

Spectral Investigation of the Interaction of Carbon Monoxide and Dioxygen with Low-Temperature Sublimates of Co(II) *meso*-Tetraphenylporphyrinate: Evidences for Oxidative Catalysis

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Abstract—The interaction of carbon monoxide and dioxygen with low-temperature ($T = 77$ K) sublimates of cobalt(II) *meso*-tetraphenylporphyrinate (CoTPP) is studied by IR spectroscopy using isotopically labeled compounds (^{13}CO and $^{18}\text{O}_2$). The obtained data confirm the coordination of CO and O_2 with the formation of axial complexes $\text{CoTPP} \cdot \text{L}$ ($\text{L} = \text{O}_2, \text{CO}$) and the mixed complex $\text{O}_2 \cdot \text{CoTPP} \cdot \text{CO}$. The heating of the complex containing CO and O_2 to 150 K leads to the appearance of lines in the IR spectrum corresponding to valence asymmetric ($\nu_{\text{as}}\text{OCO}$) and degenerated deformation (δOCO) vibrations of carbon dioxide. This is evidence for the oxidation of CO. The evacuation of CO_2 at a higher, but still low, temperature and the addition of a new portion of CO and O_2 mixture lead to the formation of new portions of CO_2 . This demonstrates the catalytic character of the process. Only low-temperature sublimates have catalytic properties. Sublimates of CoTPP obtained on the surface at room or higher temperature demonstrate neither catalytic activity nor the ability to coordinate any amount of CO and O_2 sufficient for the detection by spectroscopy.

INTRODUCTION

The most important and useful property of metal porphyrins is their ability to act as catalysts in various chemical, electrochemical, and photochemical processes. By now, considerable information on various catalytic processes with porphyrins has accumulated. The results of the investigations in this field are described in many monographs and review articles [1–3].

Low-temperature studies of oxidative catalysis are of particular interest for this work. From this point of view, the most interesting is a series of works [4–6] on the catalytic oxidation of CO by molecular oxygen. In these studies, Co(II) *meso*-tetraphenylporphyrinate (CoTPP) deposited on titanium dioxide was used. CoTPP/ TiO_2 system preliminarily treated in a vacuum at an elevated temperature demonstrates a high catalytic activity at -79°C ($0.3 \text{ mol CO}_2 / (\text{mol CoTPP min})$). In the above works, the activation of CO by CoTPP was proposed. The sites for O_2 adsorption were not discussed there, but it was suggested that these sites are located on TiO_2 surface near CoTPP.

The role of titanium dioxide in the catalytic process is not completely clear from data presented in [4–6], but the authors propose that porphyrin is modified as a result of the thermal and vacuum treatments of CoTPP/ TiO_2 . However, titanium dioxide may only play the role of porous support with a large surface area for adsorbed porphyrin molecules.

Low-temperature oxidation of carbon monoxide was also found in [7–9] on phthalocyanines, which are similar to porphyrins. It is important that not only phthalocyanines of metals monomolecularly dispersed in zeolite matrices, but also the complexes themselves without any matrix exhibited a catalytic activity. In this case, phthalocyanines were carefully crushed in an agate mortar and evacuated at 280°C for 10 h to obtain a stronger catalytic effect.

Unfortunately, in the cited papers, vibrational spectroscopy was not applied despite its successful application to catalytic processes [10, 11].

Earlier, we showed that the low-temperature sublimates of CoTPP can coordinate molecular oxygen [12]. The formation of CO_2 was found by IR spectroscopy [14] when we investigated the ability of low-temperature sublimates of CoTPP to form a mixed carbonyl–oxygen extra-complex, which is analogous to an isonitrile–oxygen complex [13]. This phenomenon can be related to the low-temperature oxidation of CO by molecular oxygen catalyzed by CoTPP. Therefore, in this work, we carried out an experiment to study this process by IR spectroscopy.

Most IR spectrophotometers have low sensitivity at $2300\text{--}2400 \text{ cm}^{-1}$ due to the absorption of IR radiation by atmospheric CO_2 . When ^{13}CO and $^{18}\text{O}_2$ gases were used in this work, the vibrational frequencies $\nu_{\text{as}}\text{CO}_2$ of CO_2 molecules formed in the process and containing

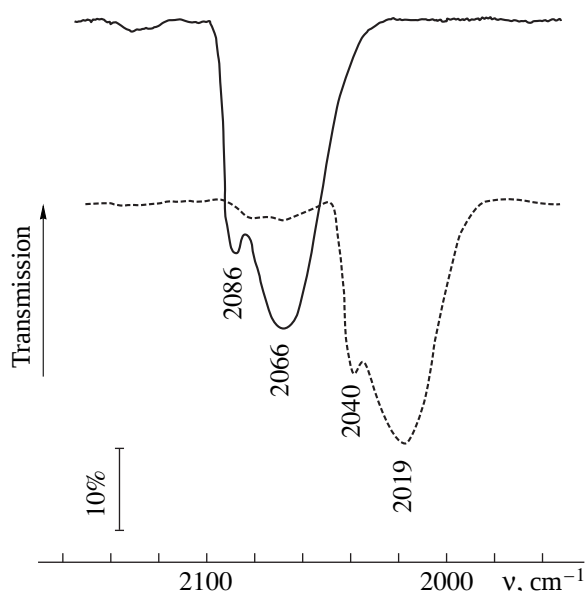


Fig. 1. IR spectra of co-condensate of CoTPP with ^{12}CO (solid line) and with ^{13}CO (dashed line) at 80 K.

these isotopes fall out of this frequency range. This makes the results of measurements more reliable.

EXPERIMENTAL

CoTPP was obtained using the method described in [15]. Before the experiment, CoTPP was additionally purified by passing through a column filled with dry alumina of the 2nd activity grade (Brokeman). Gases were dried using P_2O_5 and purified from traces of CO_2 using a high-vacuum low-temperature technique. Commercially available samples of ^{13}CO (88.4% enrichment) and $^{18}\text{O}_2$ (81.7% enrichment) were purified using the same method. The method for the preparation of sublimated CoTPP layers was described in detail in [13].

Two types of experiments were carried out to study the low-temperature interaction of CO with sublimated layers of CoTPP.

In the first type of experiments, porphyrin was sublimated under dynamic vacuum conditions onto liquid-nitrogen-cooled CsI support. CO was supplied simultaneously using a fine valve and an injector. Because boiling points of CO and N_2 are close [16], CO condensation on liquid-nitrogen-cooled support is impossible. However, it was found that the simultaneous condensation of CO and CoTPP results in the capture of CO leading to the appearance of a new intense line of the IR spectrum at 2000 cm^{-1} corresponding to coordinated CO. Then, we treated the complex with various portions of O_2 , and recorded IR spectra at different temperatures of support. Temperature was measured by chromel–alumel thermocouple. The end of the thermocouple was inserted into a tight hole in a CsI crystal. Temperature between liquid nitrogen and solid carbon

dioxide temperatures was maintained by the addition of the small portions of liquid nitrogen to a cryostat. The mass of copper holder supporting the support permitted us to maintain a desired temperature within a precision of 2–3 K during recording the IR spectrum.

In the second type of experiments, CO, O_2 , or their mixture was supplied to CoTPP layer sublimated beforehand. The gases were supplied from a chamber equipped with a gauge enabling the measurement of pressure in the cryostat. The microporous structure of low-temperature sublimates [17] of *meso*-tetraphenylporphyrinates of metals (MTPP) enabled the interaction of porphyrin with the ligand in total sublimated layer thickness.

IR spectra were recorded using a Specord M-80 spectrophotometer. The spectral broadness of slit was 4 cm^{-1} .

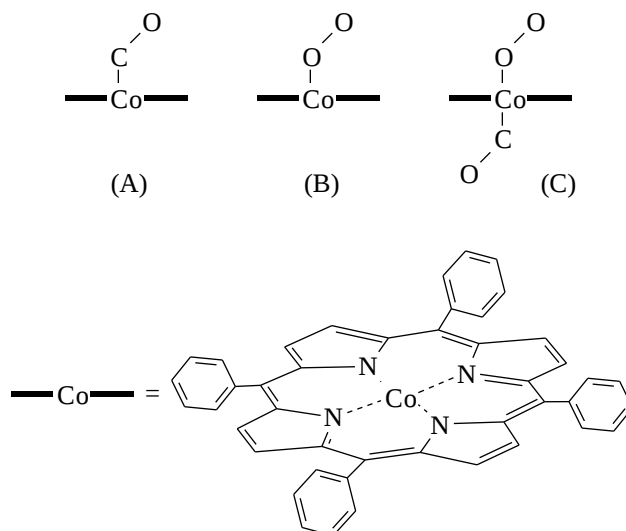
RESULTS AND DISCUSSION

Carbonyl Extra-complex CoTPP

The co-condensation of sublimated porphyrin and CO (^{13}CO) supplied onto the support at a low flow rate ($\sim 30\text{ }\mu\text{mol/h}$) leads to the appearance of broad ($\Delta\nu_{1/2} \approx 30\text{ cm}^{-1}$) absorption bands at 2066 (2019 cm^{-1}) in the IR spectrum (Fig. 1). These bands are absent from the CoTPP spectrum. The isotopic shift of these bands is in ideal agreement with calculations carried out for CO molecules in the approximation of harmonic oscillator. The frequencies of these bands are close to those observed earlier [18] for the CoTPP + CO system in Ar matrix. There is no doubt that these bands correspond to the vibrations $\nu\text{CO}(^{13}\text{CO})$ of the coordinated carbonyl group.

The spectrum presented in Fig. 1 contains, in addition to the main band, weak bands shifted by $\sim 20\text{ cm}^{-1}$ from the main band to higher frequencies. Earlier, the monocarbonyl complex CoTPP was discovered and characterized in a frozen toluene glass by EPR method [19]. It was shown in [18] that, at a low temperature, the dicarbonyl complex CoTPP can be formed in addition the monocarbonyl complex. Experiments were carried out using the matrix-isolation technique in Ar and Kr matrices. A rather broad band with a maximum at 2078 cm^{-1} (2032 cm^{-1} for ^{13}CO) was found by IR spectroscopy in an Ar matrix. This band is split into two bands at 2073 and 2077 cm^{-1} in a Kr matrix. The authors concluded from this observation that the band at 2078 cm^{-1} consists of two close bands of mono- and dicarbonyl complexes. This leads to its large halfwidth. The frequencies are close, probably because of a weak overlap of the *d*-orbitals of metal with the antibonding orbitals of CO, that is, because of a weak *trans*-effect.

The band at 2066 (2019 cm^{-1}) (Fig. 1) has large a halfwidth and can consist of two overlapping bands. In this case, high-frequency bands at 2086 (2040 cm^{-1}) can be assigned to the cophased vibrations of carbonyl ligands in the dicarbonyl complex. According to [18, 19], these ligands can be active in this case if twisted coor-



Scheme 1.

dination of CO is assumed. However, the results of our experiments damage this assumption. We did not find any change in the ratio of the intensities of the main band and the high-frequency band at a much lower rate of CO supply when the probability of the formation of dicarbonyl complex should be minimal.

In low-temperature experiments, it was difficult to exclude the presence of water traces in the system. In the experiments with matrix-isolated CO, the presence of two bands separated by $\sim 10 \text{ cm}^{-1}$ lying in the region corresponding to the vibrations of νCO is explained by this difficulty in [16]. The high-frequency band of these two is assigned to CO bound to water by a hydrogen bond [20]. The direction of the shift and the band shape are similar to those observed in our experiments. Therefore, in our experiments, it is also impossible to exclude the formation of hydrogen bond between the coordinated CO and trace H_2O molecules. We did not find absorption bands in the region $3700\text{--}3100 \text{ cm}^{-1}$ where the stretching vibration of H_2O was found, but it is not excluded that this is related to the low intensity of these bands. However, in experiments where CO was additionally mixed with water, we did not find the relative growth of high-frequency bands. This evidently contradicts to our assumption.

It is necessary to note that the Fermi-resonance nature of the band is also hardly probable, because this nature also manifests in the experiments with ^{13}CO .

In this work, the reason for the appearance of high-frequency bands at 2086 (2040) cm^{-1} was not determined. Perhaps, it is related to the features of molecule packing in the layer and with different surroundings of coordinated CO in the samples obtained by the co-condensation of reagents. This is confirmed by the experiments where CO was supplied onto preliminarily prepared layers. In these experiments, the bands are not

resolved, only shoulders on high-frequency wings of the main bands (Fig. 6a).

The frequency of the monocarbonyl complex in sublimated layer is lower than in the Ar matrix by $\sim 12 \text{ cm}^{-1}$ and lower than in the Kr matrix by 7 cm^{-1} (see Fig. 1). That is, surrounding influences considerably the frequency of the coordinated diatomic ligand. Analogous conclusions were drawn in [12] for coordinated dioxigen.

Mixed Carbonyl–Oxygen Extra-complex CoTPP

The addition of oxygen to the sublimated layer containing $\text{CoTPP} \cdot \text{CO}$ (Scheme 1A) leads to considerable changes in the spectrum in the region of νCO (Fig. 2). The intensity of the band at $\sim 2070 \text{ cm}^{-1}$ dramatically decreases, a new absorption band appears in the high-frequency region at 2119 cm^{-1} . Experiments with ^{13}CO (Fig. 3) showed that the new band can be assigned to the vibrations including CO group. The evacuation of oxygen from cryostat leads to a decrease in the intensity of new band and to an increase in bands of coordinated carbonyl group.

The frequencies of the band at 2119 cm^{-1} and its ^{13}C isotope analog at 2072 cm^{-1} are close to the frequencies of CO (^{13}CO) in the argon matrix, that is, to 2138 (2093) cm^{-1} [18]. Therefore, it is possible to suppose that oxygen substitutes CO from the coordination sphere of CoTPP, and it remains in the bulk of the layer in adsorbed (probably, physically adsorbed) state.

However, there are some arguments against this interpretation of the nature of the band at 2119 (2072) cm^{-1} . If CO (or ^{13}CO) is supplied to low-temperature sublimate of CoTPP, another band at 2136 (2086) cm^{-1} appears in the IR spectrum in addition to the band corresponding to the coordinated CO. This new band could be assigned to the physically adsorbed CO (Fig. 6a). Nev-

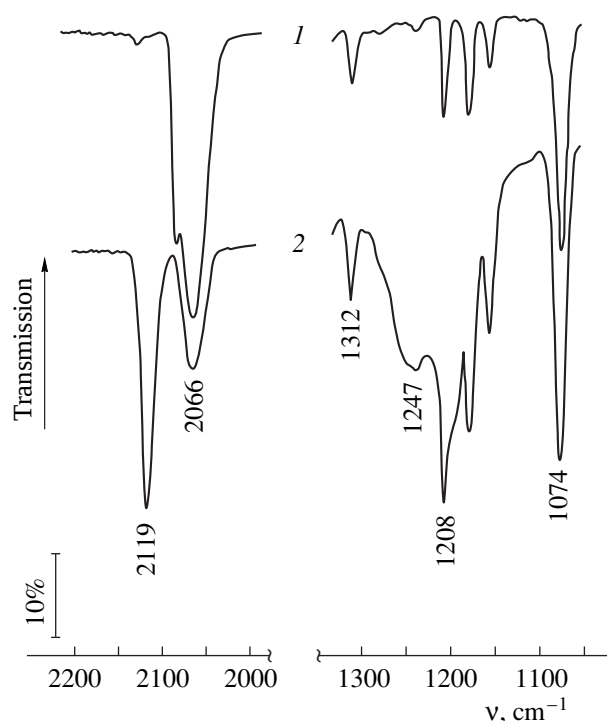


Fig. 2. IR spectra in the region of the vibration of CO and O₂ molecules at 80 K. (1) co-condensate of CoTPP with CO and (2) the transformation of spectrum 1 after the treatment of the sublimate with 90 torr of O₂.

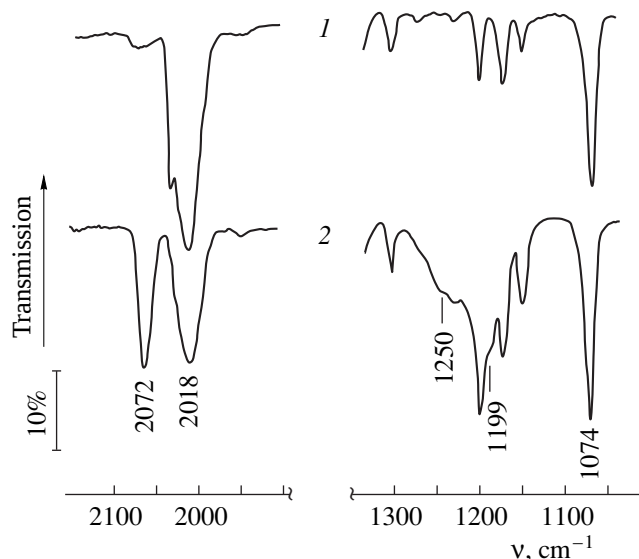


Fig. 3. IR spectra in the region of the vibration of CO and O₂ molecules at 80 K. (1) co-condensate of CoTPP with ¹³CO and (2) the transformation of spectrum 1 after the treatment of the sublimate with 50 torr of O₂.

ertheless, these arguments cannot be considered strict, because it is impossible to exclude that the structures of sublimated layers formed by co-condensation of interacting components (CO and CoTPP) and formed by the action of CO on the preliminarily formed sublimated

layer of CoTPP are different. This difference can lead to the difference in adsorption sites and CO molecule vibration frequencies.

The following objection is more serious. It is possible to see from Figs. 2 and 3 that the appearance of a new band in the region of ν_{CO} is accompanied with the appearance of a new band in the region of the vibration frequencies of coordinated dioxygen ($\sim 1198 \text{ cm}^{-1}$). This last band is shifted by more than 50 cm^{-1} toward lower frequencies with respect to ν_{O_2} of mono-oxygen complex CoTPP $\cdot$ O₂ (Scheme 1B), which was observed in the sublimated layer [17]. Here, the picture is much less clear due to the presence of the absorption bands of porphyrin itself. However, the experiments with ¹⁸O₂ (Fig. 4) where an isotope analogue of this band is recorded as the low-frequency shoulder of the porphyrin band at unambiguously support the assignment of this band to ν_{O_2} . The intensity of this band correlates with the intensity of the band at 2119 cm^{-1} , increases with an increase in the O₂ pressure, and decreases when O₂ is evacuated.

Thus, it is possible to assume that the bands at 2119 and 1198 cm^{-1} correspond to the vibrations of CO and O₂ in the mixed oxygen–carbonyl complex (Scheme 1C). This assignment is based on the fact that the substitution of CO for ¹³CO in the experiments with oxygen addition does not lead to the shift of the bands in the region of O₂ vibration (compare the data presented in Figs. 1 and 2 at $1300\text{--}1100 \text{ cm}^{-1}$). In turn, the bands corresponding to the vibrations including the carbon atom ($2000\text{--}2150 \text{ cm}^{-1}$) do not change when ¹⁸O₂ is supplied to the cryostat. This is important, because it is impossible to exclude some other reactions leading to the formation of new carbon–oxygen bonds. For example, the CO₃ radical was shown to be formed as a result of the low-temperature photolysis of CO₂ [21]. The IR spectrum of this radical contains absorption bands in the region of 2000 and 1100 cm^{-1} .

The stability of the oxygen–carbonyl complex is poor. Even at the liquid nitrogen temperature, the evacuation of oxygen leads to its slow decomposition.

The mixed carbonyl–oxygen complex was also found in the Ar and Kr matrices [18]. The frequencies of vibrations ν_{CO} and ν_{O_2} in this matrix-isolated complex are at 2089 and 1261 cm^{-1} , respectively. Although the direction of the frequency shift of these vibrations during the formation of the mixed complex is the same as in the case of the sublimated layer, an increase in ν_{CO} and a decrease in ν_{O_2} , the values of these shifts, are higher. For example, an increase in ν_{CO} when carbonyl complex is substituted for the mixed oxygen–carbonyl complex, is equal to 15 cm^{-1} , and a decrease in ν_{O_2} when the oxygen complex O₂ $\cdot$ CoTPP is substituted with O₂ $\cdot$ CoTPP $\cdot$ CO is equal to 17 cm^{-1} . For the sublimated layer, these shifts reach values of 54 and 53 cm^{-1} , respectively. This difference in the frequencies of coordinated ligands during the transfer from the iso-

lated state to the associated state can be related to extremely strong intermolecular interaction in the sublimated layer or with the difference in coordination.

It was shown in [22–24] that the molecules of tetraarylporphyrin compounds can hardly be packed in the three-dimensional space due to the large size and hardness of the molecule, as well as due to almost perpendicular orientation of aryl rings with respect to porphyrin macroring. As a result, they form macroporous structures with molecular-sized pores. That is why these structures are called “porphyrin sponges.” It is important that the pores of these compounds are long narrow channels located opposite to the axial positions of the metal. The scheme of the cross section of this channel is presented in Scheme 2A as a circle. If these compounds are precipitated from a solution, these pores are filled with the solvate molecules or with axially coordinated ligands.

In low-temperature sublimates of MTPP, these pores make it possible the diffusion of potential ligands into the bulk of the layer and the formation of axial complexes along its full thickness [17]. The analysis of structural data [22] shows that, in the system under investigation, one of the ligands can be in tight contact with another ligand coordinated by the porphyrin molecule from the layer placed through one layer from the first molecule. This is shown in Scheme 2B. These contacts are probably a reason for much more pronounced shifts of stretching vibration frequencies during the formation of the mixed complex in the sublimated layer compared to the case of matrix isolation.

We cannot exclude completely the possibility of ligand coordination from the same side of porphyrin plane accompanied by the coming of metal ion out of this plane. The possibility of the coordination of two O_2 molecules from the same side of the metal phthalocyanine plane was mentioned in [25]. In any case, the fact that the additional coordination of CO leads to the more efficient activation of molecular oxygen resulting in a further decrease in ν_{O_2} frequency and in the strength coefficient of the O–O bond is important.

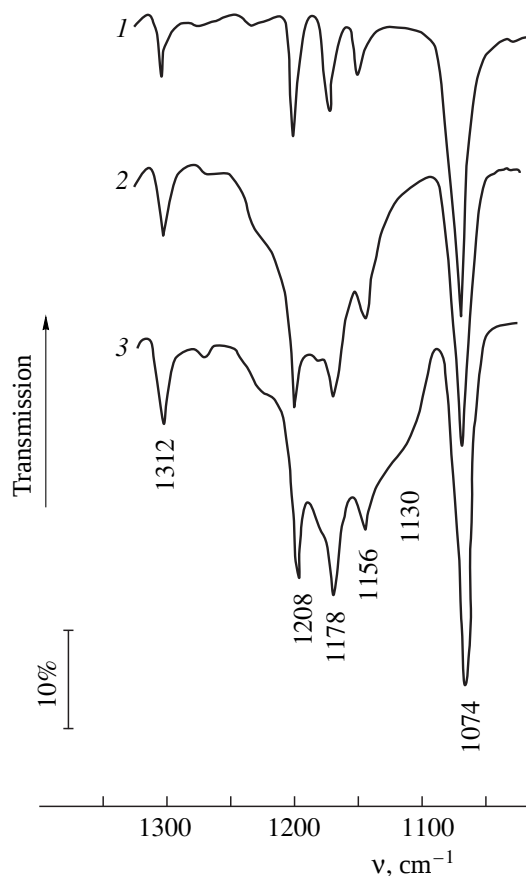
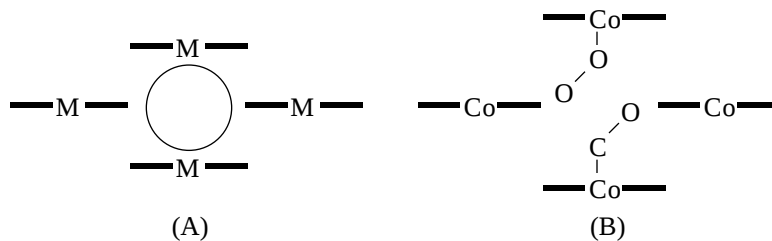


Fig. 4. (1) IR spectrum of co-condensate of CoTPP with CO in the region of oxygen vibration, (2) the transformation of spectrum 1 after the supply of O_2 , and (3) the transformation of spectrum 1 after the supply of $^{18}O_2$.

Oxidative Catalysis on Low-Temperature Sublimates of CoTPP

The heating of the co-condensate containing the mixed oxygen–carbonyl complex leads to a decrease in the intensity of ν_{CO} and ν_{O_2} bands in this complex and to an increase in the intensity of the bands at 2336 (2268) cm^{-1} (Fig. 5) and 658 (640) cm^{-1} (in the experiments with CO and ^{13}CO , respectively). These bands



Scheme 2.

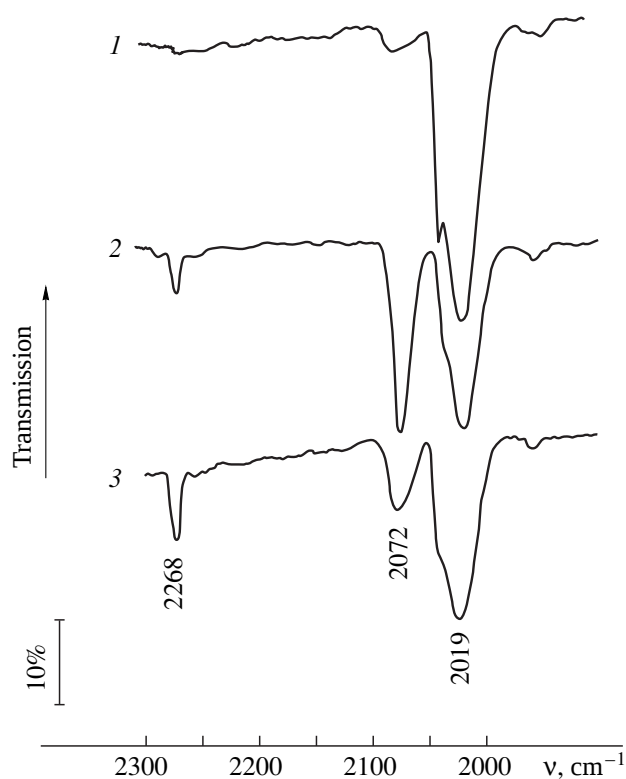


Fig. 5. (1) IR spectrum of co-condensate of CoTPP with ^{13}CO at 80 K, (2) the transformation of spectrum 1 after the supply of oxygen and heating the layer up to 130 K, and (3) the transformation of spectrum 1 after the supply of oxygen and heating the layer up to 150 K.

can clearly be assigned to νCO_2 . An increase in temperature leads to the decomposition of mixed oxygen-carbonyl complex, therefore the strict correlation between a decrease in the intensity of νCO band in this complex and an increase in the intensity of $\nu_3\text{CO}_2$ band seems to be impossible. However, it is possible to suppose that the presence of the mixed complex in the sublimated layer promotes the catalytic oxidation of CO because the O-O bond in this complex became weaker.

CO_2 formation was also detected when heating the sublimated layer of CoTPP onto which CO and O_2 were consecutively or simultaneously supplied at the liquid nitrogen temperature (Fig. 6). In this case, not only the bands corresponding to coordinated CO, O_2 , and the mixed complex were observed in the IR spectrum, but also the bands corresponding to adsorbed CO. The intensity of the band of carbon dioxide increases in this case up to a certain value and does not increase further, in spite of the presence of CO and O_2 in the cryostat. Carbon dioxide formed in the first cycle probably inhibits the further process. This effect was also observed on phthalocyanines [9]. In this case, the frequency of CO_2 vibration is higher by 12–14 cm^{-1} than the frequency found for solid CO_2 obtained by recondensation of CO_2 onto a cold support of second cryostat connected with the first one in a series. This confirms

the adsorption of CO_2 in the first case. This adsorption probably involves active catalytic sites in the layer. Indeed, after evacuation at about 160 K of initially formed CO_2 and after the subsequent supply of a new portion of CO + O_2 mixture at the liquid-nitrogen temperature, the formation of a new portion of CO_2 takes place. Thus, the low-temperature oxidation of carbon monoxide is catalytic. The IR spectrum of the sublimated layer of CoTPP after the removal of the coordinated ligand and CO_2 at an elevated temperature reproduces the spectrum of the initial CoTPP; that is, the molecules of CoTPP do not change during the process of CO oxidation.

If the mixture $\text{CO} + ^{13}\text{CO} + \text{O}_2 + ^{18}\text{O}_2$ is used, six bands at 2334, 2317, 2300, 2268, 2252, and 2233 cm^{-1} can be found in the IR spectrum. The calculations carried out for the ν_3 of the linear triatomic molecule [26] demonstrate an agreement of the frequencies of these bands with the anticipated frequencies for the molecules of CO_2 , OC^{18}O , $^{18}\text{OC}^{18}\text{O}$, $^{13}\text{CO}_2$, $\text{O}^{13}\text{C}^{18}\text{O}$, and $^{18}\text{O}^{13}\text{C}^{18}\text{O}$. If the gas content of the cryostat where the experiment was carried out, is frozen on cold support of another cryostat, these bands give absorption maxima at 2346, 2330, 2314, 2280, 2264, and 2247 cm^{-1} . Thus, the vibration frequencies of solid CO_2 and of CO_2 in the presence of sublimated layer differ by 12–14 cm^{-1} . This confirms that CO_2 molecules are concentrated inside the layer, but not on its surface in the form of a frozen film. Six bands with somewhat lower resolution were also recorded at 660–630 cm^{-1} where the bands of degenerate deformational vibrations νCO_2 of various isotopic modifications of carbon dioxide are reflected. In the experiments, we used C^{16}O and $^{13}\text{C}^{16}\text{O}$. Therefore, the presence of $^{18}\text{OC}^{18}\text{O}$ and $^{18}\text{O}^{13}\text{C}^{18}\text{O}$ as final reaction products demonstrates the possibility for the formation of a compound with two ^{18}O atoms as reaction intermediate. This could be, for example, the above-mentioned $\text{CO}_3^{\cdot}$ radical, which may have the *trans*-structure $\text{O}-\text{O}-\text{C}=\text{O}$ [27] or the structure with a three-membered ring [21].

It is interesting to note that this reaction does not take place if the mixture of CO with O_2 is supplied to the cooled sublimate obtained by the deposition at room temperature or if the low-temperature sublimate was re-cooled after heating the layer to room temperature. Without solvate molecules or axially coordinated additional ligands, this process leads to the contraction of pores [22]. This contraction must hinder the efficient diffusion of reactant molecules into the film. This was confirmed by our experiments with molecular oxygen [12]. In these experiments, we did not detect O_2 coordinated by CoTPP by spectroscopy at liquid-nitrogen temperature if the pressure of O_2 was lower than 300 torr and CoTPP layer was prepared by sublimation at room temperature or this layer was preliminarily heated to room temperature. In our opinion, the main reason for these differences is related to the activity of

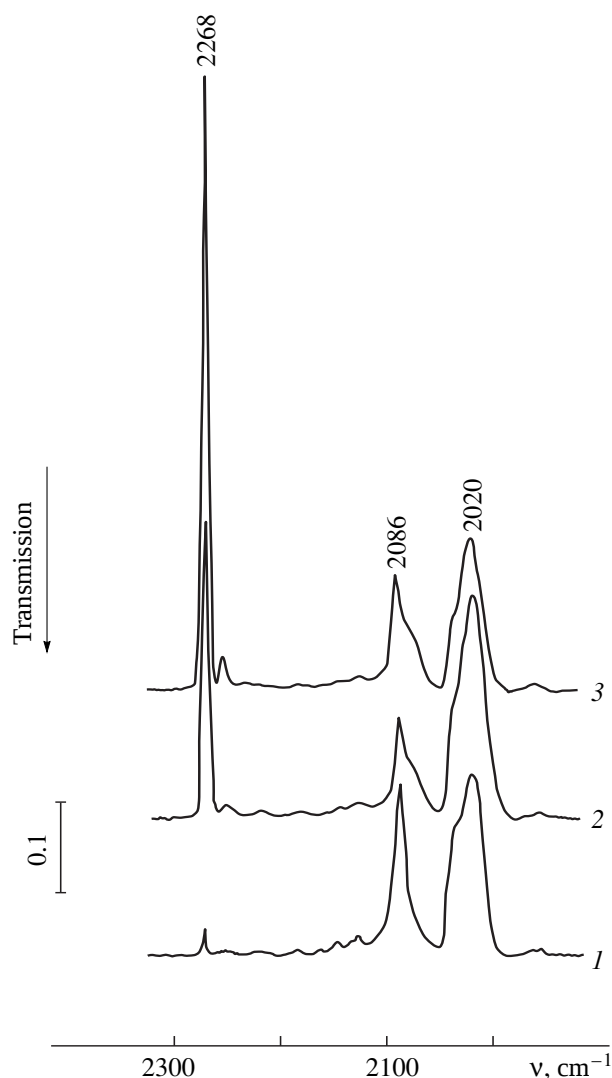


Fig. 6. (1) IR spectrum of sublimated CoTPP layer at 80 K the after supply of ^{13}CO ($P \approx 2$ torr). (2) the transformation of spectrum 1 after further supply of O_2 ($P \approx 3$ torr) and annealing at 150 K for 1 h, and (3) the transformation of spectrum 2 after the additional supply of O_2 ($P \approx 4$ torr) and annealing at 160 K for 1 h. P is equilibrium gas pressure in cryostat.

the full volume of the layer of low-temperature sublimate of CoTPP, rather than only the surface.

The presence of low-temperature sublimate is necessary for catalysis. Nevertheless, the experimental data are insufficient to conclude that all steps of the reaction take place at a low temperature in the sublimated layer. Under the experimental conditions, oxygen and carbon monoxide are always present in the gas phase due to the low thermal stability of the complexes. Therefore, it is impossible to exclude that oxygen and carbon monoxide play a certain role in the catalytic process. The necessity of the presence of CO in the gas phase for low-temperature catalysis on phthalocyanines was emphasized, for example, in [7].

Our data show, how strong the catalytic activity of the sublimated layer depends on its structure, which is in turn determined by the conditions of its formation. This dependence was mentioned many times [3, 28] for organic semiconductor materials. Thus, the supermolecular structure of sublimated layer of CoTPP plays a decisive role in the catalytic reaction of carbon monoxide oxidation by molecular oxygen.

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