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Optical studies of thin films of cryocondensed mixtures of water with carbon dioxide

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Abstract. The reasons for choosing this type of hydrate as an object of research were the actual problems of cleaning the air layer of the planet from carbon. A series of experiments was carried out to record changes in the vibrational spectra in a thin film of a cryocondensed mixture of water and carbon dioxide at various concentrations. The purpose of this study was to determine the presence of carbon dioxide hydrates in conditions of high vacuum and low-temperature condensation from the gas phase. For the frequency range, the interpretation of changes in the vibrational spectra depending on the annealing temperature of the sample and the concentration of carbon dioxide is given 2210-2260, 2270-2290, 2310-2380, 2800-3700, 3590-3610, 3580-3720, 3685-3720 cm^{-1} . The peaks of adsorption of a 15% carbon dioxide mixture with water at a condensation temperature of 15 K and further annealing of the sample are compared.

Keywords: cryocondensation, FTIR, PVD, carbon dioxide, water, clusters.

1. Introduction

Contribution to global warming due to the absorption of infrared radiation, carbon dioxide CO_2 , methane CH_4 , and nitrous oxide N_2O were recognized as the most harmful substances [1].

There are two ways to reduce the level of carbon dioxide in the atmosphere. The first is associated with the reduction of carbon dioxide emissions into the atmosphere, and the second is with the utilization of carbon dioxide that has already entered the atmosphere.

The first path has difficulties associated with the fact that it is difficult for mankind to abandon the existing energy consumption in favor of environmentally friendly methods of obtaining it. For example, even though there is an increase in the development of alternative energy sources, this quantitatively does not affect the reduction of CO_2 emissions into the atmosphere.

A recent study by scientists at the University of California, Berkeley [2] confirms that the US could get 90 percent of its electricity from zero-carbon sources by 2035. The detailed network modeling underlying the study shows that electricity demand is reliably met every hour until 2035 under various weather scenarios. Moreover, ever-cheaper wind and solar panels make it possible to achieve 90% net electricity, while the reduction in wholesale electricity trade costs 10 percent of today's level.

An analysis by the University of California, Berkeley, and the Energy Innovation team shows that America can achieve a zero-carbon electricity system without significantly raising wholesale electricity rates from today's levels through a combination of technologies that have not yet been commercialized but are currently in the pipeline project.

New methods being developed for storage are increasing interest in the study of various methods for studying the structures of clathrates. This will be facilitated by injection back into earth formations where voids are formed due to mining, as well as on the ocean floor, possibly for use in the production of concrete and synthetic fuels, as well as in the chemical industry.

There is also the idea of storing carbon in solid hydrates on the ocean floor. Thus, CO_2 can stay in the hydrate «capsule» for a long time at low temperatures and high pressure. Now, methane extraction is actively carried out from the ocean floor from methane hydrate clathrates. Carbon dioxide can also exist in the hydrate shell, which can be a promising replacement for methane clathrate hydrates by CO_2 hydrates in the places where methane clathrates are mined [3].

Non-stoichiometric inclusion compounds that have a small, usually polar (guest) molecule within ice-like hydrogen-bonded host molecules and can exist as a stable solid at high pressure and low temperature are called hydromethanes. Seafloor sediments contain this type of hydrate that can be of use as an alternative energy source. Cubic structures I and II are the major crystallographic structures of clathrate hydrates [4]. The cell occupancy ratio is what distinguishes them. In structure-I (sI), for every three large cells, there is only one small cell, and in structure-II (sII), there are twice as many small cells as large cells. Guest molecules, methane (CH_4) and carbon dioxide (CO_2), for instance, cannot create sII hydrates when the temperature is low and the pressure is high. It is thought that such guest molecules can create sI in natural clathrate hydrates and synthetic ones formed in comparable conditions. Raman spectroscopy is known to have clathrate hydrate signatures. It is used as a supplementary instrument, just like IR spectroscopy. It can be hard to utilize

IR when it comes to clathrate hydrates because of the strong water regime. It is possible for CO₂ though, and the use of IR spectroscopy makes it possible to gain important data here due to the separation of the CO₂ and H₂O spectra. Researching CO₂-containing clathrates through spectroscopy is hard since Raman spectroscopy cannot differentiate between cellular populations. There are some difficulties with NMR spectroscopy as well because isotropic chemical shifts cannot be altered for various CO₂ cellular populations. Molecules in different clathrate-related states provide unique IR vibration frequencies. To date, however, just the thin cryogenic films obtained at low pressure have been researched through FTIR.

Hydration count estimates are based on gas chromatography data obtained by conducting an analysis of infrared spectra. Raman scattering was studied using spectroscopy with pressure, ranging from 3.0 to 9.0 MPa within the high-temperature range with sll [5]. The results demonstrated [3] the creation of the sll CO₂ hydrates at the time of the formation of the pure CO₂ clathrates. According to [6] and [7,8], the sll CO₂ clathrates were observed on the tetrahydrofuran (THF) clathrate in a cryogenic state, while the sl CO₂ clathrates were found on the ethylene oxide.

Therefore, this research is aimed at studying the creation and the main characteristics of thin films of cryovacuum condensates of water molecules with CO₂. Besides, the samples condensed at low temperatures are investigated in relation to the process of relaxation and the structural transformations affected by the temperature. CO₂ and water films are used as the objects of this research. Such research may yield a result establishing a correlation between the condensation conditions such as substrate temperature and the gas phase pressure and the characteristics of the amorphous films created. Besides, one of the main objectives is to find the temperature intervals that correspond to various structures of the samples and to obtain the temperature of desorption and the relaxation times of the films created.

Major relevant studies utilized hydromethanes as objects, so CO₂ clathrate hydrates remain underresearched [9–11]. Besides, in our research, the IR studies were conducted at low pressures to gain samples. This method had not been used before. In general, Raman spectroscopy is utilized in this type of research [12–14].

2. Materials and methods

To fulfill the tasks, it is essential to utilize an integrated approach combined with certain experimental methods:

- The laser interferometry technique of two beams is utilized to obtain the rate of growth, the film level of thickness, and the index of refraction.
- IR spectrometric method is utilized to determine IR reflection spectra of films and characterize the condition of the cryovacuum condensate samples by conducting an analysis of the amplitudes of absorption and band location with respect to the typical vibrations of the unbound molecules examined.
- The technique of thermal desorption is utilized as a different method of obtaining the values of temperature of structural-phase transformations.
- Quadrupole mass spectrometry technique for residual gases.

To implement the tasks set, we use the method of cryovacuum condensation of samples from the gas phase onto a substrate cooled to low temperatures. It is well known that this

method is one of the effective ways to obtain cryofilms in various, and, importantly, well-controlled structural phase states [15–17]. In Western literature, this method is called the method of physical vapor deposition (PVD [6]) and is also widely used to study the properties of matter at low and ultralow temperatures, such as density [9], [10], optical characteristics [18,19], as well as in solving a wide range of problems in astrophysical and astrochemical studies [17,20–23].

Installing a gas analyzer and completing the substrate with an adjustable heater based on a vacuum spectrophotometer helped to quantitatively determine the concentration of components in the film. Research on the analysis of greenhouse gases by various methods is a hot topic at this time, as evidenced by recent publications in high-ranking journals [24,25].

During the experiment, the condensate growth rate and refractive indices for the number of different concentrations of CO₂ and H₂O were determined at the temperature of T=11 K. The data obtained in the course of the experiment for a mixture of water cryocondensates and carbon dioxide are presented in Table 2. Figure 1 demonstrates an experimental apparatus used to measure the dependence of the indices of refraction on the temperature of deposition. For the purpose of this research, the temperature range for the experiments was 11–310 K, which includes the changes in the structure of the samples examined. The pressure of deposition (P) was equal to P=5·10⁻⁵ Torr. The only exception were some cases when the pressure of another value was needed. The thickness remained the same throughout all the experiments for each temperature of condensation. The wavelength of the laser chosen for this research was (406 ± 0.5) nm. The laser interferometry technique with two beams was utilized to determine the index of refraction. Figure 1 demonstrates points each of which is an average value based on 2 or 3 measurements carried out. The error rate when determining the refractive index did not exceed 1.5%.

The Extorr XT100 gas analyzers were set up in a vacuum chamber. They incorporate an improved version of the Pirani gauge and a Bayard-Alpert one. The latter measures the currents of ions in relation to pressure through electron impact ionization of residual gases. The former measures vacuum through heat conduction of gases. The ion currents are measured by the analyzer through electronic technologies and fine mechanics. The operating range of the quadrupole starts at 10⁻⁴ Torr. It is also able to function below 10⁻¹¹ Torr. The start-up of the Pirani gauge requires atmospheric pressure. The Bayard-Alpert gauge can function, starting at 10⁻² Torr, and has a limit of 2x10⁻¹⁰ Torr, beyond which it cannot conduct measurements. The Extorr gas analyzer operating range is 1–100 amu.

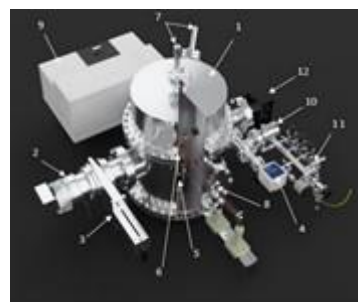


Figure 1. Cryovacuum condensation experimental setup: 1: vacuum chamber, 2: vacuum pump Turbo-V-301, 3: vacuum gate valve CFF-100, 4: pressure detector FRG-700, 5: Gifford-

McMahon refrigerator, 6: substrate, 7: photo multiplier, laser interferometer, 8: light source, optical channel, 9: IR-spectrometer, 10: high-precision gas supply leak into the chamber; 11: gas leak into the mixture production system; 12: The Extorr XT100

3. Results and discussion

The experimental dependence of the deposition rate on temperature using the example of water and carbon dioxide films is presented in Table 1. Several experiments were carried out with different deposition temperatures, because of which a linear increase in the deposition rate with a decrease in the condensation temperature at a constant pressure $P=5 \cdot 10^{-4}$ Torr is observed. Thus, the optimal deposition temperature for the given conditions was found experimentally.

Table 1. Film deposition rates versus temperature

Prepared mixture for K condensation	Temperatures, μ m/s	Deposition rate, index	Refractive, n
H ₂ O(85%)+CO ₂ (15%)	11	0.0167	1.2567
H ₂ O(85%)+CO ₂ (15%)	45	0.0141	1.3293
H ₂ O(85%)+CO ₂ (15%)	80	0.0110	1.4044
H ₂ O(85%)+CO ₂ (15%)	110	0.0052	1.2875
H ₂ O(85%)+CO ₂ (15%)	11	0.0032	1.2568
CO ₂	11	0.0230	1.2320
CO ₂	45	0.0138	1.3935
H ₂ O	11	0.0167	1.2231

The results shown in Table 1 demonstrate that at a temperature of 110 K, only water condenses onto the substrate. This confirmation was also revealed in the IR spectra. Therefore, the refractive index from tables 1 and 2 does not correspond to the given concentration and represents the value for pure water at this temperature. This is evidenced by the IR spectra of the deposited films, as well as the thermogram of this film, which does not show any signs of CO₂ in the film. During condensation, the evacuation pump from the chamber is blocked. After condensation is completed, it opens.

Table 1 demonstrates that the refractive index increased gradually from 16 K to 80 K. This increase occurs due to two main factors. Firstly, the structural characteristics of the sample influence the increase as it is amorphous. Secondly, the temperature range of 16–80 K is characterized by high levels of porosity.

Table 2. The film index of refraction on the concentration of the mixture

Substance K	Temperatures, μ m/s	Deposition rate, index	Refractive, n
CO ₂	11	0.0118	1.2320
H ₂ O(75%)+CO ₂ (25%)	11	0.0114	1.3381
H ₂ O(50%)+CO ₂ (50%)	11	0.0176	1.2860
H ₂ O(75%)+CO ₂ (25%)	11	0.0181	1.2760
H ₂ O(80%)+CO ₂ (20%)	11	0.0166	1.2703
H ₂ O(85%)+CO ₂ (15%)	11	0.0166	1.2708
H ₂ O(90%)+CO ₂ (10%)	11	0.0155	1.2539
H ₂ O(95%)+CO ₂ (5%)	11	0.0173	1.2330
H ₂ O	11	0.0167	1.2231
CO ₂ (75%)+N ₂ O(25%)	11	0.0032	1.2568
N ₂	11	0.0030	1.2257

Figure 2 demonstrates how the deposition temperature affects the nitrous oxide refractive index. It was mentioned above [23] that this gas changes its state at the temperature of 40 K to the disordered phase Pa3. That is why it is important

to understand the way this change influences the refractive index of this material. The diagram shows the gradual increase of its refractive index. At the temperature of 16 K, the refractive index (n) equals 1.254. However, when the temperature reaches 40 K, the value of n increases to 1.310. From 45 K to 52 K, the index undergoes a rapid increase, reaching the value of 1.410. After that, it continues to increase gradually.

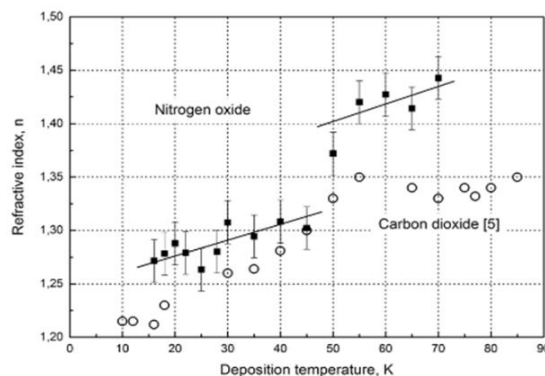


Figure 2. Influence of deposition temperature on the nitrous oxide refractive index. [23] provides the corresponding data for carbon dioxide, which is useful for comparison

In order to carry out a comparison, the corresponding data for carbon dioxide was added to Figure 2. The data were obtained in an experiment, utilizing a method similar to the one used in this research [26]. A slow increase can be observed in the range from 10 and 55 K. The increase eventually stops as the temperature rises.

The hydrate phases of CO₂ are not a new research object, and their characteristics have been researched for quite a long time [27]. Lately, these hydrate forms have been found to be useable in storing and containing CO₂. As a gas hydrate with the Type I (Pm3n) structure, each of its cells includes 6 tetrahedral cells (51262), 46 molecules of water, and two dodecahedral (512). Provided that every cell is filled separately, the composition is 5.75H₂O. Certain studies proved that in a CO₂ hydrate, molecules fill most of the cells large in size and some smaller ones in the I (sI) structure. As a result, the solvation number is in the range of 5.75 to 7.66. For the use of spectroscopy to be beneficial in cell population research, it ought to demonstrate resolved guest signatures in cells of larger (51262) and smaller (512) sizes. However, Raman spectroscopy does not provide the means to differentiate between the sizes of the cell populations [28,29].

Molecules can be characterized by the chemical bonds and functional groups inside them. One of the features of IR spectroscopy is its ability to discern the vibrations that signify the presence of these bonds or groups. The vibrations of molecules may absorb infrared radiation. This occurs in the course of the interaction between the IR and matter provided that certain conditions such as the frequencies and the bond length are met. The structure of the molecule as a whole may not affect the process of absorption though. As stated in [30], one of the methods applicable when researching gas hydrates through their FTIR spectra is the preparation of the ethylene oxide hydrate. This approach was subsequently utilized in another research to create CO₂ hydrate and find two peaks in cells of small and larger sizes in sI and sII structures. This research found that guest molecules have IR patterns that

differ a lot from what had been found in other phases. It was also observed that the lower the temperature was, the more effects such as more noticeable narrowing and shifting as well as higher peak intensity occurred. Nevertheless, the difficulty of producing the thin films of gas hydrates like carbon dioxide was highlighted, and creating mixed hydrates with a little bit of polar gas was suggested as a more plausible option.

In order to determine the viability of the ATR-FITR method and research how the spectrum of CO₂ reacts to the environment, the CO₂ IR spectrum was observed throughout various phases in the region of antisymmetric stretching.

4. Conclusions

The kinetics of the creation and decomposition of carbon dioxide hydrates require additional research. There is not enough data concerning the physical characteristics of their structure. That is why is important to carry out more experiments, involving condensation and various carbon dioxide hydrate histories.

Besides, the spectra identified are useful for finding CO₂ hydrates on celestial objects.

At atmospheric pressure, the face-centered cubic form CO₂ structure is only mentioned in [32]. As for the temperature range in our research, the development of the structure can be characterized in two ways. One explanation is based on the data obtained through IR spectroscopy that demonstrate the amorphousness of the structure below 30 K and its crystallization when exceeding 50 K. After the formation of ice at low temperatures, the annealing causes the structure to become less amorphous and more crystalline. One other explanation is based on the formation of ice through nucleation [33]: random crystalline islands are formed from the grains, and their size is influenced by the temperature. Similarly, the process of annealing leads to crystallization as the temperature increases, providing more energy, or the energy is transmitted to a molecule of gas when colliding with a solid.

Concerning the IR spectra of carbon dioxide and water cryocondensates, the correlation of data that proves the existence of a clathrate structure is evident.

The increase in refractive indices as the water concentration approaches 25% compared to other concentrations as well indicates the growth of less dense structures than amorphous condensates of carbon dioxide or amorphous ice of water.

This interesting pattern also manifests itself with other clathrate-forming mixtures, which will help attract interest in a detailed calculation of this phenomenon for various similar structures.

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Конденсацияланған су мен көмірқышқыл газ қоспаларының жұқа қабықшаларын оптикалық зерттеу

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Аңдатпа. Гидраттың бұл түрін зерттеу нысаны ретінде таңдау себептері планетаның ауа қабатын көміртектен тазартудың өзекті мәселелері болып табылды. Әр түрлі концентрациядағы су мен көмірқышқыл газының криоконденсацияланған қоспасының жұқа қабығындағы тербелмелі спектрлердің өзгеруін тіркеу бойынша бірқатар тәжірибелер жүргізілді. Бұл зерттеудің мақсаты – жоғары вакуум және газ фазасынан төмен температуралы конденсация жағдайында көмірқышқыл газы гидраттарының болуын анықтау. Жиілік диапазоны үшін үлгінің күйдіру температурасына және көмірқышқыл газының концентрациясына байланысты тербелмелі спектрлердің өзгеру интерпретациясы берілген 2210–2260, 2270–2290, 2310–2380, 2800–3700, 3590–3610, 3580–3720, 3685–3720 см⁻¹. Үлгінің 15 К конденсация температурасында және оны одан әрі күйдіру кезіндегі 15% көмірқышқыл газы мен су қоспасының адсорбция шындырын салыстырмасы берілген.

Негізгі сөздер: криоконденсация, FTIR, PVD, көмірқышқыл газы, су, кластерлер.

Оптические исследования тонких пленок криоконденсированных смесей воды с углекислым газом

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Аннотация. Причинами выбора этого типа гидрата в качестве объекта исследования послужили актуальные проблемы очистки воздушного слоя планеты от углерода. Была проведена серия экспериментов по регистрации изменений колебательных спектров в тонкой пленке криоконденсированной смеси воды и углекислого газа при различных концентрациях. Целью данного исследования было определить наличие гидратов диоксида углерода в условиях высокого вакуума и низкотемпературной конденсации из газовой фазы. Для частотного диапазона дана интерпретация изменений колебательных спектров в зависимости от температуры отжига образца и концентрации углекислого газа 2210-2260, 2270-2290, 2310-2380, 2800-3700, 3590-3610, 3580-3720, 3685-3720 см⁻¹. Дано сравнение пиков адсорбции 15%-ной смеси диоксида углерода с водой при температуре конденсации 15 К и дальнейшем отжиге образца.

Ключевые слова: криоконденсация, FTIR, PVD, диоксид углерода, вода, кластеры.

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