IRSTI 29.03.30
https://doi.org/10.53939/1560-5655_2025_1_115

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OPTICAL STUDIES OF H_2O+CO_2 THIN FILMS

Abstract. The choice of this type of hydrate as a study was the actual problems of cleaning the air layer of the planet from carbon. A series of experiments was carried out to record changes in 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 under conditions of high vacuum and low temperature condensation from the gas phase. The interpretation of changes in the vibrational spectra depending on the sample annealing temperature and carbon dioxide concentration is given for the frequency range 2210-2260, 2270-2290, 2310-2380, 2800-3700, 3590-3610.3580-3720.3685-3720 cm^{-1}. When comparing the adsorption peaks of a 15% mixture of carbon dioxide with water at a condensation temperature of 15 K and further annealing of the sample.

Keywords: decarbonization, carbon emission, cryocondensates, optical properties, water, carbon monoxide.

Introduction. All over the world, environmental problems are driven by climate change, especially with increasing greenhouse gas emissions. The growth of greenhouse gas concentrations in the atmosphere has become a serious environmental problem, as evidenced by the Kyoto Protocol. In addition to contributing to global warming by absorbing infrared radiation, carbon dioxide CO_2, methane CH_4, and nitrous oxide N_2O were declared the most harmful substances.

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 [1] 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:

- Use of hydrogen produced in gas turbines upgraded to burn pure hydrogen
- Use of hydrogen produced by green electricity in fuel cells
- Combustion of synthetic methane or biogas in existing gas installations
- Capture and sequestration of CO_2 from existing gas installations
- Direct capture of CO_2 in air from ambient air

Stages of CCUS

1. Determining the source of CO_2
2. Capture and release of CO_2
3. Cleaning and shrinking
4. Transportation
5. Storage
6. Usage

First you need to identify the source of carbon: Mobile, point (industrial emissions), atmosphere.

Many systems also exist for carbon capture: conventional, direct air capture and natural carbon sinks.

Storage is carried out by injection back into earth formations, where voids are formed because of mining, as well as on the ocean floor, use is possible 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.

Methane hydrates (clathrates) are non-stoichiometric inclusion compounds where small, usually polar (guest) molecules are trapped within a host framework of hydrogen-bonded, ice-like structures. These compounds can remain stable in solid form under high pressure and low temperature conditions. Methane hydrates found in marine sediments are considered a potential alternative energy source. There are two main crystallographic forms of gas hydrates: cubic structure I and II. [2]. The main difference between these two types is the cell occupancy ratio. The ratio of large and small cells in structure-I (sI) is 3:1, while in structure-II (sII) it is 1:2. It is known that guest molecules such as methane (CH_4) and carbon dioxide (CO_2), most abundant in natural gas hydrates, do not form sII hydrates under low temperature and high-pressure conditions. It is generally accepted that these guest molecules form sI in natural gas hydrates and in synthetic hydrates grown under similar geological conditions. It is well known that Raman spectroscopy has clear gas hydrate signatures. Raman spectroscopy and infrared (IR) spectroscopy are additional tools. The use of IR in the case of gas hydrates (IR) is difficult due to the stronger regimes of the nearby water. But for CO_2, IR spectroscopy provides vital information because the spectra of CO_2 and H_20 are well separated. Spectroscopic examination of CO_2 containing clathrates is difficult because Raman spectroscopy cannot distinguish between cell populations. NMR spectroscopy also has some complications since isotropic chemical shifts do not change for different CO_2 cell populations. But it is known that molecules in various phases related to hydrates give unique infrared vibration frequencies, but so far only thin cryogenic films obtained at low pressure have been studied using IR transmission spectroscopy.

Based on the analysis of IR spectra and knowledge of the composition of the hydrated gas from gas chromatography data, quantitative estimates of the hydration number are given.

Some spectroscopic studies of Raman scattering on synthetic methane hydrates in the pressure range of 3.0-9.0 MPa and temperatures from -15 to 15°C showed the presence of sII, [3] observed the transitional formation of sII CO_2 hydrates during the growth of pure CO_2 hydrates. [4]

and [5] reported sII CO_2 hydrates on tetrahydrofuran (THF) hydrate in a cryogenic state, as well as sI CO_2 hydrates on ethylene oxide.

Thus, this work is devoted to an experimental study of the formation and properties of thin films of cryovacuum condensates of water molecules with CO_2, as well as relaxation processes and thermally stimulated structural-phase transformations in samples condensed at low temperatures. The objects of the study are films of water and CO_2. Such studies are aimed at establishing the relationship between condensation conditions (substrate temperature and gas phase pressure) and the properties of the amorphous films formed, such as growth rate, refractive indices and polarizability. In addition, one of the important tasks is to determine the temperature intervals for the existence of various structural states of the samples, as well as to determine the desorption temperature and the degree of kinetic stability (relaxation times) of the films formed.

Since the main studies use methane clathrates as an object, hydrates with CO_2 are little studied [6–8], moreover, in our work, IR studies are carried out at low pressures to obtain samples, which has no analogues now. Basically, such works use Raman spectroscopy [9].

"CCUS should be a key element in the transition to carbon-free energy. It is the only technology group that contributes both to direct emission reductions in critical sectors of the economy and to CO_2 removal to balance unavoidable emissions". Samantha McCulloch, Head of Technology, CCUS, International Energy Agency

Experimental Technique:

An integrated approach involving multiple experimental methods is employed to address the research objectives:

- Two-beam laser interferometry is utilized to measure the growth rate, thickness, and refractive index of the cryocondensed film.
- Infrared (IR) spectrometry is applied to obtain IR reflection spectra of the films and to analyze the state of cryovacuum condensate samples by evaluating absorption amplitudes and the positions of bands corresponding to characteristic vibrations of the studied molecules in their free state.
- Thermal desorption is used as an alternative method to determine the temperatures at which structural-phase transformations occur.
- Residual gas analysis is performed using quadrupole mass spectrometry.

To achieve the research goals, cryovacuum condensation of samples from the gas phase onto a substrate cooled to low temperatures is employed. This technique is well-known as an effective method for producing cryofilms in various, and critically, well-controlled structural-phase states [4]. In Western literature, it is referred to as the physical vapor deposition (PVD [5]) method and is widely used to investigate material properties at low and ultra-low temperatures, including density [6], polarizability [7], and optical characteristics [8], [9]. Additionally, it is applied in a broad range of astrophysical and astrochemical studies [10], [12].

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 [13], [14].

The values of the growth rate and refractive indices of condensates for various concentrations of CO_2 and H_2O at a constant temperature T=11 K are obtained. Figure 4 shows the experimental data obtained for cryocondensates of a mixture of water and carbon dioxide.

Measurements of the dependence of the refractive index on the deposition temperature were carried out using the experimental setup shown in Figure 1. The experiments were carried out in the temperature range from 11 to 310 K, including structural transformations of the studied materials. All experiments were conducted at a constant deposition pressure of $P = 5 \times 10^5$ Torr, with several additional experiments conducted to optimize the pressure. The sample thickness was kept constant for each condensation temperature. A laser with a wavelength of (406 ± 0.5) nm was used, and the refractive index was measured using a two-beam laser interferometer. Each data point in Figure 2 represents the average of two or three measurements. The total error of measuring the refractive index was estimated to be no more than 1.5%.

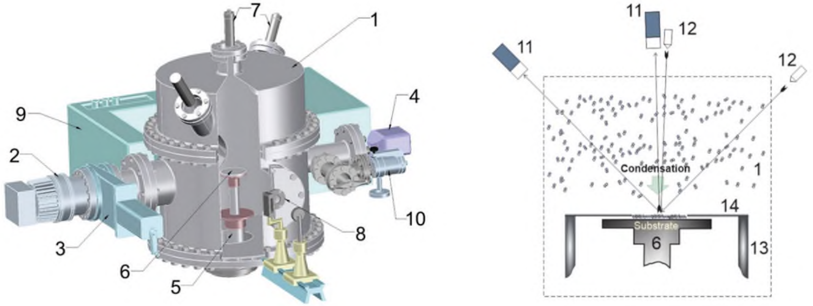

Figure 1 - Experimental setup for cryovacuum condensation: (1) vacuum chamber, (2) Turbo-V-301 vacuum pump, (3) CFF-100 vacuum shut-off valve, (4) FRG-700 pressure sensor, (5) Gifford- McMahon, (6) substrate, (7) photomultiplier and laser interferometer, (8) light source and optical channel, (9) IR spectrometer and (10) power system, (11) photomultiplier, (12) laser, (13) metal cylinder and (14) screen.

Results and discussion. The experimental dependence of the deposition rate on temperature using the example of water and carbon dioxide films is presented in Figure 2. Several experiments were conducted with different deposition temperatures, which is why a linear increase in the deposition rate is observed with a decrease in the condensation temperature at constant pressure P= 5* 10^{-4} Torr. Thus, the optimal deposition temperature for the given conditions was found experimentally.

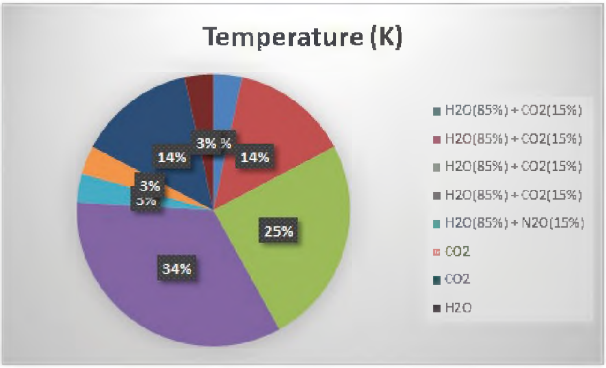

Figure 2 - Film deposition rates versus temperature

The results shown in the Figure 2 and Figure 3 demonstrates 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 Figure 2 and Figure 3 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 CO_2 in the film. During condensation, the evacuation pump from the chamber is blocked. After condensation is completed, it opens.

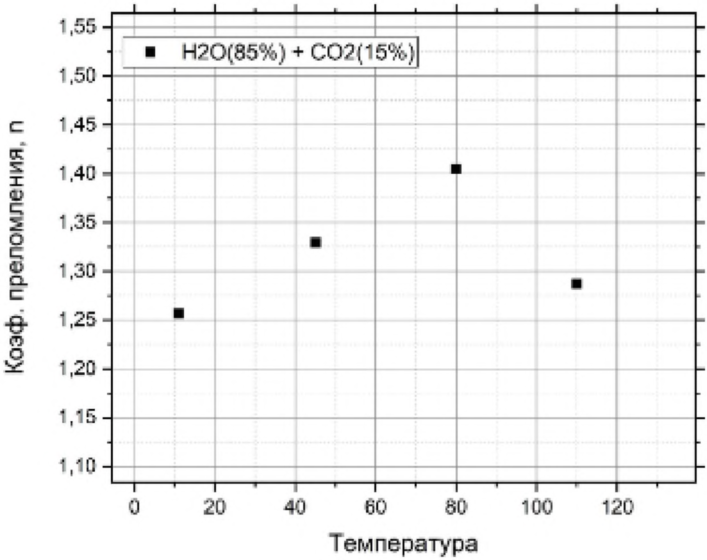

Figure 3 - Dependence of the refractive index of a thin film of cryocondensate of water and carbon dioxide at different temperatures.

As shown in Figure 2 and Figure 3, a gradual increase in the refractive index is observed within the temperature range of 16–80 K. In this range, the sample exhibits an amorphous structure with a high degree of porosity, which contributes to the observed increase in the refractive index.

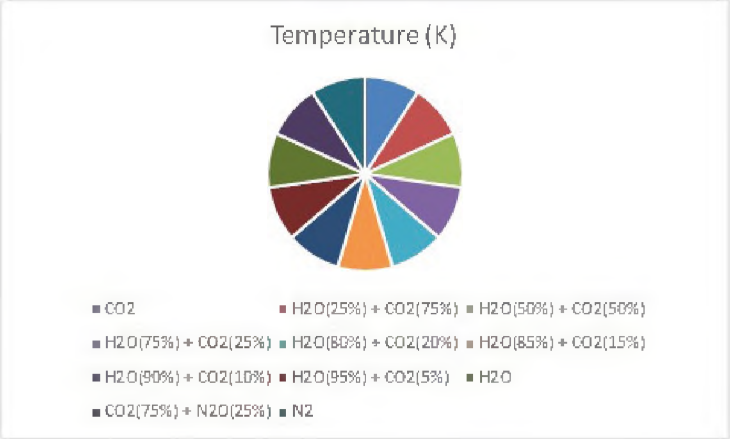

Figure 4 - The refractive index of the film on the concentration of the mixture.

The effect of the deposition temperature on the refractive index of nitrous oxide is shown in Figure 5. As previously reported [9], [15], at T = 40 K, this material undergoes a transition from a crystalline cubic face-centered phase (T > 40 K) to a partially orientationally disordered Pa3 phase (T < 40 K). This makes it particularly interesting to study how this transition affects the refractive index of nitrous oxide. As shown in the diagram, the refractive index gradually increases with increasing temperature, from n = 1.254 at 16 K to n = 1.310 at 40 K. Around 45 K, there is a sharp increase in the refractive index from n = 1.315 at T = 45 K to n = 1.410 at T = 52 K. A further increase in the deposition temperature from 50 to 70 K leads to a further gradual increase.

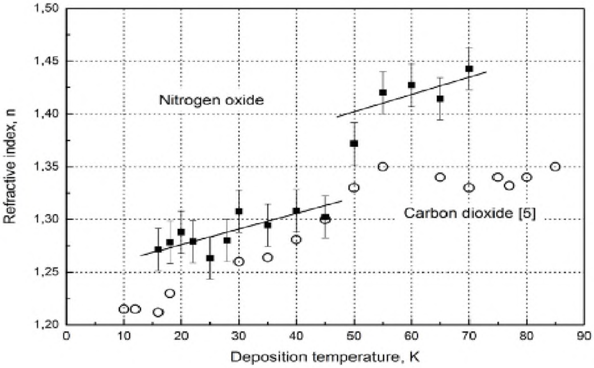

Figure 5 - Effect of deposition temperature on the refractive indices of nitrous oxide. For comparison, data for carbon dioxide are given [16].

For comparison, Figure 5 also shows the values of the refractive index of carbon dioxide, measured experimentally using a similar technique [16]. In this case, a monotonous increase is observed in the range from 10 to 55 K, after which the values reach a plateau at higher temperatures.

The fact is that CO_2 hydrate forms have been known for many years [17]. Recently, CO_2 hydrate has been considered as a means of capturing and sequestering CO_2. The CO_2 hydrate forms a type I (Pm3n) cubic structure. Its unit cell contains 46 water molecules within two dodecahedral (5_{12}) and six tetrahedral cells ($5_{12}6_2$). If all cells are occupied individually, the hydrate composition of CO_2 is 5.75 H_2O. In several spectroscopic and diffraction studies, the composition of the hydrate was considered, and it was decided that CO_2 molecules occupy almost all the large cells in the I (sI) structure, as well as some of the small cells, which gives a hydration number between 5.75 and 7.66. Spectroscopic measurements useful for distinguishing cell populations should preferably show resolved guest signatures in the large ($5_{12}6_2$) and small (5_{12}) cell hydrate lattice. Unfortunately, Raman spectroscopic measurements are not able to distinguish between large and small populations of cells in CO_2 hydrate [17], [18], [19].

Infrared spectroscopy (IR) detects vibrations characteristic of certain chemical bonds or functional groups in a molecule. When infrared light interacts with matter, the molecular vibrations that give rise to changes in the molecular dipole moment tend to absorb infrared radiation in a certain range of frequencies depending on bond lengths and angles and may be independent of the structure of the rest of the molecule. Berti and Devlin [20] prepared ethylene oxide hydrate using a cryogenic thin film vapor deposition method and established this approach as a viable option for studying clathrate hydrates by obtaining transmission FTIR spectra. Later, Fleifel and Devlin used the same method to prepare CO_2 hydrate and identify two separate peaks for CO_2 in large and small cells in sI and structure II (sII). They concluded that infrared patterns for guest molecules are usually significantly different from those temperatures often cause pronounced shifting, narrowing, and amplification of peak intensity by limiting internal rotational motions. However, they reported that it was difficult to grow thin films of simple clathrate hydrates of small non-polar polyatomic molecules such as carbon dioxide, and it was only possible to form mixed hydrates in the presence of a small amount of polar auxiliary gas such as ethylene oxide.

To assess the feasibility of the ATR-FTIR method and the sensitivity of the CO_2 spectrum to the environment, the infrared spectrum of CO_2 in the region of antisymmetric stretching was recorded for CO_2 in different phases.

Figure 6 shows that the frequency of CO_2 oscillations in different phases varies significantly, as does the bandwidth.

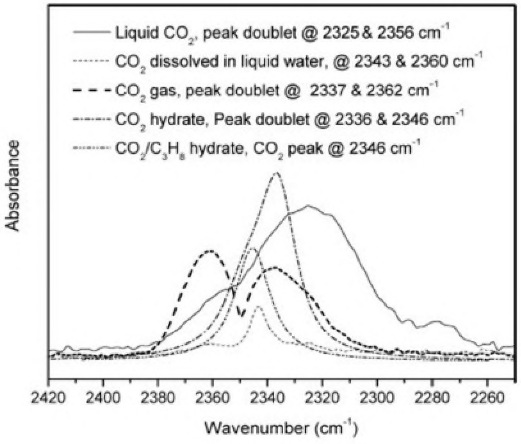

Figure 6 - ATR-IR spectra of CO2 showing unique peaks under different conditions.

No solid CO_2 was observed as the assay temperature did not drop below -50°C. Because spectra for CO_2 in different phases give unique peak positions, infrared spectra recorded by the ATR method can be usefully used to characterize CO_2 hydrate.

The formation of carbon dioxide clathrate hydrate is verified and identified using the vibrational mode v_3. The position of the absorption bands observed in our experiments at 2280 and 2283 cm^{-1} closely corresponds to the IR spectrum of type I $13CO_2$ clathrate, which corresponds to molecules trapped in small and large structures, respectively. Fluctuations of the primary isotopomer in the region of 2341 cm^{-1} are also shown in our spectra. The very weak arm visible in the 2235 cm^{-1} region in Figure 6a of our low−temperature spectra is shifted by 7 cm^{-1}. We attribute this to $C_{18}O_{16}O$, a substituted isotope of carbon dioxide, based on the shifts measured in the gas phase (Rotman, 1986) [21]. The second band, expected at a slightly higher wavenumber for $C_{18}OCO$ trapped in the second type of cell, is barely visible in our spectra due to significant overlap with the main bands of CO_2 saturation (Figure 7). In addition, a noticeable band, more noticeable above 2360 cm^{-1}, corresponds to the 3_v harmonic in the libration mode water ice (Figure 8).

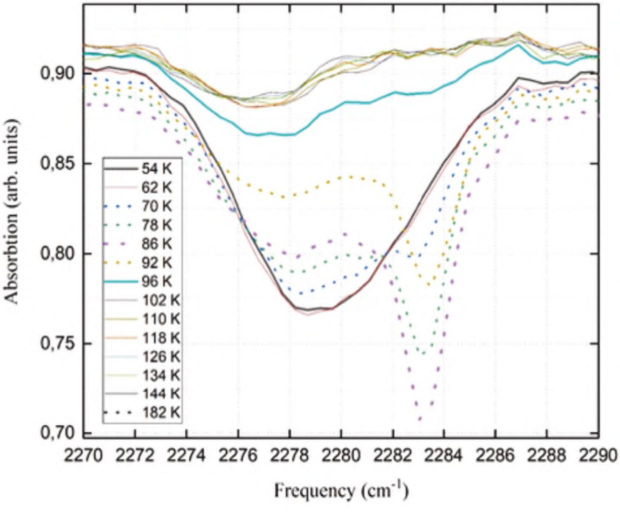

Figure 7 - Temperature-dependent spectrum in the vibrational region 2270-2290 cm^{-1} v_3 for the formed clathrate hydrate.

Weak transitions of 13 CO_2 and 18 OCO within the first range of the Fermi resonance were predicted based on the natural isotope content and band shifts observed in particles in the gas phase [21]. We applied the same approach by assigning the peak of the Fermi resonance an index starting from the highest resonance level.

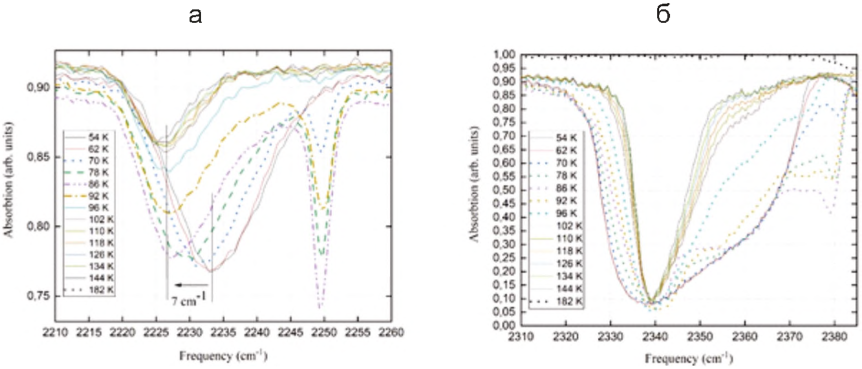

Figure 8 - Temperature-dependent spectra of carbon dioxide clathrate hydrate in the region of combination modes of the Fermi resonance $v_1 + v_3$.

The $v_1 + v_3$ transitions in CO_2 were not detected during the current experiments, and Figure 9 shows only their assumed position.This absence can be partially explained by the strong absorption by water ice. However, the ratio of the Fermi dyad intensities for this isotope seems to differ significantly from the ratio of the intensities of the main isotopic transitions. In addition, an absorption of about 3710 cm^{-1} was observed.

One of the questions concerning the origin of this band may be related to the interaction of the CO_2 v_3 mode with the harmonic libration of water ice, similar to what is observed at lower wave numbers.It is highly unlikely that this transition is related to the double presence of CO_2 in the same cells, given the large size of the CO_2 molecule compared to type I clathrate cells. In the range from 150 to 11 K, we observe spectral clarification characterized by the sharpness of individual CO_2 bands inside the clathrate shell., as well as an increase in intensity and a slight shift towards lower frequencies. For the 13CO_2 v_3 regime, the integral absorption increases approximately 3-fold from 150 K to 11 K, which indicates cell-induced polarizability in the asymmetric stretching regime, a feature observed to varying degrees in clathrate hydrates.

We summarize the observed values at 11 K for type I carbon dioxide clathrate hydrate and compare them with three other phases: CO_2 in the gas phase, pure solid CO_2, and CO_2 as a simple hydrate mixed with amorphous H_2O ice at low temperatures. In addition to band splitting caused by CO_2 entering two different type I cells of the clathrate hydrate structure, the key difference between the spectra of clathrate hydrate and simple hydrates is the absence of activation of the $2v_3$ mode in clathrate hydrate, whereas a strong band is observed at 4678 cm^{-1} during hydrate formation.

FTIR spectra of type I carbon dioxide clathrate hydrate were recorded in the near and middle infrared range at temperatures from 11 to 150 K. Characteristic double peak profiles corresponding to the same transition were observed, but for CO_2 trapped in two different types of cells - small and large - in the structure of clathrate I hydrate. These spectroscopic features, along with the location of the two components, make it possible to reliably detect CO_2 clathrate hydrate using remote spectroscopy of icy bodies in the Solar System or the interstellar medium. Reflection (or transmission) spectroscopy of the icy surfaces of planets, moons, or comets with a spectral resolution exceeding one thousand in the near and middle infrared ranges would make it possible to clearly separate the transitions associated with different cells. Although direct remote observations can provide valuable results, they are fraught with difficulties. This difficulty in detecting clathrates has led to the use of thermodynamic methods to assess their presence, as well as to study their effect on the release of elemental or molecular content. However, despite meeting the conditions necessary for the formation and stability of clathrates, care must be taken not to rely too much on these methods, emphasizing the need for their unambiguous spectroscopic determination under strict conditions.

Despite the expected filling of the cell and, as a result, the doubling of bandwidth, no direct evidence of the presence of carbon dioxide clathrate hydrate in astrophysical objects, including in our Solar System, has yet been obtained. Given that various physical interactions can occur between CO_2 (and other molecules) and water ice - interactions that are not necessarily associated with the formation of a crystallographic structure similar to clathrate hydrates - it is extremely important to be able to directly determine the content and state of various phases of CO_2 in astrophysical media using spectroscopic methods..

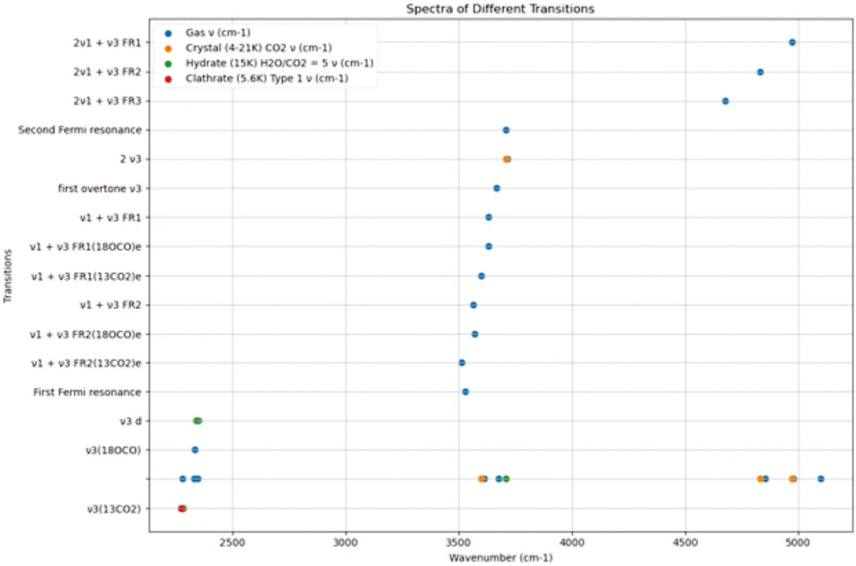

Figure 9 - Carbon dioxide: gas, pure solid, hydrate and clathrate-hydrate transitions.

The gradual transition of the absorption peak at a frequency of 3704 cm^{-1} during the annealing process is shown in Figure 10.

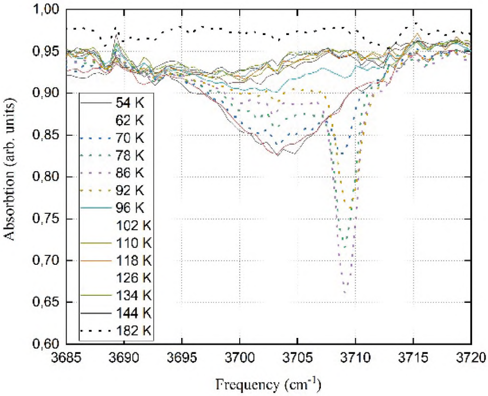

Figure 10 - Change in the absorption band of the cryocondensate mixture of water and CO_2 during annealing. Tc = 16 K, Water concentration 75%.

Conclusion. Due to the limited data on the kinetics of formation and decomposition of carbon dioxide hydrates, as well as their physical structural properties, it is necessary to obtain more experimental data with condensation and different thermal histories of potential carbon dioxide hydrate clathrates.

The obtained spectra are also important for the identification of CO_2 hydrates on space objects.

In our temperature range and under similar vacuum conditions, there are two ways to describe the structural evolution. On one hand, infrared spectroscopy data indicate that when deposited below 30 K, the structure is amorphous, while deposition above 50 K results in a crystalline structure. Once ice forms at lower temperatures, annealing tends to produce a more ordered amorphous structure or even crystallizes the solid. Another explanation involves nucleation-driven ice growth, where small crystal islands form, randomly oriented, with their size directly dependent on temperature; similarly, annealing leads to solid crystallization, with energy for this process supplied either by increasing temperature or by energy transferred during gas molecule collisions with the solid. In our laboratory, we observed these structural changes during thermally programmed desorption (TPD) experiments, where CH_4 from a CO_2-CH_4 mixture desorbed at three distinct temperatures: 35 K, typical for pure CH_4; 50 K, when a structural change in CO_2 occurs; and 90 K, when both CO_2 and CH_4 desorbed together. Based on our results, we can conclude that this structural change does not affect polarizability, as this property is intrinsic to the molecule. However, it should also be noted that changes in the polarizability tensor may not be captured by the experimental value, as the measured value represents the average of the elements on the main diagonal of the radiation pattern [10], [11], [16], [21].

Regarding the IR spectra of cryocondensates of carbon dioxide and water, the correlation of the data clearly confirms the presence of a clathrate structure.

The publication of the article was carried out with the support and funding of the Science Committee of the of Science and Higher Education of the Republic of Kazakhstan within the framework of the implementation of the grant funding project of the IRN AP19680205.

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H_2O+CO_2 ЖҰҚА ҚАБЫҚШАЛАРЫНЫҢ ОПТИКАЛЫҚ ЗЕРТТЕУЛЕР

Түйіндеме. Гидраттың бұл түрін зерттеу ретінде таңдау планетаның ауа қабатын көміртектен тазартудың өзекті мәселелері болды.

Әртүрлі концентрациядағы су мен көмірқышқыл газының криоконденсацияланған қоспасының жұқа қабықшасында тербеліс спектрлерінің өзгеруін тіркеу үшін бірқатар тәжірибелер жүргізілді.

Бұл зерттеудің мақсаты газ фазасынан жоғары вакуум және төмен температуралық конденсация жағдайында көмірқышқыл газы гидраттарының болуын анықтау болды. Үлгіні күйдіру температурасына және көмірқышқыл газының концентрациясына байланысты діріл спектрлеріндегі өзгерістердің интерпретациясы 2210-2260, 2270-2290, 2310-2380, 2800-3700, 3590-3610, 3590-3610, 32080-137-1302 $см^{-1}$ жиілік диапазонында берілген. 15 К конденсация температурасында сумен көмірқышқыл газының 15% қоспасының адсорбция шыңдарын салыстыру және үлгіні одан әрі жасыту кезінде.

Түйінді сөздер: декарбонизация, көміртегі шығарындылары, криоконденсаттар, оптикалық қасиеттер, су, көміртек тотығы.

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ОПТИЧЕСКИЕ ИССЛЕДОВАНИЯ ТОНКИХ ПЛЕНОК H_2O+CO_2

Аннотация. Выбор данного типа гидрата в качестве объекта исследования обусловлен актуальными проблемами очистки воздушного слоя планеты от углерода.

Проведена серия экспериментов по регистрации изменений колебательных спектров в тонкой пленке криоконденсированной смеси воды и углекислого газа при различных концентрациях

Целью данного исследования было определение наличия гидратов углекислого газа в условиях высокого вакуума и низкотемпературной конденсации из газовой фазы. Приведена интерпретация изменений колебательных спектров в зависимости от температуры отжига образца и концентрации углекислого газа для диапазона частот 2210-2260, 2270-2290, 2310-2380, 2800-3700, 3590-3610,3580-3720,3685-3720 $см^{-1}$. При сравнении пиков адсорбции 15% смеси углекислого газа с водой при температуре конденсации 15 К и дальнейшем отжиге образца.

Ключевые слова: декарбонизация, углеродный выброс, криоконденсаты, оптические свойства, вода, оксид углерода.

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