Fine Structure in the ³Σ Ground State of the Oxygen Molecule, and the Rotational Intensity Distribution in the Atmospheric Oxygen Band

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The formula developed by Kramers (and recently on different lines by Hebb) to represent the fine structure of the ground state of oxygen is compared with the experimental data. It is pointed out that the currently accepted values of the parameters are in error. The measurements are compared with a more accurate formula, which takes into account the fact that the rotation does not completely decouple the spin from the axis of the molecule, and values of the parameters are found which give excellent agreement. The rotational intensity distribution in the atmospheric O_2 bands is recalculated on the assumption of incomplete decoupling; the intensities in the ^PP and ^RR branches are found to be unchanged, while those in ^PQ and ^RQ become more nearly equal than with complete decoupling, a result in harmony with the measurements.

1. INTRODUCTION

A MULTIPLET structure of the ordinary kind, due to magnetic interaction between the total spin S ($=1$ for a triplet state) and the quantized component of the orbital electronic angular momentum along the axis of figure, does not arise in Σ states, for in them the latter component vanishes. It was, however, shown by Kramers[1] that the spin-spin interaction of the uncompensated electrons, invoked by Heisenberg to explain the fine-structure of the orthohelium terms, is equivalent to an interaction between S and the axis of figure, with energy proportional to $3\cos^2\theta - 1$, where θ is the angle between them. Kramers calculated the energy levels in first approximation by averaging the coupling energy over the "end-over-end" rotation of the molecule (quantum number K), and found that each rotational level K was split by the interaction into three, corresponding to the three different ways of constructing a total angular momentum vector J ($=K-1$, K, $K+1$) out of K and $S=1$.

There is a further effect[2,3] due to the interaction between the uncompensated spins and the magnetic field set up by the rotation of the molecule as a whole, which is equivalent to a cosine coupling between S and K. These two effects together give[1] for the three energy levels W_J associated with a given value of K the following expressions.

$$W_{K+1} = W_0 - 2\lambda(K+1)/(2K+3) + \mu(K+1),$$
$$W_K = W_0, \tag{1}$$
$$W_{K-1} = W_0 - 2\lambda K/(2K-1) - \mu K.$$

Here W_0 is the usual rotational energy $h^2 K(K+1)/8\pi^2 I$. The constant λ ($=3A/2$ in Kramers' notation) is a measure of the $\cos^2\theta$ coupling between S and the axis, and μ ($=$ Kramers' $-B$) is a measure of the cosine coupling between S and K.

There is a further cause of fine structure, not taken into account by Kramers. Although on the average the electronic orbital momentum of the molecule in a Σ state is null, this angular momentum has a precessing component perpendicular to the axis of figure, which interacts with the total spin S, an interaction which clearly involves an influence of neighboring $^3\Pi$ states on the $^3\Sigma$ state. The theory of this effect in the rotating molecule has been given recently by Hebb,[4] and the remarkable result has emerged that in first approximation the energy levels are given by expressions of exactly the same form as (1), the constants λ and μ having of course a different interpretation. Until suitable wave functions are available, and the various matrix elements on which the constants depend are worked out, it is not possible to disentangle accurately the contributions of the different causes of the fine structure to the values of λ and μ. But in any case it should be possible to represent the fine structure of a $^3\Sigma$ state by a formula of the type (1), regarding λ and μ as

[1] H. A. Kramers, Zeits. f. Physik 53, 422 (1929).
[2] F. Hund, Zeits. f. Physik 36, 657 (1926); 42, 93 (1927).
[3] J. H. Van Vleck, Phys. Rev. 33, 467 (1929).
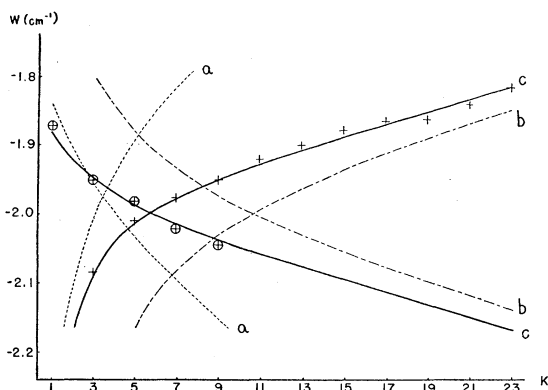[4] M. H. Hebb, Phys. Rev. 49, 610 (1936).

FIG. 1. In the figure the crosses represent the observed positions of two components $J=K-1$ (+) and $J=K+1$ ($\oplus$) of the fine structure of the $^3\Sigma$ ground state of the oxygen molecule (vertical scale in cm^{-1}), plotted against rotational quantum number K (horizontal scale); the positions of the observed points are given relative to the third component $J=K$ at ordinate 0 cm^{-1} (not shown). The curves (a), (b), (c), give the calculated positions of the components $J=K\pm1$, relative to $J=K$ at ordinate 0 cm^{-1}. (a) Kramers' formula, with $\lambda=0.726$ cm^{-1}, $\mu=-0.025$ cm^{-1} (the usually accepted values of the parameters), the levels $J=K\pm1$ having been arbitrarily reduced by 1.21 cm^{-1} as explained in the text. (b) Kramers' formula (Eq. 1), with $\lambda=1.985$ cm^{-1}, $\mu=-0.008$ cm^{-1}. (c) More complete formula (Eq. 2), with $\lambda=1.985$ cm^{-1}, $\mu=-0.008$ cm^{-1}.

parameters to be adjusted to fit the observations. The formula (1) will be referred to as Kramers' formula.

2. COMPARISON OF KRAMERS' FORMULA WITH EXPERIMENT IN OXYGEN

For oxygen, in connection with which Kramers originally developed his theory, the agreement is merely qualitative. As it has been stated several times in the literature that the agreement is good, it may be well to emphasize that Kramers says explicitly that his formula is inadequate for the quantitative description of the fine structure. The values of the parameters which he gives, and which have found their way into the literature ($\lambda=0.726$ cm^{-1}, $\mu=-0.025$ cm^{-1} in our notation) were obviously not meant to be taken very seriously; in order to obtain anything like agreement using these values, Kramers found it necessary to raise the level $J=K$ by an amount 1.21 cm^{-1} ($=1.67\lambda$, or 2.5A in Kramers' notation) relative to the others, an *ad hoc* shift for which he claimed no theoretical justification.

In Fig. 1 the crosses represent the observed relative positions of the components of the $^3\Sigma$

level plotted against K. Only two components of the triplet, *viz.* $J=K-1$ and $J=K+1$ are shown, marked by plain and circled crosses, respectively. The third component $J=K$ is too far distant to appear in the figure, but would be represented by a series of points parallel to the K axis at ordinate 0 (scale on left in cm^{-1}). The data are taken from Dieke and Babcock's measurements[5] of the B band of atmospheric oxygen. This band has been chosen in preference to the A band, with which Kramers originally compared his formula, because Dieke and Babcock assign greater weight to their determinations of wave-length in the B band. In any case the intervals derived from the two bands differ only slightly, and the A band could have been taken without materially affecting the conclusions.

The dotted line (a) in the figure gives the levels as calculated from Kramers' formula (1), using the commonly accepted values of the parameters $\lambda=0.726$ cm^{-1}, $\mu=-0.025$ cm^{-1}. The *ad hoc* shift mentioned above has here been taken account of by lowering the levels $J=K\pm1$ by 1.21 cm^{-1}. Even with this shift the agreement is very poor indeed.

Approximate values for the parameters which will give better agreement can be obtained from a rough consideration of the points representing the observations. From (1) we see that $-\mu$ is the asymptotic slope of W_{K-1} plotted against K; and also that the interval between W_K and the mean of W_{K+1} for $K=K'-2$ and W_{K-1} for $K=K'$ is independent of K' and equal to $-\lambda-\mu/2$. If we take the asymptotic slope from the observations as 0.08 cm^{-1} in 10 units of K, and note that the interval in question is actually approximately constant, having a mean value -1.981 cm^{-1}, we find $\lambda=1.985$ cm^{-1}, $\mu=-0.008$ cm^{-1}. The broken lines (b) in the figure give the energy levels calculated from (1) as functions of K, with these values of the parameters. The agreement, although better than before, is still poor, especially at lower values of K; in particular, the intersection of W_{K+1} and W_{K-1} falls near $K=11$ instead of near $K=6$. I am indebted to Professor Kramers for the information that he had himself noted that his formula as it

[5] G. H. Dieke and H. D. Babcock, Proc. Nat. Acad. Sci. **13**, 670 (1927).

stands could be made to agree moderately well with the observations at large values of K; but he did not place much weight on this agreement, and did not publish the corresponding values of the parameters, as the formula fitted very badly at low values of K, where the experimental points were believed to be more reliable.

3. Correction to Kramers' Formula

Kramers himself indicated a possible cause for the failure of his formula in oxygen, but did not pursue the question. The formula is exact only as far as the first power of the ratio of the fine structure separations to the rotational separations, or in other words, is valid when the $^3\Sigma$ state considered conforms closely to Hund's case (b), where the spin is almost completely decoupled from the axis of figure. This is more likely to be the case in molecules with small moments of inertia, such as the hydrides, than in oxygen.

The correction to be made, assuming that the cause of the fine structure is the spin-spin interaction of the uncompensated electrons, has been given implicitly by Hill and Van Vleck,[6] starting from case (b) as the unperturbed system, and also by the author,[7] starting from case (a). After superposition of the terms representing the coupling of the spin and the magnetic field due to rotation, the formulae for the fine structure are as follows.

$$W_{K+1} = W_0 + (2K+3)B - \lambda$$
$$- [(2K+3)^2B^2 + \lambda^2 - 2\lambda B]^{\frac{1}{2}} + \mu(K+1),$$
$$W_K = W_0, \qquad (2)$$
$$W_{K-1} = W_0 - (2K-1)B - \lambda$$
$$+ [(2K-1)^2B^2 + \lambda^2 - 2\lambda B]^{\frac{1}{2}} - \mu K,$$

where B is the usual constant $h^2/8\pi^2 I$, and λ and μ are the parameters introduced above. These expressions agree with Kramers' formula as far as the first power of λ.

If we assume that the cause of the fine structure is the interaction between $^3\Sigma$ and $^3\Pi$ states, it is easy to show from the secular determinant of the problem, given by Hebb,[4] that when the fine structure is no longer small compared with the rotational separation, it is

given by formulae of exactly the same form as (2), provided the $^3\Pi$ states are sufficiently remote from the $^3\Sigma$ state, and the terms in μ are much smaller than those in λ. To show this, it is only necessary to diagonalize that part of Hebb's determinant referring to $^3\Sigma$, then to take account approximately of interaction with $^3\Pi$ by putting the appropriate first order terms in $1/h\nu(\Sigma\Pi)$ on the diagonal, and finally to solve the secular problem involving the three $^3\Sigma$ states accurately as regards λ, supposing μ to be small, so that only the terms linear in μ are retained. Thus the agreement between the fine structure formulae arising from two completely different mechanisms, which was noted by Hebb to hold as far as the first powers of λ and μ, holds even when higher powers of λ are included; in oxygen μ turns out to be so much smaller than λ that the neglect of higher powers of μ seems perfectly legitimate.

4. Comparison of the Corrected Formula with the Observed Fine Structure in Oxygen

It is of interest to see whether the observations can be represented more accurately by the corrected formula (2) applicable when the fine structure and rotational separations are comparable, than with Kramers' formula (1), which assumes almost complete rotational decoupling of the spin. It will be noticed that the asymptotic slope and the mean of the levels $J = K \pm 1$ determine λ and μ in exactly the same way as before (§2), and lead to the same numerical values of these parameters.

The full lines (c) in Fig. 1 represent the levels $J = K \pm 1$ plotted from formula (2) with the values $\lambda = 1.985$ cm^{-1}, $\mu = -0.008$ cm^{-1}. The constant B for the ground state of the oxygen molecule has been taken as 1.438 cm^{-1}. The component $J = K$ is at ordinate 0. Agreement with the experimental points is most satisfactory, especially when regard is had to the open scale of ordinates which has been adopted. The intersection of $J = K \pm 1$ is now accurately reproduced.

The conclusion is that Kramers' formula, suitably corrected, is adequate to represent the fine structure of the $^3\Sigma$ state in oxygen quantitatively, but the values of the parameters differ considerably from those usually assumed.

[6] E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928).

[7] R. Schlapp, Phys. Rev. **39**, 806 (1932).

In the hydride molecules NH, PH, PD, OH⁺, Kramers' original formula has been found to represent the fine structure sufficiently well; this is what one would expect in view of the smallness of the moment of inertia for these molecules, which makes the constant B large, so that (2) differs little from (1).

5. INTENSITY DISTRIBUTION IN $^1\Sigma \leftarrow {}^3\Sigma$ BANDS

Van Vleck[8] has shown that these bands are associated with magnetic dipole transitions rather than with electric dipole transitions of the ordinary type. This fundamental modification of earlier views regarding the nature of these bands does not however invalidate the intensity formulae given by the author.[7] These formulae were based on the assumption of complete decoupling of the spin from the molecular axis. It has been seen above that as regards energy levels this assumption is certainly inadequate, at least in oxygen, and even the next approximation, in which only the first power of λ is retained, is insufficient. We may therefore expect that the incomplete decoupling will have an influence on the intensities.

The origin of the intersystem transitions is that orbit-spin interaction of the type $\Sigma a_i(l_i s_i)$ rather than $A(L \cdot S)$ blends the $^1\Sigma$ state with $^3\Pi$ states, and the $^3\Sigma$ state with $^3\Pi$ and $^1\Pi$ states. It is the blending of $^1\Sigma$ with $^3\Pi$, and of $^3\Sigma$ with $^1\Pi$ that makes intersystem transitions possible, the blending of $^3\Sigma$ with $^3\Pi$ gives no contribution to the intensity of these transitions. It is therefore justifiable to confine attention to the $^3\Sigma$ states (appropriately modified by blending with $^1\Pi$) without considering interaction with $^3\Pi$ in calculating intensities. In the paper referred to above,[7] the intensities were calculated for pure case (b), corresponding to $\lambda/B=0$. It is a comparatively simple matter to recalculate the intensities for any given value of λ/B. It is found at once that the rotational intensity distribution in the branches ^RR, ^PP is independent of the value of λ/B, i.e., of whether the $^3\Sigma$ state is case (a) or case (b) or intermediate between them. On the other hand the intensity distribution in ^PQ and ^RQ depends on the value of λ/B. For $\lambda/B=4/3$, which is roughly the value in oxygen, the in-

[8] J. H. Van Vleck, Astrophys. J. 80, 101 (1934).

TABLE I. *Comparison of experimental and calculated intensities.*

BRANCH	INTENSITY				
	Obs.[10]	Obs.[9]	Calc. $\lambda/B=0$[7]	4/3	2
$^PP=P_2$	$\frac{1}{2}(J+2)$	$\frac{1}{2}(J+2)$	$\frac{1}{2}(J+2)$	$\frac{1}{2}(J+2)$	$\frac{1}{2}(J+2)$
$^PQ=P_3$	$\frac{1}{2}(J+1)$	$\frac{1}{2}(J+\frac{1}{2})$	$\frac{1}{2}J$	$\frac{1}{2}(J+\frac{3}{4})^*$	$\frac{1}{2}(J+1)$
$^RQ=R_1$	$\frac{1}{2}J$	$\frac{1}{2}(J+\frac{1}{2})$	$\frac{1}{2}(J+1)$	$\frac{1}{2}(J+\frac{1}{4})^*$	$\frac{1}{2}J$
$^RR=R_2$	$\frac{1}{2}(J-1)$	$\frac{1}{2}(J-1)$	$\frac{1}{2}(J-1)$	$\frac{1}{2}(J-1)$	$\frac{1}{2}(J-1)$

*Asymptotic values.

tensities in these branches for larger values of J are approximately $\frac{1}{2}(J+\frac{3}{4})$ and $\frac{1}{2}(J+\frac{1}{4})$, respectively, being given for any value of J by the expressions

$$2J(J+1)(2J+1)[8J^2+8J+1$$
$$\pm(16J^2+16J+1)^{\frac{1}{2}}]$$
$$\div[64J^4+128J^3+84J^2+20J+1$$
$$\pm(12J^2+12J+1)(16J^2+16J+1)^{\frac{1}{2}}],$$

which do not however differ appreciably from the asymptotic values $\frac{1}{2}(J+\frac{3}{4})$, $\frac{1}{2}(J+\frac{1}{4})$ from $J=2$ upwards.

With $\lambda/B=2$ the calculated intensities in ^PQ and ^RQ are, respectively, $\frac{1}{2}(J+1)$ and $\frac{1}{2}J$, as contrasted with $\frac{1}{2}J$ and $\frac{1}{2}(J+1)$, respectively, for $\lambda/B=0$. It also appears that for a value of λ/B intermediate between 4/3 and 0 the calculated intensities of the two branches should be equal (as Childs and Mecke[9] have concluded them to be from their experiments) for all but the smallest values of J.

Although the intensity measurements are not sufficiently consistent to give an independent determination of λ/B, it is satisfactory that the experimental intensities given by Childs and Mecke are reproduced rather more accurately with the value of λ/B deduced from the energy levels (approximately 4/3) than with $\lambda/B=0$. In this connection it is not without interest to note that in their preliminary report[10] Childs and Mecke gave the intensities of the two branches ^PQ and ^RQ as $\frac{1}{2}(J+1)$ and $\frac{1}{2}J$, respectively.

For convenience Table I is given showing the experimental intensities according to Childs and Mecke, and the calculated intensities on the various hypotheses as to the value of λ/B.

I wish to record my thanks to Professor Van Vleck for valuable discussions.

[9] W. H. J. Childs and R. Mecke, Zeits. f. Physik 68, 344 (1931).
[10] W. H. J. Childs and R. Mecke, Nature 125, 599 (1930).