

Structure and phase transition peculiarities in solid nitrous oxide and attempts at their explanation

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Received October 15, 2012

Cryogenic vacuum deposited films of nitrous oxide were studied at the following conditions: a mirror-like silver-coated copper substrate; deposition temperature 16 K; gas phase pressure during deposition 10^{-3} Pa. Analysis of the IR-spectrometric and thermodesorption data leads to the following conclusion. The transition from the amorphous to crystalline state in the vicinity of 40 K proceeds in several steps which reflect relaxation processes related to different molecular vibrations. The differences in the temperature intervals of the transitions are determined by the activation energies of relevant vibrations. It was shown that cryocondensation at 16 K is accompanied by appearance of flashes on the condensate surface. Based on the uniform nature of the observed processes, a model based on several possible isomorphous molecular states of nitrous oxide is suggested.

PACS: **61.50.-f** Structure of bulk crystals;
78.30.-j Infrared and Raman spectra;
78.30.Hv Other nonmetallic inorganics.

Keywords: IR-spectrometric investigation, phase transition.

1. Introduction

Earlier we investigated the dependence of the rate of nitrous oxide deposition on gas pressure and substrate temperature. It was observed that the process of cryogenic deposition was accompanied by emission of electromagnetic radiation in the visible spectrum, which was a direct evidence of the gas-solid phase transition [1]. Studies of this phenomenon have revealed a range of characteristic peculiarities referring to thermodynamic parameters of both film deposition and light emission. In particular, cryogenic deposition of N_2O is accompanied by radiation only in the case when the substrate temperature does not exceed $T = 130$ K. On the hand, when the deposition temperature is below $T = 90$ K intensity of the radiation decreases. Besides this, for every deposition temperature in the interval between 90–130 K there is an optimal value of gas phase pressure corresponding to a maximum of emission intensity. The study of spectral composition of radiation [2] established the presence of two maxima in the vicinity of 380 and 700 nm.

Additionally, IR-spectrometric investigations were conducted on cryogenically deposited films of nitrous oxide in the interval between 12 K and the sublimation temperature [3,4]. A cryogenic film of N_2O was deposited at $T = 12$ K and subjected to slow heating. It was found that in the vi-

cinity of $T = 40$ K the state of the sample had a stepwise transformation which was reflected in the change of the position and shape of characteristic IR absorption bands (Fig. 1). Heating of the sample, whilst monitoring the evolution of IR absorption at a fixed frequency, allowed determining the temperature interval of the transition with high precision.

The following electron diffraction studies of the discovered phenomenon [5,6] led to a conclusion that the sample obtained at $T = 12$ K was in an amorphous state. When heated to $T = 40$ K it undergoes a transition into a crystalline state with a cubic lattice.

So far, the experimental evidence described above did not have a reliable interpretation which caused an interest in additional studies in this area. Moreover, in recent years a number of papers presented new results, in our opinion, directly related to the earlier data. Thus, Ref. 7 reports that in the process of N_2O film deposition a positive potential is spontaneously formed at the film-vacuum interface relative to the film-substrate interface. The potential difference may reach several volts depending on film thickness, demonstrating strong temperature dependence, especially for thinner films.

In Ref. 8 IR-spectrometric studies of the molecules of nitrous oxide isolated in cryogenic matrices of xenon, ar-

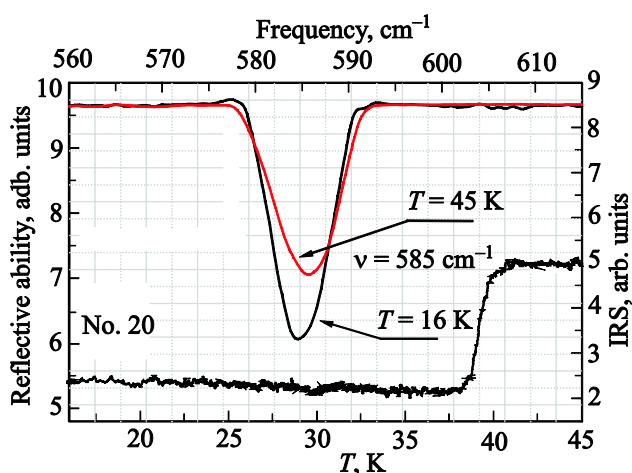


Fig. 1. IR-spectrometric studies of transitions in cryogenically deposited films of nitrous oxide [3]. Upper curves—change in the position of the absorption band corresponding to deformation vibrations of a nitrous oxide molecule when temperature increases from $T = 16$ K to $T = 45$ K; lower curve—evolution of the IR signal at 585 cm^{-1} upon heating of the sample. The sample deposition temperature was $T = 16$ K with sample thickness of $d = 2.5\text{ }\mu\text{m}$ and the heating rate of 1 K/min .

gon and nitrogen were conducted. These studies revealed anomalous behavior of absorption intensities of different vibration modes of N_2O during the matrix heating: the first derivatives of the dipole moments corresponding to symmetrical and asymmetrical vibrations had opposite signs. It must be noted that these changes occurred at the interval of $15\text{--}45\text{ K}$ which agrees with the results presented herein.

In the studies of adsorption of the nitrous oxide molecules [9] it was found that depending on the nature of the substrate the character of molecule-surface bonding varied. This was described by a change in an angle between the molecular axis and the plane of the substrate made of either copper or silver. To rationalize this observation the authors proposed an idea of an existence of two resonant forms of the molecule of nitrous oxide.

The body of the above evidence was an additional motivation for detailed studies of the process of nitrous oxide cryogenic deposition and properties of the formed films.

2. Idea and experiment

This paper presents experimental results regarding the studies of peculiarities in the transitions observed in cryogenically deposited films of nitrous oxide in the vicinity of $T = 40\text{ K}$ during thermal cycling. The studies were aimed at elucidating how the deformational and translational vibration modes of the solid state of nitrous oxide react to these transformations. In other words, they were aimed at finding whether the observed changes correspond to a single transition simultaneously affecting all transition modes of a nitrous oxide molecule, or there is a set of sequential

transitions corresponding to a certain type of vibrations. In addition, there were further investigation of the temporal parameters of the flashes, accompanying the process of N_2O cryocondensation.

The studies were conducted using a setup and a methodology described in our earlier works [10,11]. A considerable difference from the earlier studies of nitrous oxide was in the use of a combination of optical and thermal desorption methods simultaneously producing two independent sets of data. In the past, this approach was successful in investigating structure and phase transitions in cryogenic films of water and ethanol [12,13].

In the present work, cryogenic vacuum deposited films of nitrous oxide were studied which were formed at the following conditions: a mirror-like silver-coated copper substrate with diameter of 40 mm used as a deposition surface; deposition temperature of $T_c = 16\text{ K}$; gas phase pressure of $P = 10^{-3}\text{ Pa}$; sample thickness of $d = 2\text{ }\mu\text{m}$; sample heating rate of $t = 1\text{ K/min}$; nitrous oxide gas phase purity of 99.92% . By, first, measuring vibration spectra of the samples and, then, recording changes in amplitude and position of a characteristic absorption band, it is possible to determine the temperature and nature of thermally stimulated transformations in cryogenic films of nitrous oxide.

The experiments were conducted in the following manner. The vacuum chamber was pumped down to $2 \cdot 10^{-5}\text{ Pa}$ followed by cooling of the substrate down to $T = 16\text{ K}$. Using a leak valve, gaseous nitrous oxide was injected into the chamber until the set deposition pressure (10^{-3} Pa) was reached. After this, formation of a cryogenic film of N_2O on the substrate was observed with simultaneous measurement of its growth rate and refractive index using a two-beam laser interferometer. When the required film thickness had been obtained, injection of the gas was stopped and after a $5\text{--}10\text{ min}$ wait period IR spectra of the samples were recorded at the interval of $400\text{ to }4200\text{ cm}^{-1}$. Further, the IR-spectrometer was set at a fixed frequency corresponding to a molecular vibration mode under study. The sample was slowly heated with simultaneous measurement of the spectrometer signal at the selected observation frequency. Additionally, gas phase pressure in the chamber was measured to monitor possible release of impurities (such as nitrogen) captured during the film deposition stage. It is expected that such impurity release may be induced by structural transformations in the film and may provide an additional piece of information independent of the optical methods.

3. Results

Figure 2 demonstrates the influence of temperature of thin cryogenic films of nitrous oxide during heating on the shape and position of the absorption bands corresponding to deformational and longitudinal vibrations of the N_2O molecule.

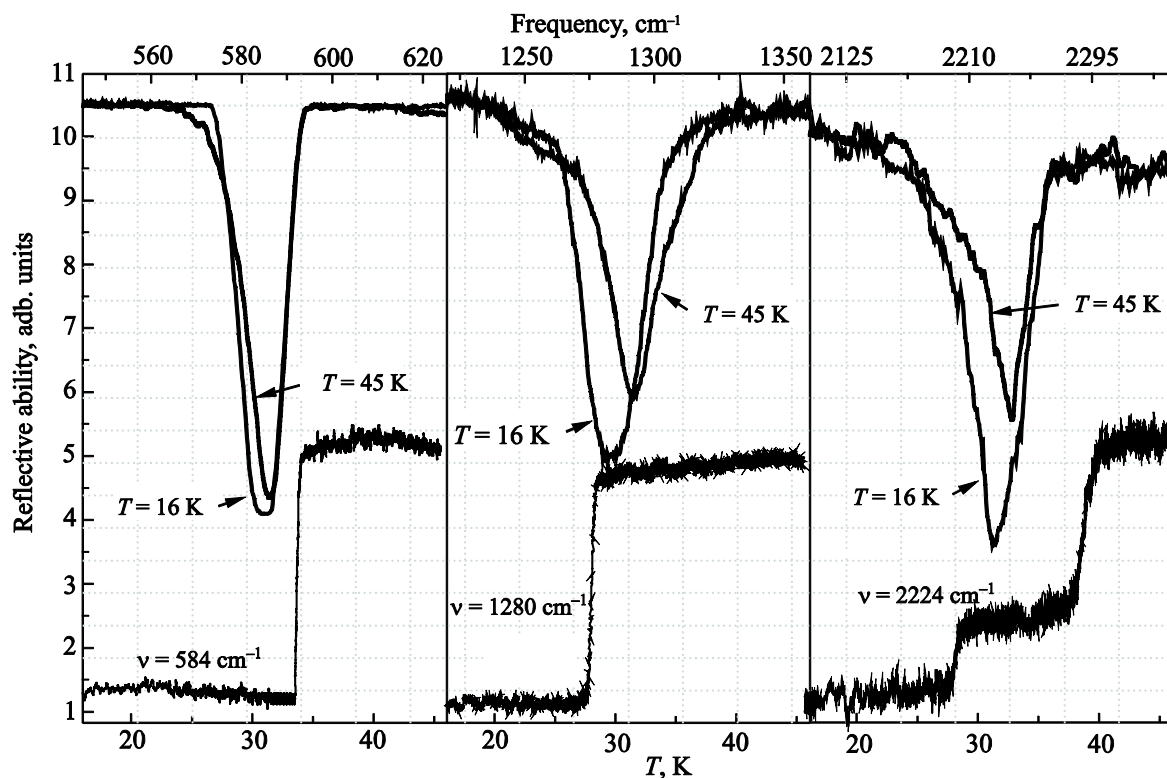


Fig. 2. Influence of temperature of thin cryogenic films of nitrous oxide on the shape and position of the absorption bands corresponding to deformational and longitudinal vibrations of the N_2O molecule. The spectra were obtained at the deposition temperature of $T = 16$ K and after heating to $T = 45$ K. The lower part of the graphs shows thermal evolution diagrams of the IR spectrometer signal in the process of heating at a fixed observation frequency. The film thickness was $d = 2$ μm .

As seen in the figure, there is a set of characteristic spectral peculiarities of various types of vibrations.

1. The $560\text{--}600\text{ cm}^{-1}$ interval corresponds to deformational vibrations. Heating of the film leads to noticeable narrowing of the absorption band and a shift towards higher wavenumbers, while the high-frequency edge of the absorption band retains its position. The change in full width at half maximum is $\Delta\nu = 1.3\text{ cm}^{-1}$. The IR intensity measurement at a fixed observation frequency of $\nu = 584\text{ cm}^{-1}$ demonstrates a stepwise change in the interval between $T = 33.3$ and 34 K.

2. The $1200\text{--}1400\text{ cm}^{-1}$ interval corresponds to longitudinal asymmetric vibrations. Heating of the film leads to a shift of the whole band to higher frequencies and a reduction in the absorption amplitude. The change in full width at half maximum is $\Delta\nu = 9.1\text{ cm}^{-1}$. The IR intensity measurement at a fixed observation frequency of $\nu = 1280\text{ cm}^{-1}$ demonstrates a stepwise change in the interval between $T = 27.2$ and 28.7 K.

3. The $2100\text{--}2300\text{ cm}^{-1}$ interval corresponds to longitudinal symmetric vibrations. Heating of the film from $T = 16$ to 45 K leads to a rapid narrowing of the absorption band accompanied by its shift to higher frequencies and a significant reduction in the absorption amplitude. The change in full width at half maximum is $\Delta\nu = 13.1\text{ cm}^{-1}$. The IR intensity measurement at a fixed observation frequency of $\nu =$

$= 2224\text{ cm}^{-1}$ demonstrates that the transition proceeds in two steps. The first stepwise change is observed in the temperature interval between $T = 27.4$ and 29.4 K. Between $T = 29.5$ and 35 K the signal shows relative stability. The second, more gradual, transition is observed in the $35\text{--}40.3$ K interval.

Analysis of the data given in Fig. 2 leads to the following conclusion. Transition from the amorphous state of nitrous oxide to the crystalline state proceeds in several steps which reflect relaxation processes related to a certain type molecular vibrations. Difference in the temperature intervals of the transitions is determined by activation energies characteristic of a certain type of vibrations.

Also, we measured the time parameters of the cryocondensing emission of nitrous oxide. Signal change of the photomultiplier during N_2O cryodeposition is shown in Fig. 3. As can be seen, the process of cryocondensation is accompanied by a spontaneous increase of the photomultiplier signal that corresponds to the appearance of flashes on the condensation surface. These data are in agreement with our previous experimental results [1].

Figure 4 shows the detailed time scans of individual bursts corresponding to different time periods of condensation. Measurements showed that the maximum radiation time set for different intervals of time of observation is less than 0.5 s.

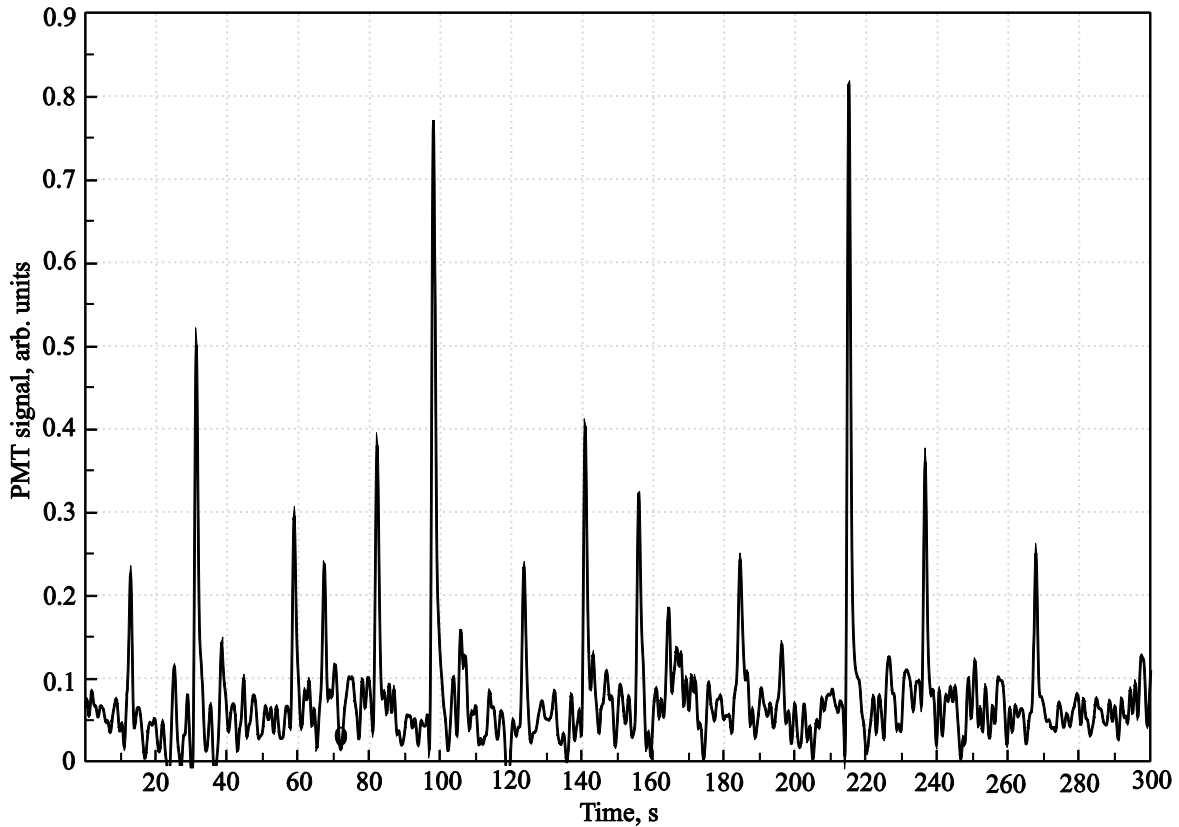


Fig. 3. Registration of the photoemission during the process of N_2O cryodeposition. Temperature of condensation $T = 16$ K; pressure of condensation $P = 10^{-2}$ Torr.

4. Discussion and conclusions

Despite a considerable difference in experimental methods employed and type of data obtained, the evidence presented herein, both our own and that of our colleagues, is, in our opinion, a manifestation of characteristic peculiarities of nitrous oxide, and in particular, of the presence two resonant forms of the N_2O molecule [14–16]. Without going into quantum-chemical details of this phenomenon, we limit our description by stating that these two forms of

the nitrous oxide molecule are different in the character of valence bonds, electronic configuration of external shells and, consequently, in the size of the dipole moments. In this regard, it may be both interesting and productive to use results of the theoretical studies [17] highlighting principal possibility of existence of isomorphous forms of N_2O (Fig. 5). Figure shows as a result of successive electronic reorganizations of valence bonds nitrous oxide molecule goes from the ground state I to quasi-stable state V with energy different between this state's of 2.81 eV.

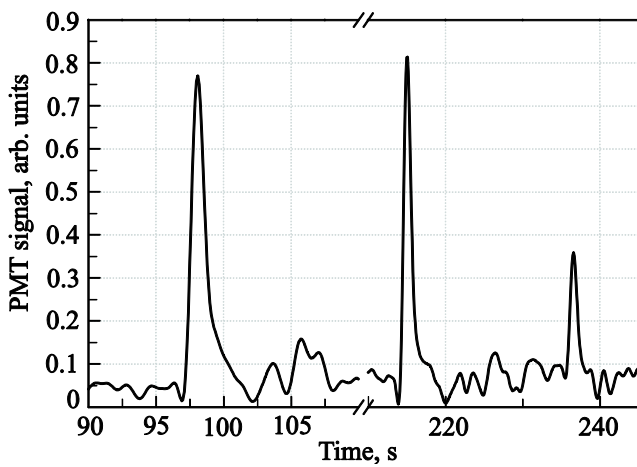


Fig. 4. Detailed time scans of individual bursts corresponding to different time periods of condensation.

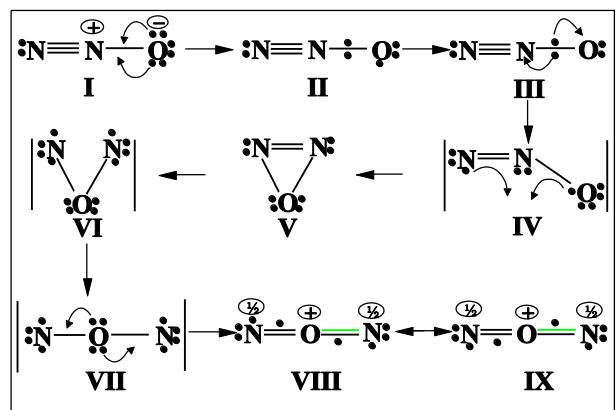


Fig. 5. Qualitative valence bond representation for the electronic reorganization that may be associated with an isomerization (using data from [17]).

Based on the above arguments, one may attempt to explain our data, both obtained earlier and presented herein. However, in our opinion, before this several important assumptions must be made:

First, nitrous oxide in the gas phase represents a mixture of two resonant forms at equilibrium and in a certain concentration ratio.

Second, equilibrium concentrations of the two resonant forms of nitrous oxide are significantly different in the gas and solid state.

Third, equilibrium concentration of the two forms of nitrous oxide in solid state depends on both the deposition temperature and the current temperature of the sample.

Fourth, the solid state of nitrous oxide is characterized by relaxation processes related to non-equilibrium in concentration of the two resonant forms; the dynamics of these processes are determined by a thermodynamic history of formation and evolution of the samples.

Taking into account these assumptions, we propose the following explanation of the data presented here.

(a) The phenomenon of light emission by nitrous oxide during cryogenic deposition [1,2]. The process of nitrous oxide cryogenic deposition is accompanied by a stepwise change in equilibrium concentration of the two resonant forms of N_2O in the solid state relative to the gas. At relatively high deposition temperatures (90–130 K) the mobility of molecules is sufficiently high and relaxation processes proceed intensively. Meanwhile, a rapid change in dipole moments of a considerable proportion of nitrous oxide molecules occurs both in magnitude and in spatial orientation. This results in generation of electromagnetic radiation in the form of brief high-intensity flashes. When the deposition temperature is lowered, this results in freezing of non-equilibrium configurations, which may undergo transition into a steady state upon heating of the film. As a result, radiation characterized by continuous glowing is observed.

(b) The shift of characteristic vibrational absorption bands of nitrous oxide in the vicinity of $T = 40$ K (Figs. 1, 2). Our attempt at rationalizing this phenomenon is also based on the idea of the existence of isomorphous structures of nitrous oxide. Both below and above the transition temperature of $T = 40$ K the cubic lattice points may be occupied by the molecules of nitrous oxide corresponding to either cyclic or linear isomorphs. Transition from one form to another is accompanied by changes in characteristic frequencies of fundamental intramolecular vibrations as observed in our experiments. The fact that for every type of vibrations the transition occurs at a different temperature interval may be related to the difference in binding energies and corresponding activation energies.

Thus, the key moment to explain both structural transformations in nitrous oxide cryocondensates and in cryocondensate radiation could possibly be presence of isomorphous structures in N_2O molecule and its thermo-stimulated transformation. This idea is more or less used in works of our colleagues [8,9], and also can be used to explain the phenomenon of spontaneous dipole alignment in films of N_2O [7].

The work is supported by Science Committee of Republic of Kazakhstan, Grant IPC-43/2012.

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