Exciton and exciton-magnon absorption of light in antiferromagnetic-oxygen

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Absorption of light in the antiferromagnetic α-phase of oxygen at $T = 1.5$°K is measured at frequencies corresponding to the ${}^1\Delta_g \leftarrow {}^3\Sigma_g$ and ${}^1\Sigma_g \leftarrow {}^3\Sigma_g$ transitions in the O_2 molecule. It is shown that these transition in α-oxygen are primarily of an exciton-magnon nature. The observed fine structure of the absorption bands is ascribed to anisotropy of the exciton and magnon bands in α-oxygen. Values of the transition oscillator strengths are presented and the bandwidths of the excited states are estimated.

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1. INTRODUCTION

Experimental and theoretical investigations of molecules in oxygen crystals have been carried out systematically for many years. This increased interest in oxygen is due in particular to its unique magnetic and particularly spectral properties due to the uncompensated spin of the O_2 molecule (ground state ${}^3\Sigma_g^-$). Thus, for example, the absorption spectra of the compressed gas and liquid reveal already three series of bands which are missing from the spectrum of the O_2 molecules and correspond to simultaneous direct excitation of two molecules by one photon. In this case each of the molecules of the pair goes over from the ground triplet state into one of two lowest excited singlet states ${}^1\Delta_g$ and ${}^1\Sigma_g^+$, so that the final state is one of the states $\Delta\Delta$, $\Delta\Sigma$, or $\Sigma\Sigma$. In the antiferromagnetic modification of oxygen (α-O_2, a two-sublattice collinear antiferrodielectric), all the bands of this double or bimolecular absorption reveal at T = 4° K a fine structure,[1,2] some of the features of which have been theoretically interpreted.[3,4]

Much attention has been paid and is still being paid to the absorption of oxygen with excitation of the states $\Delta\Delta$, $\Delta\Sigma$ and $\Sigma\Sigma$. At the same time, the regions of the transitions ${}^1\Delta_g \leftarrow {}^3\Sigma_g^-$ and ${}^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ have been far from sufficiently investigated, especially in crystals. Thus, the bands of these transitions were investigated in [5,6] under conditions that were not very favorable for the observation of a fine structure. Recent papers cite more detailed information on the position and structure of the bands of these transitions.[7-9] In all the calculated papers it was assumed that the absorption of this frequency region is due to transitions of individual O_2 molecules into corresponding excited states, and only Litvinenko, Eremenko, and Garber[7] have advanced the hypothesis that two O_2 molecules may take part in the vibronic transition of the ${}^1\Delta_g$ band.

In this study we have investigated experimentally and theoretically the absorption of light in the region of the excited states ${}^1\Sigma_g^+$ and ${}^1\Delta_g$ of α-oxygen at T = 1.5° K. We show that the observed absorption and its intensity are due mainly to exciton-magnon transitions. Starting from the collective nature of the excited states of the crystal, we present theoretical arguments that explain the observed singularities of the structure of the absorption bands, and also help estimate the widths of the exciton and magnon bands.

2. DETAILS OF THE EXPERIMENT

Pure oxygen was crystallized from the liquid phase in quartz cells in a cryostat, where further cooling to 1.5° K took place (pumped-on liquid helium). The gaps between the flat quartz windows of the cells ranged in the different experiments from 0.2 to 2.5 mm. The cracking of the crystal during the course of its cooling, owing to the phase transitions, leads to an increase of the length of the optical path in comparison with the size of the gap. This circumstance does not play any particular role in the determination of the line frequencies, but is important when it comes to measurement of the absorption coefficient. To prevent errors connected with the scattering of light by the boundaries of the microblocks, we established the relation between the measured absorption intensity of each of the bands and the value of the gap in the cell. A certain increase of the absorption coefficient due to scattering with increasing length of the sample was approximated by us at small thicknesses by a straight line, extrapolation of which to "zero thickness" has made it possible to reduce to a minimum the error due to the scattering. In addition, wherever possible the measurements of the various bands were made with one and the same cell. The small error introduced by the dependence of the scattering coefficients on the wavelength of the light can be neglected because of the smallness of the employed frequency interval.

The spectrum was recorded with a large-aperture SDL-1 spectrophotometer with a diffraction grating. The dispersion in the investigated region was 32 Å/mm; the spectral width of the slit did not exceed 1.6 cm^{-1}; the light source was an incandescent lamp, and the receiver an FÉU-62 photomultiplier. The spectrophotometer was calibrated against the mercury lines.

Transition	Absorption band	O_2 [10]		α-O_2, $T=1.5$ K				
		ω, cm^{-1}	$F\cdot10^{-10}$	Total intensity		ω, cm^{-1}	A, cm^{-2}	$F\cdot10^{-10}$
				A, cm^{-2}	$F\cdot10^{-10}$			
${}^1\Delta_g \leftarrow {}^3\Sigma_g^-$	0—0	7882.4	0,0414	1300	512	7988	308	122
						8005	8.3	3.27
	0—1	9365.9		900	355	9471	172	67.7
						9482	123	48.5
	0—2			80	31.5	10933	14.3	5.62
						10944	9.4	3.72
${}^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$	0—0	13120.9	2,47	40	15.7	13168	2.3	0.90
	0—1	14525.7		5.7	2.26	14582	0.23	0,090

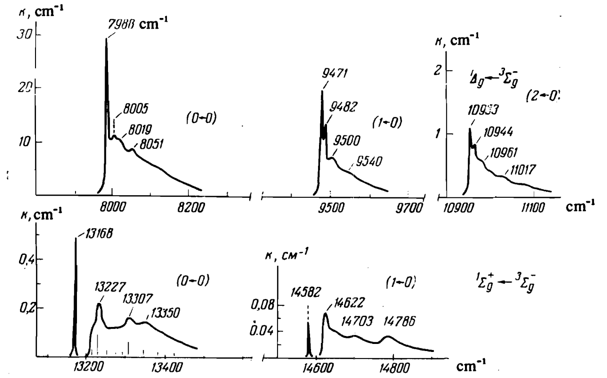

FIG. 1. Absorption curves of α-O_2 at T = 1.5° K.

The calibration was monitored by the narrow 13168-cm^{-1} α-O_2 absorption line (electronic line of the $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^{-1}$ transition), which was measured earlier with high accuracy.[8] The positions of the maxima were measured accurate to 1–2 cm^{-1} for the narrow and strong components of the absorption bands, and to 5–10 cm^{-1} for the broader ones. To identify the observed intrinsic absorption of α-O_2 and to compare it with the absorption of the O_2 molecules in the matrix, we used certain information obtained from the absorption spectra of O_2-N_2 solid solutions measured under the same experimental conditions.

3. EXPERIMENTAL RESULTS

a) The $^1\Delta_g \leftarrow {}^3\Sigma_g^-$ transition. Out of the five α-O_2 absorption bands observed in this region, we measured three, one electronic and two vibronic. The corresponding absorption curves are shown in Fig. 1, where the frequencies of the observed absorption peaks are indicated. The table lists the values of the oscillator strengths F, both the total strengths for each of the bands, and for the initial absorption peaks separated in them.

The total oscillator strength was calculated from the total area under the corresponding absorption curve, while the oscillator strength of each of the separated peaks was estimated as the area under the peak.

From a comparison of the oscillator strengths of this transition in the α-O_2 gas and in the crystal it follows that the total intensity of only the electronic band exceeds the intensity of the transition in the spectrum of the gas by four orders of magnitude; the first vibronic band in the crystal hardly differs in its strength from the electronic one, whereas in the gas spectrum they differ by two orders of magnitude.[10,11]

As seen from Fig. 1, the bands of this transition have a well-developed structure. A number of observed peaks (for example, 8019 and 8051 cm^{-1} in the 0–0 band) can be attributed to libronic replicas of the initial maximum, since similar intervals (32 and 70 cm^{-1}) were observed in the $\Delta\Delta$ transition.[2] In addition, it is seen that the initial lines of the bands are doublets, which are most clearly pronounced in the vibronic bands with distances 11 cm^{-1} between components in both bands. The doublet in the electronic band, with splitting 17 cm^{-1} and with components that differ greatly in strength, is somewhat less pronounced. We propose that the weak line separated by this interval pertains precisely to the doublet and not to the remaining structural components of the electronic band. It is also sharper than the others and is observed only in the electronic band, whereas the remaining maxima have their analogs in the vibronic bands.

It is important that the corresponding absorption curves in the O_2–N_2 solution do not have a similar doublet structure and the initial absorption lines in these curves are essentially single.

b) The $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ transition. Two observed bands of the $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ transitions are shown in Fig. 1; the oscillator strengths are given in the table. Both bands, electronic and vibronic, begin with single sharp lines 0–0 and 1–0, which appear to be strong because of the small half-width, but which in fact, as seen from the table, are weak. The interval between them is 10 cm^{-1} larger than the corresponding interval in the spectra of the gas and of the solution, this being way in excess of the measurement errors. The lines 0–0 and 1–0 are separated from the remaining fine structure components of the electronic and vibronic bands by narrow interval of almost total transparency. Outstanding in their intensity are, in the fine structure of both bands, broad lines located 60 cm^{-1} away from the 0–0 line in the electronic band and 40 cm^{-1} from the 1–0 line in the vibronic band. Each of these is connected with a number of weaker libronic lines.[8]

4. THEORY

A. The experimental data presented above show that the bands of the $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ transition, unlike the $^1\Delta_g \leftarrow {}^3\Delta_g^-$ transition, begin with sharp relatively weak lines that are separated from the continuous-absorption region. To understand the origin of these lines and also to explain on the whole the nature of the α-O_2 absorption in this frequency region, we have investigated the dependence of the integrated intensity of the absorption bands of an O_2–N_2 solution on the O_2 concentration. The results for the electronic bands are shown in Fig. 2; the vibrational bands behave analogously. We see that for the $^1\Delta_g \leftarrow {}^3\Delta_g^-$ transition this dependence is purely quadratic, thus indicating that two molecules take part simultaneously in the absorption. At the same time, in the case of $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ transition, in addition to the quadratic contribution, there is a linear contribution to the concentration dependence, which indicates that in this case part of the absorption is due to transitions of individual molecules. Accordingly, bimolecular transitions this energy region in α-O_2 can be attributed to exciton-magnon absorption, and single-molecule transitions to pure exciton absorption. In this case exciton absorption, which is allowed in the magnetic-dipole approximation, corresponds to the separated lines 0–0 and 1–0 of the $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ transition.[1)]

No analogous lines appear in the $^1\Delta_g \leftarrow {}^3\Sigma_g^-$ transi-

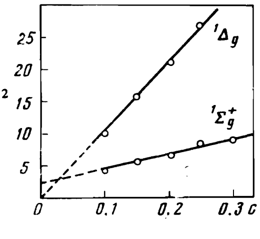

FIG. 2. Dependence of the intensity of the electronic absorption bands of the O_2–N_2 solution on the oxygen concentration c.

tion, in spite of the general appreciable enhancement of the absorption in O_2 in comparison with the gas. This is due to the smallness of the oscillator strength of the magnetic-dipole component in the $^1\Delta_g \leftarrow {}^3\Sigma_g^-$ transition, which, just as in the free molecule, is much weaker than the corresponding component for the $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ transition. It should be noted here that the 1–0 band of the $^1\Delta_g \leftarrow {}^3\Sigma_g^-$ transition was already attributed to exciton-magnon absorption.[7] This was done by comparing the relative position of this band in the α-O_2 spectra and in the spectra of the O_2–N_2 solutions at high O_2 concentration. However, the data on the concentration dependence of the integrated intensity offer convincing evidence that the other observed 0–0 and 2–0 bands of this transition should also be regarded as due to exciton-magnon absorption.

As to the exciton-magnon transitions in α-O_2, a group-theoretical analysis shows that they are allowed even in the electric-dipole approximation. These transitions are due to simultaneous excitation of the nearest molecules from different magnetic α-O_2 sublattices. Unfortunately, owing to the low group symmetry of the excited pair in the α-O_2 (group C_i), the direction of the dipole moment of the transition of a pair of molecules cannot be determined. If it is assumed that the crystalline environment does not lead to significant changes of the magnitude and direction of the dipole moment, calculated for the free pair [12,13], then it turns out that the dipole moments of the transitions, in which one of the O_2 molecules is excited in a state $^1\Delta_g$ or $^1\Sigma_g^+$ and the other changes the spin projection, are perpendicular to the plane of the pair, and the transition with excitation of the $^1\Delta_g$ state is more intense by approximately one order than the transition $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$.

B. The coefficient $K_j(\omega)$ of the exciton-magnon absorption of light of frequency ω and polarization j is determined, according to [14], by the expression

$$K_j(\omega) = -\frac{4\pi\omega}{Nc\eta v} \lim_{\varepsilon\to+0} \operatorname{Im} G_j(\omega+i\varepsilon),$$

where c is the speed of light, η is the light reflection coefficient, v is the volume of the unit cell, N is the number of cells, and $G_j(\omega)$ is the Fourier transform of the retarded Green's function

$$-i\theta(t)\langle[P^j_{eff}(t), P^j_{eff}(0)]\rangle,$$

in which

$$\theta(t) = \begin{cases} 1, & t \geqslant 0, \\ 0, & t < 0, \end{cases}$$

$$\mathbf{P}_{eff} = \sum_{\mathbf{n}\alpha,\mathbf{m}\beta,f} (1-\delta_{\alpha\beta})\mathbf{p}_{\mathbf{n}\alpha,\mathbf{m}\beta}(f) B_{\mathbf{n}\alpha}(f)\, b_{\mathbf{m}\beta} + \text{э. c.} \tag{1}$$

is the operator of the effective dipole moment of the transition of the crystal.[3] In (1), $\mathbf{p}_{\mathbf{n}\alpha,\mathbf{m}\beta}(f)$ is the dipole moment of the transition of the pair of molecules $\mathbf{n}\alpha$ and $\mathbf{m}\beta$ ($\mathbf{n}$ and $\mathbf{m}$ label the cells; α and β label the magnetic sublattices), in which the molecule $\mathbf{n}\alpha$ goes over into the f-th electronic state (f = $^1\Delta_g$, $^1\Sigma_g^+$), and the molecule $\mathbf{m}\beta$ changes the spin projection; $B_{\mathbf{n}\alpha}(f)$ and $b_{\mathbf{m}\beta}$ are the annihilation operators of the f-th electronic and spin excitations, respectively.

It is convenient to calculate $K_j(\omega)$ by changing over from the exciton to the magnon representation with the aid of the transformations

$$B_{\mathbf{n}\alpha}(f) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k},\mu} e^{i\mathbf{k}\mathbf{n}\alpha} U_{\alpha\mu}(\mathbf{k}) B_\mu(\mathbf{k}; f),$$

$$b_{\mathbf{n}\alpha} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k},\mu} \{e^{i\mathbf{k}\mathbf{n}\alpha} u_{\alpha\mu}(\mathbf{k})\, b_\mu(\mathbf{k}) + e^{-i\mathbf{k}\mathbf{n}\alpha} v_{\alpha\mu}(\mathbf{k})\, b_\mu^+(\mathbf{k})\},$$

where

$$\{U_{\alpha\mu}(\mathbf{k})\} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix},$$

and the coefficients of the u-v transformation for the spin excitations of αO_2 can be easily obtained from the results of the preceding paper.[15]

In the investigation of exciton-magnon absorption processes one frequently uses the approximation of noninteracting quasiparticles. This approximation is justified in most cases, since the matrix elements of the exciton-magnon interaction are as a rule small in comparison with the total width of the exciton and magnon bands, and allowance for this interaction does not lead to qualitative changes in the form of the absorption spectrum.[3,14]

We shall henceforth assume that the approximation of free exciton and magnons is suitable also for the α-O_2 crystal. Then, assuming that the main contribution to the effective dipole moment (1) is made by the nearest molecules from different magnetic sublattices, we obtain directly that the absorption of the wave polarized along and across the monoclinic axis is described by the coefficients

$$K_\parallel^f(\omega) = \frac{16\pi^2\omega}{Nc\eta v} \mathbf{p}_\parallel^2(f) \sum_{\mathbf{k},\mu} \cos^2\frac{\mathbf{ka}}{2} \sin^2\frac{\mathbf{kb}}{2} u_\mu^2(\mathbf{k})\, \delta[\omega-\varepsilon_\mu(\mathbf{k})-E_f(\mathbf{k})],$$

$$K_\perp^f(\omega) = \frac{16\pi^2\omega}{Nc\eta v} \mathbf{p}_\perp^2(f) \sum_{\mathbf{k},\mu} \sin^2\frac{\mathbf{ka}}{2} \cos^2\frac{\mathbf{kb}}{2}$$
$$\times\, u_\mu^2(\mathbf{k})\, \delta[\omega-\varepsilon_\mu(\mathbf{k})-E_f(\mathbf{k})]$$

(f ≡ $^1\Delta_g$. $^1\Sigma_g^+$). Here $p_\parallel(f)$ and $\mathbf{p}_\perp(f)$ are the dipole moments of the transition along and across the monoclinic axis of the crystal for the corresponding excitations, $u_\mu(\mathbf{k})$ are the coefficients of the u-v transformations: $u_1 \equiv u_{11} = u_{21}$; $u_2 \equiv u_{22} = -u_{12}$; $\epsilon_\mu(\mathbf{k})$ and $E_f(\mathbf{k})$ are respectively the energies of the magnon branch μ (μ = 1, 2) and of the f-th exciton (in collinear antiferromagnets, the exciton branches are degenerate[16]), the explicit expressions for which are

$$\varepsilon_\mu(\mathbf{k}) = \{[\varepsilon_0 + I_\mathbf{k} + (-1)^\mu \gamma J_\mathbf{k}]^2 - J_\mathbf{k}^2\}^{1/2}, \tag{2}$$

$$E_f(\mathbf{k}) = \varepsilon_f + L_f(\mathbf{k}), \tag{3}$$

$$I_\mathbf{k} = 2I\cos\mathbf{kb}, \quad J_\mathbf{k} = 8J\cos\frac{\mathbf{ka}}{2}\cos\frac{\mathbf{kb}}{2},$$

$$L_f(\mathbf{k}) = 2L_f\cos\mathbf{kb},$$

where ϵ_f and ϵ_0 are the energies of the f-th electronic and spin excitations of the O_2 molecule in the crystal, and γ ($|\gamma| < 1$) is a constant connected with the magnetic-anisotropy energy of α-O_2.[15] As to the formulas for I_k, J_k, and $L_f(\mathbf{k})$, they were written out with allowance for the strong anisotropy of the crystal lattice of α-O_2 ($|\mathbf{b}| < |\mathbf{a}|$, $|\mathbf{c}|$ [17]) and under the assumption that the exchange interaction between the different antiferromagnetic ab planes can be neglected ($\mathbf{b}$ is parallel to the monoclinic axis of α-O_2). Then I is the matrix element of the exchange interaction between the nearest molecules of one sublattice, J corresponds to different magnetic sublattices, and L_f is the matrix element of the resonant transfer of the f-th electronic excitation.

Using (2) and (3), we find that the absorption coefficient $K_\parallel^f(\omega)$ has a maximum at a light frequency

$$\omega_\parallel = \varepsilon_f + \varepsilon_0 - 2(I + L_f),$$

while the absorption coefficient $K_\perp{}^f(\omega)$ has a maximum at

$$\omega_\perp=\varepsilon_f+\varepsilon_0+2(I+L_f),$$

and the distance $\omega_\perp - \omega_{\|} = 4(L_f + I)$ between these frequencies is due to the anisotropy of the exciton and magnon bands.

5. DISCUSSION

A. The observed doublet splitting of the lines of the ${}^1\Delta_g \leftarrow {}^3\Sigma_g^-$ transition, in accordance with the formulas given above, can be connected with the difference between the width of the exciton and magnon bands along the directions of the anisotropic lattice of α-O_2. In principle this splitting could have two additional causes: 1) the lifting of the degeneracy of the state ${}^1\Delta_g$ and the molecule O_2 in the crystal field of α-O_2 (Bethe splitting) and 2) the mixing of the components of the state ${}^1\Delta_g$ due to the resonant interaction between the molecules and the crystal. However, if the former degeneracy-lifting mechanism were to operate, then, first, the splitting would be the same for the electronic as well as for all the vibronic bands of the series and, second, it would lead to a triplet structure of two-exciton $\Delta\Delta$ absorption. Experiment does not yield such a structure.[2] As to the latter cause, the splitting due to it would either be absent from the vibronic terms, or else would be strongly dependent on the serial number of the vibronic term.

Since the widths of the vibronic bands are very small and can be neglected (the change of the equilibrium distance between the atoms in the O_2 molecule under the considered excitations is ~1%, and the change of the frequency is large), it follows from (4) and (5) that the observed splitting is due entirely to the anisotropy of the magnon band, and its magnitude

$$|\omega_\perp-\omega_{\|}|=4|I|=11 \text{ cm}^{-1}$$

determines the matrix element of the exchange interaction between the nearest neighbors in one sublattice. The sign of I cannot be determined from the absorption spectra. Let us assume for the sake of argument that both inside the sublattices and between the sublattices there is antiferromagnetic exchange (I > 0). Favoring this assumption is the decrease of the intensity of the bimolecular transitions in O_2-N_2 solutions in strong magnetic fields at low temperature.[18]

The strongest component of the doublet splitting of the lines of the exciton-magnon absorption should be the one polarized along the monoclinic axis (see subsection A of the preceding section). We then obtain from (4) and (5) that the exciton band due to the ${}^1\Delta_g$ excitation (Δ exciton) is characterized by a negative effective mass and has a width

$$4|L_f|=17 \text{ cm}^{-1}-11 \text{ cm}^{-1}=6 \text{ cm}^{-1}$$

B. As stated above, the narrow lines of the absorption bands of the ${}^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ transition were attributed by us to magnetic dipole excitations (Σ-exciton excitation). From the 10 cm^{-1} increase of the interval between these exciton lines in the α-O_2 crystal relative to both the gas spectrum and the spectrum of the O_2-N_2 solution, and also neglecting the width of the vibronic band, it follows directly that there exists an exciton band with a width 20 cm^{-1} and with a positive effective mass.

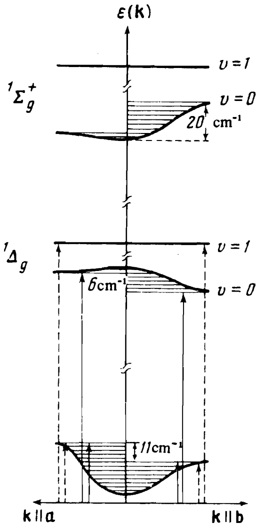

FIG. 3. Energy spectrum of α-O_2 for the directions a and b in the crystal.

The exciton-magnon absorption in the region of this state is much weaker than the corresponding ${}^1\Delta_g \leftarrow {}^3\Sigma_g^-$xx transition bands. From the distribution of the intensity in the structure part of the bands it can be assumed that from among the components of the doublet splitting, which are the analogs of the bright ${}^1\Delta_g \leftarrow {}^3\Sigma_g^-$ doublets, one can see only the strongest peaks, which should be polarized along the monoclinic axis of α-O_2; the frequencies of the maxima of these peaks are indicated in Fig. 1. From the distances between the corresponding magnetic-dipole lines and the maxima of the exciton-magnon bands one can find that the energy of the magnons at the edges of the Brillouin zone in the direction of the monoclinic axis is close to 40 cm^{-1}, which agrees with the data of [19]. The distance 60 cm^{-1} in the purely electronic band is due to the total width of the Σ-exciton band and the magnon band along the b direction of the lattice, while the 40 cm^{-1} distance is due to the width of only the magnon band, since the width of the vibronic band can be neglected. The energy spectrum of α-O_2, which corresponds to the observations made above and to the theoretical analysis, is shown in Fig. 3.

As indicated in Sec. 3, the structure of the absorption bands of both transitions contain many lines that are separated from the initial maxima by intervals that are characteristic of libronic oscillations of the molecules in α-O_2. These maxima are due to direct excitation of three quasiparticles: exciton, magnon, and libration phonon (of course, the intramolecular oscillations also take part in the bands 1–0 and 2–0). As to the exciton-phonon replicas of the ${}^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ transition, in view of their relative weakness they are concealed by the intense exciton-magnon absorption.

6. CONCLUSION

Our investigation of the absorption of light in α-O_2, which corresponds in energy to the transitions ${}^1\Delta_g \leftarrow {}^3\Sigma_g^-$ and ${}^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ in the O_2 molecule, has shown that it is both a pure-exciton and an exciton-magnon character in the crystal. The exciton-magnon transitions turn out to be much stronger than the exciton transitions and account for the total integrated intensity of the absorption in this frequency range. The already noted different relation between the intensities of the

0–0 and 1–0 bands for the gas and for the crystal is precisely due to the fact that the absorption bands are due to one-molecule transitions in the gas and to bimolecular (exciton-magnon) transitions in α-O_2. The collective nature of the excited states and the presence of anisotropy of the quasiparticles of the crystal bands lead to a fine structure of the absorption band at low temperatures, a structure not observed in spectra of solutions. This shows that it is important to take into account the exchange resonance interactions in α-O_2, the role of which was pointed out by us earlier.[4]

We note that our numerical values for the widths of the exciton and magnon bands are approximate. In particular, they may be altered when account is taken of the interaction between the planes or when the exchange integral I is of opposite sign. On the other hand, the qualitative picture of the spectrum remains the same.

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[1] Unfortunately, measurement of the concentration dependence of the integrated intensity of each of the band components of the ${}^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ transition is impossible, because the energy of the spin excitation of the O_2 molecule is comparable with the widths of the absorption lines of the O_2–N_2 solutions. As a result it is impossible to separate the one-molecule (magnetic dipole) and bimolecular (electric-dipole) absorptions in the spectrum.

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