Intensities in $^2\Pi-{}^2\Sigma$ Transitions in Diatomic Molecules

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Simple intensity expressions for $^2\Pi-{}^2\Sigma$ and $^2\Sigma-{}^2\Pi$ transitions in diatomic molecules have been developed for cases in which the $^2\Pi$ state is intermediate between Hund's case (a) and case (b), by specializing the general formulas given by Hill and Van Vleck. Numerical values have been worked out for all branches in typical $^2\Pi$ cases, for low values of J.

SEVERAL years ago Hill and Van Vleck[1] developed formulas based on the new quantum mechanics giving the amplitudes necessary for finding the intensities of electronic transitions in diatomic molecules. These formulas are applicable to transitions in which either initial or final state, or both, is intermediate between case (a) and case (b) as classified by Hund.[2] The amplitudes are functions of the rotational quantum number J and of a parameter $\lambda=A/B$ for each state. $\lambda=\pm\infty$ in case (a), 0 in case (b). The present work involves the application of these general formulas to $^2\Pi\rightarrow{}^2\Sigma$ transitions, the reduction of the resulting expressions to surprisingly simple forms, and the substitution of numerical values to facilitate comparison with experimental data. Hill and Van Vleck gave formulas for these transitions, but did not put them in as simple explicit algebraic form as in the present paper. It is found experimentally that the $^2\Sigma$ state is nearly always case (b), but that the $^2\Pi$ state lies intermediate between case (a) and case (b). Accordingly the amplitude expressions were developed for arbitrary λ in the $^2\Pi$ state but $\lambda=0$ in the $^2\Sigma$ state, squared to give intensities, and simplified; the resulting expressions for the intensities of the twelve possible branches become the following functions of λ (in the $^2\Pi$ state) and J:

$^2\Pi\rightarrow{}^2\Sigma$	$^2\Sigma\rightarrow{}^2\Pi$	*Intensity*
P_2 $^{PP}P_{12}$	R_2 $^{RR}R_{21}$	$\dfrac{(2J+1)^2\pm(2J+1)\,U(4J^2+4J+1-2\lambda)}{32(J+1)}$
$^{Q}P_{21}$ P_1	$^{Q}R_{12}$ R_1	$\dfrac{(2J+1)^2\mp(2J+1)\,U(4J^2+4J-7+2\lambda)}{32(J+1)}$
Q_2 $^{P}Q_{12}$	Q_2 $^{R}Q_{21}$	$\dfrac{(2J+1)[(4J^2+4J-1)\pm U(8J^3+12J^2-2J+1-2\lambda)]}{32J(J+1)}$
$^{R}Q_{21}$ Q_1	$^{P}Q_{12}$ Q_1	$\dfrac{(2J+1)[(4J^2+4J-1)\mp U(8J^3+12J^2-2J-7+2\lambda)]}{32J(J+1)}$
R_2 $^{Q}R_{12}$	P_2 $^{Q}P_{21}$	$\dfrac{(2J+1)^2\pm(2J+1)\,U(4J^2+4J-7+2\lambda)}{32J}$
$^{RR}R_{21}$ R_1	$^{PP}P_{12}$ P_1	$\dfrac{(2J+1)^2\mp(2J+1)\,U[4J^2+4J+1-2\lambda]}{32J}$

where[3]

$$U=[\lambda^2-4\lambda+(2J+1)^2]^{-\frac{1}{2}}.$$

The designation of the branches for both $^2\Pi\rightarrow{}^2\Sigma$ and $^2\Sigma\rightarrow{}^2\Pi$ transitions is in the notation of Mulliken;[4] however, in any case the value of J is that in the $^2\Pi$ state. The level before the arrow is the upper state in emission. The intensity expressions as written include the statistical weight factor $2J+1$, but do not include an arbitrary factor which is independent of J. They are valid for all positive and negative values of λ (normal and inverted doublets), and for all values of $J>\frac{1}{2}$. For the case $J=\frac{1}{2}$, due to an anomalous correlation discussed by Hill and Van Vleck,[1,5] the formulas must be specially considered and give the values shown in the curves and tabulated as follows:

$J=\frac{1}{2}$	$^2\Pi\rightarrow{}^2\Sigma$	$^2\Sigma\rightarrow{}^2\Pi$
$\lambda>0$	$^{PP}P_{12}=P_1=\frac{1}{6}$ $^{P}Q_{12}=Q_1=\frac{1}{3}$	$^{RR}R_{21}=R_1=\frac{1}{6}$ $^{R}Q_{21}=Q_1=\frac{1}{3}$
$\lambda<0$	$P_2=^{Q}P_{21}=\frac{1}{6}$ $Q_2=^{R}Q_{21}=\frac{1}{3}$	$R_2=^{Q}R_{12}=\frac{1}{6}$ $Q_2=^{P}Q_{12}=\frac{1}{3}$.

The intensities of the other branches are identically zero for $J=\frac{1}{2}$.

[1] Hill and Van Vleck, Phys. Rev. **32**, 250 (1928).
[2] Hund, Zeits. f. Physik **36**, 657 (1926).
[3] The positive square root is to be used.
[4] Mulliken, Phys. Rev. **30**, 785 (1927).
[5] The standard Mulliken notation, which we use, is really a misnomer when $J=\frac{1}{2}$, $\lambda>0$ as the superscript no longer always gives the K behavior correctly in this exceptional case.

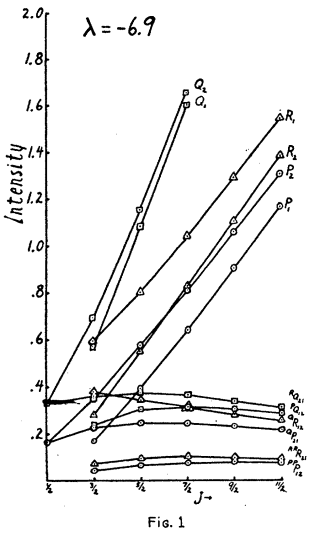

Fig. 1

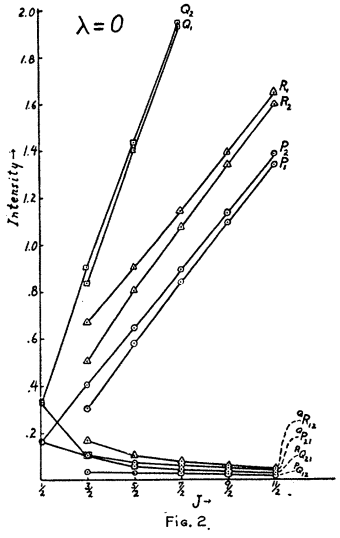

Fig. 2

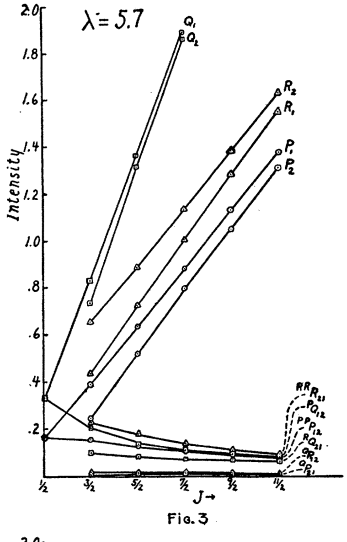

Fig. 3

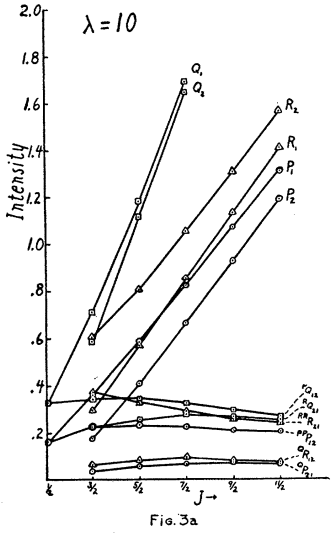

Fig. 3a

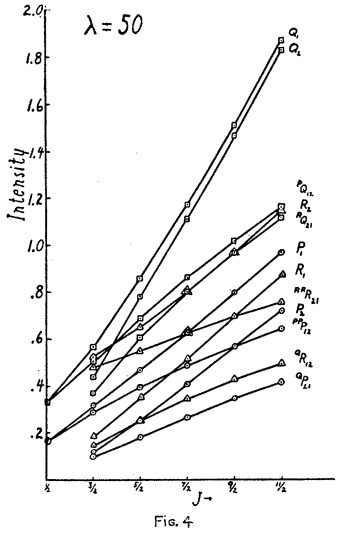

Fig. 4

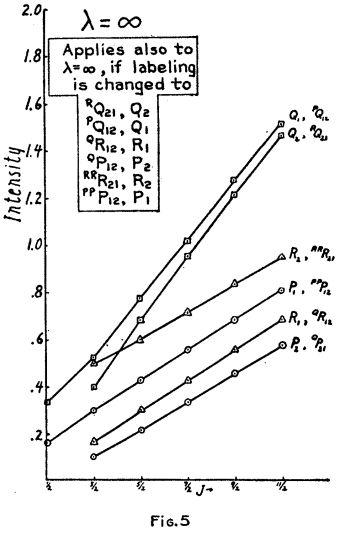

Fig. 5

Errata to Fig. 5: The following corrections should be made in the legend in the box: $\lambda = -\infty$; in the third line from the bottom, ${}^{Q}P_{21}$.

The accompanying curves show the rise of the two branches ${}^{PP}P_{12}$ and ${}^{RR}R_{21}$ (forbidden in case (b)) and the four satellite branches ${}^{Q}R_{12}$, ${}^{P}Q_{12}$, ${}^{R}Q_{21}$, ${}^{Q}P_{21}$ to intensities equivalent to those of the strong branches P_1, Q_1, R_1, P_2, Q_2, R_2, as λ increases. The notation on the curves is that appropriate to ${}^2\Pi \rightarrow {}^2\Sigma$ transitions. The relative position of the various branches varies fairly smoothly with λ in the regions intermediate between the various figures. The expressions given above are in agreement with the numerical values for the intensities in HgH ($\lambda = 560$) as calculated by Kapuscinski and Eymers.[6]

Appreciation is due and gladly given to Professor J. H. Van Vleck for his suggestion of this topic and his guidance in the work, which was done at the University of Wisconsin.

[6] Kapuscinski and Eymers, Zeits. f. Physik **54**, 246 (1929).