

FORMATION OF NANOCLUSTERS IN THE TRANSITION OF CARBON DIOXIDE TO THE SUPERCRITICAL STATE

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Supercritical fluid extraction (SFE) with CO₂ is widely used to extract biological materials, metal complexes and their isotopes. Supercritical CO₂ (SC-CO₂) is an environmentally friendly, efficient, and affordable solvent. However, the change in the chemical and physical properties of CO₂ in the transition to the supercritical (SC) state has not been studied so far. The paper proposes to consider such a change as a result of the formation of elementary linear, flat or volumetric nanoclusters, from which large nanoclusters can also be formed. Based on the theory of repulsion of valence electron pairs, the geometry of the arrangement of atoms in elementary nanoclusters is described. The change in the chemical and physical properties of CO₂ is confirmed by absorption spectra in the IR range for wavelengths of 4.2...4.4 μm in sub- and SC-CO₂.

INTRODUCTION

Supercritical fluid extraction (SFE) – extraction by substances at temperatures and pressures above critical values. Most often, CO₂ is used for SFE due to its non-toxicity, availability, explosion and fire safety, and low cost. In addition, it has low critical parameters for temperature T_c over 31.06 °C and pressure P_c above 7.38 MPa. CO₂ at a temperature above T_c with an increase in pressure from $P < P_c$ to $P > P_c$ passes from gaseous carbon dioxide to supercritical (SC), called "fluid".

SC-CO₂ is not subject to radiolysis [1], which makes it technologically efficient when working with radioactive materials. The decrease in pressure and/or decrease in temperature converts the supercritical fluid to a gas. In this case, it is possible to ensure the recycling of the solvent after separation of the extracted substance from it in a dry and compact form. The SFE-CO₂ method has been tested and is used for the extraction of biological materials, complexes of lanthanides and actinides [2].

Currently, there is a large amount of research on the study of SFE-CO₂ extraction of heavy metal complexes (see, for example, [3, 4]). Ongoing studies of SFE-CO₂ extraction of heavy metal complexes have shown that it is possible to extract not only metal complexes, but also to carry out targeted isolation of isotope complexes of these metals. This possibility has been demonstrated for uranium-238 and uranium-235 isotopes [5], as well as medical isotopes of molybdenum: molybdenum-98 and molybdenum-100 [6].

The main stage in carrying out SFE-CO₂ complexes of heavy metals is the sample preparation process, which is necessary for the transition of target heavy metals into chemical compounds (complexes) that can be dissolved in SC-CO₂. Therefore, the search for reagents for the formation of heavy metal complexes soluble in SC-CO₂ is an important task of the SFE.

Several works note the decisive influence of the presence of water on the efficiency of extraction of metal complexes [7, 8]. In the absence of water micro additives, SFE-CO₂ of heavy metal complexes are not observed.

Water is present in the form of microdroplets 50...100 μm in size in SC-CO₂ at a pressure of up to 18 MPa was experimentally shown in [8]. The metal complexes formed on the basis of tributyl phosphate become hydrophilic at extraction temperatures and therefore concentrate in water microdroplets. This explains the decisive role of water in the SFE processes of metals.

Despite the important role of water in the processes of SFE-CO₂ of metal complexes, the basis of the extraction process lies on SC-CO₂. However, the change in the molecular structure of carbon dioxide during the SC transition remains unclear so far.

Analysis of such changes can be carried out using IR spectrometry. To do this, it is necessary to consider the change in the IR spectra of carbon dioxide depending on the pressure at a constant temperature exceeding the critical T_c . Since the atomic composition of carbon dioxide does not change, new absorption bands may appear in the IR spectrum, which are not characteristic of CO₂ in the normal state. These bands may indicate the appearance of nanoclusters with a molecular structure formed from CO₂ atoms.

This article considers possible combinations of new chemical compounds combined into a nanocluster of C and O atoms, which at temperatures above T_c can appear because of a decrease in the distance between atoms due to an increase in pressure. The consideration was carried out for the isotopic composition of CO₂ marked with the numbers 262 [9].

1. CHARACTERISTIC IR ABSORPTION BANDS OF CO₂ IN THE SUB- AND SC-STATES

The elemental composition of carbon dioxide during the transition to the SC state remains unchanged. However, the method of chemical association of atoms during such a transition may change due to the overlap of the electron shells of atoms. The question of what kind of connections may appear remains unclear to this day. In our opinion, the answer can be obtained based on the

analysis of changes in the IR spectrum of CO₂, for example, as a result of an increase in pressure at a temperature above the critical one. In this case, the configuration of a chemical compound can be determined by the belonging of the IR absorption bands to the characteristic wavelengths of known compounds, or by the wavelengths of deformation vibrations of the formed nanoclusters. In the latter case, the characteristic wavelengths of oscillations are determined by their geometric dimensions.

Let us discuss the results of studying the IR spectra of CO₂ in various aggregate states.

In [10], the IR spectra of CO₂ in the gaseous, CS, and liquid states were considered.

In the gaseous state, carbon dioxide is characterized by transparent IR regions that are wide in wavenumber, as follows from Fig. 1,a. In two groups of bands (3717, 3603 cm⁻¹ and 2399, 2283 cm⁻¹), strong absorption of the IR spectrum is observed in the bands 3500...3800 cm⁻¹ and 2200...2500 cm⁻¹. These two groups of bands also exist in liquid (see Fig. 1,b) and SC (see Fig. 1,c) states. Based on the position of the absorption bands, it can be concluded that there are no functional groups of chemical compounds for them that could be identified by Supercritical Fluid Chromatography-Fourier Transform Infrared Spectrometry (SFC/FTIR) methods by their fundamental frequencies.

In contrast to the gaseous state, in the IR spectrum of carbon dioxide in the liquid and SC states, two additional absorption bands appear at 2070, 1944 cm⁻¹ and 1387, 1282 cm⁻¹ [10] or 2064, 1949 cm⁻¹ and 1388, 1286 cm⁻¹ [11]. These bands are attributed to the Fermi resonance between the forbidden transition of the Raman active symmetric band at 1300 cm⁻¹ and the second harmonic of the infrared active, doubly degenerate bending vibration band at 667 cm⁻¹ [12]. It was noted that the intensity and width of these bands increase in the transition from the SC to the liquid state. The appearance of other bands in the IR absorption spectrum at 1064, 958, and 3010 cm⁻¹ was also found, but they can be neglected. It follows from the analysis of the results obtained in [10–12] that during the transition from a gaseous a) to a liquid b) state, absorption bands appear, which increase in width and amplitude with increasing pressure.

In the range of wavenumbers 2200...2500 cm⁻¹ [13], the transition from a) to b) (see Fig. 1) is accompanied by a decrease in absorption, and during the transition from b) to c) – its growth. At the same time, absorption increases with increasing pressure, as can be seen in Fig. 1,c.

As the pressure increases, a loss in the rotational structure is observed [13]. In [13], a version was proposed that explains the loss of the rotational structure. Such a loss can be associated either with sample compression (collisional broadening of the spectrum) or with a specific CO₂-CO₂ intermolecular interaction.

However, based on Fig. 2, it is not possible to explain the broadening of the spectrum either due to collisions or due to the intermolecular interaction of CO₂-CO₂. To separate these two effects, pure carbon dioxide was injected into the IR cell to a pressure of 40 bar, and then the inert gas argon was introduced into the cell.

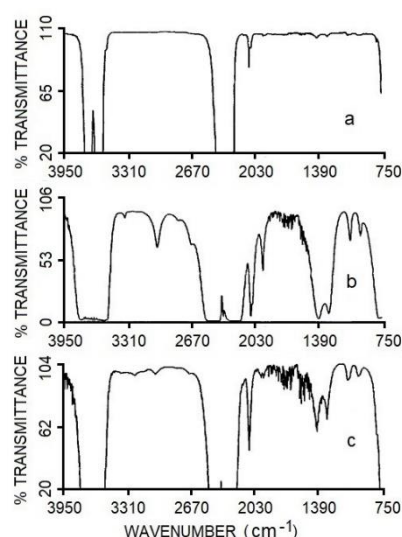


Fig. 1. The transmittance of carbon dioxide in the IR range depending on its physical state [10].

Optical path length – 1 cm, resolution – 4 cm⁻¹:

a – gaseous (122 atm, 21 °C); b – liquid (222 atm, 11 °C); c – SC (178 atm, 41 °C)

Argon was used to increase the pressure in the cell. The introduction of argon is due to that its intermolecular interaction with carbon dioxide is minimal. Therefore, the changes observed in the spectrum can be attributed to the specific intermolecular interaction of the solvent.

From the results of experiments with pure carbon dioxide and argon, it was concluded that freedom of rotation is maintained at subsequent higher pressures, even if the overall density of the system is increased. This can be seen from the rotational fine structure observed in the argon/carbon dioxide system at pressures above 104 bar. Based on this, it was concluded in [13] that the results of the experiment with pure carbon dioxide, the broadening of the absorption spectrum, to a large extent, is a consequence of the manifestation of a specific intermolecular interaction CO₂-CO₂ – the presence of a rotational degree of freedom.

In addition to the version proposed in [13] of the broadening of the absorption spectrum due to the presence of a rotational degree of freedom, another one can be proposed. It assumes that nanoclusters consisting of C and O are formed during the transition of carbon dioxide to the SC state. It follows from the experiments that, in the subcritical state, the IR absorption curve is a two-peaked function (see Fig. 2, 32 bar), and as the SC pressure level is overcome, the maxima of the absorption spectrum approach each other. At high pressures, the maxima merge and form one curve described by a Gaussian function with a maximum at a wavenumber value of 2318.11 cm⁻¹ (wavelength 4.31 μm) (see Fig. 2, 104 bar).

This behavior of the absorption spectrum curve is possible if the resonant frequencies of the IR spectrum of CO₂ are synchronized near one of the natural vibrational frequencies of the nanocluster [14], which is formed because of the transition of the medium to the SC state.

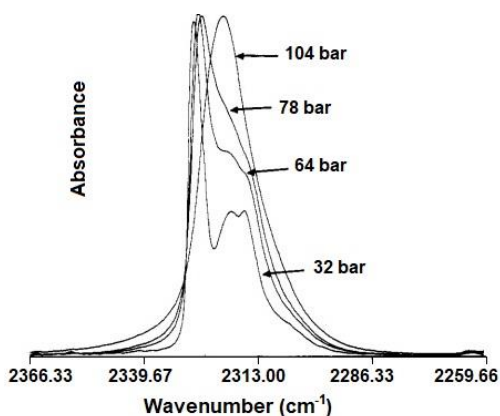


Fig. 2. Curves of IR absorption spectra in the wavenumber range 2260...2366 cm^{-1} [13] for SC- CO_2

Let us consider possible chemical compounds from which geometric structures can be formed, which we will refer to as nanoclusters in what follows. Since the nanocluster contains C atoms, it is natural to consider the formation of nanoclusters based on compounds of carbynes with oxygen [15].

2. CARBINES AND THEIR COMPOUNDS WITH OXYGEN

It is known that in the process of identification of α - and β -carbynes by ozonolysis [16], chemical compounds C and O of the form are formed:

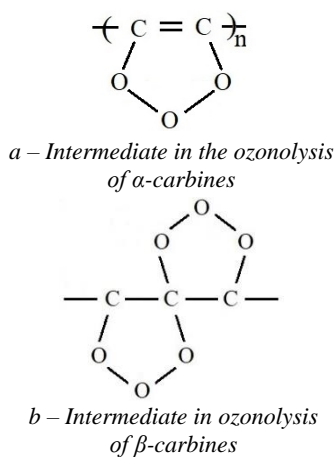


Fig. 3. Chemical compounds arising from ozonolysis of carbynes

In SC- CO_2 in the chemical combination of C and O atoms in Fig. 3,a, due to the preservation of the ratio of the number of C and O atoms, a fourth O atom must be added, as shown in Fig. 4,a. This chemical compound C and O can be formed on the basis of α -carbynes.

Another configuration of the chemical combination of C and O atoms in SC- CO_2 can be obtained from the configuration of Fig. 3,b if middle oxygen atoms are removed from this compound. On Fig. 4,b shows the chemical compound of C and O atoms in SC- CO_2 , which can be formed based on β -carbynes.

Possible types of chemical compounds arising in SC- CO_2 based on carbynes are shown in Fig. 4.

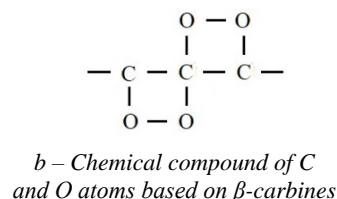
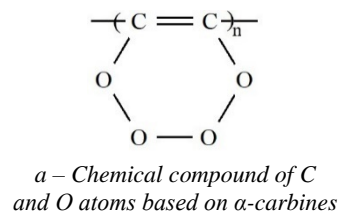


Fig. 4. Chemical compounds arising in SC- CO_2 based on carbynes

2.1. LINEAR NANOCLUSTERS

From chemical compounds Fig. 4, it is possible to form carbyne-like nanoclusters, which are formed by connecting atomic structures with active bonds – C. The final nanocluster will have two active bonds, which, apparently, explains the good dissolving properties of SC- CO_2 . The length of linear nanoclusters will be of the order: $L = p \cdot d_i$, where $p = 1, 2, 3, \dots$ are integers, d_i is the bond length type of i , $i = \text{"C=C"}$ corresponds to the bond length for the chemical combination of C and O atoms based on α -carbynes, $i = \text{"C-C"}$ corresponds to the bond length for the chemical combination of C atoms and O based on β -carbynes.

In various sources, the length of bonds between carbon atoms and a carbon and oxygen atom is determined by the values given in Table.

Bond lengths between atoms

Bond length	Value, Å			
	[17]	[18]	[19]	[20]
C – C	1.36	1.379	1.54	1.54
C = C	–	1.282	1.33	1.33
C \equiv C	1.19	1.207	1.21	1.21
C – O	–	–	–	1.43
C = O	–	–	–	1.23
C \equiv O	–	–	–	1.13

It should be noted that the bond length may decrease with increasing pressure [21].

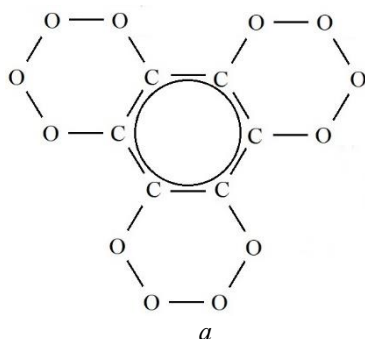
Average values of d_i are about 1.2...1.4 Å. Therefore, to ensure the resonance of natural deformation vibrations of linear nanoclusters with vibrations of the IR spectrum in the range of 4.2...4.4 μm , the integer p must take sufficiently large values.

The resonance conditions for natural vibrations of linear nanoclusters with natural vibrations of SC- CO_2 will be considered below.

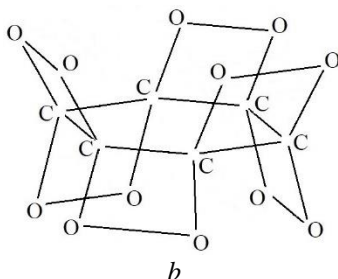
2.2. FLAT AND VOLUMETRIC ELEMENTARY NANOCLUSTERS

From the chemical compound Fig. 4,a it is possible to form a flat elementary nanocluster (EN). So, for example, at $n = 6$, the atoms of the chemical compound C and O are in the same plane, while the C atoms are connected into a benzene ring, where the double electronic bond is not fixed [22]. This representation of the electronic bonds in the benzene ring is like the hypothesis of Linus Pauling, who proposed to depict the benzene molecule as a hexagon with an inscribed circle, which is equivalent to the presence of a conjugated 6π electron cloud covering all six carbon atoms. The oxygen atom, according to the theory of repulsion of valence electron pairs [20], is located at an angle of 120° to the benzene C–C bond. Such a symmetrical arrangement of atoms makes the benzene molecule nonpolar.

A schematic representation of such a flat EN is shown in Fig. 5,a.



Flat EN from C and O atoms based on α -carbines



Volumetric EN from C and O atoms based on β -carbines

Fig. 5. EN in SC-CO₂ based on carbines

On Fig. 5,b shows a schematic representation of a volumetric EN in the form of a benzene ring with attached petals in the form of a quadrilateral, at the vertices of which there are COOC atoms. The benzene arrangement of carbon atoms can be formed from the configuration Fig. 4,b by the connection of 6 C atoms through simple active chemical bonds. The arrangement of the planes of the petals and the benzene ring in terms of angle is determined according to the theory of repulsion of valence electron pairs [20], as shown in Fig. 5,b. According to this theory, in the equilibrium state, the plane of the petal, which can approximately be considered a rectangle, is located at an angle of about 120° to the plane of the benzene ring. This arrangement of the petal ensures the preservation of the non-polar status of SC-CO₂, which CO₂ had in the subcritical state.

Shown in Fig. 5 EN have a flat or volumetric configuration. They are characterized by sets of natural deformation vibrations of the atoms that make up them. However, the frequencies of these vibrations are far from the absorption frequencies of SC-CO₂ in the IR range, since they are determined by their characteristic geometric dimensions. Therefore, it is necessary to consider the possibility of forming large clusters from a large set of ENs, which would have resonant frequencies that fall into the IR absorption bands of SC-CO₂. Symmetric bending vibrations of atoms of large nanoclusters do not contribute to the IR spectra, as can be seen from the example of a nonpolar CO₂ molecule. Therefore, below we consider asymmetric vibrations of bound atoms in a large nanocluster, which fall into the absorption band in SC-CO₂ in the wavelength range from 4.2 to 4.4 μm (from 2400 to 2200 cm^{-1}) of the IR range [23]. But first, let's consider the vibrations of individual elements of EN, falling in the range from 4.2 to 4.4 μm .

3. ROTATIONAL DEGREES OF FREEDOM IN OSCILLATIONS OF FLAT AND VOLUMETRIC EN

We will proceed from the fact that in the subcritical state CO₂ molecules in the IR range experience absorption in the wavelength range of 4.2...4.4 μm . These vibrations, as noted earlier, refer to rotational degrees of freedom. Let us briefly discuss the energy characteristics of such oscillations. The energy of the rotational motion of a CO₂ molecule is determined by the expression:

$$W_{CO_2} = \frac{1}{2} I_{CO_2} \omega_{CO_2}^2, \quad (1)$$

where $I_{CO_2} = \sum_{i=1}^2 m_{iO} r_{iO}^2$ the moment of inertia of a linear CO₂ molecule about the axis of rotation, which passes through the carbon atom and is perpendicular to the distance between the oxygen atoms, $m_{iO} = M_O$, r_{iO} – mass and distance of the i -th oxygen atom from the C atom [24], $i = 1, 2$ – number of atom oxygen, $\omega_{CO_2} = \frac{2\pi c}{\lambda}$, λ – frequency and wavelength of rotational oscillations of the CO₂ molecule, c is the speed of light. The moment of inertia of a CO₂ molecule is equal to $I_{CO_2} = 2M_O d_{C=O}^2$.

Under identical pressure and temperature conditions, the average total kinetic energy is uniformly distributed over the degrees of freedom (the virial theorem [24]). Therefore, for the same frequencies of the IR range, the moments of inertia of different configurations of the EN must be equal. It follows from here that the moments of inertia of atoms O of the configurations Fig. 5 must be equal or the same order to the moment of inertia of a linear CO₂ molecule.

Based on what is shown in Fig. 4,b the arrangement of O atoms, it can be concluded that the moment of inertia of a volumetric EN from C and O atoms based on β -carbines is of the order of the moment of inertia of a linear CO₂ molecule (the lengths of the C and O bonds in CO₂ and EN can be comparable, see Table).

Thus, the rotational degrees of freedom and associated oscillations of volumetric EN based on β -carbines are in the IR wavelength range of 4.2...4.4 μm .

4. LENGTH EVALUATION OF A LARGE-SIZED RESONANT NANOCUSTER

Elementary clusters based on α -carbynes have a flat geometry with a radius of the circumscribed circle of the order $R \approx 3 \cdot d_b$, where $d_b = 1.39 \text{ \AA}$ bond length of carbon atoms in the benzene ring [17, 25].

Radial wave numbers of axially symmetric oscillations of elementary clusters based on α -carbynes of the order $k \sim 1/R \approx 10^8 \text{ cm}^{-1}$, and are far from the range of wavenumbers shown in Fig. 2. Therefore, elementary clusters based on α -carbynes are unsuitable for interpreting IR absorption spectra in SC-CO₂.

Combining elementary clusters based on α -carbynes into large flat clusters is impossible due to geometric considerations. Therefore, we will consider the possibility of combining EN based on β -carbynes. Elementary clusters based on β -carbynes can have a three-dimensional structure. To do this, it is necessary to attach the C atom of the benzene ring to the C atom of another benzene ring through the bond $-\text{C}-\text{O}-\text{O}-\text{C}-$. In this way, two benzene rings can be combined into a large nanocluster. On Fig. 6 shows a schematic representation of a nanocluster with two benzene rings.

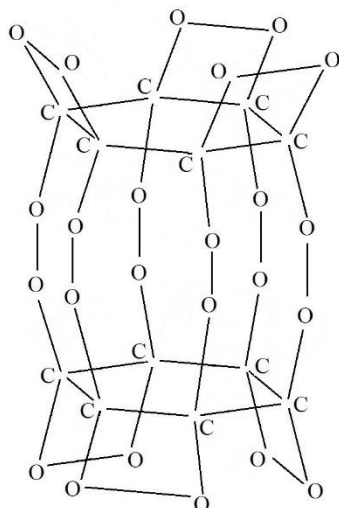


Fig. 6. Nanocluster with two benzene rings in SC-CO₂

N such compounds of benzene rings can form a hexagonal prism with a hexagonal cross section periodically changing in height, where the number N can reach large values. For large N , the hexagonal prism has a sufficiently large length. In this case, it can be considered a thin string, and the theory of vibrations of a string with fixed ends can be used to describe the natural vibrations of such a structure [26, 27]. On a stretched string fixed at both ends, transverse vibrations are excited in the form of standing waves with nodes at the places where the string is fixed. In a string with fixed ends, only such vibrations are excited, half of the wavelength λ of which fits an integer number of times over the length of the string. Hence follows the condition: $L = m \cdot \frac{\lambda}{2}$, where $m = 1, 2, 3, \dots$, L – string length.

For oscillations with one antinode ($m = 1$) the wavelength is related to the length of the string by the relation $L = \frac{\lambda}{2}$. This relation gives the condition for the

existence of a maximum in the IR absorption spectrum at high pressures (see Fig. 2). The length of a string consisting of n , where $n = 1, 2, 3, \dots$, double benzene rings, is given by:

$$L_n = n \cdot (d_{\text{O-O}} + 4 \cdot d_{\text{C-O}}) + (n - 1) \cdot d_{\text{O-O}}, \quad (2)$$

where $d_{\text{O-O}} = 1.5 \text{ \AA}$ – simple bond length O–O [28], $d_{\text{C-O}} = 1.43 \text{ \AA}$ – simple bond length C–O [20, 29]. Consequently, the length of the string at large $n \gg 1$ is estimated by the magnitude of the order: $L \cong n \cdot (1.5 + 4 \cdot 1.43) + (n - 1) \cdot 1.5 = n \cdot (3 + 5.72) \text{ \AA}$.

On the other hand, the string length is: $L = \frac{\lambda}{2} = \frac{4.34 \cdot 10^4}{2} = 2.17 \cdot 10^4 \text{ \AA}$. Hence, considering that $n \gg 1$, we determine the number of pairs of benzene rings included in the nanocluster: $n \cong 2.17 \cdot \frac{10^4}{8.72} \cong 250$.

Carbine-like nanoclusters Fig. 4, formed by joining chemical compounds through active bonds $-\text{C}$, can contain many C atoms. The conclusions regarding the representation of a large nanocluster by a string with fixed ends are applicable to carbine-like nanoclusters. In this case, the string length should also be on the order of 2.17 \mu m . In this case, about 10^4 carbon atoms can be integrated into the string, which reduces the realistic formation of such extended nanoclusters in comparison with nanoclusters based on β -carbynes.

It should be noted that the dependence of the number of nanoclusters based on β -carbynes on their length (the distribution function of the number of clusters along their length) repeats the curve of the IR absorption spectrum in SC-CO₂, shown in Fig. 2 at pressures of 104 bar or more. Based on the form of the distribution function of nanoclusters along their length, one can estimate their average values of the parameters.

CONCLUSIONS

The paper analyzes the possibility of the formation of nanoclusters in CO₂ during its transition to the SC state. Since the elemental composition of the medium is unchanged, the analysis is based on the study of the IR spectra of CO₂ in both subcritical and SC states. For this, changes in the IR spectra of carbon dioxide in the wavenumber range of $2200 \dots 2500 \text{ cm}^{-1}$ were studied depending on the pressure at a constant temperature exceeding the critical T_c . This range was chosen due to the specific dependence of the absorption curve on pressure: the transition from the gaseous state to the liquid state is accompanied by a decrease in absorption, and the transition from liquid to SC is accompanied by an increase. At the same time, in the subcritical state, the IR absorption curve is a two-peaked function, and when the SC pressure is overcome, the maxima of the absorption spectrum approach each other and merge at high pressures. It has been suggested that such a behavior of the absorption spectrum curve is possible if the resonant frequencies of the IR spectrum of CO₂ are synchronized near one of the natural vibration frequencies of nanoclusters formed as a result of the transition of the medium to the SC state.

Possible configurations of chemical compounds called nanoclusters are considered. The presence of C and O atoms in nanoclusters made it possible to consider

the process of EN formation based on compounds of carbynes with oxygen.

It is shown that EN can have a linear, flat, or volumetric configuration. The last two are formed with the participation of the benzene ring. EN are characterized by sets of natural vibrations of the atoms included in their composition. However, their characteristic dimensions are small, which does not allow such oscillations to fall into the IR range. For them to fall into the IR range, it is necessary that the EN can form large nanoclusters or have rotational vibrations from this wavelength range.

It is shown that linear carbyne-like nanoclusters have a large length, about 10^4 bond lengths –C. However, it is concluded that the large length of nanoclusters reduces the realism of the formation of such extended nanoclusters in SC-CO₂. Based on the theory of repulsion of valence electron pairs, the arrangements of atoms in planar and bulk ENs are proposed.

It is shown that the rotational degrees of freedom and associated oscillations of volumetric EN based on β -carbynes fall in the IR wavelength range of 4.2...4.4 μm . It has been shown that planar nanoclusters based on α -carbynes cannot combine into large nanoclusters.

Volumetric nanoclusters based on β -carbynes can form long nanoclusters in the form of a hexagonal prism, with a base in the form of a carbon benzene ring and a cross section periodically changing along the length between the benzene rings. The transverse vibrations of a nanocluster in the form of a long hexagonal prism with a cross section periodically varying along the length between the benzene rings are considered. Due to the large length of the nanocluster, its transverse vibrations are modeled by vibrations of a string with fixed ends. It is shown that vibrations of such a string in the IR range are observed under the condition that half the wavelength of 2.17 μm is equal to the length of the string. The number of pairs of benzene rings included in a large nanocluster was determined: $n \cong 2.17 \cdot \frac{10^4}{8.72} \cong 250$. An assumption is formulated that at pressures of 104 bar and more, the resonant frequencies of the IR spectrum of SC-CO₂ are synchronized near one of the natural vibration frequencies of a long nanocluster.

For pressures of 104 bar and more, the distribution function of the number of nanoclusters versus length repeats the curve of the IR absorption spectrum in SC-CO₂ in the range of wave numbers 2200...2400 cm^{-1} . Based on the form of this function, one can estimate the average values of the nanocluster parameters.

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ФОРМУВАННЯ НАНОКЛАСТЕРІВ ПРИ ПЕРЕХОДІ ДІОКСИДУ ВУГЛЕЦЮ В НАДКРИТИЧНИЙ СТАН

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Надкритична флюїдна екстракція CO₂ широко використовується для вилучення біологічних матеріалів, комплексів металів та їх ізотопів. Надкритичний CO₂ є екологічно чистим, ефективним та доступним розчинником. Однак до цього часу не досліджено зміну хіміко-фізичних властивостей CO₂ при переході до надкритичного стану. У роботі запропоновано розглядати таку зміну як результат формування елементарних лінійних, плоских або об'ємних нанокластерів, з яких можуть формуватися нанокластери великих розмірів. На основі теорії відштовхування валентних електронних пар описано геометрію розташування атомів у елементарних нанокластерах. Зміна хіміко-фізичних властивостей CO₂ підтверджується за допомогою спектрів поглинання в ІЧ-діапазоні для довжин хвиль 4,2...4,4 мкм у до- та надкритичному CO₂.