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Excitons in α-Oxygen Crystals

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The investigation results of exciton, exciton-magnon and biexciton absorption by α-oxygen at $T = 1.5$ K are reported.

It is shown that the doublet structure of exciton-magnon bands is due to anisotropy of the exciton and magnon bands; the doublet structure of the bands in the two-particle absorption results from the bound two-exciton states, the biexcitons, present in α-O_2.

Investigations of oxygen crystals have a long history, the first papers dating back to 1930's, however, a progress in understanding of its complicated spectra was gained only in the recent years. An analysis of the spectra in terms of collective excitations and their interactions has provided a new insight of the phenomena involved. Investigations of the low-temperature oxygen modification, i.e. of α-oxygen, have proven the most effective. This paper surveys some facts and concepts resulting from the study of this molecular antiferromagnet with unique molecular crystals properties. The exciton approach to the spectra developed in these studies made it possible to consistently interpret a number of their features. It was found that the spectral abundance is the result of complex collective excitations due to a simultaneous creation of several quasi-particles: excitons, vibrons, magnons, phonons. The research of α-O_2 has essentially widened the scope of exciton concepts for organic molecular crystals, largely contributed by the activities of Vladimir L'vovich Broude. This paper is devoted to his memory.

1. MOLECULAR AND BIMOLECULAR ABSORPTION OF O_2

Electron absorption of the crystalline oxygen is due to transitions in a O_2 molecule from the ground level $^3\Sigma_g^-$ to those of the normal-$^1\Delta_g$ and $^1\Sigma_g^+$ and the first excited electron configuration $^1\Sigma_u^-$, $^3\Sigma_u^+$, $^3\Delta_u$. In a free molecule all these transitions are for some reasons forbidden. The respective weak absorption series are located in the region 1–2 ev and, after the large transparency region, at 4–5 ev. For the low energy transitions internuclear equilibrium distances r_e are little changed. The electron bands are the strongest, there are a few vibronic repetitions and for the transition ${}^1\Delta_g \leftarrow {}^3\Sigma_g^-$ only two bands: the electron and first vibronic.[1] On the contrary, for the high energy transitions, r_e changes considerably. The number of terms is large, their intensities increase with the vibrational number. The electron bands are the weakest. The first vibrational numbering proposed by Herzberg[2,3] was repeatedly modified. For the strongest of the forbidden transitions ${}^3\Sigma_u^+ \leftarrow {}^3\Sigma_g^-$ it was established from the spectrum of O_2 discharge[4] and supported by the analysis of O_2 isotope mixture.[5] The electron band of the transition ${}^1\Sigma_u^- \leftarrow {}^3\Sigma_g^-$, by 3–4 orders weaker, is known only from the gas discharge spectrum.[6] The evidence on the weakest transition ${}^3\Delta_u \leftarrow {}^3\Sigma_g^-$ is very scarce. The electron band position is unknown, of the vibronic bands Herzberg observed only two near the fourth and the fifth bands of the ${}^3\Sigma_u^+ \leftarrow {}^3\Sigma_g^-$ transition.[3] Calculations of the potential energy curves show that the state lies about 0.1 ev lower than ${}^3\Sigma_u^+$.[7] The vibrational constants of these states, so similar in energy, seem to be also very near. The constants of the O_2 molecule states are tabulated in Table I.

All the bands of the free molecule spectrum have a developed fine rotational structure, their intensities depend linearly on pressure. With the pressure increasing even up to several atmospheres the oxygen spectrum exhibits a new absorption due to the intermolecular interactions arising from molecule collisions. The intensities of its broadened structureless diffuse bands are quadratically pressure-dependent; two molecules participate in an absorption act. Owing to exchange interactions during a collision (a O_2 molecule has spin equal to unity), of a considerable probability become bimolecular transitions when two molecules are simultaneously excited by a quantum of energy required. The transitions to the singlet electron states in a pair of molecules occur without a change of the total spin and are dipole-allowed. The corresponding absorption is essentially stronger than the forbidden in a molecule. If both absorptions lie in the direct vicinity, then with the increasing pressure the bimolecular absorption quickly inhibits the molecular, providing an illusion of the favouring the forbidden transitions, though, in fact, its intensity remains as low. This is the case when a molecule is excited into one of the states with a simultaneous spin flip in the other which requires an additional energy of several cm^{-1}. If both molecules are simultaneously excited to the same or different ${}^1\Delta_g$, ${}^1\Sigma_g^+$, states, the bimolecular absorption falls within the transparency region of the molecular spectrum and can be investigated without interferences. In the bimolecular $(\Delta\Delta)$ $(\Delta\Sigma)$, $(\Sigma\Sigma)$ states the coherently excited molecules interact with each other. Then the $(\Delta\Sigma)$ state is split since it is permutation degenerate. The splitting

TABLE I
Constants of O_2 molecule states and their analogs in other absorption series

		O_2 gas Molecular			α-O_2 crystal Exciton		
State	T_0 cm^{-1}	ω_e cm^{-1}	$\omega_e x_e$ cm^{-1}	r_e Å	ν_0 cm^{-1}	ω_e cm^{-1}	$\omega_e x_e$ cm^{-1}
$^3\Sigma_g^-$		1580.19	11.98	1.207			
$^1\Delta_g$	7,882.39	1509.3	12.9	1.216	7,954[a]	1511	13
$^1\Sigma_g^+$	13,120.91	1432.67	13.93	1.227	13,168	1433[b]	—
$^1\Sigma_u^-$	32,664.1	794.29	12.74	1.517	32,745[a]	796	12.15
$^3\Sigma_u^+$	35,007.15	799.08	12.16	1.521			
					Two-exciton		
(ΔΔ)					15,865	1512	14
(ΔΣ)					20,891–95[c] 20,992[c]	[d]	
(ΣΣ)					26,308–32	1429	14.5
	From triplet series of compressed gas				From triplet series		
	34,350	824.9	12.22	(1.5)	34,132 34,285 34,434	816.76	12.78

[a] Calculated from exciton-magnon absorption.

[b] Taken from molecular $^1\Sigma_g^+$-series.

[c] 20,891–95 cm^{-1} is a biexciton doublet in the (ΔΣ)-state; 20,891–95–20,992 is permutation splitting of the (ΔΣ)-state.

[d] Vibrations in the (ΔΣ)-state arise from vibration frequencies of O_2 molecule in the states $^1\Delta_g$ and $^1\Sigma_g^+$.

[e] An assignment of the triplet series as the $^3\Delta_u$ or $^3\Sigma_u^+$-state is being open to question.

effect indicative of this interaction is not exhibited by the gas because of the band width, but is pronounced for the crystal.

Bimolecular absorption in the middle uv, the so-called Wulf series,[8] located in the region of ($^3\Delta_u \leftarrow {}^3\Sigma_g^-$, $^3\Sigma_u^+ \leftarrow {}^3\Sigma_g^-$) transitions, is of a quite different character. The intensity of these bands depends quadratically on pressure, with two molecules participating in the absorption act. At low pressures the Wulf bands are overlapped by the structural absorption related to both molecular transitions; with the higher density of gas only one bimolecular series, consisting of a number of triplets, remains in the spectrum. The triplet components are wide peaks, the middle the strongest, the side ones markedly weaker. Separations between the peaks are 150 cm^{-1} giving the total splitting magnitude about 300 cm^{-1}. The bands of these series, weak in the beginning, become stronger with the increasing vibration number, as the bands of the molecular transitions, and converge to about the same limit. Herzberg,[3] presumably attributed the triplet series to transition to the $^3\Delta_u$ state, markedly strengthened by the intermolecular interaction.

Thus, the spectrum of gaseous oxygen consists of molecular and bimolecular excitations even at low pressures. Of essential interest is the spectrum of a crystal where molecule excitations transform to collective states yielding a complicated absorption.

2. α-O_2 ABSORPTION NEAR 1K

a. Exciton absorption

Of the three modifications of crystalline oxygen – γ, β and α, the latter, stable below 23.8 K, is antiferromagnetic. Two molecules of a α-O_2 monoclinic cell lie in a site and the centre of the (a, b)-plane, differ in the spin direction and belong to different magnetic sublattices. The molecular axes are parallel, therefore, a simplest unit cell contains one molecule[9] (see Figure 1).

As in any molecular crystal, electron molecular levels in α-O_2 transform to exciton bands. Because of its symmetry, the spectral lines do not undergo exciton splittings. The spectrum shows only one exciton line belonging to the triplet-singlet transition ${}^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ and its vibronic repetition, the former much stronger, both symmetric, single, sharp and narrow. Though the absorption coefficient in the exciton line maximum is high, the area under the absorption curve is small i.e. the oscillator strength is small. In the crystal the transition is forbidden, as is in the gas.

The separation between the electron and vibronic lines in α-O_2 is by $10\,cm^{-1}$ larger than that in the molecular spectrum. Considering that the

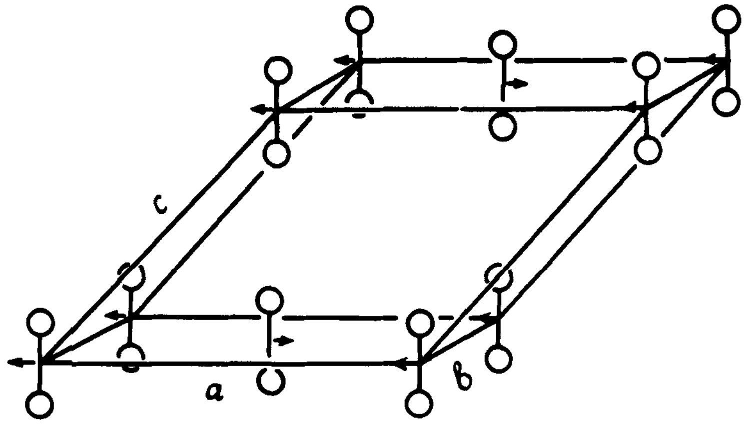

FIGURE 1 An α-oxygen unit-cell. The space group C^3_{2h} $z = 2$; $a = 5.403$ Å; $b = 3.429$ Å; $c = 5.086$ Å; $\beta = 132°53'$. Directions of arrows indicate different magnetic sublattices.

transition in the crystal occurs to the exciton band bottom and that the vibronic band is very narrow, the value obtained for the exciton band width[10] is 20 cm^{-1}. The exciton lines, corresponding to the $^1\Delta_g$ and $^1\Sigma_u^-$ excitations, are still weaker, as in the molecular spectrum and are not observed in the experiment. Thus, the exciton spectrum of α-O_2 is found to be extremely meager.

b. Exciton-magnon absorption

Electron excitation of one of a pair of molecules with a simultaneous spin flip in the other is in the crystal adequate to simultaneous creation of an exciton and magnon. In absorption the magnon on the edge of the Brilloin zone with the energy[10] of about 40 cm^{-1} is active, leading to a large separation between the exciton and magnon lines. Only in the $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$-series one can see both exciton and magnon lines. In the involved fine structure of its bands there are pronounced strong diffuse magnon peaks differing in its shape from the sharp exciton lines. A spacing between the exciton line and the magnon peak is 60 cm^{-1}, between that and the vibronic line is 40 cm^{-1} because of the different band width. A distinct resolution of the exciton lines and magnon peaks in this series indicate that the exciton-magnon coupling is weak. Created simultaneously, both quasi-particles propagate further independently. The structure of the magnon peaks in the series is poorly resolved.

Such is not the case for the crystal excitation in the region of the molecular $^1\Delta_g \leftarrow {}^3\Sigma_g^-$ transition where several strong bands with a separation of the order of the vibrational frequency in the $^1\Delta_g$-state are located. Neither exciton lines, nor their vibronic or phonon repetitions are observed. All the bands which are doublets with the splitting 17 cm^{-1} in the initial and 11 cm^{-1} in the rest can be interpreted as exciton-magnon absorption. The doublet structure of bands displays anisotropy of the α-O_2 magnon band, the splitting of the first doublet is also contributed from the Δ-exciton band width. A knowledge of the exciton and magnon band widths provides the energy value of the Δ-exciton given in Table I.

Another exciton-magnon transition connected with the molecular transition is located in the middle uv. As it was mentioned above, the initial bands of these series are observed neither in the spectrum of gas nor of the crystal. However, the latter shows a number of vibronic bands from whose arrangement one can determine the series origin. It agrees with that found from the O_2 isotope mixture absorption[11] and is given in Table I. The doublet lines with the constant splitting near that observed in the Δ-excitation are distinctly seen in the band structure. These doublets result from the splitting of the spin wave branches in the anisotropic crystal.

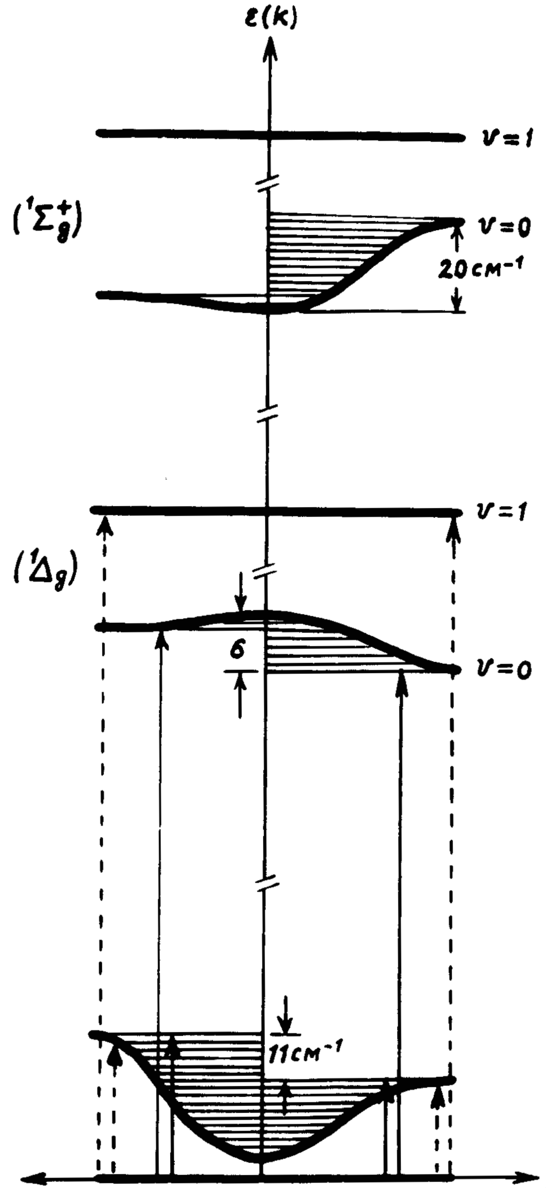

FIGURE 2 α-oxygen energy spectrum in the region of ${}^1\Delta_g$- and ${}^1\Sigma_g^+$-states.

A quite unusual absorption, called polyexciton, also belongs to the exciton-magnon absorption. It arises from a simultaneous excitation of four molecules: two molecules to the (ΔΔ)- and one to the Σ-state and two to the (ΣΣ)- and one to the Δ-state; in both cases the fourth molecule is spin-excited, i.e. a magnon is created. A series of weak bands with a complicated structure in the near uv and several weak bands in the middle uv correspond to this excitation. Belonging of this absorption just to oxygen rather than to any impurity is evidenced by the spectra of O_2 isotopes.[12]

Investigations of the α-O_2 exciton-magnon absorption provide a new information on the crystal energy spectrum. From the studies of the Δ and Σ-excitations such important characteristics as the widths of the Δ- and Σ-exciton bands, the signs of the exciton effective masses in these states, etc. were determined. The results, as given in Ref. 10, are shown in Figure 2. Revealing of anisotropy of the magnon and exciton bands, as well as determination of the magnon energy on the edge of the Brilloin zone from the spectral data are essential. Also it is important that from the exciton-magnon absorption it is possible to locate weak exciton lines for the forbidden transitions and obtain an information on the weak transitions.

c. Two-exciton absorption

The electron bimolecular (ΔΔ), (ΔΣ), (ΣΣ) states transform in a crystal to two-exciton bands three absorption series—the red, blue and violet corresponding to transitions to these bands. Each series consists of 4–6 bands with the intervals of the order of a molecular vibration. Peculiarities of the series and their bands' fine structure are due to the excitation interactions in a crystal. It should be noted that interactions of excited molecules are noticeably exhibited not only by the crystal, but also by the compressed gas and solid oxygen solutions.

The above bimolecular states (ΔΔ) and (ΔΣ) are degenerate due to orbital momentum degenaracy of the Δ-term and, in addition, the state (ΔΣ) is permutation degenerate. This degeneracy can be removed by the molecule interaction. It can be shown that in the α-O_2 crystal, transitions are allowed only to the two of four splitting components of the (ΔΣ)-term. Therefore, the blue series is composed doublet bands with splitting of the order of 100 cm^{-1}. We refer to these wide doublets as permutational. Since it is necessary to take into account interaction of excited molecules it is impossible to determine the parameters of excited states from the two-exciton absorption spectra using trivial vibronic methods. Thus, in the blue series the distances between bands do not correspond to the values of the molecule vibrational frequencies, and only by allowance for the resonance interaction their correct values can be obtained. The situation is simplified in the red and violet series composed of only one vibrational frequency each. They have an illusory resemblance to the molecular absorption since the strongest are the lines corresponding to simultaneous transitions to the two-exciton and vibronic bands whereas simultaneous transitions to the different vibronic bands are essentially weaker.

The collective nature of excitations in a crystal affects the intensities and sharply different shapes of the two-exciton and vibronic bands, the serial intensity distributions, causes violations of the vibrational intervals, etc.[13] But its strongest effect is in unexpected doublet splittings of the order of $10\,\mathrm{cm}^{-1}$, abundant in the α-O_2 spectrum. These fine splittings are specific only to the crystal and are not encountered in any other aggregate oxygen states. They are due to new quasi-particles, biexcitons, arising from interactions of two simultaneously created excitons.

3. BIEXCITON ABSORPTION

A two-exciton state, having formed in a crystal, can either dissociate into two excitons propagating further independently as an exciton and magnon or remain bound if interactions between excitons are sufficiently strong. Such a dissociation is displayed as wide bands, the exciton-exciton binding, on the contrary, as narrow lines. If the exciton-exciton coupling is so strong that the two quasi-particles can be characterized by one common wave vector it implies that a new collective biexciton state is created. The calculation shows that in the α-O_2 this state has two branches the transition to which are polarized along and normal to the monoclinic axis. Unfortunately, it is impossible to observe polarization of lines experimentally since all the attempts at growing a single crystal of α-O_2 are unsuccessful at least so far, but the spectrum shows many doublets ascribed to biexcitons.

The biexciton splitting is essentially different from the exciton splitting which is known to be due to resonance interaction of an excited molecule with translationally nonequivalent unexcited molecules. It should be recalled (see Section 2(a)) that the exciton oxygen spectrum does not show line splittings. When a biexciton propagates in a crystal, the excitation migrates from one pair of molecules to another, each of the excitons, created by this pair, staying in its own magnetic sublattice due to the intercombinational selection rules. However, the exciton-exciton coupling is so considerable that separation between them remains constant. The biexciton splitting magnitude is determined by the exciton band widths and for the vibronic repetitions depends also on the difference of the exciton band vibrational constants.

Such a splitting of the violet series lines is most demonstrative since their doublet structure is pronounced, though the $(\Sigma\Sigma)$ state does not undergo the other-nature splitting, as it was aforesaid. The biexciton splitting magnitude of the vibronic lines amounts to 10 cm^{-1}, in a two-exciton band it is 20 cm^{-1}, in agreement with the above Σ-exciton band width (see Section 2(a)). Very effective is biexciton splitting in the blue series, especially of the long-wavelength component of the first permutational doublet whose lines are so sharp that a splitting of 4 cm^{-1} is quite visible. Doublets are also seen in the other terms of the blue series (see Figure 3). Similar splitting is also inherent in the (ΔΔ) series but because of the complicated structure of its bands (due to degeneracy of this term) it is difficult to distinguish components of biexciton splitting and also to determine the width of the exciton band.

4. TRIPLET ABSORPTION

The Wulf triplet series[8] has spectrum an analog in the α-O_2: a series of 12–14 terms converging to the limit of about 42,000 cm^{-1}. The intensities of its initial bands are very weak, increasing further with the vibrational number. In the fine structure of each band one can distinctly see the line triplets whereby the series is referred to as the triplet series. The triplet splitting magnitude is 300 cm^{-1}, the distance between the long-wavelength and the central components is 155 cm^{-1}, between the central and the short-wavelength components is 145 cm^{-1}. These distances are almost constant all over the series and only slightly decrease in its high terms. The long-wavelength line is the sharpest and strongest in the triplet, its width is 3–5 cm^{-1}. The two others are somewhat wider, slightly more diffuse and weaker, especially the third—the weakest. The triplet line frequencies and the frequency differences are given in Table II. The band structure is shown in Figure 4. Each of the triplet components is accompanied by a set of three weaker lines at the constant distances of 30, 50 and 80 cm^{-1}, the latter the strongest. The whole group consisting of 12 lines repeats regularly in all the series terms. By varying the thickness of absorbing layers one can reveal the structure of almost all the bands, except for the highest terms masked by continuous absorption near the series limit. The long-wave triplet components are most pronounced, it is from their frequencies that the serial relationships were established.[14]

Interpretation of this absorption described at length above is rather involved. By the energy value the triplet series could be compared with one of two transitions ${}^3\Sigma_u^+ \leftarrow {}^3\Sigma_g^-$ or ${}^3\Delta_u \leftarrow {}^3\Sigma_g^-$ in an O_2 molecule. Let us consider both of them.

The first transition corresponds to a comparatively strong band series, the second to a considerably weaker one in the gas spectrum, therefore, it

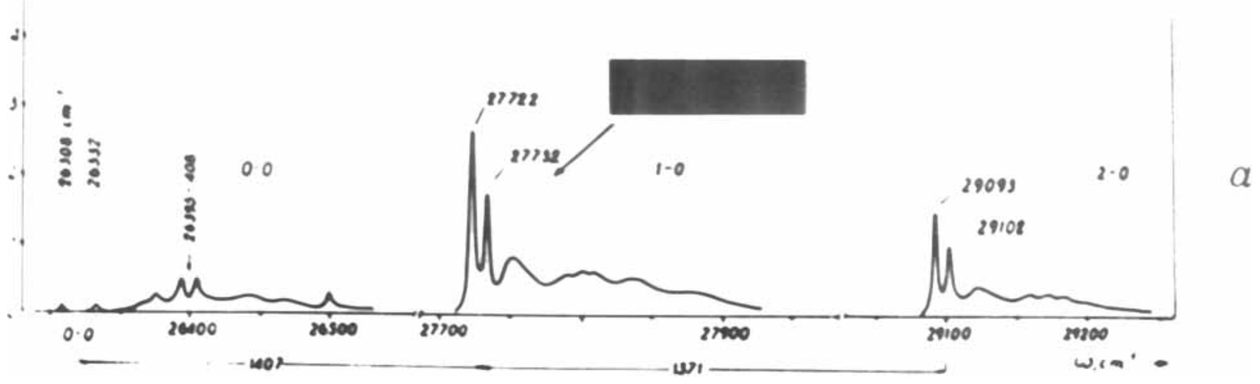

FIGURE 3 α-O_2 absorption band profiles. (a) is a violet series, (b) is a blue series.

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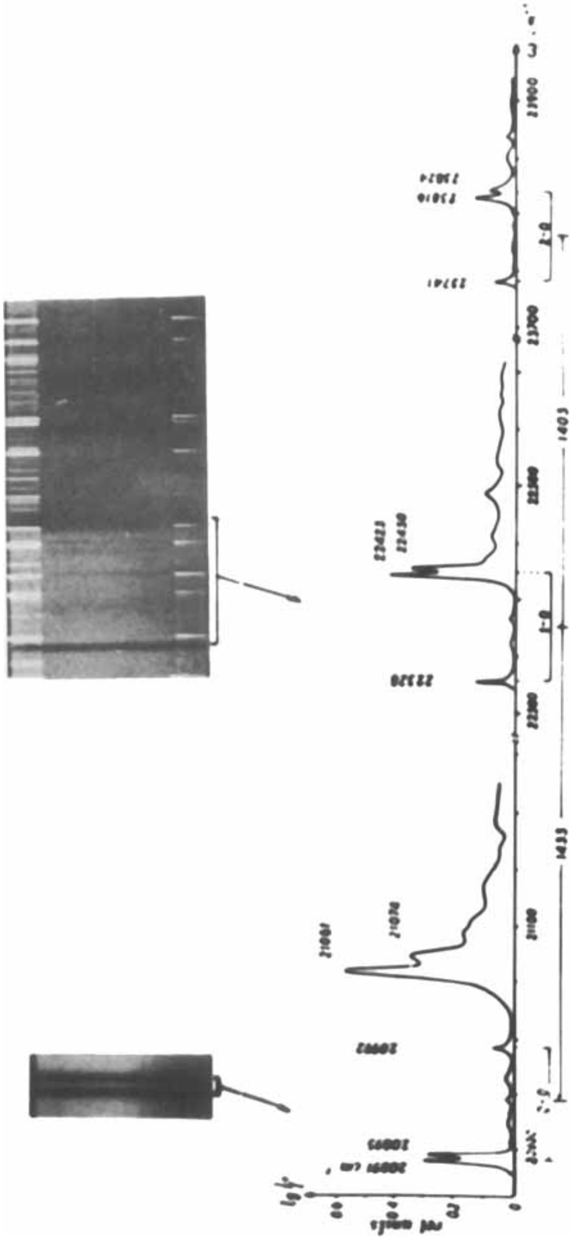
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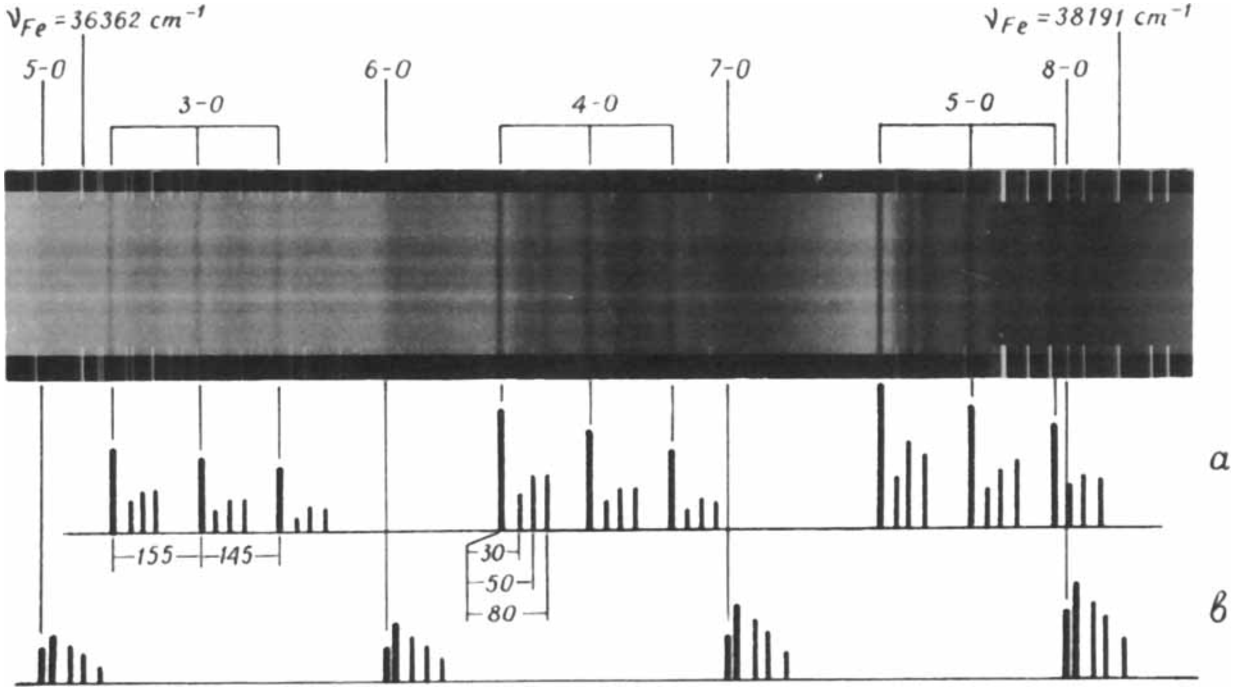

FIGURE 4 α-O_2 *absorption spectrum at* $T = 1.5°K$. *(a) a triplet series bands, (b)* ${}^1\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ series bands.

TABLE II

Absorption line frequencies and frequency differences in α-O_2 triplet series at 1.3 K

v'–0	ν, cm^{-1}	$\Delta G_{v'+1/2}$, cm^{-1}	$\Delta_2 G$, cm^{-1}	v'–0	ν, cm^{-1}	$\Delta G_{v'+1/2}$, cm^{-1}	$\Delta_2 G$, cm^{-1}
0–0	34,132			7–0	39,002		
	285				156		46
	434				294		
		791				546	
1–0	34,923			8–0	39,548		
	35,082		30		696		49
	228				39,839		
		761				497	
2–0	35,684			9–0	40,045		
	841		30		185		51
	990				330		
		731				446	
3–0	36,415			10–0	40,491		
	573		31		628		56
	36,716				—		
		700				390	
4–0	37,115			11–0	40,881		64
	270		34			326	
	416						
		666		12–0	41,207		(68)[a]
						(258)	
5–0	37,784						
	37,937		37	13–0	(41,465)		
	38,079						
		629		14–0	(41,651)		
6–0	38,410						
	567		37				
	38,707						
		592					

[a] In brackets are the values calculated from extrapolation of the dependence of ν on the vibration number.

would be natural to compare absorption in the crystal just to the first transition. Indeed, by changing the vibrational numbering in the gas spectrum by unity it is possible to attain a very near agreement between the serial regularities and the similar ones in the crystal. However, determination of the vibrational numbering by the isotopic method[5] does not allow to do this. If the numbering remains unchanged, the gas-crystal shift is found to be too large compared with that for other transitions in α-O_2.

Also it is difficult to explain the triplicity of bands.

The second possibility, i.e. a comparison between the crystal absorption and the transition to the $^3\Delta_u$ state removes this difficulty and enables us to explain the large triplet splitting value as the spin-orbital interaction. However, in this case it has to be assumed that a very weak in a molecule transition $^3\Delta_u \leftarrow {}^3\Sigma_g^-$ becomes by 6–7 orders stronger, whereas a stronger transition is entirely absent in the spectrum. Thus, both interpretations appear contradictory.

A question arises whether these states could mix in the crystal spectrum. They are in parameters and have the same multiplicity. The difference of their electron excitation energies is near the energy of molecular vibration. It is possible that just due to this similarity the mixing occurs, the vibrational constants of both states become identical and only one vibronic series remains in the crystal spectrum.

However, neither these nor the other explanations of the series have been sufficiently analyzed and the triplet series still awaits for its correct interpretation.

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