromine chlorine compound contains some bromine gas hydrate. Furthermore the observed wavenumber is very close to the gas-phase value of the stretching vibration in bromine and it is also in accordance with the wavenumber of a far more intense band found in pure bromine gas hydrate.

(iii) *Br₂ gas hydrate.* In bromine gas hydrate the bromine stretching vibration is observed as a relatively broad band at 318 cm^{-1} . No isotope shift was observed in this case, probably because of instrumental conditions. The band center at 318 cm^{-1} is assigned to $^{79}\text{Br}^{81}\text{Br}$. The isotope shift for $^{79}\text{Br}^{79}\text{Br}$ and $^{81}\text{Br}^{81}\text{Br}$ has been calculated to about $\pm 2 \text{ cm}^{-1}$, respectively. The relative intensity ratio between $^{81}\text{Br}^{81}\text{Br}$: $^{81}\text{Br}^{79}\text{Br}$: $^{79}\text{Br}^{79}\text{Br}$ should be approximately 1:2:1. It is therefore very reasonable that the line broadening is due to overlap of the three bands mentioned above. The wavenumber is given in Table 1 together with the wavenumbers in other phases.

It can be seen from the table, that the stretching vibration wavenumbers in both bromine- and chlorine gas hydrate are very close to the gas-phase values, whereas the matrix values are close to the liquid-phase wavenumbers. This indicates remarkably little interaction between the guest molecules and the surrounding host molecules, far smaller than is the case in a "normal" matrix. Because the enclosed molecules behave very nearly as in the gas-phase it indicates, that there is only trapped one guest molecule in each cavity.

There is a more pronounced deviation between the gas-phase and gas hydrate wavenumbers for the fundamental in bromine chloride, than is the case for the two former mentioned compounds. It is possibly due to the fact that

bromine chloride has a small permanent dipole moment, which can interact with the surrounding water lattice. However, there cannot be any doubt about the existence of bromine chloride as a gas hydrate. It should be mentioned that bromine chloride trapped as a gas hydrate was stable several weeks, when stored in a refrigerator, although bromine chloride itself is an unstable compound.

The spectra below 200 cm^{-1}

Bands observed in this region may be due to external vibrations of the water lattice together with translational and hindered rotational motions of the guest molecules in the cavities. In each of the three compounds there has only been observed one band below 200 cm^{-1} at 103 cm^{-1} (s), 88 cm^{-1} (s), and 130 cm^{-1} (m,br) in chlorine, bromine chloride, and bromine gas hydrates, respectively.

The band observed in each compound can hardly be due to a translational or "rattling" motion of the guest molecules, because it then would have been expected that the wavenumber decreased as the mass of the enclosed molecule increased. Furthermore the translational motions should not be active in the Raman spectrum according to the point group symmetry of the free guest molecules, unless the interaction with the lattice has violated the selection rules.

The rotational constants of the free molecules are in each case small ($B < 0.3 \text{ cm}^{-1}$). This means that the rotational Raman spectrum must be very close to the exciting line in the free unhindered case. As the interaction between guest and host molecules is supposed to be strongest in the case of bromine chloride one would expect, that a band due to a hindered rotational motion would have been observed at higher wavenumber in this compound than in the two other gas hydrates. Because this is not the case, it is unlikely that the bands are due to rotational motions. Furthermore the potential barriers should be relatively high to make the bands appear at a wavenumber as high as observed and this is not in accordance with the small interaction suggested above.

It seems therefore most reasonable to assign these bands to lattice vibrations, although the wavenumbers deviate somewhat from com-

pound to compound. According to Taylor and Whalley²¹ in most of the ice modifications only one band — sometimes two — is observed in the low frequency Raman spectrum. This band is observed between 150 and 225 cm^{-1} and is assigned to a translational motion of the water lattice. The observation of only one band also in the gas hydrates is in accordance with the Raman spectra of the pure water modifications. The shift towards lower wavenumber in the gas hydrates could be due to an increasing interaction between the guest molecules and the lattice in the order $\text{BrCl} > \text{Cl}_2 > \text{Br}_2$. This order is in accordance with the spectra above 200 cm^{-1} and the bands below 200 cm^{-1} are therefore tentatively assigned to translational vibrations of the lattice.

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