

It has been customary to expand the exponential in Eq. (A.1) leading to the familiar result that the power absorption is proportional to αl . However, for a long absorption cell so that $\alpha' l$ is no longer much less than unity, expansion of Eq. (A.1) must be carried out to higher-order terms, i.e.,

$$\Delta P \simeq P_0 \exp(-\alpha_0 l) (\alpha l - \frac{1}{2} \alpha^2 l^2 + \frac{1}{6} \alpha^3 l^3). \quad (\text{A.4})$$

Equation (A.3) is now substituted in Eq. (A.4). Since the detection system is tuned to the modulation frequency, we are concerned only with the fundamental frequency component of ΔP . Neglecting higher

power of ω' on account of $\omega' \ll \Delta\nu$, we have

$$\langle \Delta P \rangle_{\text{fund}} \propto - \frac{2(\nu - \nu_0)}{[(\nu - \nu_0)^2 + (\Delta\nu)^2]^2} + \frac{2\alpha' l (\Delta\nu)^2 (\nu - \nu_0)}{[(\nu - \nu_0)^2 + (\Delta\nu)^2]^3} - \frac{\alpha'^2 l^2 (\Delta\nu)^4 (\nu - \nu_0)}{[(\nu - \nu_0)^2 + (\Delta\nu)^2]^4}. \quad (\text{A.5})$$

The frequency difference between the two peaks of this function is denoted $2(\delta\nu)_l$. From (A.5) it is easy to show that

$$(\delta\nu)_l = (\Delta\nu/\sqrt{3}) (1 + \frac{1}{4} \alpha' l + \frac{1}{16} \alpha'^2 l^2)$$

which then gives Eq. (2).

Absolute Intensities of the Discrete and Continuous Absorption Bands of Oxygen Gas at 1.26 and 1.065 μ and the Radiative Lifetime of the ${}^1\Delta_g$ State of Oxygen

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Laboratory measurements have been made of the absolute intensities of the discrete-line absorption band at 1.26 μ , and of the continuous bands at 1.26 and 1.065 μ in oxygen gas at pressures up to 4.3 atm. It has been shown that discrete and continuous absorptions are quite independent features, the one being a measure of the intrinsic transition probability in isolated molecules, the other of its enhancement in collision complexes. In the former the lines show significant pressure broadening, but the integral molecular absorption coefficients are constant; in the latter they are proportional to pressure and continuous absorption dominates in the 1.26- μ region at about $\frac{1}{2}$ atm oxygen pressure.

The radiative half-life of isolated ${}^1\Delta_g$ oxygen molecules is estimated to be 45 min, and the effect of gas pressure on the rate of decay has been predicted.

INTRODUCTION

IN conjunction with a study of ozone, we recently observed in this laboratory the absorption at 1.26 μ , due to the doubly forbidden ${}^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition of oxygen, and it occurred to us that, although this transition is extremely weak, it might nevertheless be possible to make a reasonably reliable measurement of the absolute intensity and transition probability under controlled laboratory conditions. The lifetime of the ${}^1\Delta_g$ state of oxygen is now of considerable interest owing to several recent observations relating to this state. In particular, Vallance Jones and Harrison¹ tentatively identified the (0-1) band of the above-mentioned transition in the early evening airglow, and subsequent high-altitude observations have demonstrated the (0-0) band in both the daytime² and nighttime³ emission,

* Contribution No. 3276.

¹ A. V. Jones and A. H. Harrison, *J. Atmospheric Terres. Phys.* **13**, 45 (1958).

² J. F. Noxon and T. P. Markham, *J. Geophys. Res.* **68**, 6059 (1963).

³ (a) J. F. Noxon and A. Vallance Jones, *Nature* **196**, 157 (1962); (b) H. P. Gush and H. L. Buijz, *Can. J. Phys.* **42**, 1037 (1964).

and have positively identified the emitter. Vallance Jones and co-workers^{1,4} in attempting an explanation of this airglow have made estimates of the transition probability at low pressures, based on the intensities of weak absorption lines of oxygen in the solar spectrum, but such estimates involve a number of uncertainties. For example, it has not been entirely clear that they may not be falsified by contributions from the collision-induced transitions observed by Ketelaar.⁵

EXPERIMENTAL

Laboratory Observations on the Oxygen Bands

The laboratory studies were made using a 1-m spectrometer previously described,⁶ which has since been considerably modified and integrated with a White absorption cell which is matched to it in optical aper-

⁴ A. Vallance Jones and R. L. Gattinger, *Planetary Space Sci.* **11**, 961 (1963).

⁵ J. A. A. Ketelaar, *Nuovo Cimento Suppl.* **11**, 763 (1955).

⁶ R. M. Badger, L. R. Zumwalt, and P. A. Giguère, *Rev. Sci. Instr.* **19**, 1861 (1948).

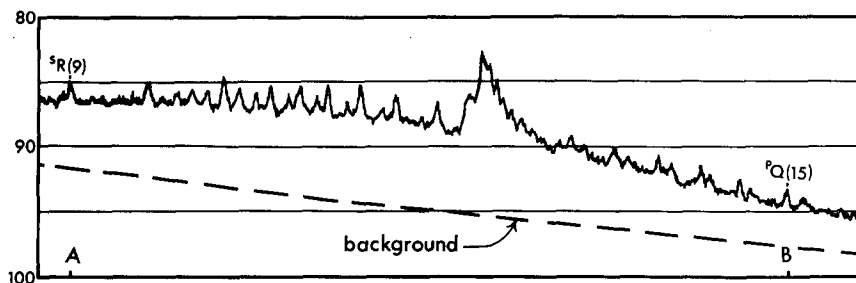


FIG. 1. Absorption spectrum of oxygen gas in the (0-0) band of the ${}^1\Delta_g\text{-}{}^3\Sigma_g^-$ system at $1.26\ \mu$. ($T=298^\circ$, $P=4.31\ \text{atm}$, $l=32\ \text{m}$, slitwidth $0.4\ \text{\AA}$.) Designations and frequencies of two lines are indicated as A 7942.2 and B 7837.0.

ture. This cell is 1 m in length, employs gold mirrors, and in the $1.26\text{-}\mu$ region routinely permits 32 traverses with a light loss of about 50%. Moderate pressurizing is possible.

The observations were made chiefly in the third order of a 7500-line/in. grating, which was well isolated by a filter consisting of $\frac{1}{8}\text{-}\frac{1}{4}$ in. of water, depending on the spectral region, and a glass with very sharp short wave cutoff at about $0.95\ \mu$. The detector was a diffused-junction germanium diode, usually cooled to about 5°C , used in conjunction with a lock-in amplifier at 720 cps.

RESULTS AND INTERPRETATIONS

As may be seen in Figs. 1 and 2, in the absorption spectrum of pure oxygen at 4 atm and 32-m path, the very weak, discrete-line bands characteristic of the ${}^1\Delta_g\text{-}{}^3\Sigma_g^-$ system are overlaid by continuous absorptions. In both (0-0) and (1-0) regions, at 1.26 and $1.065\ \mu$, respectively, continuous absorption bands are found which have slightly asymmetrical bell-shaped contours, steeper on the long-wave side. The respective maxima are at 7895 and $9373\ \text{cm}^{-1}$, about $13\ \text{cm}^{-1}$ to the violet of the centers of the discrete bands. The width of the former at half-maximum intensity is about $160\ \text{cm}^{-1}$; the latter appears to be somewhat broader ($\sim 200\ \text{cm}^{-1}$).

It is evident from the following that, although the continuous- and discrete-line absorptions occupy essentially the same spectral regions, they must be regarded as two distinct features; the former definitely does not develop out of the latter with increase in pressure. The discrete absorption lines show a moderately large pressure broadening, but the integral *molecular* absorption coefficients appear to be independent of pressure.

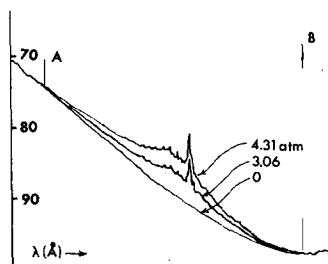


FIG. 2. Absorption spectrum of oxygen gas near $1.26\ \mu$ at two pressures in the ratio $2\frac{1}{2}/1$. ($T=298^\circ$, $l=32\ \text{m}$, slitwidth $=1.5\ \text{\AA}$.) A, 12 559; B, 12 836.

In the continuous bands, on the contrary, the integral molecular coefficient is proportional to pressure; in the $1.26\text{-}\mu$ region the continuous absorption in pure oxygen dominates at pressures above $\frac{1}{2}$ atm. The intensity distributions in discrete and continuous absorptions are quite different. In the former more than $\frac{1}{3}$ of the intensity of the band is localized in the very prominent Q branches, in a region less than $20\ \text{cm}^{-1}$ wide. Any correspondingly conspicuous feature is absent from the smooth contours of the continuous bands.

It is now clear that the intensity of the discrete-line spectrum may be taken as a measure of the probability of the ${}^1\Delta_g\text{-}{}^3\Sigma_g^-$ transition in isolated molecules. On the other hand the intensity data on the continuous bands may provide means for estimating the radiative decay of the ${}^1\Delta$ state at higher pressures, through processes involving collision complexes, and may furnish an analytical tool for estimating concentrations of ${}^1\Delta$ molecules.

It is remarkable that, although the ratio of the intensities of the (0-0) and (1-0) discrete-line bands probably exceeds $200/1$,⁷ we find that the integral absorption coefficients ($\int \alpha d\nu$) of the underlying continuous bands are practically equal when the pressurized gas is pure oxygen (see Table II below). This confirms the observations of Ketelaar⁸ at higher pressure who found, however, that any continuous band underlying the (2-0) discrete band is very weak. The same sequence of intensities is found in condensed oxygen,^{10,11} where a fourth extremely weak member of the progression is also observed.

Ketelaar⁸ found that pressurization with foreign gases was effective in developing the 7895-cm^{-1} continuous band; indeed CO_2 was about 1.3 times as effective as oxygen itself, though N_2 was only 0.3 as effective. However, of the gases mentioned, oxygen appears to

⁷ We draw this conclusion from the published solar spectra of Refs. 8 and 9, in which the (1-0) band does not appear in observations made near the zenith, although there is nearly total absorption in the Q branches of the (0-0) band.

⁸ O. C. Mohler, *Table of Solar Spectrum Wave-lengths and Photometric Atlas of the Near Infrared Solar Spectrum* (University of Michigan Press, Ann Arbor, Michigan, 1950).

⁹ L. Delbouille and G. Roland, *Mem. Soc. Roy. Sci. Liège*, Vol. Hors Ser. 4, (1963).

¹⁰ J. W. Ellis and H. O. Kneser, *Publ. Astron. Soc. Pacific* 46, 106 (1934); *Z. Physik* 86, 583 (1933).

¹¹ V. I. Dianov-Klokov, *Opt. Spectry.* 6, 290 (1959) [*Opt. i Spektroskopiya* 6, 457 (1959)].

be unique in also developing the 9373-cm⁻¹ band. Ketelaar observed that CO₂ was ineffective, and in a subsequent section we present evidence that this is likewise true of N₂.

It is reasonable to attribute 7895-cm⁻¹ to the (0-0) transition of an oxygen molecule in a collision complex in which the partner is not necessarily also oxygen. However, if we are to attribute 9373 cm⁻¹ to the (1-0) transition, we must assume that oxygen as the collision partner is uniquely able to cause a partial relaxation of vibrational selection rules. The (O₂)₂ complex is of course unique in that the vibrational excitation might occur either in the electronically excited molecule or in its partner.¹² The very low intensities of the succeeding members of the progression do, however, seem a little odd.

Estimation of Intensities and Einstein Coefficients for the Discrete-Line Spectrum

The errors in our estimation of absolute intensities are unfortunately rather large. The maximum absorption at the peaks of discrete lines was at most about 2%, whereas the rms noise level in the spectra at higher resolution was about 0.3% of full-scale deflection. The broad, weak wings of the continuous absorption bands introduced some uncertainty in the fitting of zero-absorption background curves to the spectra, particularly in the 9373-cm⁻¹ band, and an objective partition of the (0-0) band into discrete-line and continuous absorption was not easy. At pressures necessary to obtain significant absorption the lines are broad and overlap sufficiently that the points of minimum absorption lie considerably above the true background for the discrete-line absorption.

This problem was met by computing a series of synthetic spectra, using the known spacing and theoretical relative intensities of the lines, and a line shape which was an adequate simulation of the convolution of a Gaussian slit function (slitwidth=0.4 Å) with a Lorentz absorption line. With a Lorentz half-width γ_L between 0.5 and 0.6 Å we obtained very satisfactory agreement with the 4.31-atm observations in respect to resolution of closely neighboring lines, relative peak heights, etc. One or two lines may exhibit slightly anomalous peak heights, but in the region of the more intense lines we found no evidence of significant variation or trend in linewidth. We estimate the pressure broadening constant γ_L^0 in pure oxygen to be about 0.08 cm⁻¹·atm⁻¹.

It is presumably legitimate to present the intensity data for the discrete-line spectrum in terms of an Einstein coefficient of absorption, $B''(0-0)$, and to estimate the radiative lifetime of the ¹Δ_g state in the limit of zero pressure from the coefficient $A'(0-0)$, calculated in the usual way. From our observation above one

TABLE I. Einstein coefficients for the ¹Δ_g-³Σ_g⁻ transition in isolated molecules.

	Laboratory measurements	Solar spectrum	Vallance Jones and Gattinger ^a
$B''(0-0)$ (erg ⁻¹ ·sec ⁻¹ ·cm ²)	0.070	0.085	0.04
$A'(0-0)$ (sec ⁻¹)	2.58×10^{-4}	3.10×10^{-4}	1.5×10^{-4}

^a Reference 4.

may predict that transitions with $\Delta v \neq 0$ make a trivial contribution to the decay of this excited state.

From a comparison of the observed and synthetic spectra, the position of the background of the discrete-line spectrum was estimated, and a weighted-average value was obtained for the ratio R of theoretical line intensity RS to observed intensity S . We define $RS = S_J \exp(-\epsilon''/kT)$, where S_J is the line strength factor calculated by Van Vleck,¹³ and ϵ'' is the energy of the lower state. For uniformity with a later section we represent the observed line intensity by $S = N \int \alpha_m d\lambda$, where α_m is the *molecular* absorption coefficient and N is the number of molecules in a column of unit cross section and length equal to the absorption path. The Einstein coefficient of absorption, $B''(0-0)$ (defined in terms of intensity), was then calculated by the relation

$$B''(0-0) = \frac{4}{3} Q_r'' / (h\lambda_0 RN), \quad (1)$$

where the factor $\frac{4}{3}$ is the reciprocal of that required to effect the appropriate normalization of the S_J 's, Q_r'' is the rotational partition function in the ground electronic state, and λ_0 and R^{-1} are in the same units. The inaccuracy of the data amply justifies the approximation that λ is constant over the portion of the band used in our analysis.

Our calculated Einstein coefficients are presented in Table I, together with those obtained in another manner, described below.

Rate of Radiative Decay of the ¹Δ_g State at Higher Pressures

In view of recent observations on emission from ¹Δ oxygen molecules at pressures around 1 atm,¹⁴ it may be useful to attempt the application of our data on the continuous absorptions in predicting the contribution of collision-induced radiative processes to the decay of these molecules. There appear to be several processes involving collision-complex intermediates¹⁵

¹³ J. H. Van Vleck, *Astrophys. J.* **80**, 161 (1934).

¹⁴ R. T. Browne and E. A. Ogryzlo, *Proc. Chem. Soc.* **1964**, 117.

¹⁵ Although we have, throughout, referred to the "carriers" of the continuous bands as *collision complexes*, we have intended no implication regarding their specific nature. Our treatment in this section is, indeed, formulated in terms of *equilibrium complexes*, but an equivalent treatment leading to the same end result can equally well be made in terms of molecules in the act of colliding.

¹² Suggestion made privately by O. R. Wulf.

TABLE II. Data on continuous absorption bands in pure oxygen gas.

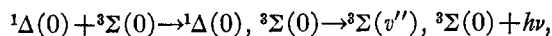
Transition	Integral molecular absorption coefficient per atm ^a (cm ² sec ⁻¹ ·atm ⁻¹)	\mathcal{B}'' per atm (erg ⁻¹ ·sec ⁻¹ cm ² atm ⁻¹)	\mathcal{A}' per atm (sec ⁻¹ ·atm ⁻¹)
7895 cm ⁻¹ (0-0)	1.09×10 ⁻¹²	0.16	5.9×10 ⁻⁴
9373 cm ⁻¹ (1-0)	1.07×10 ⁻¹²	0.13	12.3×10 ⁻⁴
~6417 cm ⁻¹ (0-1)	4.0×10 ^{-4b}

^a $(1/\bar{N}P)\int\alpha P d\nu$, where \bar{N} is number of O₂ molecules per cubic centimeter at P atm.

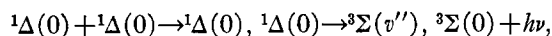
^b Estimated as described above.

which may contribute to this decay, of which the more important are represented by the following:

(a) and (b)



(c) and (d)



where in (a) and (c), $v''=0$; in (b) and (d), $v''=1$.

We neglect (c) and (d), since they involve processes which are second order in ¹Δ molecules, and qualitative considerations indicate that they will make only a minor contribution relative to (a) and (b), unless the concentration of these molecules is very high. Under the conditions achieved by Browne and Ogryzlo,¹⁴ we estimate that (c) and (d) may have contributed 10% of the radiative decay.

In our treatment of (a) and (b) we make a formal extension of the concept of the Einstein coefficients to the collision complexes, on the assumption that the usual equilibrium considerations are valid. Obviously we cannot calculate the B_c'' and A_c' characteristic of the complexes, because the concentrations are unknown, but we can obtain the quantities \mathcal{B}'' and \mathcal{A}' , which are measures of the contribution of the complexes to the behavior of the equilibrium system.

The process in which the 7895-cm⁻¹ continuous absorption originates is presumably the reverse of (a), and from the integral absorption coefficient at some given pressure we can consequently obtain

$$\mathcal{B}''(0-0) = X_c'' B_c''(0-0) = \frac{1}{h\bar{N}} \int \frac{\alpha}{\nu} d\nu \approx \frac{1}{h\bar{N}v_0} \int \alpha d\nu, \quad (2)$$

where \bar{N} is the total number of O₂ molecules, and $X_c''\bar{N}$ the number of ³Σ(0), ³Σ(0) complexes, per unit volume.

From the usual equilibrium considerations, taking into account the relative statistical weights of excited and ground states of both isolated molecules and complexes, we then obtain for the coefficient of spontane-

ous emission of the excited complex

$$\mathcal{A}'(0-0) = X_c' A_c'(0-0) = (g_i''/g_i') X_c'' B_c''(0-0) 8\pi h c (v_0/c)^3, \quad (3)$$

where X_c' is the fraction of ¹Δ molecules in the form of complexes, and g_i''/g_i' is the ratio of the statistical weights of the ³Σ and ¹Δ states of isolated molecules.

From the observed intensity sequence in absorption it seems very probable that $\mathcal{A}'(0-1)$ is relatively large, but that $\mathcal{A}'(0-2)$, etc., are negligible, as was indeed observed in the doubly excited complex (¹Δ, ¹Δ).¹⁴ Consequently, by invoking the sum rule, we equate the transition moments for the (1-0) and (0-1) transitions, and calculate $\mathcal{A}'(0-1)$ from the absorption data on the 9373-cm⁻¹ continuous band. By similar arguments we conclude that, when the collision partner is a foreign gas molecule, only $\mathcal{A}'(0-0)$ is significant.

For the total probability of radiative decay of ¹Δ molecules in oxygen gas under equilibrium conditions, we may then write an effective \bar{A} , or reciprocal mean lifetime:

$$\tau_m^{-1} = \bar{A} = [X_i' A_i'(0-0) + \mathcal{A}'(0-0) + \mathcal{A}'(0-1)], \quad (4)$$

where X_i' , the fraction of ¹Δ molecules not in complexes, is practically unity, and $A_i'(0-0)$ is the coefficient of spontaneous emission of these molecules.

To what extent the \bar{A} so calculated can be used to predict decay in conditions far from equilibrium seems to depend on whether the first steps in Processes (a) and (b) above, and their reverse, are rapid in comparison with the second steps. This seems probable when one considers that on the average each ¹Δ molecule experiences of the order of 10¹³ kinetic theory collisions with other molecules before a resulting complex emits.

Our calculated Einstein coefficients are given in Table II, and in the concluding section we present an expression for the rate of decay as a function of pressure, including an estimate of the effects of two foreign gases deduced from the observations of Ketelaar.

COMPARISON WITH OBSERVATIONS ON THE SOLAR SPECTRUM

As a check on the laboratory observations we have attempted an independent estimate of the intensity of the discrete-line absorption by a systematic use of the high-resolution observations on the solar spectrum in the 1.26-μ region.⁸ In using the solar data one encounters several obstacles which limit the reliability of any conclusions. The observations reported were all made near the zenith, at essentially the same air path, so that the ordinary curve of growth procedure is inapplicable. Furthermore the atmosphere is neither isopiestic nor isothermal and the thermal structures at the times of observation are unknown.

Our treatment of the solar data essentially involves

TABLE III. Curve of growth parameters for 1.26- μ discrete oxygen band in solar spectrum and derived Einstein coefficient.

Triplet component in ground state	$J''=K''-1$	$J''=K''$	$J''=K''+1$	Av.
$R[(m\text{\AA})^{-1}]$	0.0081	0.0110	0.0089	0.0093
$\gamma'_L(m\text{\AA})$	34	38	32	35
$\gamma_L^0(\text{cm}^{-1}\cdot\text{atm}^{-1})$				0.027
$B''(0-0) (\text{erg}^{-1}\cdot\text{sec}^{-1} \text{cm}^2)$				0.085 ± 0.013

the extrapolation of a plot of observed equivalent width W versus theoretical relative line intensity RS into the region of linear relationship. If the atmosphere were isothermal and all lines exhibited the same (Lorentz) pressure broadening, such a plot would be equivalent to a curve of growth, and should conform to the equation

$$W = 2\pi^{\frac{1}{2}}\gamma'_L \Gamma(\beta + \frac{1}{2}) / \Gamma(\beta), \quad (5)$$

where γ'_L is a Lorentz half-width, $\beta = S/2\pi\gamma'_L$, and S is the equivalent in this situation of the line intensity defined above. This equation is applicable to the condition in which the pressure gradient in the atmosphere transforms the Lorentz absorption line into what we may call the Pedersen,¹⁶ Strong, Plass,^{17,18} or PSP line. The γ'_L above is the Lorentz half-width at the maximum pressure (i.e., at the bottom of the atmosphere).

In plotting the data the equivalent widths used were the best averaged values recorded in the *Table of Solar Spectrum Wave-lengths*,⁸ although some original photometric tracings, made available to us by the courtesy of Mohler, have been of considerable assistance. The theoretical relative line intensities, $RS = S_J \exp(-\epsilon/kT)$, have been calculated for an average temperature of 251°K. We have plotted separately the lines involving the three components of the triplet ground state, partly to detect any systematic differences, and partly to assist in estimating the probable error in curve fitting. Figure 3 presents the data on the ^SR, ^QQ, and ^QP branches of the 1.26- μ band, and is typical in all respects.

For reasons implied above, one need not expect that the points of such a plot should fall on any single curve. Nevertheless they do conform reasonably well to the PSP curve of growth as may be seen in Fig. 3. The deviations, though fairly large, appear to be perfectly random; they are not common to sets of lines having common upper or lower states. Furthermore there is no indication of any large systematic decrease in γ'_L with line number, which would introduce a point of inflection in the plot just above the "knee," where the

transition from the linear to the square-root relation between W and S occurs. In any case, although the fit of the PSP curve of growth in the region of high intensities may have limited significance, it does become increasingly valid as the linear region is approached. We have consequently made use of the curve in the extrapolation to this region, with confidence that the intensities of the weaker lines obtained from the curve fitting have significance, though this may be less true of the pressure-broadening parameter.

A number of uncertainties arise from the thermal gradient in the atmosphere, but we comment only on the one which is most serious in regard to the weaker lines on which our conclusions largely depend. These lines involve high rotational states, and the error introduced by assuming an average temperature in calculating relative intensities is not trivial, but is probably small in comparison with that which might arise from an incorrect choice of this temperature. The value which we have assumed, 251°K, is the mass-weighted average corresponding to the White Sands average atmosphere.¹⁹ Although the thermal structures above Mt. Wilson at the times of the measurements are not known, an examination of radiosonde measurements at several stations in the southwest leads us to conclude that the error in our estimate probably does not exceed 5°.

The values of the parameters required to fit the PSP

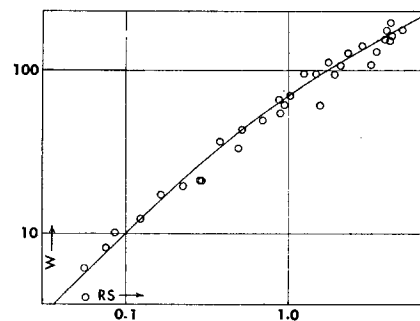


FIG. 3. Log-log plot of equivalent width, W (milliangstroms) versus theoretical relative line strength, for lines in the ^SR, ^QQ, and ^QP branches of the 1.26- μ oxygen band in the solar spectrum. Solid line represents the PSP curve of growth.

¹⁹ J. A. Van Allen *et al.* (The Rocket Panel), *Phys. Rev.* **88**, 1027 (1952).

¹⁶ E. F. Pedersen, *Meteorologische Annalen* (Norske Meteorologiske Institut) **1**, 117 (1942).

¹⁷ J. Strong and G. N. Plass, *Astrophys. J.* **112**, 365 (1950).

¹⁸ See also R. Goody, *Physics of the Stratosphere* (Cambridge University Press, London, 1954).

curves of growth to the data in the three plots mentioned are given in Table III, where the parameter γ_L^0 , the pressure-broadening constant, is defined by the relation $\gamma_L = \gamma_L^0 P$, where P is in atmospheres. The ratio R has been defined above, where we have outlined the method of calculating B'' . We have taken $N = 3.65 \times 10^{24}$ for a vertical path in the atmosphere above Mt. Wilson, and $T = 251^\circ\text{K}$, throughout. Results of the calculations are presented in Table I. The discrepancy between the value for the pressure-broadening constant quoted above, and the one found from the solar data, $\gamma_L^0 = 0.027 \text{ cm}^{-1} \cdot \text{atm}^{-1}$, seems to deserve comment, even though the former applies to pure oxygen, and the latter to air.

It is obviously impossible to estimate the intensity of any underlying continuous absorption in the $1.26\text{-}\mu$ region, from the high-resolution solar spectra. Nevertheless in low-dispersion spectra it is possible to estimate a plausible background, as Ellis and Kneser¹⁰ have done in the spectra of Abbot and Freeman.²⁰ This leads to an estimate of integral absorption of the order of twice the sum of the equivalent widths of the oxygen lines in this region, measured under high resolution. This is in qualitative agreement with our data which predict that in an air column at an average pressure of $\frac{1}{2}$ atm the ratio of integral absorption coefficients in the continuous and discrete bands, respectively, is about 0.5. Due to the line structure in the latter the ratio of *absorptions* should, however, be larger by more than a factor 2, which seems to have been ignored by several authors. In the $1.065\text{-}\mu$ region conditions are less favorable due to the intrusion of other bands, but there seems to be no evidence in the solar spectrum for any significant continuous absorption by oxygen. This is the basis for our earlier statement that nitrogen is ineffective in relaxing the vibrational selection rules.

²⁰ C. G. Abbot and H. B. Freeman, Smithsonian Inst. Misc. Collections **82**, 1 (1931).

CONCLUSION

The results of our investigation are collected in Tables I and II. From the degree of self-consistency of the data we estimate that the probable error in our intensity measurements, and in the coefficients derived directly from these data, does not exceed $\pm 15\%$. For the discrete-line transition, the values of $B''(0, 0)$ and $A'(0, 0)$ derived from the laboratory measurements, and the solar spectral data, agree well within this limit. The previous estimates of Vallance Jones and Gattinger,⁴ given for comparison, are considerably smaller, and we believe are outside the limit of our error.

In our prediction of the effect of gas pressure on the rate of decay we may be on less firm ground. Nevertheless from the available data we predict for the reciprocal mean lifetime of $^1\Delta_g$ oxygen molecules subject to decay *only by radiative processes*, which are moreover first order in excited molecule concentration:

$$(1/\tau_m) (\text{sec}^{-1}) = \bar{A} \\ = (2.6 \times 10^{-4}) (1 + 3.8P_{\text{O}_2} + 3.0P_{\text{CO}_2} + 0.7P_{\text{N}_2}), \quad (6)$$

where the P 's are partial pressures in atmospheres. The half-life of an isolated $^1\Delta_g$ molecule is then about 45 min, which, in pure oxygen, is reduced to 9.2 min at 1 atm. If some of the oxygen is vibrationally excited, as was observed by Browne and Ogryzlo,¹⁴ one may expect the decay to be somewhat more rapid owing to the availability of more paths of decay.

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