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Clathrate Hydrates

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Abstract

The clathrate hydrates represent a distinctive, unusual, scientifically significant, and practically important class of solid state materials. Since their discovery in the early nineteenth century, their widespread distribution in oceans and permafrost regions and their ability to trap atoms and small molecules—particularly methane and other small hydrocarbons—has led to the realization that they are simultaneously a tremendous energy source and, in the face of global warming, a potential greenhouse gas release disaster of unprecedented magnitude just waiting to happen. In the twentieth century, it was realized that solid methane clathrate hydrate could plug natural gas pipelines and disrupt oil drilling processes. On the environmental positive side, clathrate hydrates can store hydrogen and sequester carbon dioxide. A brief historical review of the formation, structure, and uses of clathrate hydrates forms the backdrop for a discussion of modern scientific investigations of these solids employing spectroscopy, structure determination methods, isotopic studies, computational-theoretical modeling, and interrogations of guest-host interactions via special guests. For example, the use of colored halogens in clathrate hydrate hosts enables UV-visible spectroscopic methods to be employed to study clathrate hydrate structure.

Keywords: clathrate, clathrate hydrate, guest, host, lattice clathrate, methane clathrate hydrate, halogen clathrate hydrate, alkane clathrate, hydrogen bonding network, greenhouse gas, enclathration, sequestration, solidification

1. Introduction

Pure water solidifies (i.e., freezes) at 0°C at the normal atmospheric pressure of 1 bar. Pure chlorine gas solidifies at -101°C at ambient 1 bar pressure. However, as Humphery Davy [1] famously noted in 1811 “the solution of oxymuriatic gas (chlorine) in water freezes more readily than pure water.” It turns out that chlorine-water solutions solidify at temperatures well above 0°C. This phenomenon is by no means restricted to chlorine-water solutions. Aqueous solutions into which many types of small non-polar or modestly polar gas atoms or molecules

are dissolved (e.g., xenon, bromine, iodine, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethane) exhibit this enhanced solidification temperature effect also. Application of modest pressures further increases the solidification temperatures of these solidified gas-water solutions. For example, at 50 bar, a methane-water solution solidifies around 8°C. It turns out that the gas molecules or atoms become guests encased in a three-dimensional lattice network of water molecules called a clathrate hydrate host. Many clathrate hydrate host cage structures, sizes, and geometries are possible. If the guest molecule is methane and the host system is water, the solidified guest-host system is called methane clathrate hydrate. The interaction between the host cage water molecules in the clathrate hydrate and the guest gas atoms or molecules is of the non-covalent van der Waals type. The distinctive and fascinating solidification behavior of gas-clathrate hydrate systems is the subject of this chapter.

The scientific history of clathrates dates back to the year 1811 when Sir Humphrey Davy first studied and identified clathrates comprised of solidified mixtures of gases, particularly methane, and water [1]. A distinctive property of these natural gas clathrate hydrates is their capacity to remain in the solid state well above the 273.15 K melting point of pure water. A quantitative study of the composition of gas clathrate hydrates was later taken up by Michael Faraday [2]. After reading Schroeder's 1927 review of clathrate hydrates [3], Hammerschmidt [4] in the mid-1930s came the realization that solidified methane clathrate hydrates were responsible for the blocking of natural gas transmission pipelines, a major problem in the petroleum industry. From the 1930s to the present, the petroleum industry has expended an enormous amount of effort in developing techniques to detect and remove/dislodge solid gas clathrate hydrates or prevent their formation. It is now known that massive amounts of methane are sequestered in clathrate hydrates in the deep ocean and permafrost regions of planet Earth. This enclathrated methane has the potential to be extracted and used as a fuel. On the negative side, global warming will increase ocean temperatures and destroy permafrost regions, resulting in a potentially catastrophic release of methane – a major greenhouse gas – into the atmosphere. It is speculated that clathrate hydrates are widespread in the universe, and possibly exist in comets, asteroids, Mars, Pluto, and the moons of Jupiter and Saturn in our Solar System [5].

Clathrates are defined by the IUPAC to be inclusion compounds in which the guest atoms or molecules are constrained or trapped in cages formed by the host molecule or by a lattice of host molecules. Host molecules and guest atoms or molecules interact via van der Waals or hydrogen bonding forces. The word clathrate comes from the Latin word *clatratus*, which means a lattice or with bars. The traditional use of the word clathrate in science and engineering is in reference to materials comprised of hosts that are polymers trapping guests that are atoms or molecules. However current use of this word now extends to many other molecular host systems such as calixarenes [6], cyclodextrins [7], and even to inorganic polymeric systems such as zeolites [8] and chibaites [9]. Hofmann compounds [10] and metal organic frameworks (MOFs) [11] can also serve as clathrate hosts for small aromatic guest molecules such as carbon tetrachloride, benzene, toluene, and xylene. These types of clathrate host systems have the potential to serve as a new class of stationary phases capable of achieving heretofore unattainable chromatographic separations. Clathrates may also be separated into two general types depending upon how the host molecules encapsulate the guest atoms or molecules. In molecular clathrates, each guest atom or molecule is trapped in a site located in a single host molecule. Such clathrates are stable in both the liquid solution

and solid states. However, in lattice clathrates, the trapping sites for guests are formed from multiple host molecules arranged in a lattice or array. Thus, lattice clathrates only exist in the solid state since dissolving or melting destroys these intermolecular host lattice trapping sites. Perhaps the most famous and well known example of a lattice clathrate is methane clathrate hydrate. Each methane guest molecule is trapped in a cage formed from a three-dimensional network of hydrogen-bonded host water molecules. It turns out that there are many other examples of clathrate host molecules that form hydrogen bonded networks capable of trapping guest atoms and molecules. The compounds hydroquinone, urea, thiourea, and Dianin's compound, (4-p-hydroxyphenyl-2,2,4-trimethyl chroman) are notable examples [12, 13]. The clathrate hydrate host lattice can form hydrogen bonded water molecule cages of various sizes and geometries capable of trapping a wide variety of guest atoms and molecules. Examples of clathrate hydrate guest moieties include a number of small alkanes, hydrogen, the noble gases, the halogens, nitrogen, oxygen, and carbon dioxide, carbon monoxide, and ozone.

2. Clathrate hydrate applications and uses

2.1. Petroleum industry

Clathrate hydrate plugs in gas pipelines have been very problematic for energy industries, causing significant economic loss and environmental risks. In 2010, the Macondo Project Deep Horizon well blew up and created an oil spill of 4.9 million barrels in Gulf of Mexico, which simultaneously released large amounts of hydrocarbons [14]. The hydrocarbons that were released ended up forming methane clathrate hydrates with surrounding water vapors. Unfortunately, the accumulation of methane clathrate hydrates blocked the well caps and prevented a 100-ton containment structure from being sealed after the blowout (**Figure 1**).

2.2. Environmental issues

A long-term concern for natural clathrate hydrates is the slow release of methane gas into the atmosphere [15]. For instance, when oil companies drill hot oil through hydrate-bearing



Figure 1. Recovered gas hydrate plug from a subsea pipeline off the coast of Brazil (courtesy of Petrobras).

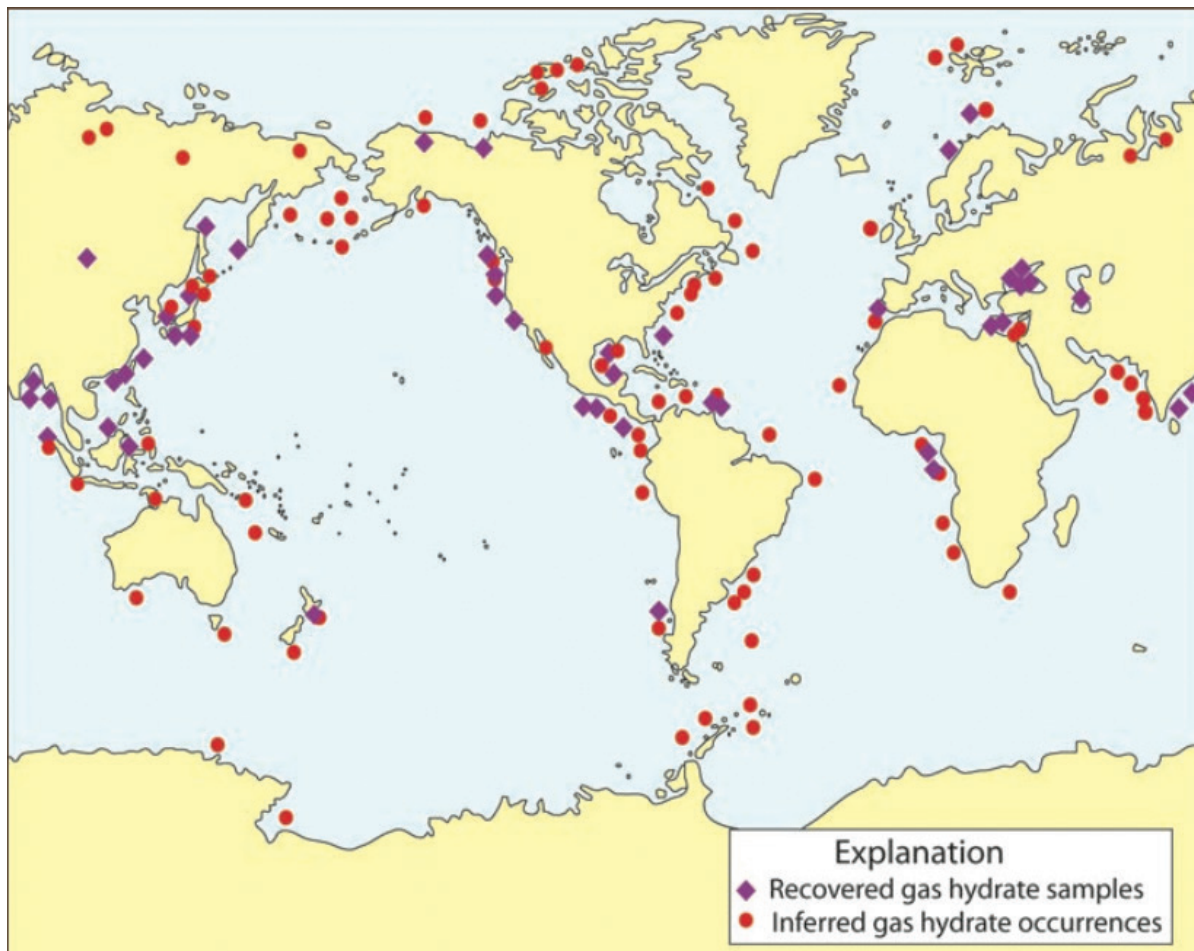
sediments, the high temperature of the oil encourages melting and thus dissociation of clathrate hydrates. Then, large amounts of methane gas are released, surrounding sediments are weakened, and pockets of highly pressured gas are generated. The effect of global warming on the stability of methane clathrate hydrate is another concern. The rising temperature results in a steady release of methane, a key greenhouse gas, from methane clathrate hydrates in the Arctic where there are large deposits of methane clathrate hydrates. The dramatic dissociation of methane hydrates, also known as the clathrate gun hypothesis, exacerbates global warming and poses a significant threat to our climate [16]. Recently, large craters and blow-outs from the Barents Sea floor that are produced from decomposing methane hydrates in the ocean floor have been discovered [17, 18].

2.3. Clathrate hydrate as energy source

Clathrate hydrates have been also studied as a potential energy source and fuel storage/transportation technology. Moreover, they are readily available; there exist extensive clathrate hydrate deposits along continental margins and in the Arctic. In particular, methane clathrate hydrates have been found in deep ocean layers, sediments below the Arctic, and permafrost areas where there is a combination of high pressure and low temperature. A reliable estimate done by DOE and USGS researchers suggests that there are about 3×10^{15} cubic meters of methane or ~1800 gigatons of carbon in hydrates that can be utilized as a potential energy source. In the US alone, the mean estimate of the amount of gas sequestered in clathrate hydrates is around 9×10^{21} m³ [19]. Another USGS survey indicates that the potential energy stored in methane clathrate hydrates exceeds the combined global fossil fuel reserves! Thus, natural gas stored in the form of clathrate hydrates may be a significant alternative energy source in the future (**Figure 2**).

Extracting combustible gases, especially methane, already stored in natural clathrate hydrates is a prospect, but using the clathrate hydrates to hold gas molecules that can serve as fuels is also a subject of study. Storing gases in a solid state clathrate hydrate “container” may be more cost-effective than storage in the liquid or gaseous state in many cases. For instance, building a LNG plant is much more costly than storing natural gas in clathrate hydrates. Clathrate hydrates also offer an easier method of transportation compared to pipelines in many instances. Clathrate hydrates are also able to sequester hydrogen, the ultimate, carbon-free, environmentally friendly fuel. In the past decades, researchers have tested different types of promoters to increase hydrate formation rate and decrease induction time in order to enhance clathrate hydrates as a storage method.

Large scale trapping of carbon dioxide molecules in clathrate hydrates is a potentially viable way to reduce atmospheric CO₂ levels and thus inhibit the acidification of ocean waters [20]. Other applications of clathrate hydrates include the separation of gases such as CO₂ from flue gases and desalination. Clathrate hydrates can be used in flue gases to separate CO₂ by encouraging the formation of CO₂ clathrate hydrate in a flue gas mixture. Seo et al. [21] found that forming clathrate hydrates is a feasible method of recovering CO₂ from flue gases in silica gel pores. Another useful application is hydrate-based desalination. The process begins when clathrate hydrate forming agent is injected into seawater that has a surrounding temperature lower than clathrate hydrate forming temperature. The condition promotes



*Location of sampled and inferred gas hydrate occurrences worldwide.
(Map courtesy of Timothy S. Collett, USGS)*

Figure 2. World map of recovered and inferred gas hydrate locations (map courtesy of Timothy S. Collett, USGS).

condensation of water molecules around the hydrate formers, and a slurry of clathrate ice and brine form. Once they form, brine is separate from the slurry of clathrate ice. The clathrate ice is then melted via heat exchange with warmer surface water of the ocean. During the last decade, the United States, Canada, Japan, India, and South Korea have conducted extensive research on clathrate hydrates. While much is now known, much still remains to be discovered. To advance understanding concerning the physical properties and practical uses of clathrate hydrates, further research is necessary.

3. Clathrate hydrates in space

The possible presence of clathrate hydrates in Mars, Pluto, Saturn's and Jupiter's moons, Kuiper Belt objects, comets, and asteroids is a hotly debated topic. In the cosmos, the giant planets may provide a cold, gaseous environment for clathrate hydrates to form as grains of water

ice and gaseous guest molecules collide. Primordial sources of volatiles in space can be found in clathrate hydrates that formed in the presolar nebula. They have remained stable in low pressure-low temperature condition. Based on current information, it is speculated that natural gas hydrates may exist on Mars, Saturn, Uranus and Neptune and their moons. During the past decades, ammonia and methane clathrate hydrates have been the focus of space research because they have been considered to be the main sources of nitrogen and carbon species.

Titan, one of Saturn's moons, has been extensively investigated for the presence of clathrate hydrates because of its likely conditions. Titan's atmosphere and surface contain atmospheric gases such as nitrogen, methane, ethane, carbon dioxide, propylene, water vapor that typically form clathrate hydrates. However, since the atmosphere has only a limited amount of water vapor presence despite an abundance of hydrate guests, the amount of available water regulates clathrate hydrate formation. Osegovic and Max [22] suggested that the overabundance of hydrate forming guest molecules in Titan may exhaust all water vapor supply on the surface. In the event that water is introduced to the surface such as in cryovolcanism, the newly introduced water vapor would most likely form clathrate hydrates with guest molecules in the atmosphere unless a more thermodynamically favorable water vapor sink consumes water molecules first. In Titan, compound clathrate hydrates may form in which two or more guest molecules are trapped in a single clathrate cage. These clathrates usually assume sII or sH type structures. They tend to have higher reaction rates and faster induction time compared to pure clathrate hydrates.

The most common type of clathrate hydrate conjectured to be stored below the surface of Titan is methane clathrate hydrate since methane gas is one of the most common types of gases in Titan, as discovered by the Cassini-Huygens space probe, and methane clathrate hydrates have a broad spectrum of stability. Loveday et al. [23] reported that methane clathrate hydrates undergo structural transition at about 1 and 2 GPa and are able to remain stable up to 10 GPa. They are very stable in high pressure settings up to 42 GPa as well. After accretion, Lunine and Stevenson have suggested that the condensed methane in Titan is stored beneath a pure rock layer [24]. The inner core (~20–35 kilobars) of Titan thermodynamically prefers low pressure phases such as methane clathrate and ammonia monohydrate rather than equilibrium ices. Considering methane clathrate hydrates' characteristics and Titan's environment, it is likely that methane has been stored in clathrate hydrates in Titan for a long time.

Recent studies have also discussed the presence of ammonia in the cosmos including two of Saturn's moons, Titan and Enceladus [25]. Ammonia has previously been considered to be water-ice antifreeze and methane hydrate inhibitor, contributing to decreases in dissociation temperature of methane clathrate hydrates. Structurally, ammonia is around the molecular size of methane. However, ammonia is hydrophobic, which is atypical of most clathrate guest compounds. Previous experiments have shown that low pressure ammonia dihydrate and high pressure phase II of ammonia monohydrate resemble semiclathrate structures. Hence, Ripmeester et al. [25] experimented with ammonia clathrate hydrates and suggested that low temperature methane gas helps stabilize ammonia hydrate. Conversely, ammonia has been found to help activate ice nearby to initiate ammonia clathrate hydrate formation at temperatures where methane by itself does not normally form clathrate hydrates. They concluded that ammonia's inhibition effect on methane clathrate hydrates is not due to ammonia's instability as a guest molecule but instead due to their stabilizing effect of guest molecules at the aqueous phase [25].

4. Clathrate hydrate crystal structure types and physical properties

As mentioned earlier, clathrate hydrates are nonstoichiometric, solid lattice inclusion compounds with a crystalline water cage that enclathrates small gas molecules. Generally there are vacant cages in the clathrate hydrates, but a sufficient amount of gas molecules are needed inside the cages to stabilize the structure. Typically, there is one molecule per cage. However in a high pressure environment [26] (>0.1 GPa), it is possible for a cage to contain more than one gas molecule. Thus, clathrates have similar physical properties as water including physical appearance, refractive index, and density. However, they also differ from water when considering properties like mechanical strength, heat capacity, thermal conductivity.

In the 1950s, von Stackelberg and Muller [27] were the first to determine a clathrate hydrate crystal structure using X-ray diffraction. They determined that CO₂ hydrates had the sI crystal structure. Since then, three most common crystal structure types of clathrate hydrates, have been identified by X-ray diffraction. The types are structure I (sI), structure II (sII), and structure H (sH). The sI structure is a body-centered cubic structure and has two cage types - a small pentagonal dodecahedral cage (5¹²) and a large tetrakaidecahedral cage (5¹²6²). The structure sII is a diamond lattice within a cubic framework and has two cage types - small cage (5¹²) and a large hexacaidecahedral cage (5¹²6⁴). The sII structure fits molecules in natural gases or oils that are larger than ethane but smaller than pentane. The sI and sII structures are of interest for gas companies because they form when natural gas molecules interact with

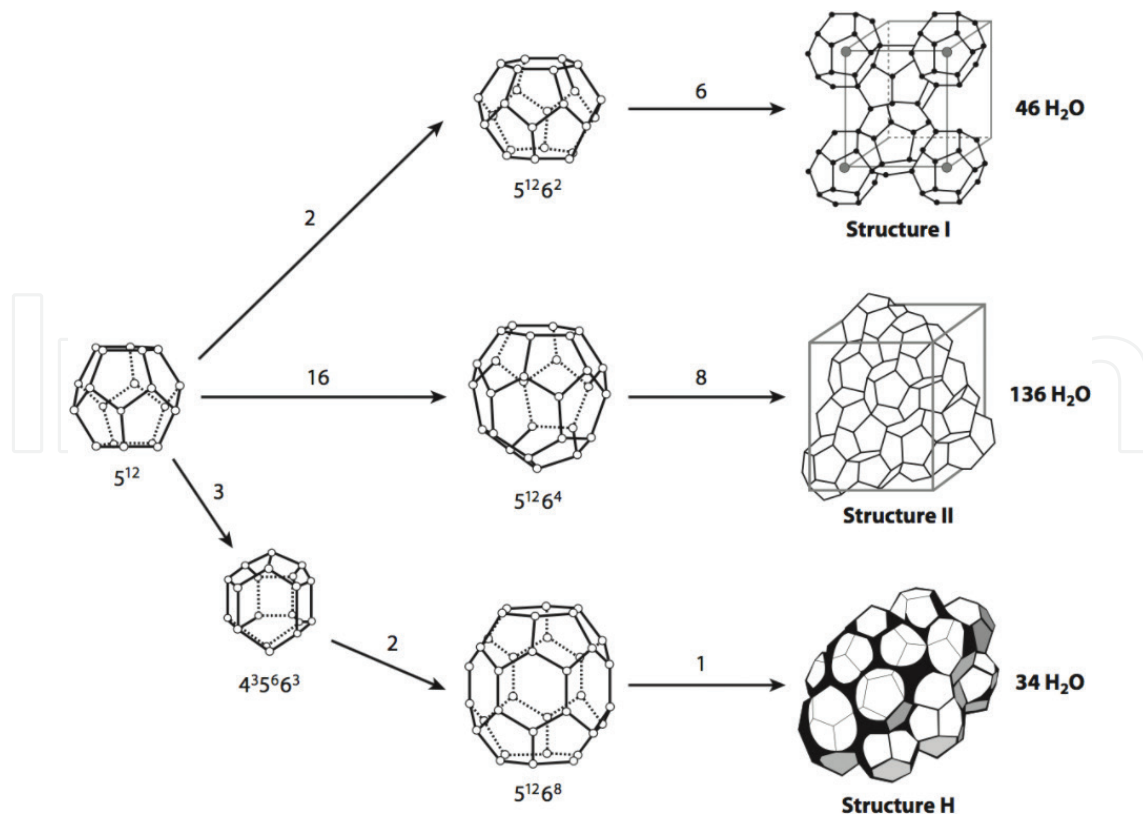


Figure 3. Common clathrate hydrate structures (sI, sII, sH) (courtesy of Koh et al.).

water near gas pipelines or deep ocean areas. The sH structure has a hexagonal framework and three cage types: a small 5^{12} cage, a mid-sized $4^35^66^3$ cage, a large icosahedral cage $5^{12}6^8$. Understanding of sH hydrate structure is particularly important for the oil industry because it is able to fit larger molecules contained in crude oils.

The cage size is determined by the size of the largest guest molecule. For example, methane can fit into both the small and large cages of sI whereas other large hydrocarbon molecules such as propane are too large to fit into the large cage of sI. Instead, they can fit into the larger cages of sII. In fact, clathrate hydrates formed near oil and gas pipelines are mostly of sII structure because they contain larger hydrocarbon molecules like propane and isobutane. Spectroscopy has been used to analyze guest occupancy. It has been found that molecules below 0.35 nm will not stabilize sI and above 0.75 nm will not stabilize sII [28]. When a large organic molecule is combined with a clathrate hydrate promoter, it is possible to form hydrates with atypical crystal structures. More new structures are being discovered as researchers produce clathrate hydrates with different types of gases in laboratory settings (**Figure 3**).

5. Memory phenomenon

Clathrate hydrate memory phenomenon suggests that clathrate hydrates nucleate faster from a dissociated hydrate solution than from a freshly made solution. It is an interesting phenomenon has been observed and recorded for over 100 years. However, some studies [29] have shown that memory phenomenon does not occur in all cases of clathrate hydrates. Thus, it has been suggested that heating the hydrate system at a high temperature can destroy the memory effect. However, even at high temperatures, researchers have observed the memory effect. Two possible explanations for the memory effect are either there is residual clathrate hydrate cage structure or clusters of high concentration gas left behind in the dissociated hydrate system. Buchanan et al. have observed that there are no significant signs of memory effect before and after the hydrate formation [30].

6. Models of thermodynamics, structure, and dynamics including solidification

Density functional theory (DFT) is the predominant method employed by researchers for modeling the structural, dynamical, thermodynamic, and spectroscopic properties of clathrate hydrates. Ramya and Venkatnathan have calculated interaction energies, free energies, and reactive energies of clathrate cages using DFT [31]. However, simulations based upon statistical mechanics, classical DFT, and Monte Carlo (MC) methods are also employed as shown in the work of Alavi and Ripmeester [32]. For example, Lasich and Ramjugernath used a simple lattice gas approximation with classical DFT coupled with Platteuw theory to model clathrate hydrate phase equilibria for several hydrate guest molecules [33]. Standard DFT calculations were used by Chattaraj et al. to probe the structure, stability and reactivity

of H₂ clathrates [34]. Using B3LYP HuzIII-su3 DFT, Siuda and Sadlej calculated NMR parameters (¹³C and ¹H shielding constants and spin–spin coupling constants for 5¹², 5¹²6², and 5¹²6⁴ cages hosting methane, ethane, and propane guests) [35]. Mondal and Chattaraj used ab initio molecular dynamics (AIMD) via atom-centered density matrix propagation (ADMP) methodologies to study time-dependent structural behavior of noble gas hydrates on the timescale of ~500 fs [36]. Sun et al. carried out DFT calculations using the M06-2X method to determine the relative stabilities of guest species in various clathrate hydrate host sites [37]. They predict that the guest molecules N₂ and NO are more stable in a 5¹²6⁴ cage and that the SI NO hydrate is less stable than the SII NO hydrate. For the guest N₂, the Type II hydrate structure with single occupancy provides more stability than a type I structure with multiple occupancy. DFT calculations predict severe deformations when CS₂ is enclathrated in 5¹² and 5¹²6² cages. The 5¹², 5¹²6², and 5¹²6⁴, cages can enclathrate up to 2 N₂ molecules. Two H₂S molecules can be enclathrated in a 5¹²6⁴ cage. DFT modeling and other types of modeling involving halogen guests in clathrate hydrate hosts are discussed in Section 10.

7. Clathrate hydrate structural studies

7.1. X-ray structural studies of clathrate hydrates

Much of the structural work on clathrate hydrates and their guests is based upon investigations of X-ray scattering from crystalline powders. Takeya et al. have determined structures of clathrate hydrates containing the guests CO₂, C₂H₆, C₃H₈, and methyl cyclohexane + CH₄ using X-ray methods with Rietveld analysis [38]. Shin et al. [39] have studied clathrate hydrate hosts with methanol guests via X-ray diffraction [39]. Davidson et al. carried out variable low temperature (18–250 K) powder X-ray investigations of THF clathrate hydrate from which its thermal expansion coefficient could be determined. Powder diffraction data of the CO₂--clathrate hydrate collected by Hartmann et al. obtained using synchrotron radiation as the X-ray photon source yielded structural information of extremely high precision via Rietveld refinements.

7.2. NMR, Raman, infrared spectroscopy

A diverse repertoire of spectroscopic techniques has been employed to investigate clathrate hydrate structure, bonding, composition, and dynamics. Chief among these techniques are X-ray crystallography, neutron diffraction, and infrared, Raman, and NMR spectroscopy. More exotic techniques include X-ray Raman and various time-resolved spectroscopies. For guest species that absorb near UV and visible light (e.g., the halogens), UV-visible absorption spectroscopy can be a useful tool by which to elucidate guest-host interactions. The interactions of clathrate hydrate hosts with xenon guests have been probed by ¹²⁹Xe NMR [48]. Similarly, ¹³C NMR has been employed by Ripmeester and Ratcliffe [48] and Kida et al. [46] to investigate the dynamics of CO₂ and various alkane guests encapsulated in clathrate hydrate hosts. Chemical shift and linewidth variations can be correlated with the local guest-host interactions [42]. Infrared spectroscopy is a powerful tool for probing the compositions of extra-terrestrial objects. Evidence derived from laboratory infrared reflectance spectroscopy

of the clathrate hydrate-CO₂ system at cryogenic temperatures by Oancea et al. [41] is inconsistent with corresponding reflectance spectra of Jupiter, Saturn, and the Martian poles suggesting that the observed spectral features do not come from clathrate hydrate-CO₂, although this does not rule out its existence beneath the surfaces of these bodies. Petuya et al. [43] have shown that Raman spectroscopy can be quite useful in determining the extent of partitioning of a CO guest in a clathrate hydrate host lattice containing several different host sites. The FTIR spectroscopy studies of Dartois et al. [40, 44] regarding the possibility of astrophysical remote detection of clathrate hydrates on Pluto and Triton lead to the observation that the methane (CH₄) associated with these bodies was not encapsulated in clathrate hydrates. Raman and resonance Raman investigations of halogen clathrate hydrates are most helpful in elucidating host-guest interactions in these highly colored systems.

8. Clathrate hydrates involving isotopic guests and hosts

Clathrate hydrate lattices formed out of ¹⁸O and/or D are excellent model systems for probing the host lattice and guest vibrational behavior including the phonon density of states. A comparison of H₂O vs. D₂O as clathrate hydrate cage-forming molecules demonstrates that D₂O stabilizes the lattice better than H₂O. The crystalline D₂O clathrate hydrates are noticeably more stable thermodynamically than H₂O clathrate hydrates. The D₂O clathrate hydrates have assumed great importance in X-ray and neutron diffraction work in elucidating positions of the hydrogen atoms and thus the nature of hydrogen bonding in the clathrate hydrate structure. The use of isotopic substitutions (D vs. H and/or ¹⁸O vs. ¹⁶O) in varying proportions in clathrate hydrates provides the capability to adjust the clathrate host scattering intensity with respect to the guest scattering intensity in neutron inelastic scattering studies [45]. Isotopic substitution in alkane guests, particularly methane (e.g., ¹²CH₄, ¹²CD₄, ¹³CH₄, ¹³CD₄), provides unparalleled opportunities to investigate host-guest interactions through NMR, infrared, and Raman spectroscopies [46]. The NMR active ¹²⁹Xe guest has proven to be an exceedingly valuable as an NMR probe of clathrate hydrate properties [47, 48]. Through NMR, time-resolved probes of clathrate hydrates formation and decomposition can be studied; magnetic resonance imaging of clathrate hydrates is also possible [49]. Isotopes, even in an indirect way, can assume importance in studies involving clathrate hydrates. For example, observations of the isotopic content of deep ocean water indicate a direct correlation between ¹⁸O concentration and the presence or one time existence of methane clathrate hydrates in deep ocean sediments [50].

9. Clathrate hydrate inhibitors and promoters

Inhibitors are chemicals that delay or prevent formation of clathrate hydrates under conditions where they would normally form. Promoters are chemicals that speed up the formation of and or stabilize the already formed clathrate hydrates under conditions where they might not normally be stable. There is tremendous incentive, particularly on the part of the petroleum and energy industries worldwide, to design better inhibitors and promoters that do not adversely affect the environment.

9.1. Inhibitors

Clathrate hydrate formation is a crystallization process, and thus is affected by temperature, pressure, and other inhibiting or promoting factors. Clathrate hydrate growth inhibition has been a research focus since mid-1930s when, as previously noted, Hammerschmidt determined that man-made clathrate hydrates caused pipeline blockage. In order to inhibit clathrate hydrate formation, it is favorable to thermodynamically shift phase boundaries to high pressure and/or low temperature.

Modern thermodynamic programs based on a Gibbs energy extension of the van der Waals and Platteeuw method [51] calculation of hydrate stability temperature and pressure within a range. However, the low temperature and high pressure in the ocean where most pipelines are located create ideal hydrate-forming regions. To combat pipeline plugging, the oil industry has been injecting large amounts of hydrogen bonding fluids such as methanol or glycols that have antifreezing qualities. Introduction of hydrogen bonding fluids inhibits clathrate hydrate growth because they form hydrogen-bonds with available water, exhausting water from clathrate hydrate formation. Ultimately, it shifts the phase boundaries away from the hydrate forming zone. Methanol, in particular, has been widely used because it is easy to concentrate in water cages when injected as vapors. However, high concentrations (e.g., 40 vol%) of methanol pose a severe environmental threat. Large methanol contamination greater than 50 ppm in refinery feedstocks is severely fined [52]. Annually, in the US \$220 million of methanol is being injected to inhibit hydrate growth (P.K. Notz). For instance, it requires about $4000 \text{ L} = 4.0 \text{ m}^3$ of methanol to treat a gas pipeline that transports approximately $2430 \text{ m}^3/\text{d}$ of gas. The methanol prevents clathrate hydrate formation but also carries the risk of contaminating the reflux water and increasing the potential for corrosion. The toxicity of methanol to humans and many other organisms is also a matter of grave concern.

Recently, hydrocarbon clathrate hydrate formation has been occurring in extreme environments that require a lot of methanol or other type of hydrogen bonding fluids, often too costly economically and environmentally, to successfully shift phase boundaries. Hence, much effort has been made to develop low-dosage hydrate inhibitors (LDHIs) in the past decade. The two type of LDHIs are kinetic hydrate inhibitors (KHIs) and anti-agglomerate chemicals (AAs). Their most significant benefit is that they pose little threat to the environment even in cases of leakages or mishandling. Thus, it is much safer to employ LDHIs in storage and transportation.

KHIs directly interfere in crystal lattice structures of clathrate hydrates, preventing crystal growth and nucleation, ultimately delaying or preventing hydrate formation. They are similar to enclathrated gas molecules and generally do not change the thermodynamics. They are supposed to be incorporated into growing clathrate hydrates and block further development. Some examples of polymeric kinetic hydrate inhibitors are poly(N-methylacrylamide), poly(N-ethylacrylamide), poly(2-ethylloxazoline) [53]. Recent studies have found that certain poly(vinyl caprolactam) (PVCap), a type of KHIs, changes the thermodynamics by increasing the dissociation temperature.

Anti-agglomerants (AAs) can be a solution to gas pipelines in very cold areas where thermodynamic inhibitor is impractical. AAs only work in the presence of an oil phase such as oil pipelines. They do not entirely prevent clathrate hydrates from forming but rather from

agglomerating. AAs keep clathrate hydrate particles small and in a slurry so that they can be flushed out along with the fluids in the pipe. Many AAs have been made with halogen content. The high reactivity of halide compounds posed some threats with gas pipelines, and a lot of research has gone into developing low-halogen or no halogen AAs.

Considering long-term uses of inhibitors in gas pipelines, biodegradability has been one of the biggest concerns. As mentioned before, poly(vinylpyrrolidone) PVP and poly(vinyl caprolactam) PVCap are somewhat biodegradable. On the other hand, different types of esters such as pyroglutamic acid esters have high levels of biodegradability also have shown to function as gas hydrate inhibitors. Recently, researchers have been trying to create “bio-KHIs” [54] from natural living systems such as ocean pouts and mealworms that have proteins to help sustain frigid temperatures. The proteins may be applied to preventing pipeline plugging.

9.2. Promoters

In the recent decades, the use of clathrate hydrates as a storage and transportation method for gases such as methane, ethane, hydrogen, and carbon dioxide, has gained much attention. Unlike their liquid or compressed state counterparts, solid clathrate hydrates are much safer to handle and often cost-effective. Thus, many experiments have been conducted to examine promoters that increase induction time and growth rate and expand cage occupancy of clathrates. In essence, promoting additives work to drive clathrates away from the thermodynamic equilibrium or increasing reaction rates through efficient reactors. Some also work to increase stability of clathrate hydrates and increase clathrate occupancy. However, there have been concerns that promoter additives may take up space in the clathrate, limiting the occupancy for guest gas molecules.

Chemical additives that are generally considered as promoters are THF, surfactants, cyclopentane, acetone, propane. These types of additives do not alter the water cage structure. On the other hand, promoters like tetrabutylammonium salts and $[(n-C_4H_9)_4NBH_4]$ change the cage structure [53]. Recent studies have experimented with combining different promoters to discover synergistic effects that can drive clathrate hydrate growth as well as stability. Some methods [55] of increasing clathrate hydrate formation are vigorous mixing, using micron-sized ice particles or dry water, and using micron-sized ice particles, using hollow silica, metal packing media, porous materials to increase heat and mass transfer rate.

Tetrahydrofuran is a five-sided cyclic ether structure organic solvent that has been widely studied as a promoter. It has been generally considered a promoter due to its ability to form structure II hydrates with water and increase methane hydrate occupancy and stability [56]. THF additive has been observed to significantly reduce the hydrate formation pressure. The use of THF in methane hydrates has been suggested for upscaling the SNG technology as a more cost-effective and safer method to LNG. Furthermore, in methane clathrate hydrates (sII), THF increases the cage occupancy. Recently studies done by Veluswamy et al. [57] have reported that THF is an excellent kinetic and thermodynamic promoter for clathrate hydrate growth for CO_2 clathrate hydrates at moderate temperature (301.7 K) and pressure (1 MPa) of an unstirred tank reactor configuration. A potential application is using THF to improve natural gas storage in a solid state as clathrate hydrates. THF-promoted solid natural gas storage technique has potential to reduce significant cost in natural gas driven economies.

Surfactants are additives that reduce surface tension between two liquids or liquid and a solid, thereby increasing mass transfer. Surfactants do not change the thermodynamics of clathrate hydrates, but they have been found to alter clathrate hydrate kinetics. Karaaslan and Parlaktuna [58] have found that anionic surfactants increase hydrate formation rate at all concentration, cationic surfactants increase hydrate formation rate at low concentration, and nonionic surfactants have little distinguishable effects on hydrate formation rate. SDS is a commonly used surfactant that is known to increase hydrate stability. Arora et al. [59] conducted an interesting work developing a biosurfactant with *Pseudomonas aeruginosa* strain A11, which was characterized as rhamnolipids. 1000 ppm rhamnolipids solution increased methane hydrate formation and reduced methane hydrate's induction time. Biosurfactant research may lead to environmentally safe methods to use gas hydrates as an energy source.

Cyclopentane is a hydrophobic, cycloalkane compound. Lim et al. [60] conducted experiments comparing hydrate growth at different levels of cyclopentane, and observed that the system with 0.9 mL CP had a faster hydrate formation compared to the system with 0.45 mL CP. In the same experiment, it was noted that hydrates grow faster on metal surfaces due to better heat transfer. However, cyclopentane is not always effective as a clathrate hydrate promoter. Although cyclopentane is an efficient sII hydrate promoter at high temperatures (283 K), Herslund et al. [61] suggested that in its study of water-cyclopentane-carbon dioxide clathrate hydrate, cyclopentane's efficiency decreases at lower temperatures because cyclopentane clathrate hydrates are more likely to form than mixed carbon dioxide-cyclopentane hydrates at temperatures below 281 K and pressures above 0.4 MPa.

Tetra-n-butyl ammonium bromide (TBAB) is an additive that alters the clathrate hydrate cage and forms a semi-clathrate. In a semi-clathrate, the cage is broken so that the large TBAB molecule can fit inside. One advantage of semi-clathrates in storage purposes is that it allows for more guest molecules compared to promoters like THF, which do not alter the cage. Li et al. [62] examined a hydrate-based CO₂ separation process from a fuel gas mixture and observed that TBAB range of 0.14–1.00 mol% increased the induction time and hydrate growth rate while also increasing CO₂ storage capacity of the clathrate.

An interesting phenomena similar to the effects of promoters that occurs in methane hydrates is self-preservation [55]. Self-preservation is when clathrates under ice layers form insulating ice shells that prevent dissociation. Thus, methane hydrate resists mass and heat transfer, allowing it to be kinetically stable in temperatures beyond the three equilibrium boundary.

9.3. Mixed promoters

Researchers have studied the presence of mixed promoters in clathrate hydrate formation to examine the synergistic effect on increasing hydrate formation rate and decreasing induction time. In a comparative study conducted by Kumar et al. [55], THF and SDS as mixed promoters for methane hydrates were tested. A concentration of 5.56 mol% THF was observed to induce the fastest rate of hydrate formation whereas 0.1 wt% of SDS was observed to increase the most gas storage capacity. Thus, a combination of THF and SDS has been suggested to optimize induction time and storage potential for methane hydrates. Partoon and Javanmardi [63] noted that a mixture of promoters, propanone and sodium lauryl sulfate (SDS), can work

to increase induction time and initial formation rate of methane hydrates. However, the combination of the two promoters decreases self-preservation at low pressures and temperatures below the ice point and storage capacity of the hydrate. However, SDS by itself, expands the storage capacity compared to its theoretical value. The synergistic effect of mixed promoters needs to be further examined regards to cases in which a significant amount of pure promoter hydrates form at low temperatures.

9.4. Switching effects

Some additives have switching effects. For example, Mohammadi and Richon [64] found that while THF of 5–7 mol% has a promoting effect on clathrate hydrate formation, THF at high concentration (>10 mol %) in aqueous solution shifts phase boundaries to high pressure and thus plays an inhibiting role. Similarly, methanol and ethanol, typically inhibitors, have been found to act as a promoter for sII hydrates. Further research needs to be done on different types of additives that can either promote or inhibit hydrate formation depending on concentration and isotopic conditions.

10. Clathrate hydrate with halogen guests

Although halogen clathrate hydrates were among the first clathrate hydrates discovered, they have not attracted the level of scientific scrutiny that has been given to clathrate hydrates with hydrocarbon guests. Simply put, halogen clathrates do not plug natural gas pipelines. Recently, however, the value of studying this class of clathrates as model systems has been shown in a series of studies involving theoretical/computational modeling and experimental spectroscopy (Figure 4).

10.1. Theoretical and computational models of halogen clathrate hydrates

Over the past decade, theoretical and computational models of halogen clathrate hydrates of increasing sophistication have been utilized with considerable success to elucidate various aspects of halogen clathrate hydrate structure, thermodynamics, and spectroscopy.

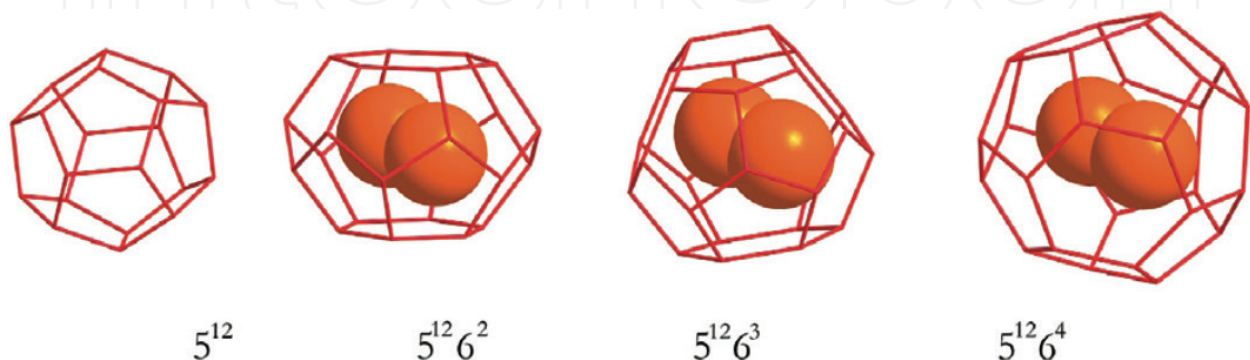


Figure 4. Common halogen clathrate hydrate structure types (courtesy of Janda et al.).

Kerenskaya et al. [65] in 2007 used simple models and force field calculations to estimate the association energy between the clathrate hydrate host and the halogen guest. Schofield and Jordan [66] in 2007 carried out calculations modeling the ground and excited electronic states of Cl_2 trapped in 5^{12} and $5^{12}6^2$ clathrate hydrate lattice sites. A 700 cm^{-1} spectral blue shift was predicted for Cl_2 trapped in a distorted 5^{12} clathrate hydrate cage. Ramya and Venkatnathan [67] in 2013 employed DFT with a dispersion corrected (B97-D) functional to model the Raman spectra of H_2 --a model system for the halogen X_2 guest molecules--encapsulated in pure and THF doped clathrate hydrates. Their computational results predicted a 700 cm^{-1} blue shift of the H_2 breathing mode in the THF doped clathrate hydrate guest vs. the pure clathrate hydrate. Molecular dynamics (MD) simulations, used by Nguyen and Molinero [68] in 2013 in conjunction with the coarse-grained model of water, were employed to model the thermodynamic stabilities of vacant and guest-filled sI, sII, TS, and HS-1 clathrate hydrate types. Bernal-Uruchurtu, Janda, and Hernandez-Lamonedá [69] developed a simple semi-empirical quantum mechanical model in 2015 incorporating, via molecular dynamics trajectories, the impact of movement of bromine molecules in clathrate cages on the UV-visible spectra of bromine clathrate hydrates. A simple electrostatic model of the clathrate hydrate cage predicts a blue shift in the UV-visible spectra, which agrees with experiment. Ochoa-Resendiz, Batista-Romero, and Hernandez-Lamonedá [70] in 2016 employed ab initio calculations and natural bond order analysis to investigate Cl_2 and Br_2 guests in various clathrate hydrate host sites. The picture that emerges is that of an interaction between the lone pair of the nearest oxygen atom in the clathrate hydrate host with the sigma LUMO of the halogen dimer X_2 but only when the halogen is out of its central equilibrium position in the cage, thus allowing a significant cage-halogen interaction. Breaking of O–H hydrogen bonds in the cage is not necessary in this interaction model. Dureckova et al. [71] in 2017 also used ab initio calculations and natural localized molecular orbital analysis in isolated cages and cages with one shell of coordinating atoms to elucidate halogen guest interactions with clathrate hydrate hosts.

10.2. Electronic and vibrational spectroscopy

Although halogen clathrate hydrates have been investigated extensively since their discovery in the early 1800s, there is a paucity of experimental spectroscopic data in the literature pertaining to the interaction between the halogen guest molecules and water host lattice in the clathrate. At this writing, the only halogen clathrate electronic and vibrational spectroscopic studies in the literature are the Raman investigations of Anthonisan [72], and the electronic (UV-visible absorption) and vibrational (Raman and resonance Raman) studies of Janda and co-workers [73]. Halogen clathrate hydrates absorb visible and near UV light but do not luminesce, even at cryogenic temperatures. The clathrate lattice efficiently dissipates the excited electronic state energy of the halogen chromophore through nonradiative channels. The UV-visible and Raman spectra measured Janda et al. [65, 74, 75] clearly show greater perturbations of the spectral properties of the enclathrated halogen guest when the water lattice host cage is smaller than when the lattice host cage is larger. For example, the UV-visible band maximum of the $X \rightarrow C$ transition of gas phase bromine is $24,270\text{ cm}^{-1}$ but this transition frequency increases to $24,630\text{ cm}^{-1}$ when the bromine is confined in a large $5^{12}6^4$ clathrate hydrate cage. Encapsulation of the bromine in a small $5^{12}6^2$ clathrate hydrate cage further increases the transition frequency to $25,150\text{ cm}^{-1}$

(Figure 5). An almost identical frequency increase with decreasing guest cavity size is seen in the $X \rightarrow B$ electronic transition of bromine. This trend shows that tighter guest halogen confinement in a smaller host clathrate hydrate site--with consequently increased clathrate halogen interactions--also increases the B and C excited state energies relative to the energy of the X ground state. In effect, it is a particle in a box situation; a smaller box, in this case a smaller clathrate host lattice cage, gives rise to more widely spaced electronic energy levels and larger $X \rightarrow B$ and $X \rightarrow C$ transition frequencies (Figure 6). A molecular orbital explanation posits that an interaction between the halogen LUMO and the valence oxygen orbitals in the clathrate hydrate will result in a blue shift of the associated valence electronic bands of the water-encapsulated halogen. In contrast, the $X \rightarrow B$ transition frequency for gas phase chlorine is $30,300 \text{ cm}^{-1}$ and for chlorine molecules trapped in small $5^{12}6^2$ clathrate cages this transition is also $30,000 \text{ cm}^{-1}$. This suggests that even the small $5^{12}6^2$ clathrate hydrate lattice minimally perturbs the valence orbitals of the encapsulated chlorine molecules, which are significantly smaller than bromine and iodine molecules. At the other extreme is iodine, the largest of the halogens studied by Janda et al. [75], whose gas phase $X \rightarrow B$ transition frequency of $18,870 \text{ cm}^{-1}$ increases to $20,310 \text{ cm}^{-1}$ when confined in a large $5^{12}6^4$ cage. The vibrational anharmonicity term $w_e x_e$ in bromine clathrate hydrate decreases from 1.06 cm^{-1} in the gas phase, to 0.82 cm^{-1} in a $5^{12}6^2$ cage, and finally to 0.7 cm^{-1} in a larger $5^{12}6^4$ cage. This is consistent with the idea that the smaller and tighter the clathrate hydrate host trapping site becomes, the more harmonic the X ground state potential surface in the guest Br_2 becomes. The clathrate hydrate cage in effect “pushes on” the Br_2 potential surface via van der Waals interactions, rendering it more harmonic.

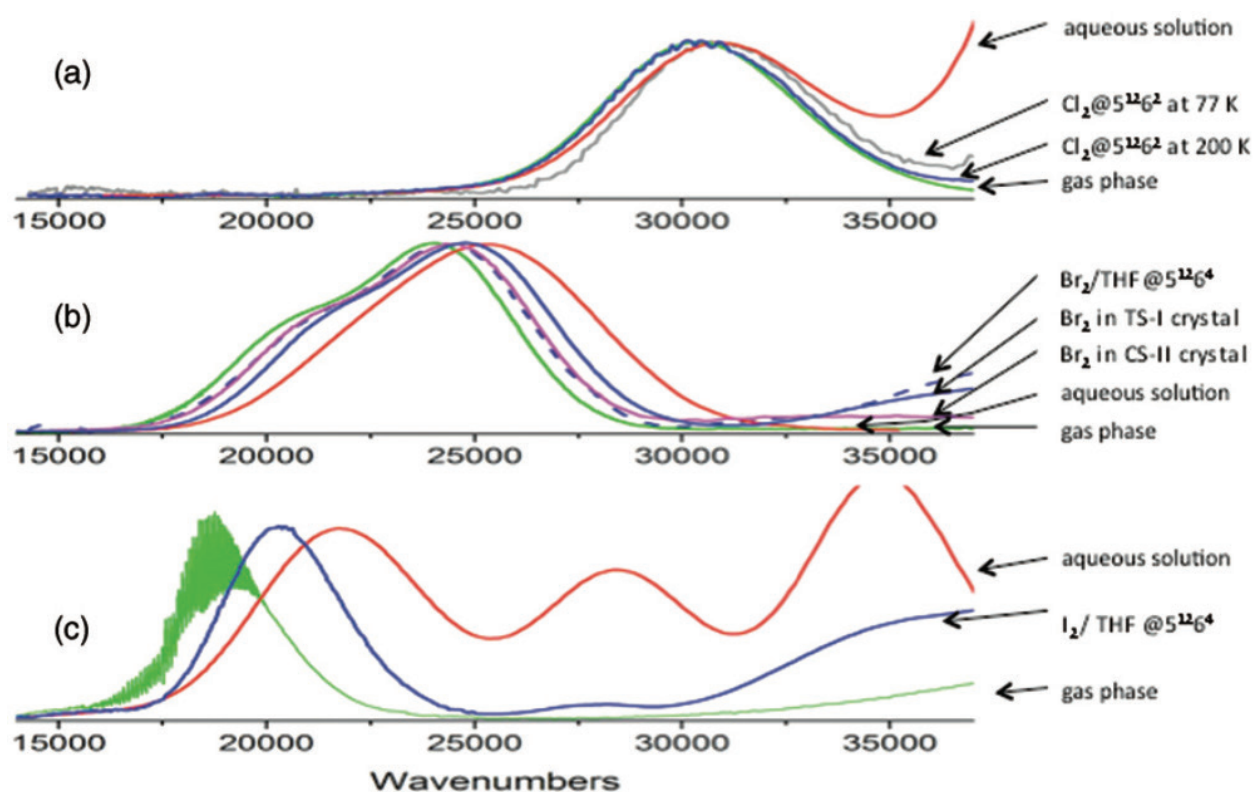


Figure 5. Spectra of (a) chlorine, (b) bromine, and (c) iodine in various environments. In each case, green curve is the gas phase spectrum and the red curve is for an aqueous solution. (Courtesy of Janda et al.).

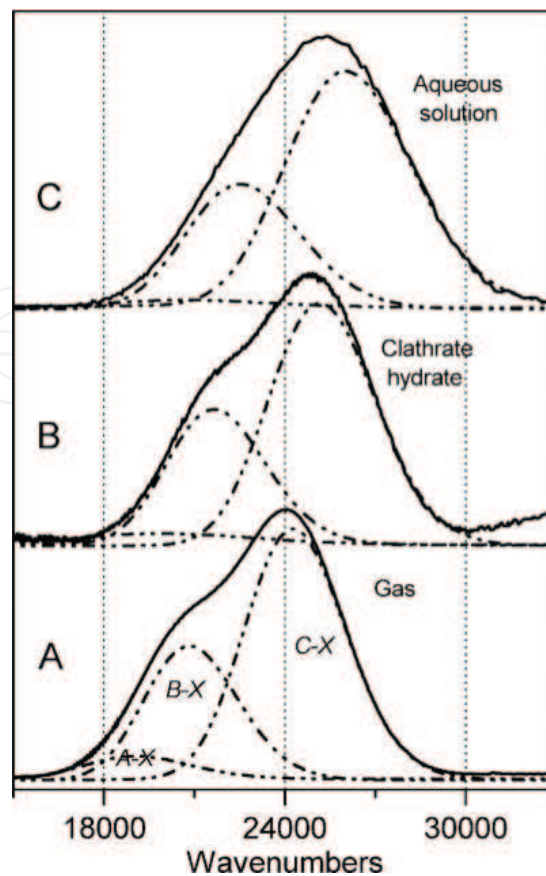


Figure 6. Br₂ absorption spectra in: (A) gas phase (293 K), (B) clathrate hydrate (250 K), and (C) liquid water (293 K). (Courtesy of Janda et al.).

11. Future research

Future research on encapsulated guests in clathrate hosts will undoubtedly focus to a certain extent on the design and execution of experiments that will yield definitive experimental confirmations of the existence of clathrate hydrates in other environments in the Solar System than Earth. Such experiments will undoubtedly include the landing of probe vehicles on the objects of interest in the Solar System. The probes will be capable of accessing, retrieving, and analyzing sub-surface samples where clathrate hydrates are thought to reside. Spectroscopic interrogations of extra-Solar planets will also include “clathrate hunting” in their task lists. On the practical side, the search for more effective and more environmentally friendly clathrate hydrate promoters and inhibitors will continue. Scientists and engineers will continue to study clathrate hydrates as possible storage/transport media for fuels such as methane and hydrogen. The possible use of clathrate hydrates as sequestering agents for carbon dioxide will continue to be investigated. Increasing scientific research attention will be given to the impact of global warming on methane clathrate hydrate degradation and subsequent release of methane into the oceans and atmosphere. In the realm of pure science, ever more sophisticated spectroscopic, structural, isotopic, thermodynamic, and theory/computational tools will be employed to provide a picture of unprecedented detail that encompasses the dynamics

of clathrate formation, thermal degradation, and host-guest interactions. Expect also to see multi-spectroscopic/structural probes being used to investigate the same sample at essentially the same time under the same experimental conditions.

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