# WEAKLY BOUND MOLECULAR COMPLEXES IN THE ATMOSPHERE

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*The role of van-der-Waals molecules in physical-chemical transformations of atmospheric particles and their interaction with radiation are reviewed. Data on the content of binary complexes in planetary atmospheres are presented. It is shown that the presence of van-der-Waals molecules in the atmosphere must be taken into account when modeling atmospheric processes.*

## INTRODUCTION

Investigations of the gas composition of the earth's atmosphere are undertaken primarily for purposes of predicting and monitoring possible changes of the composition. It goes without saying that any molecular or atomic components of the troposphere and stratosphere which are at all significant are well known and have been determined quantitatively. The conditions of the atmospheres of the nearest planets have been studied in much less detail, though existing data from space probes and astronomical observations indicate that the composition and conditions of the planetary atmospheres are very diverse. It is well known, for example, that the atmospheres of the nearest terrestrial planets consist almost entirely of carbon dioxide gas, while the atmospheres of the giant planets consist of light hydrogen and helium gases. The atmospheres of all planets contain many minor gaseous components (MGCs), which can significantly affect the temperature and climate of different atmospheric layers. Thus in studying radiant energy transfer in the earth's atmosphere a number of climatically important MGCs, whose content is of the order of $10^{-4}$–$10^{-9}$, must be taken into account. They include chemically stable gaseous components such as, for example, $H_2O$, $CO_2$, and others. However no single list of MGCs, no matter how detailed, contains any indication of the number of van-der-Waals and hydrogen-bonded complexes, formed by molecular and atomic components of the atmospheres. Meanwhile, the need for studying dimerized molecules has been specially stressed in the recommendations of the Atmospheric Spectroscopy Applications Workshop.[2]

In the last few years the physics of weakly bound molecular systems has been developing rapidly, stimulated primarily by significant progress in quantum chemistry and experimental methods of optical and microwave spectroscopy. The literature on the properties of weakly bound complexes is extensive; the main results are reviewed in Refs. 3–7. It is now possible, for the first time, to treat weakly coupled molecules as special molecular impurities, whose content can vary over wide limits depending on the thermodynamic conditions. They can be termed MGCs of the second kind, since they are derivatives of the standard gaseous components of the atmosphere and they exist only in the gas-phase environment of the parent molecules. It is noteworthy that all known atomic and molecular particles form such weakly bound complexes, and in addition, the energies of the intermolecular bonds of the complexes vary over wide limits: from hundredths of kcal/mole for dimers of inert gases up to tens of kcal/mole for the hydrogen-bonded ionic complexes of associated radicals. It is not difficult to show that N atomic or molecular particles can form $N(N + 1)/2$ different bimolecular complexes. Thus the number of possible van-der-Waals complexes that can be formed by standard gaseous components of the atmosphere is more than an order of magnitude greater than the number of components. Of course, in most cases the content and role of the complexes in atmospheric processes is negligibly small. However it is wrong to drop them from the list a priori, in view of the fact that these exotic molecular objects are exceedingly poorly understood.

Intermolecular forces link particles at large distances several times greater than the typical lengths of chemical bonds. For this reason, to a first approximation, it would seem that the mutual influence of particles in a weakly bound pair can be neglected. However the observation of a number of new physical effects makes such an approximation unacceptable. First, the enlargement of a complex does not reduce simply to arithmetic addition of the energies of the bonds formed - the nonadditivity of the energy of attachment of the consequent particles must be taken into account in the description of the starting stages of homogeneous condensation from the gas phase. Second, the formation of directed intermolecular bonds results in the appearance of metastable binary complexes in collisions between particles, and such complexes play an important role at intermediate stages of chemical and photochemical reactions in the atmosphere. Third, the change in the moments of inertia and selection rules and the appearance of new vibrational degrees of freedom of the particles in the complex results in the appearance of new spectral features. In particular, all neutral dimers of polyatomic gases absorb long-wavelength infrared radiation owing to intermolecular vibrational transitions. Finally, fourth, the role of complexes in the relaxation of intramolecular excitations cannot be ignored. The latter could be related, for example, with the absorption of radiation or with collisions with light or heavy particles. It has been shown that the existence of associated molecules in a gas substantially changes the rate of relaxation of the rotational, vibrational, or electronic energy, the thermodynamic equilibration time, and the characteristics of processes determined by dissipation.

In this review we summarize the data on the possible manifestations of weakly bound neutral complexes in planetary atmospheres and thereby call attention to the need for a detailed study of the bound and quasibound states of molecules for problems of atmospheric physics and chemistry.

## 1. THE FORMATION OF COMPLEXES AND THEIR ROLE IN TRANSFORMATIONS OF ATMOSPHERIC PARTICLES

### 1.1. WHAT IS A WEAKLY BOUND COMPLEX?

The answer to this question is by no means unequivocal. The term "weakly bound complex" (as a rule, bimolecular) is most often employed to denote pairs (groups) of atoms or molecules coupled by the van-der-Waals interaction. The van-der-Waals bond energies, as a rule, do not exceed 1 kcal/mole, and the intermolecular bonds are two or more orders of magnitude weaker than the intramolecular chemical bonds. Hydrogen bonds are sometimes put into a separate category; such bonds are characterized by energies ranging from one to several tens of kcal/mole and by a distinct directionality of the bond formed by the hydrogen atoms. Molecules capable of forming hydrogen bonds constitute minor impurities in the atmospheres of all planets, but their role in physical-chemical and radiation processes could turn out to be significant. An example are water molecules in the earth's atmosphere or ammonium and phosphene molecules in the atmospheres of Jupiter and Saturn.

A characteristic feature of weakly bound complexes is that they lose their rigid structural form on excitation as a result of collisions with other particles or absorption of a quantum of light. For this reason, great care must be exercised in transferring to the conditions of real atmospheres any inferences made about the most stable structure of complexes obtained, for example, under extremely low temperatures under laboratory conditions. In addition, the intermolecular interaction, which in most cases is anisotropic, depends strongly on the internal state of the constituent particles of the complex. Thus the at first glance insignificant difference of the rotational energies of the ortho- and para-modifications of heavy water, as shown in Ref. 8, results in appreciable differences in the efficiency of complex formation and absorption of molecules.

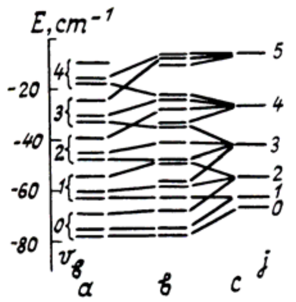

*FIG. 1. The correlation of the bound states of the complex $N_2$ ... Ar (b) with the levels of a rigid-rotator-harmonic-oscillator molecule (a) and molecules with free internal rotation (c). The translational quantum number $v_s = 0$; $v_b$ is the quantum number of the deformation vibration; j is the rotational quantum number of the $N_2$ molecule in the complex.*

In the region of the bound states of a pair of particles the energy spectrum may not have anything in common either with the spectrum, of a harmonic oscillator or with the spectrum of the molecules freely rotating in a complex, and then the models most often employed' and developed for standard molecules turn out to be inapplicable. Figure 1 shows the spectrum of the bound states of the complex $N_2$...Ar, calculated in Ref. 9. One can see that the usual rigid rotator—harmonic oscillator approximation can be employed for modeling the spectrum of the complex only at very low temperatures. The approximation of free internal rotation of the particles in a complex is valid only near the dissociation limit. The intermediate region of bound states has a complicated spectrum, which, as a rule, cannot be simply interpreted.

Discrete states also exist in the region of the continuous spectrum of van-der-Waals complexes above the dissociation threshold; these states play a non-negligible role in the spectroscopy, thermodynamics, and chemistry of weakly bound complexes. The nature of these metastable states could be related, in the simplest cases, with rotational resonances, while for polyatomic molecules it could be related with the more complicated redistribution of energy between the rotational and vibrational degrees of freedom of the particles in the complex. A detailed discussion of the problem of metastable states of van-der-Waals complexes falls well outside the scope of this paper; some aspects of this problem are discussed in special publications.[10] We note only that the relative role of metastable and bound states in an equilibrium gas is strongly temperature dependent.

### 1.2. THE CONTENT OF COMPLEXES IN THE ATMOSPHERE

More than one hundred years has passed since Janssen[11] reported on the observation of diffuse bands in the spectrum of the earth's atmosphere, which were later ascribed to molecular complexes – short-lived oxygen dimers. However in spite of the fact that the existence of pair molecular formations in the atmosphere has been known for such a long time there are no accurate data on their content in the atmosphere. The diversity of the processes- and nonuniformity of conditions in real atmospheres are not the only problems involved in determining the equilibrium composition of an associating gas mixture. The determination of the content of weakly bound complexes in a gas mixture remains a difficult problem to solve, even under well-controlled laboratory conditions. At low densities the relative fraction of the complexes is so small that it is difficult to separate their contribution to the thermodynamic, transport, and spectral properties of the gas in a pure form, comparing it, in the process, with the contribution of complexes of a definite size and structure. For high densities the properties of the complexes, as pointed out above, can change, a large number of isomers and polymers form, and the problem of determining their content in the gas becomes much more complicated.

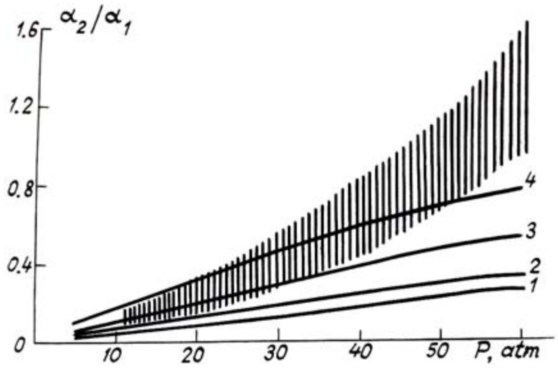

*FIG. 2. The pressure dependence of the ratio of the mass fractions of dimers $a_2$ and monomers $a_1$ in carbon dioxide gas. The hatched region was determined from analysis of the IR absorption band;*[12] *the curves 1, 2, 3, and 4 were taken from Refs. 13, 14, 15, and 16, respectively.*

As an example Fig. 2 shows the pressure dependence obtained in Ref. 12 for the relative fraction of dimers $(CO_2)_2$ in pure carbon dioxide gas from analysis of the IR absorption bands of $CO_2$ measured in the laboratory. One can see that, first of all, the error in the experimentally determined relative fraction of dimers is significant and, second, the existing theoretical estimates vary over wide limits. Only the order of magnitude of the content of dimers in an equilibrium gas can be estimated. For example, Fig. 3 shows the altitude profiles of the content of the dimmers $(CO_2)_2$ for the conditions of the atmosphere of Venus. At the surface of the planet several percent of the $CO_2$ molecules are associated. Thus, formally, the dimers $(CO_2)_2$, together with nitrogen, are the second most abundant constituent of Venus' atmosphere. For the problem of the radiation balance of Venus' atmosphere the strong complexes $CO_2...H_2O$, present in the atmosphere in significantly smaller quantities (see Fig. 3), could possibly play an even larger role. We note that the latest data on the altitude distribution of the van-der-Waals complexes in the atmospheres of planets give rise to serious doubts. To say the least, the profiles of the dimers $(CO_2)_2$ in the atmospheres of Venus and Mars as well as the profile of the content of the complexes $N_2...Ar$ in the earth's atmosphere, which were calculated in Ref. 17, disagree sharply with existing estimates based on independent calculations of the equilibrium constants.[14,15,18] For this reason the data of Ref. 17 on the content of the dimers $(H_2O)_2$ in the atmospheres of Jupiter and Saturn and of the complexes $H_2...N_2$ and $N_2...Ar$ in the atmosphere of Titan require careful checking.

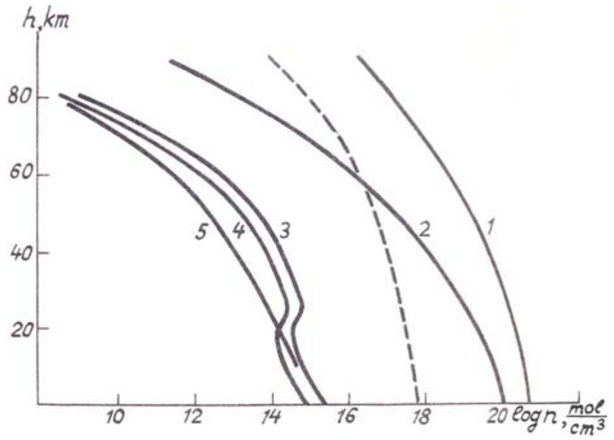

*FIG. 3. The altitude profiles of the concentration of the dimers $(CO_2)_2$, $CO_2...H_2O$, and $CO_2...Ar$ in the atmosphere of Venus. 1) Density profile; 2) density profile of $(CO_2)_2$); 3, 4) $CO_2...H_2O$; 5) $CO_2...Ar$; 3, 5) based on the equilibrium constants; 2, 4) calculation performed by the authors (together with G.V. Chlenova); the dashed line is the density profile of $(CO_2)_2$ from Ref. 17.*

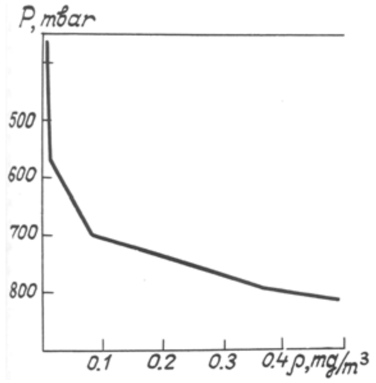

*Fig. 4. The density of water dimers in the earth's atmosphere.*[19]

Water vapor, whose absorption in the IR region is strong, determines to a significant degree the heat balance of the earth's atmosphere. Here it is apparently precisely the water dimmers that are responsible for the continuum absorption in the transmission window

8–13 μm (see Sec. 2.2). The molar fraction of the dimers $(H_2O)_2$ near the surface is only about $10^{-3}$–$10^{-4}$. Figure 4 shows Z. Slanin's calculations of the altitude profile of water dimers in the atmosphere.[19]

Estimates show that in the atmospheres of the large planets – Jupiter and Saturn – the molar fraction of ammonium dimers is of the order of $10^{-4}$, right down to the level of the tropopause. It has not been excluded that the capability of ammonium, phosphene, or methane to form hydrogen bonds can play just as important a role in the atmospheres of giant planets as does the analogous capability of water molecules under the conditions of the earth's atmosphere.

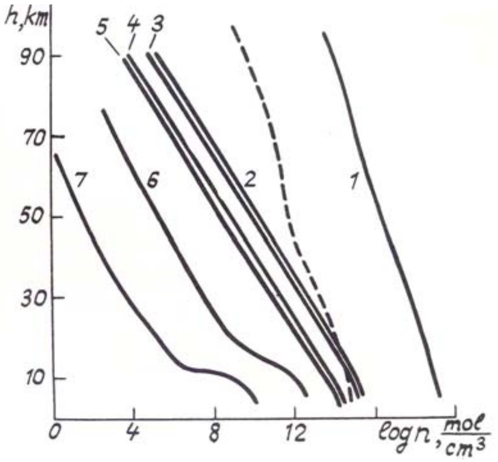

*FIG. 5. The altitude profiles of the content of some complexes in the earth's atmosphere:*[18] *1) total density; 2)* $(N_2)_2$; *3)* $N_2...O_2$; *4)* $(O_2)_2$; *5)* $N_2...Ar$; *6)* $N_2...H_2O_2$; *7)* $(HO)_2$; *the dashed line is the profile of* $N_2...Ar$ *according to the data of Ref. 17.*

A detailed analysis of the content of complexes in the atmospheres of planets has not yet been performed owing to the lack of reliable data on the equilibrium constants. For estimates it is simplest to employ the semiempirical relations of the type derived by Stogryn and Hirschfelder (see, for example, Refs. 7, 20, and 21 for methods for determining the equilibrium composition of an associating gas). For the conditions of the earth's atmosphere such estimates have been obtained in Ref. 18 for more than ten complexes. The altitude profiles obtained in Ref. 18 for the content of some weakly bound complexes are presented in Fig. 5. We note that all starting constituents of the indicated complexes are well mixed in the atmosphere, so that the profiles have a monotonic character. The altitude distribution of an entire series of other complexes, formed by components such as ozone, $SO_2$, $O_2$, $(^1\Delta_g)$, $HNO_3$, and other molecules, will be substantially more complicated, depending on the temperature distribution and the partial pressures of the parent molecules. The study of such complexes is of interest, first of all, for investigating the kinetics of stratospheric ozone and, second, for describing the homogeneous condensation, in particular, the formation of the stratospheric aerosol layer, connected with emission of large masses of gas in volcanic eruptions into the stratosphere.

## 1.3. WEAKLY BOUND COMPLEXES AND AEROSOL

Studying only the simplest – dimer-complexes cannot, of course, give a complete picture of the mechanism of nucleation from the gas phase, since the condensation nuclei consist of hundreds or thousands of molecules. In the last few years, however, on the one hand, significant progress has been made in the experimental and theoretical studies of the nonadditivity of intermolecular bonds and, on the other hand, there is a tendency to employ in models of nucleation the real properties of associated particles. The latter trend can be clearly seen, for example, in works on the study of the homogeneous condensations of $CO_2$, $N_2O$, and $H_2O$ in freely expanding gas jets.[22,23]

The study of the initial stages of the nucleation of water vapor is of greatest interest. The use of model potentials, together with nonempirical and semiempirical quantum calculations of the "water-water" interaction, have made it possible to study the properties of structures such as clathrates or fragments of hexagonal ice,[24 26] which are potentially important for the nucleation of cold supersaturated vapor.

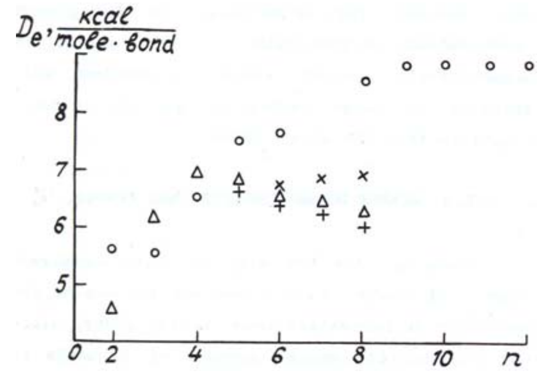

*FIG. 6. The binding energy (per H-bond) versus the size of associates of water.* ○ *- Ref. 27;* Δ, +, × *– Ref. 28 (spherical, cyclic, and irregular structures).*

The dependence of the binding energy of associated water molecules on the sizes of the associates was analyzed in Refs. 27 and 28. Figure 6 shows the dependence found by the semiempirical one-MNDO method in Ref. 27, and the dependence obtained by Clementi et al.[28] using the AFHF potential fitted to the ab initio calculations (see also Ref. 29). One can see that Clementi's calculation, which ignores nonadditivity, gives values that are much too low. In reality, the energy of the hydrogen bond (per bond) already saturates for $n \simeq 10$. This means that solid aerosol particles, coated with a very thin hydrate shell can be regarded as water drops when modeling condensation processes.

Some data indicate that the “gas-particle” transformation in the formation of sulfate aerosol occurs with the participation of molecular complexes. Moreover, the formation of aerosols in both the average atmosphere and a relatively unpolluted troposphere passes through a stage in which cluster particles interact (Ref. 30, p. 33).

In polluted air photooxidation of $SO_2$ to $SO_3$ occurs several orders of magnitude more rapidly than in a clean atmosphere,[31] so that it is very likely that gas-phase $SO_2$ complexes are entrained into this process. In Ref. 2 it is shown that in a low-temperature oxygen matrix direct photooxidation of the dimers $(SO_2)_2$ to $S0_3$ occurs, while $SO_2$ monomers are photochemically inert under the same conditions. This confirms the important role that $(SO_2)_2$ dimers apparently play in the formation of "acid rains."

*Table I.*

| Complex | μ, D | | References |
|---|---|---|---|
| | M = $SO_2$ | M = $SO_3$ | |
| AR...M | 1.5 | 0.2676 | 33,34 |
| $N_2$...M | – | 0.46 | 34 |
| $SO_2$ M | 1.4052 | – | 35 |
| $H_2O$...M* | 6.94 | 7.28 | 36,37 |

**CNDO/*2

The dimers $(SO_2)_2$ as well as a number of other bimolecular complexes of sulfur oxides have been studied experimentally and theoretically. Thus the study of purely rotational spectra of complexes forming in gas jets expanding freely into a vacuum has made it possible to determine the geometric parameters and the dipole moments of the complexes (see Table 1). The precise symmetry of the ground state of $(O_2)_2$ has still not been established; in Ref. 35 it is shown that the orientation of the monomer components is different from the mutual orientation of the nearest neighbors in a sulphur dioxide crystal. Experimental data on the parameters of the potential surfaces and spectroscopic constants of the complexes make it possible to verify the results of quantum-chemical calculations. The latter are now employed in nonempirical ab initio and semiempirical schemes for calculating the possible paths of gas-phase reactions and the kinetics of formation of sulphate molecules.[37-41] Spectroscopic studies of phototransformations in inert cooled matrices are also very useful. In particular, as shown in Ref. 42, the transformation of $SO_3$ into $H_2SO_4$ occurs in the presence of two or more molecules of water. The spectra of $H_2O$ and $SO_2$ complexes have been studied in Refs. 43 and 44, and the role of hydrogen-bonded dimmers $(H_2S)_2$ in the photooxidation of $H_2S$ under the action of ultraviolet irradiation of $H_2$ in an $O_2$ matrix at $T = 13$ K was studied in Ref. 45.

## 1.4. THE ROLE OF COMPLEXES IN ATMOSPHERIC CHEMISTRY

Most chemical reaction in the atmosphere are trimolecular. One or several constituent particles of a van-der-Waals complex can play the role of an internal third body in a chemical reaction, so that a reaction with the participation of complexes proceeds with a high efficiency. In recombination reactions the third body can simply carry away the excess energy. In more complicated cases the deformation of the potential surfaces of the ground and excited states accompanying the formation of a complex can result in the redistribution of the reaction products and (or) a distribution of the energy over the degrees of freedom. Thus, for example, in the reaction of $CO_2$ with barium atoms, resulting in the formation of BaO, the $(CO_2)_2$ dimers are four times more efficient than the monomers, and the rotational temperature of barium oxide in the reaction with the dimers is an order of magnitude lower than in the reaction with $CO_2$ monomers.[46,47] Another example is the reaction of oxygen atoms in the ground state O ($^3$P) with $(NO)_2$ and NO ... Ar complexes, studied in Ref. 48 by the method of crossed atomic-molecular beams. The angular distribution of the $NO_2$ products turned out to be isotropic in the case of the reaction with $(NO)_2$ and anisotropic for NO...Ar. The lifetime of complexes, which determines the angular distribution, is substantially different owing to the difference in the binding energies and the density of states of the complexes.

It is obvious that a detailed analysis of the flow of reactions involving complexes will be possible only if the potential surfaces and dynamics of the redistribution of internal energy are studied, i.e., after reliable models of elementary processes are constructed and data based on the properties of the complexes are accumulated. In this paper we shall restrict our attention to several examples of special interest for atmospheric chemistry.

In Ref. 49 it is shown that the oxidation of the hydroperoxide radical

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (1)$$

proceeds at low pressures through the formation of the complex $(HO_2)_2$. The very important role of the $HO_2$ radical in the kinetics of hydrogen-oxygen mixtures makes it necessary to study more carefully the properties of $(HO_2)_2$ dimers as well as other related complexes. The latter include, for example, the complexes $HO...HO_2$, $NO_2...HO_2$, and $NH_3...HO_2$. The observed rate of the reaction (1) is 2.5 times higher than (at 298 K) in the presence of several torr of $H_2O$ or $NH_3$ owing to the formation of 1:1 complexes, which are more reactive than $HO_2$ monomers. Figure 7 shows the structures of the complexes $HO_2...H_2O$, $HO_2...NH_3$, $HO_2...NO_2$, and

$HO...HO_2$ based on quantum-mechanical calculations. According to Ref. 51, at $T$ = 298.16 K and 100% relative humidity ($P_{H_2O}$ = 23.76 mm Hg) approximately 3.5% of the $HO_2$ molecules form $HO_2...H_2O$ complexes. Thus the content of these complexes cannot be regarded as negligibly small and they must be taken into account in models of the lower atmosphere.

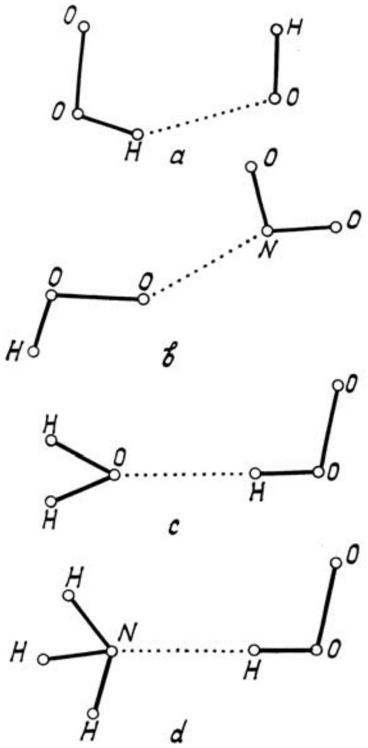

*FIG. 7. The structure hydroperoxide radical:*
*a) $R_{O...H}$ = 2.003 Å; $D_e \cong$ 4.6 kcal/mole*[50];
*b) $R_{O...N}$ = 1.418 Å; $D_0$ = 23 kcal/mole*[51];
*c) $R_{OO}$ = 2.776 Å; $D_e$ = 9.1 kcal/mole*[51];
*d) $R_{NO}$ = 2.75 Å; $D_e$ = 12.0 kcal/mole*[52].

The main sulphur-containing gas in the earth's atmosphere is sulphur dioxide $SO_2$. Volcanic gases contain from 1 to 10% $SO_2$ and, for example, the emission of $SO_2$ into the atmosphere constituted 900 tons/day in the eruption of the Mt. St. Helens volcano.[53] In the period from 1971 to 1978 more than one half of the sulphate aerosol in the lower stratosphere was of volcanic origin (Ref. 54, p. 261). The mechanism of the transformation of sulphur dioxide into sulphuric acid, proposed by Calvert and Stockwell, includes the following chain of reactions:

$$SO_2 + OH + M \rightarrow HOSO_2 + M \tag{2}$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \tag{3}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{4}$$

followed by reduction of hydroxyl in the reaction of $HO_2$ with NO. Calculations performed with the help of the semiempirical CNDO/2 method of quantum chemistry[37] have shown that the activation barrier between the complex $H_2O...SO_3$ and $H_2SO_4$ molecule is equal to about 3.3 kcal/mole. According to the data of Refs. 37 and 56 the isomerization of $H_2O...SO_3 \rightarrow H_2SO_4$ occurs within several hundreds of microseconds. As one can see from Fig. 8, however, a more accurate *ab initio* calculation predicts a much higher isomerization barrier, ranging from 23 to 31 kcal/mole, depending on the basis employed. For this reason, the probability of a spontaneous transformation of $H_2O...SO_3$ into $H_2SO_4$ turns out to be low, and in most cases the complex decomposes into the starting product.

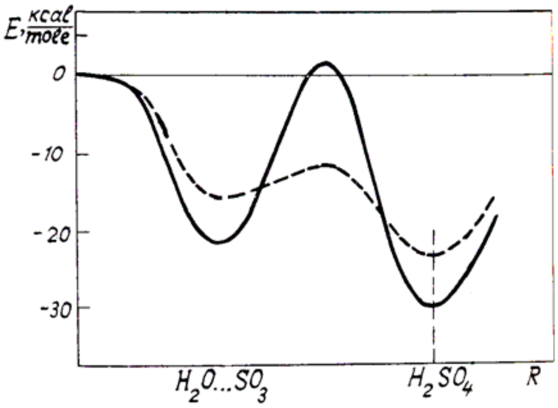

*FIG. 8. The interaction potential for* $H_2O$ *and* $SO_3$ *along the reaction coordinate R: the solid curve is the result of an ab initio calculation;*[38] *the dashed curve is the result of a CNDO/2 calculation.*[39]

It is obvious that further investigations will be required in order to finally determine the degree to which complexes participate in the formation of sulphuric acid particles in the atmosphere. There exist data indicating that intermediate complexes are formed in an entire series of other atmospheric chemical processes,[30,54,57] for example,

$$NO + O_3 \rightarrow NO...O_3 \rightarrow NO_2 + O_2 \tag{5}$$

$$OH + NO_2 \rightarrow HOONO \rightarrow HNO_3. \tag{6}$$

Processes connected with the "ozone hole" have been of special interest in the last few years. In particular, the catalytic cycle proposed in Ref. 58. includes the photodissociation reaction

$$Cl_2O_2 + h\nu \rightarrow Cl + ClOO \tag{7}$$

with the participation of a dimer, formed by the radical ClO. The structure and properties of this dimer have not been established precisely, but the temperature dependence of the equilibrium dimerization reaction constant

$$ClO + ClO + M \rightleftarrows (ClO)_2 + M \tag{8}$$

has made it possible to determine[59] the enthalpy of the reaction $\Delta H_1^0 = -72.5 \pm 3.0$ kJ/mole. Under the conditions of the Antarctic circumpolar vortex (middle of September, altitude of 18–20 km, [CIO] = $1.8 \cdot 10^9$ mole/cm$^3$) the reaction (8) is slowest, and it is precisely this reaction that determines the rate of the catalytic destruction of ozone with the participation of the radical CIO.

The last example in this section is connected with the photochemistry of ozone. Thus far $(O_2)_2$ particles — oxygen dimers — have been ignored in the study of protochemical transformations of ozone. As shown in Ref. 60, ozone molecules can appear as a result of the direct photodissociation of oxygen dimers $(O_2)_2$ accompanying the absorption of radiation with wavelength $\lambda = 2480$ Å.

It is also known (see, for example, Ref. 54, p. 7) that one of the catalytic cycles of ozone results in the existence of a correlation between $O_3$ and CO that depends on the local concentration of nitrogen oxides.

$$\begin{array}{l} CO + OH \rightarrow H + CO_2; \\ H + O_2 + M \rightarrow HO_2 + M; \\ HO_2 + NO \rightarrow OH + NO_2; \\ NO_2 + h\nu(<400\ nm) \rightarrow NO + O; \\ O + O_2 + M \rightarrow O_3 + M \\ \hline CO + 2O_2 \rightarrow CO_2 + O_3. \end{array} \qquad (9)$$

The reaction (9), however, could be a single-stage reaction. In this case it can proceed, as pointed out in Ref. 61, with the participation of excited oxygen dimers

$$CO + (O_2^*)_2 \rightarrow CO_2 + O_3. \qquad (10)$$

Oxidation of trace gases such as CO by oxygen dimers is possible if the dimers are not in the ground state, but rather in electronically excited states, for example

$$^1\Delta_g + {}^1\Delta_g \text{ or } {}^1\Sigma_g^+ + {}^1\Sigma_g^+. \qquad (11)$$

In this case the excitation energy (~ 2 and 3.6 eV) permits overcoming the high activation barrier of the oxidation reaction. Unfortunately, the radiative decay of oxygen and collisional quenching of the excited states of oxygen dimmers have not been adequately studied. This makes it impossible to establish, at the present time, definitely the degree of importance of processes of the type (10) for ozone photochemistry. It is interesting that the concentration of singlet oxygen molecules, engendering dimers in the stratosphere, is not so low; at altitudes from 30 to 50 km $[O_2(^1\Delta_g)]$ varies from $10^8$ up to $10^{10}$ mole/cm$^3$, i.e., its concentration is higher than that of CIO and is of the order of the concentrations of NO, $NO_2$, and $HNO_3$ (Ref. 62, p. 80). For this reason, in the stratosphere, even oxygen dimmers in the metastable states (11) can apparently be as abundent as, for example, the radical OH, Cl atoms, or $H_2O_2$ molecules.

In addition, free chlorine atoms and the radical CIO, as is well known,[63] efficiently generate singlet oxygen in reactions with hydrogen peroxide, and this makes it possible, in particular, to realize chemical pumping of an iodine laser.[64] It seems very probable that singlet oxygen and the dimers formed by it are an important part of the stratospheric ozone cycle and they must be taken into account in the construction of models.

## 1.5. THE ROLE OF COMPLEXES IN THE RELAXATION OF THE INTERNAL ENERGY OF MOLECULES

It was pointed out above that the rates of collisional quenching of electronically excited complexes are unknown. Unfortunately, there is also obviously not enough data on the relaxation of the other forms of energy in weakly coupled complexes. Relaxation processes can be divided into intra- and intermolecular. The former are related with the redistribution of energy within a complex, for example, accompanying the transfer of electronic or vibrational excitation of the constituent particles of the complexes to low-frequency modes, associated with weak coupling. In those cases when the excitation energy exceeds the energy of dissociation of a weak bond, one can talk about the process of predissociation of complexes and the lifetime of the complex is determined by the rate of energy exchange between the fast and slow subsystems. The vibrational predissociation of van-der-Waals complexes forms the basis of one of the methods of the spectroscopy of complexes and is widely studied theoretically and experimentally.[65]

There is no doubt that the association of molecules allows for more rapid intermolecular relaxation of energy, in particular, in VT and VV′ processes.[66,67] It is well known that the VT relaxation process is determined by the lowest vibrational quantum $\omega_{min}$ of a molecule,[68] and in addition $\ln \tau_{VT} \sim \omega_{min}$. Moreover, for a fixed vibrational energy $E$ the density of vibrational states $\rho(E)$ increases significantly with the formation of a complex, since

$$\rho(E) \simeq \frac{E^{s-1}}{(s-1)\prod_{i=1}^{s} \hbar\omega_i},$$

where $s$ is the number of active vibrational degrees of freedom and $\omega_1$ are the vibrational frequencies.

It has been proved experimentally[69] that the vibrational relaxation of $\nu = 1$ states of the molecules DF and HF in collisions with $(DF)_2$ dimers proceeds via the formation of an intermediate complex, which decays after redistribution of vibrational energy in it. The relaxation time is actually determined by the rate of formation of the complexes.

Investigation of the vibrational relaxation of molecules in water vapor$^{70-7}$2 showed that the dispersion and damping of ultrasound in humid air are determined by the association of molecules. Ultrasonic measurements have made it possible to determine the enthalpy and entropy of dimerization of water molecules and to estimate the content of the larger associates.

The problems of the kinetics of relaxation with the participation of van-der-Waals molecules are closely related with metastable states formed in pair collisions of molecular particles. Detailed information about the metastable and stable states of complexes can be obtained by modern spectroscopic methods.

## 2. INTERMOLECULAR PAIR INTERACTIONS AND RADIATION ABSORPTION IN THE ATMOSPHERE

### 2.1. GENERAL IDEAS ABOUT THE SPECTRA OF BIMOLECULAR COMPLEXES

The spectral manifestations of van-der-Waals complexes are subject to large variations depending on the temperature and density of the gas, since the concentration of the complexes is related nonlinearly with the density, while the dissociation limit is reached at comparatively low temperatures. The potential barriers for transpositions of particles within a complex are low: the nonrigidity of a complex results in a complicated structure of vibrational-rotational states. The form of the spectrum depends not only on the thermal excitation, but also on the selective excitation, and in addition the spectral lines are broadened differently with selective pumping of different modes.

| Monomer mode | $\nu_{com} - \nu_{mon}$ cm$^{-1}$ |  | Ref. |
|---|---|---|---|
|  | $(CO_2)_2$ | $(CO_2)_3$ |  |
| $\nu_1 + \nu_3$ | -0.850 | - | [74] |
| $2\nu_2 + \nu_3$ | -1.294 | 0.978 |  |
| $\nu_3$ | 1.63 | - | [75] |
| $\nu_1$ | -4.1 | - | [76] |

The shifts of the vibrational bands accompanying the formation of van-der-Waals complexes are, as a rule, small. The magnitudes of the shifts are determined by the type of vibrations as well as by the geometry of the complex and the binding force. For example, with the formation of a hydrogen bond the perturbation of the frequency of the stretching vibration of the proton-donor molecule cannot be regarded as small. The square of the frequency of the $\nu_{OH}$ vibration depends linearly on the force constant of the H bond.[73] For example, in the water dimmer $(H_2O)_2$ the frequency shift $\Delta\nu = \nu_{OH}$ (free) $- \nu_{OH}$ ((bound) is greater than 100 cm$^{-1}$. As one can see from Table II, the shifts of the intramolecular frequencies accompanying the formation of more weakly coupled $CO_2$ associates do not exceed several cm$^{-1}$. In Refs. 77–79 it is shown theoretically and experimentally that if molecules having degenerate vibrations are entrained into a complex, then the removal of the degeneracy owing to the intermolecular interaction can result in the appearance of new vibrational transitions. One can see from Fig. 9 that even in the weakly bound dimmer $(CO_2)_2$ the new intramolecular vibrations are split, in this case, by several tens of cm$^{-1}$ from the monomeric vibrations engendering them. This example demonstrates that in some cases the van-der-Waals complexes can efficiently absorb energy at frequencies that are completely unrelated with the frequency shifts accompanying complex formation and they are shifted by large amounts from the allowed transitions for monomeric molecules.

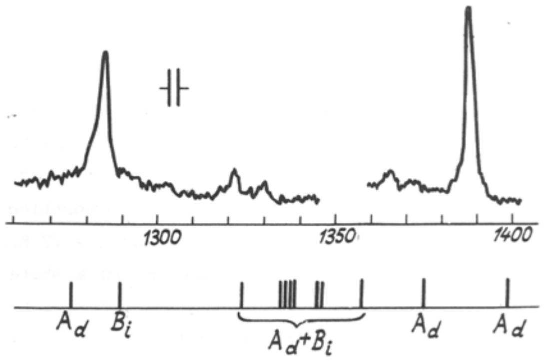

*FIG. 9. The region of the Fermi doublet in the spontaneous Raman scattering spectrum in a jet of carbon dioxide gas expanding into a vacuum.*[79] *The bottom part of the figure shows the theoretical spectrum of the P-dimer of* $CO_2$.[78]

The formation of a complex changes the selection rules and induces previously forbidden transitions. In a number of cases diffuse spectra of van-der-Waals complexes can be identified with collision-induced spectra.[80] According to the usually adopted definition, the latter are related with a short-time dipole moment, induced in one of the molecules in the process of collisional interaction (during the collision time $\tau_{col}$) with another molecule. Indeed, the rotation of monomers effectively averages the intermolecular potential, though, as model trajectory calculations show,[81] the anisotropy of the potential affects decisively the appearance of quasibound and bound states. For this reason, in the simplest systems (for example, atom-diatomic molecule) the relative fraction of the bound and quasibound states can be small, whereas for anisotropically interacting polyatomic molecules at not too high temperatures it can be assumed that the relative fraction of states with lifetimes $\tau > \tau_{\text{col}}$ will predominate over the "free" states with $\tau \lesssim \tau_{\text{col}}$. .At the same time, in many cases the lifetime $\tau$ of a coherent train of vibrations of a complex is less than the time between collisions $\tau_{\text{f.f.}}$, so that the spectral lines of complexes are strongly broadened. Since the density of states is high and the rotational constants of the complexes are small it can be expected that diffuse, unresolved bands will form even at low temperatures. Such diffuse bands should look like the contours of col 1 is ion-induced bands.

## 2.2 DIMER INTERPRETATION OF ABSORPTION BANDS OBSERVED IN THE ATMOSPHERE

The interpretation of diffuse bands as collision-induced bands gives in most cases the qualitatively correct picture of the spectrum. Figure 10 shows the spectrum of the absorption bands of nitrogen at $P = 739$ torr and $T = 77$ K; this spectrum was obtained in Ref. 82 in a White cell with wavelength $L = 154$ m. The area under the theoretical curve, corresponding to the "induced" absorption, was arbitrarily chosen to be equal to 90 % of the area under the experimental curve. The difference of the experimental and theoretical spectra in Fig. 10 is attributed by McKellar[82] to the spectrum of bound states of $(N_2)_2$ dimers, but as shown in Ref. 82 the interpretation of the spectrum of nitrogen dimers still presents insurmountable difficulties.

McKellar studied in an analogous manner, under laboratory conditions, the far-IR spectrum of hydrogen.[83] In this region of the spectrum peaks corresponding to the transitions $l = 1 \leftarrow 2$, where $l$ is the rotational quantum number of the dimer $(H_2)_2$, can be clearly seen against the background of the induced-absorption spectrum. The van-der-Waals coupling in the hydrogen dimer is so weak that only states with $l = 0$ and 1 are actually bound, while for $l = 2$ and 3 rotationally metastable states are formed. The free states with $l > 3$ correspond to the induced spectrum.

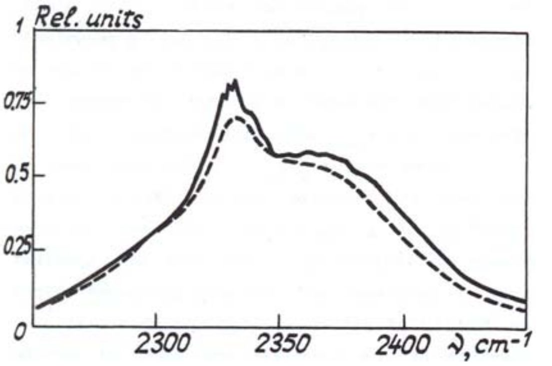

*FIG. 10. The IR spectrum of nitrogen at $T = 77$ K and $P = 739$ torr.[82] The dashed curve shows the theoretical induced-absorption spectrum.*

As shown in Fig. 11 the transition with $\omega = 351\ \text{cm}^{-1}$ in the laboratory spectrum of $(H_2)_2$ dimers is clearly manifested in the IR spectrum obtained by the Voyager space probe in Jupiter's atmosphere. An analogous spectrum was obtained by Voyager during the Saturn flyby. Thus the proposition first stated in Refs. 84 and 85 was proved, and thereby the existence of stable dimerized molecules was first proved in the atmospheres of the planets. Hydrogen comprises 89 and 94% of the atmospheres of Jupiter and Saturn, respectively.[86] The volume content of the minor components, such as methane and ammonium, is $\sim 10^{-4}$, but they are incomparably more capable of forming bound molecules than is hydrogen. The ratios of the binding energies of the corresponding dimers to the binding energy of $(H_2)_2$ constitute at least an order of magnitude for methane and a factor of 50 for ammonium.[87,88]

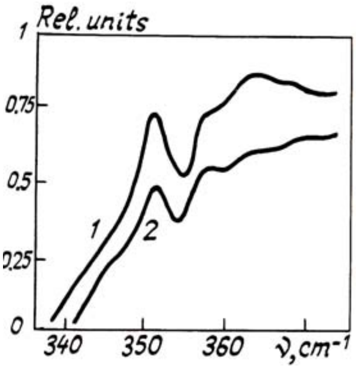

*FIG. 11. Comparison of the laboratory (1) spectrum of hydrogen[83] with the Voyager-1 spectrum in Jupiter's atmosphere (2).*

Binary complexes of oxygen and nitrogen are probably the only representatives of van-der-Waals molecules whose absorption in the visible and near-IR regions of the spectrum has been recorded spectroscopically in the earth's atmosphere. The fact that the observed bands do not have a rotational structure makes it possible to associate them with the spectra of short-lived metastable particles, which occupy an intermediate position between the spectra of stable dimers and the spectra "induced" by collisions. A complete description of the spectra of such molecules can be obtained based on an analysis of all possible bound and q.uasibound states of a colliding pair, so that the observed diffuse bands are best interpreted as anomalously broadened bands of metastable dimers. As we have already pointed out, the bands belonging to the molecules $(O_2)_2$ ($\lambda = 6299$, 5769, and 4773 Å), were first observed by Janssen[12] in the absorption spectra of the atmosphere with the sun low on the horizon. A fundamental study of the spectra of oxygen in different aggregate states was performed by V.I. Dianov-Klokov.[89–91] In particular, he studied the diffuse bands in the near-IR region of the spectrum ($\lambda = 1.26$ μm and $\lambda = 1.06$ μm), which belong to dimers or, more precisely, $(O_2)_2$ collisional pairs in the atmosphere. These bands are the analog of the

”atmospheric” and ”IR-atmospheric” bands of oxygen $^3\Sigma_g^- + ^1\Delta_g(0) \leftarrow 2^3\Sigma_g^-$ and $^3\Sigma_g^- + ^1\Delta_g(1) \leftarrow 2^3\Sigma_g^-$, where 1 in parentheses indicates vibrational excitation. We note that in the molecule $(O_2)_2$ the electronic and vibrational excitation in the state $^3\Sigma_g^- + ^1\Delta_g(1)$, for example, can be regarded as localized both in the same $O_2$ molecule and in different molecules.

According to the data of Ref. 92 the 1.26 μm band in the spectrum of $(O_2)_2$ dimers is approximately three times stronger than the 1.06 μm band, while the analogous ratio in the spectrum of the $O_2$ molecules is about 200. The exact reason for this increase of the intensity has not been established. Possibly, the deformation of the upper electronic state accompanying the formation of the complex results in an increase of the Franck-Condon factor for the 1.06 μm transition 1 ← 0. There are also other speculative explanations of this fact.[72] An increase of the intensity of the 1.06 μm band results in the fact that under atmospheric conditions this band is virtually completely determined by oxigen dimers (its strength depends quadratically on the pressure), while the O—O band of the 1.26 μm transition is masked by the fine structure of the ”atmospheric” band of $O_2$.

The ground state of the molecule $O_2(X^3\Sigma_g^-)$ has the spin $s = 1$, which makes this molecule a rare exception among the usually singlet ($s = 0$) diatomic molecules. When a dimer forms, in accordance with the rules for adding angular momenta the spin of the ground state $s = 0$, 1, or 2. Thus near the triplet state there arise singlet and quintet states. The study of the spectra of isotopically substituted $(O_2)_2$ molecules in a low-temperature matrix of Ne atoms[93] has shown that the singlet-triplet splitting of the ground state is equal to about 55 $cm^{-1}$. Model calculations of the spectra of intermolecular dimers $(O_2)_2$ (see, for example, Ref. 94) shows that the frequencies of the four low-frequency vibrations of the dimer are equal to approximately 10—50 $cm^{-1}$. Thus near the ground state the structure of the electronic-vibrational terms of the $(O_2)_2$ molecule is extremely complicated. Theoretical modeling of the spectrum of the energy states of oxygen dimers in Ref. 95 showed that when the retarded internal rotation is taken into account the complex spin-rotational fine structure of the spectrum turns out to be very sensitive to the geometry of the dimer, the nature of the internal motions, and the magnetic interaction constants. The study and establishment of these characteristics is an urgent problem for high-resolution spectroscopy, and it apparently can be solved using the gas-dynamic method for generating oxygen complexes.

## 2.3. THE MANIFESTATION OF DIMERIZATION OF MOLECULES IN THE CONTINUOUS ABSORPTION SPECTRA

In the spectroscopic part of this review it would be impossible not the mention water dimmers in the atmosphere and the problem of continuous absorption. The question of the role of water dimmers in the continuous absorption of IR radiation by water vapor, especially in the region 8—13 μm, is still the subject of lively discussions (see, for example, Refs. 96—102). There is no doubt that the physical nature of the continuous absorption is connected with intermolecular interactions. However the question of whether the bound and quasibound states must be taken into account in order to explain this effect or whether it is sufficient to take into account the corrections to the shape of the spectral linesowing to “free” flyby interactions of $H_2O$ molecules remains open. We believe that the essence of this discussion is largely one of choosing a better apparatus for describing a complicated physical phenomenon.

It is well known that the association of molecules is manifested in the thermodynamic,[103] transport,[104] and spectral[73,105] properties of water vapor via the formation of hydrogen bonds. It is difficult to imagine that the formation of bound and quasibound states can be completely ignored under the conditions of the atmosphere. One of the most common arguments against the ”dimer” hypothesis of absorption in the continuum of water vapor is the analysis of frequencies and intensities of intermolecular transitions (see, for exajnple, Refs. 97 and 106). Indeed, the wings of the librational, highest-frequency bands of intermolecular vibrations decay rapidly on the short-wavelength side for ω ≳ 600—700 $cm^{-1}$, while the continuum absorption varies relatively slowly as a function of the frequency. It can be shown, however, that the entire region of the 8—13 μm transmission window of the atmosphere is closely filled with overtones and combination bands of intermolecular vibrations. [107,108] In addition, even in the harmonic approximation their intensities are comparable to the intensities of first-order transitions.[108] The first attempt to obtain a more complete solution of the anharmonic problem by a variational method showed[109] that when the mechanical and electron-optical anharmonicities are taken into account the high-order bands are strong enough in order for the continuum absorption to be interpreted from the viewpoint of the dimer mechanism.

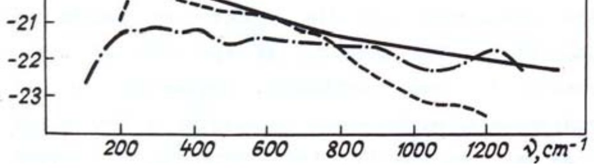

*FIG. 12. The spectral dependence of the absorption of $(H_2O)_2$ dimers for $\lambda > 8$ μm, $T = 300$ K, $P_{H_2O} = 10$ mbar, the molar fraction of the dimers $x_2 = 3 \cdot 10^{-4}$; the dashed line is taken from Ref. 108; the dot-dashed line corresponds to the data of Ref. 109; the solid line represents the experimental continuous absorption.*[106]

As shown in Fig. 12, the qualitative behavior of the absorption spectrum agrees with the observed behavior. Nonetheless the question cannot be regarded as solved. First of all, great efforts will probably be required to determine more accurately the characteristics of the potential surface of water dimers that would make it possible to perform calculations with the required accuracy. Second, it is necessary to construct a theoretical model for describing the broadening of spectral lines that ultimately leads to the formation of the continuous absorption spectrum and describing its anomalous temperature behavior.[110] A step in this direction was made in Ref. 111, where it is shown that the number of metastable dimers (the discussion concerns only vibrational ly excited molecules) can be large at temperatures much less than the dissociation energy of the complexes. Metastable molecules can decay spontaneously over a time shorter than the intercollision time. Thanks to this their spectral lines are broadened significantly more strongly than in the impact-collision mechanism of broadening and thus continuous absorption can be formed.

One of the most convincing arguments against the dimer mechanism of absorption in the water vapor continuum was recently put forth in Ref. 100, where the line and continuous absorption at the lasing frequencies of the $CO_2$ laser were specially studied. Measurements performed with the help of a sensitive opticoacoustic cell showed that the temperature dependences of the continuous absorption of water vapor at the lasing frequencies of the $CO_2$ laser 10P(20), 10P(24), and 10P(30) agree with the assumption of dimmer absorption in a wide temperature range $T = 253$–$345$ K. For the 10P(30) line, which depends least on the effect of close lines of water vapor, the dimer binding energy was found to be $D_e = -6.31$ kcal/mole, while the absorption cross section $\sigma_d = 2.6 \cdot 10^{-20}$ cm$^2$/mole. Measurements of the line and continuous absorption were also performed in Ref. 100 in a diffusion chamber, in which a constant vertical temperature gradient was maintained. This made it possible to achieve a state of supersaturation of water vapor, which had a maximum along the vertical axis of the chamber. For the comparatively low supersaturations achieved $1 \lesssim S \gtrsim 1.5$ the dimer concentration is proportional to the squared degree of saturation $s$, and not the squared local partial pressure $P$. Indeed, the dependence of the continuous absorption on the 10P(20) line on the height revealed a distinct maximum, while the line absorption on the 10R(20) line varies nonotonically over the height. Estimates showed that if the absorption at the maximum is identified with dimer absorption, then the absorption cross section $\sigma_d$ on the indicated laser line does not exceed $10^{-21}$ cm$^2$/mole. This magnitude is significantly less (by more than an order of magnitude) than the value obtained previously by measurements under static conditions. Based on the results obtained in experiments in supersaturated vapor it was concluded in Ref. 100 that the absorption cross sections of the dimers are too small to explain the observed continuous absorption. However a number of objections can be raised against the arguments put forth in Ref. 100. Theoretical estimates of the dimer concentrations (necessary in order to estimate the absorption cross sections based on the experimental data) can also be performed for equilibrium conditions to within an order of magnitude. Furthermore, the stability of the processes in a diffusion chamber and the possibility of interpreted unequivocally raises some doubts. Hinderling et al.[100] themselves point out that the theoretical description of the line absorption as a function of the height, relating the absorption with the stratification of water vapor and the buffer gas (nitrogen) in the chamber, is inadequate. In our opinion, analogous experiments using the gas-dynamic method for creating supersaturated vapor could be more convincing. In this case, practically any degree of supersaturation can be created under stationary and well-controlled conditions.

The results, presented above, of some theoretical and experimental studies of absorption in the 8–13 μm transmission window of water vapor show that it is not yet possible to achieve quantitative agreement between *a priori* theoretical models and the experimental data. The reason for this undoubtedly lies in the very superficial level of knowledge about the formation of the absorption spectrum of a nonrigid pair of interacting molecules of water. A quite complete theoretical description of the spectrum can now be obtained only for the simplest systems, for example, for $N_2$...Ar. Even for complexes with four atoms, for example, $(N_2)_2$, the theoretical models do not agree with the experiment.[82, 112]

We note that the dimers $(N_2)_2$ were used in Ref. 113 to interpret the continuous absorption in the collision-induced 4-μm band of nitrogen in the atmosphere In Ref. 113 it was also suggested that the continuum beyond the edge of the 4.3 μm band of $CO_2$ is connected with $CO_2$...$N_2$ complexes, while the absorption near 4.2 μm is determined by $N_2$...$H_2O$ complexes. Direct estimates of the envelope of the low-frequency vibrational-rotational spectrum of hydrogen-bonded complexes $N_2$...$H_2O$ were made in Ref. 114, but these calculations must be substantially improved based on more accurate molecular characteristics of the complex and better spectroscopic models.

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