Associating and dissociating sines and cosines we arrive after some transformations at the simple value of (39):

$$K''-K'=(k^2/4\pi c\lambda)J_1(\lambda).$$

If $ct<r$ we write

$$ckt=\lambda' \sinh\alpha, \quad kr=\lambda' \cosh\alpha,$$
$$\lambda'^2=k^2(r^2-c^2t^2)=-\lambda^2.$$

Here λ is imaginary, and the result is

$$K''-K'=0.$$

(37) thus yields the exact solution

$$V''-V'=ck^2\int_{-\infty}^{t}\int\int\int J_1(\lambda)\lambda^{-1}\rho(\xi\eta\zeta\tau)d\tau d\xi d\eta d\zeta, \tag{40}$$

where

$$\lambda^2=k^2[(ct-c\tau)^2-(x-\xi)^2-(y-\eta)^2-(z-\zeta)^2].$$

The $\xi\eta\zeta$-integral is extended over values that make λ real.

Subtracting $V''-V'$ from the well-known Maxwell solution V'' with the same charges as sources one obtains the exact solution of the Yukawa equation.

OCTOBER 1, 1941 PHYSICAL REVIEW VOLUME 60

Intensities in Perturbations

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Quantitative formulae for the intensities of lines from a pair of interacting states to a common lower state are applied to perturbations in band spectra. It appears that rotational and vibrational perturbations show quite a different behavior. In the former there is a direct superposition of intensities of the two interacting states whereas in the latter interference effects give an entirely different picture. The general formulae are applied to a few cases in the H_2 spectrum.

THE so-called perturbations in molecular spectra are a special case of interaction between a pair of quantum-mechanical states. So far the energy shifts due to the perturbations have been well studied but very little definite information is available in the literature about the intensities except some general qualitative statements. The perturbations are often of great importance for the interpretation of complex spectra and the intensities may be just as helpful as the frequency shifts.

In the present paper the general theory of the intensities in perturbations is given which follows directly from the general quantum-mechanical treatment of interaction of states, and is then applied to a few special cases.

§1. General Theory

Assume that ψ_1 and ψ_2 are the wave functions of two states satisfying

$$H^0\psi_n=W_n{}^0\psi_n, \quad n=1, 2,$$

and that ψ_a and ψ_b are the corresponding wave functions of the perturbed problem[1]

$$(H^0+H^1)\psi_m=(W_1{}^0+E_m)\psi_m, \quad m=a, b.$$

We assume further that only the interaction between ψ_1 and ψ_2 is appreciable. This is an assumption very well realized in most molecular perturbations,[2] and means that the problem can be treated without further approximations. We shall drop this restriction in certain cases later on in this paper. We can express the neglect of the other interactions by assuming all matrix elements of the perturbation matrix to be zero[3]

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[1] Throughout this paper indices 1 and 2 will refer to the unperturbed and a and b to the perturbed states. ψ_a corresponds to ψ_1 and ψ_b to ψ_2 in the sense that ψ_1 furnishes the largest contribution to ψ_a, etc.

[2] We leave the influence of the electron spin out of consideration. The results are then strictly applicable only to singlets and to those multiple terms where the multiplet separation is small compared to the distance of the interacting states. The considerations can easily be expanded to the more general case.

[3] This does not necessarily mean that the other matrix elements are actually small compared to H'_{12}. Even if they

except H'_{12} and H'_{21} and we call

$$H'_{12}=\bar{H}'_{21}=S \quad \text{and} \quad S=Re^{i\alpha}. \tag{1}$$

We take in general ψ_1 to belong to the lower of the two unperturbed levels and ψ_a the lower of the two perturbed states. The correlation between the perturbed and unperturbed states is then perfectly defined except when $W_1{}^0=W_2{}^0$ when it does not matter. If the distance between the unperturbed states is

$$2\delta=W_2{}^0-W_1{}^0$$

we have

$$E_{a,b}=\delta\mp(R^2+\delta^2)^{\frac{1}{2}}. \tag{2}$$

The absolute value of the shift for either level is

$$\epsilon=|E_a|=E_b-2\delta=(R^2+\delta^2)^{\frac{1}{2}}-\delta. \tag{3}$$

The perturbed wave functions are

$$\psi_a=\frac{R}{(R^2+\epsilon^2)^{\frac{1}{2}}}\left(\psi_1-\frac{\epsilon}{R}e^{-i\alpha}\psi_2\right), \tag{4a}$$

$$\psi_b=\frac{R}{(R^2+\epsilon^2)^{\frac{1}{2}}}\left(\psi_2+\frac{\epsilon}{R}e^{i\alpha}\psi_1\right). \tag{4b}$$

ϵ/R lies between zero and one. If $R\ll\delta$, $\epsilon/R=R/2\delta$.

If both ψ_1 and ψ_2 can combine with the same final state ψ'' then the intensities of the two resulting lines are[4]

$$I_1=|q_1|^2, \quad I_2=|q_2|^2,$$

where the amplitudes are

$$q_n=\int\bar{\psi}_n q\psi''d\tau, \quad n=1, 2. \tag{5}$$

q is proportional to one of the components of the dipole moment if we are concerned with dipole radiation to which we shall restrict ourselves. The results for quadrupole radiations are analogous if we substitute for q the various components of the quadrupole moment. If q is proportional to x, I_1 is the radiation polarized in the x direction, etc.

The perturbed amplitudes can be expressed in terms of the unperturbed ones because of (4) and (5)

$$q_a=\frac{R}{(R^2+\epsilon^2)^{\frac{1}{2}}}\left(q_1-\frac{\epsilon}{R}e^{-i\alpha}q_2\right), \tag{6a}$$

$$q_b=\frac{R}{(R^2+\epsilon^2)^{\frac{1}{2}}}\left(q_2+\frac{\epsilon}{R}e^{i\alpha}q_1\right), \tag{6b}$$

from which it follows that the intensities are

$$I_a=\frac{R^2}{R^2+\epsilon^2}\left[I_1+\frac{\epsilon^2}{R^2}I_2-\frac{2\epsilon}{R}(I_1I_2)^{\frac{1}{2}}\cos(\alpha-\beta)\right], \tag{7a}$$

$$I_b=\frac{R^2}{R^2+\epsilon^2}\left[I_2+\frac{\epsilon^2}{R^2}I_1+\frac{2\epsilon}{R}(I_1I_2)^{\frac{1}{2}}\cos(\alpha-\beta)\right], \tag{7b}$$

in which β is the phase difference between ψ_2 and ψ_1. This phase difference is entirely arbitrary, as the phases of the wave functions are not determined by the wave equation and the boundary and normalization condition, and no physical quantity should depend on it. The dependence of the intensities on it is only apparent, for if we increase β by an arbitrary amount γ the perturbation matrix element

$$H_{12}'=\int\bar{\psi}_1H'\psi_2d\tau=Re^{i\alpha}$$

is multiplied by $e^{+i\gamma}$, i.e., α increased by γ. $\alpha-\beta$ which occurs in (7) is therefore completely independent of the phases of the wave function as it should be.

We shall call the terms in (7) containing the cosine the interference terms.

A direct consequence of (7) is that

$$I_a+I_b=I_1+I_2. \tag{8}$$

The sum of the intensities of two lines due to the combination of two levels with a common lower level is independent of the interaction between the two initial states.

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are not small their influence is negligible if the levels lie far away from $W_1{}^0$ and $W_2{}^0$. Furthermore by assuming $H'_{11}=H'_{22}=0$ we do not restrict the generality of the problem as these terms have only a trivial influence on the result and do not affect the interaction. Treatment of the intensities in a more complicated case in He_2 is given by Kronig and Fujioka, Zeits. f. Physik **63**, 168, 175 (1930).

[4] If the q_i are proportional to the coordinates then $I\sim\nu^4|q_i|^2$, where the proportionality factor now contains only general constants. In general the perturbed and unperturbed lines lie so close together that the factor ν^4 is a constant and can be left out. In comparing the intensities of lines in different wave-length regions, however, the factor ν^4 would become important. In order to avoid carrying this factor in all the formulae we use in this paper quantities which are proportional to the real intensities divided by ν^4.

The formulae (7) apply to any interacting pair of levels in any atomic or molecular system. A special case, for example, is furnished by the Raman effect of CO_2 treated by Fermi.[5]

When both I_1 and I_2 are different from zero, the phase α of the perturbation element is very important. (We take the arbitrary phase difference β to be zero which corresponds to the conventional form of the wave functions in almost all cases), and we shall see that the two different types of perturbations usually recognized in spectra of diatomic molecules to which we shall restrict ourselves from now on differ fundamentally in this respect.

When $I_2=0$, the interference term always is absent and we have

$$I_a=\frac{R^2}{R^2+\epsilon^2}I_1,\quad I_b=\frac{R^2}{R^2+\epsilon^2}I_1.$$

We get the so-called extra line with the intensity I_b but as the intensities are entirely independent of the phases in this case, we cannot draw any conclusions regarding the type of interaction from the intensities.

As the intensities depend on ϵ/R we can have considerable intensity anomalies even for small wave-length perturbations, provided ϵ and R are both small. This will happen when two very feebly interacting states lie very close together.

In the approximate treatment of a molecule certain terms are left out of the Hamiltonian. Some of these terms can be interpreted as interaction between electronic motion and rotation, and the perturbations caused by them are called *rotational* or type A perturbations. Type B or *vibrational* perturbations are caused by terms which express the interaction between electronic motion and vibration. In a typical perturbation of either kind the usual manifestation of the perturbation is an irregularity in the spacing of the *rotational* levels. From this point of view the terms "rotational" and "vibrational" perturbation are somewhat misleading, but there can be no ambiguity if they are used in the above sense.

The two types of perturbations differ in many of their properties[6] and we shall see that they are quite radically different in the behavior of their intensities.

§2. ROTATIONAL (TYPE A) PERTURBATIONS

The interaction function for rotational perturbations is[6]

$$H^{(3)}=Bi\left[\operatorname{ctg}\theta(M_\xi+iM_\eta M_\zeta+iM_\zeta M_\eta)\right.$$
$$\left.+2\operatorname{cosec}\theta M_\eta\frac{\partial}{\partial\varphi}+2M_\xi\frac{\partial}{\partial\theta}\right],$$

where ξ, η, ζ are Cartesian coordinates fixed to the molecule and θ and ϕ the angles which determine the orientation of the molecule. M_ξ, M_η, $M_\zeta=\Lambda\hbar$ are the components of the electronic angular momentum and $B=h^2/8\pi^2mr^2$. The matrix element for the interaction between the states $\psi_1(\Lambda\pm1, K, m)$ and $\psi_2(\Lambda, K, m)$ is (all others are zero)

$$S=2(\Lambda\pm1|BM_\eta|\Lambda)$$
$$\times[(K+\tfrac{1}{2}-\Lambda\mp\tfrac{1}{2})(K+\tfrac{1}{2}+\Lambda\pm\tfrac{1}{2})]^{\frac{1}{2}}.$$

With the conventional choice of coordinates and wave functions $(\Lambda\pm1|BM_\eta|\Lambda)$ is purely imaginary,[7] which means that the interference term in (7) disappears and we get for the perturbed intensities

$$I_a=\frac{R^2}{R^2+\epsilon^2}\left(I_1+\frac{\epsilon^2}{R^2}I_2\right),\tag{9a}$$

$$I_b=\frac{R^2}{R^2+\epsilon^2}\left(I_2+\frac{\epsilon^2}{R^2}I_1\right).\tag{9b}$$

This has a well-known elementary interpretation. The perturbed states can be regarded as mixtures of the unperturbed states, and the properties of the perturbed states are accordingly mixtures of the properties of the unperturbed

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[5] E. Fermi, Zeits. f. Physik **71**, 250 (1931).

[6] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929). See also G. H. Dieke, Phys. Rev. **47**, 870 (1935). The notation of the latter paper is followed closely in this article.

[7] $$M_\xi\pm iM_\eta=\hbar e^{i\chi}\left(\pm\frac{\partial}{\partial\psi}-\frac{i}{\sin\theta}\frac{\partial}{\partial\chi}\right)$$

has only real elements, if the connection between the Cartesian coordinates ξ, η, ζ and the polar coordinates ρ, ψ, χ is in the usual form

$$\xi=\rho\sin\psi\cos\chi,\text{ etc.}$$

and the dependence on the cyclic variable χ is in the form $\exp(\pm i\Lambda_\chi)$. It is easily seen that nothing is changed if the dependence on χ is taken in the form $\cos\Lambda\chi$ and $\sin\Lambda\chi$ which is more suitable for molecular levels. From this it follows that the elements of M_ξ are real and those of M_η purely imaginary.

states. The perturbed intensities are weighted averages of the unperturbed ones and the weight factors are the probabilities with which the unperturbed states occur in the perturbed state. It must be noted, however, that we get this simple result only because the interference term is absent.

If the interaction terms are small but the interacting levels close together we call the effect perturbations proper. For larger values of the interaction with the interacting levels at a great distance we have Λ-doubling. If the levels are close together and interact strongly we get *l*-decoupling. In the latter case our results are only valid for a *p*-complex as, for *d*- and higher complexes, the interaction of more than two levels has to be considered.

There are many cases known where anomalous intensities have been observed in band spectra perturbations but quantitative measurements of such anomalies are scarce. The interpretation of such measurements, even when they exist, is complicated by the fact that the actual intensities of the lines depend often in a complicated way on the discharge conditions so that it is difficult to know what the unperturbed intensities should be. Ratios of intensities of lines coming from the same upper level have more significance. Such a pair of lines in a band are $R(K-1)$ and $P(K+1)$ and the ratio

$$f(K)=I_{R(K-1)}/I_{P(K+1)}$$

has a definite value for the different types of bands, e.g., for

$$\begin{array}{cccc} \Sigma\rightarrow\Sigma & \Pi\rightarrow\Sigma & \Sigma\rightarrow\Pi & \Pi\rightarrow\Pi \\ \dfrac{K}{K+1} & \dfrac{K+1}{K} & \dfrac{K-1}{K+2} & \dfrac{(K-1)(K+1)^2}{K^2(K+2)} \end{array} \quad \text{etc.}$$

Let us call these ratios f_1 and f_2 for the unperturbed lines, then

$$f_a=\frac{f_1+(\epsilon^2/R^2)A^2f_2}{1+(\epsilon^2/R^2)A^2}=\frac{f_1+\alpha^2f_2}{1+\alpha^2}, \tag{10a}$$

$$f_b=\frac{f_2+(\epsilon^2/AR^2)f_1}{1+(\epsilon^2/AR^2)}, \tag{10b}$$

where

$$\alpha=(\epsilon/R)A, \quad A^2=I_2^P/I_1^P. \tag{11}$$

These values lie between f_1 and f_2. If the perturbation is only small $f_a\sim f_1$ and $f_b\sim f_2$. It may be noted that these simple relations are only true if the perturbation element is imaginary. Otherwise f_a and f_b might have any value between 0 and ∞.

TABLE I. *Values of the ratio f_a.*

K	f_1	f_2	Observed f_a			
			$0\rightarrow0$	$1\rightarrow1$	$2\rightarrow2$	$3\rightarrow3$
1	2.00	0.50			1.55	1.51
2	1.50	0.67		1.35	1.08	1.00
3	1.33	0.75				0.84
4	1.25	0.80	0.85		0.82	
5	1.20	0.83				
6	1.17	0.86	0.74			

§3. EXAMPLE IN THE H_2-SPECTRUM

A test of these relations is generally of value only for small values of K as otherwise the f_n values are so close to one that they cannot be distinguished experimentally. There are quantitative measurements of the f_a quantities in the Fulcher bands of hydrogen[8] which are summarized in Table I. The Fulcher bands are a $\Pi\rightarrow\Sigma$ transition and the f values for this transition are given in column f_1. The initial $3p^3\Pi$ state is known to be perturbed by the $3p^3\Sigma$ state and the f values of the $\Sigma\rightarrow\Sigma$ transition are given in column f_2. We see that the observed f_a values all lie between f_1 and f_2 except the somewhat doubtful value for $K=6$ of the $0\rightarrow0$ band. (Kapuscinski and Eymers give 0.92 for this value.)

Whereas this qualitative result agrees with what we expect, we find serious discrepancies in the quantitative results. The magnitude of the perturbation is expressed in the Λ-doubling and from it follows[9] that the value of $\epsilon/R=0.041\times[K(K+1)]^{\frac{1}{2}}$. The order of magnitude of $A^2=I_2/I_1$ is less than 10. Under these circumstances we would expect only a very slight departure from f_1. (For $K=1$ and $A=10$ we would obtain $f_a=1.95$ instead of the observed 1.53.)

The reason for the discrepancy can be either that the experimental values are wrong or that the calculations do not represent the true picture.

As far as the experimental values are concerned, it is immediately obvious that the only source of errors responsible for the anomalous values can

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[8] N. Ginsburg and G. H. Dieke, Phys. Rev. **59**, 632 (1941).

[9] G. H. Dieke, Phys. Rev. **48**, 610 (1935).

be the calibration of the plate for different wave-lengths. This involves the calibration of the standard comparison lamp. As the measurements referred to were made with all reasonable care and agreed besides quite well with those of Kapuscinski and Eymers[10] which were made under entirely different circumstances, though with essentially the same method, there is very little doubt that the discrepancy cannot be due to experimental errors.

If the anomalous values for the R/P ratios cannot arise from the interaction with the $3p^3\Sigma$ state which gives rise to the regular Λ-doubling, we must look for other interactions which, though giving rise to unnoticed wave-length perturbations, may affect the intensities strongly. We have seen earlier that the possibility for such perturbations exists. The perturbing state can be only a $^3\Sigma$ state, as a $^3\Delta$ state, although capable of giving rise to strong wave-length perturbations, cannot produce anomalies of the intensity ratios in a $\Pi\rightarrow\Sigma$ transition, as a $\Delta\rightarrow\Sigma$ transition does not exist. It is easy to convince oneself that the higher vibrational states of $3p^3\Sigma$ cannot be responsible. Other $^3\Sigma$ states in the immediate vicinity of $3p^3\Pi$ are not known. There certainly can not be another $^3\Sigma$ state with the right symmetry in a suitable position, with the possible exception of states with both electrons excited about the position of which we know nothing.

The other remaining possibility is that the abnormal intensity ratios do not arise from the interaction with only one state but by the cooperating influence of several states, and we have to investigate this possibility next.

§4. INTERACTION WITH SEVERAL LEVELS

If more than a pair of states interact, the calculations become much more complicated. However, when the influence of the other states on state one is small, their contributions are additive and we obtain in first-order approximation according to (4)

$$\psi_a=N\left(\psi_1-\sum_n\frac{\epsilon_n}{R_n}\exp\left(-i\alpha_n\right)\psi_n+\sum_m\frac{\epsilon_m}{R_m}\exp\left(i\alpha_m\right)\psi_m\right),$$

where N is the normalizing factor

$$N^2=\Big[1+\sum_{n,\,m}\left(\epsilon_l^2/R_l^2\right)\Big]^{-1}$$

and the first sum extends over all states below and the second over all states above ψ_1.

Let us take a state ψ_1 with a definite value of Λ. Then the interacting states can either have $\Lambda_n=\Lambda-1$ or $\Lambda_n=\Lambda+1$. In the former case $\exp(-i\alpha_n)=i$, which makes $\exp(i\alpha_m)=-i$. For $\Lambda_n=\Lambda+1$ the signs are exactly reversed so that we have

$$\psi_a=N\left(\psi_1\mp i\sum\frac{\epsilon_n}{R_n}\psi_n\right),$$

where the summation extends now over all states and the minus sign refers to the states with $\Lambda-1$ and the plus sign to those with $\Lambda+1$. Only for $\Lambda\rightarrow\Lambda$ transitions do we have to consider both terms for the R/P ratios.

We have

$$I_a=N^2\left[I_1+\left(\sum\pm\frac{\epsilon_n}{R_n}A_n\right)^2\right]. \tag{12}$$

This makes the ratio

$$\frac{I_R}{I_P}=f_a=\frac{f_1+\left[\sum\pm(\epsilon_n/R_n)A_nf_n^{\frac{1}{2}}\right]^2}{1+\left[\sum\pm(\epsilon_n/R_n)A_n\right]^2},$$

where, as before, $A^2{}_n=I_n/I_1$ for the P lines. All the values of f_n belonging to a given sign are identical, so that we can write also

$$f_a=\frac{f_1+(\alpha f_2^{\frac{1}{2}}-\beta f_3^{\frac{1}{2}})^2}{1+(\alpha-\beta)^2}, \tag{13}$$

where

$$\alpha=\sum(\epsilon_n/R_n)A_n,\quad f_2=I_2^R/I_2^P, \tag{14}$$

for the states with $\Lambda_n=\Lambda-1$ and β and f_3 the corresponding values for the states with $\Lambda_n=\Lambda+1$. If only one type of states needs to be considered, as, e.g., for a $\Pi\rightarrow\Sigma$ transition, we have

$$f_a=(f_1+\alpha^2f_2)/(1+\alpha^2),$$

which is identical with (10a) except for the more general definition (14) of α.

These relations also hold when the perturbing states are continuous. In that case we have with the proper normalization of the wave functions

$$\alpha=I_1^{-\frac{1}{2}}\int\frac{R_\nu}{2\delta_n}|q_\nu|d\nu.$$

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[10] W. Kapuscinski and J. G. Eymers, Proc. Roy. Soc. **A122**, 58 (1929).

$\int |q_\nu^2| d\nu$ is the total intensity[4] of the continuous spectrum originating from transitions between the state ψ'' and the continuous states. A fairly accurate numerical calculation of α can be made if the wave functions of the three states ψ'', ψ, and ψ_ν are known.

We return now to the anomalous f_a values in the Fulcher bands of H_2. We must take the contributions of all $^3\Sigma_u$ states. Those which do interact strongly with $2p^3\Pi$ and at the same time combine strongly with the lower state (large A_n) are most important. There is no other discrete state known which combines strongly enough with the lower state. If it existed, it would undoubtedly have been discovered.

Of the continuous states, those lying above $3p^3\Pi$ with only one electron excited also can be excluded, as they do not combine with sufficient strength with $2s^3\Sigma$. However, the well-known continuous state $2p\sigma^3\Sigma$, the combination of which with $2s^3\Sigma$ is held responsible for most of the strong continuous spectrum of H_2, satisfies all requirements.

It would be feasible to calculate numerically the value of α with the wave functions of James and Coolidge. However, only those for $2s^3\Sigma$ and $2p^3\Sigma$ are known and the calculations would be quite laborious in any case. We can come to a very rough estimate of the order of magnitude by assuming the action of the continuous spectrum to be replaced by a single lines which has the total intensity of the continuous spectrum and the lower state of which interacts with $3p^3\Pi$ as all the continuous levels together. We assume this line to coincide roughly with the maximum of the continuous spectrum at about 35,000 cm^{-1}. This means $2\delta \sim 5\times 10^4$. $R^2 = 2BK(K+1) \sim 120$ for $K=1$.

$$\alpha^2 = \frac{R^2}{4\delta^2} A = \frac{120}{25} \times 10^{-8} A = 0.5\times 10^{-7} A.$$

In order to obtain the experimentally observed value 0.5 for α^2 we would have to assume that the total intensity of the continuous spectrum would be about ten million times that of the Fulcher bands. No measurements exist of this ratio, but it seems definitely much too high. On the other hand, a more exact calculation of α^2 would probably increase its value, as it would give greater emphasis to the states with smaller δ. With the present state of our information we can therefore conclude that the anomalies in the R/P ratios of the Fulcher bands probably cannot be due to the interaction with the continuous $2p^3\Sigma$ state although that possibility cannot be completely excluded.

There remains the possibility that a continuous state with both electrons excited lies close to the initial state $3p^3\Pi$ of the Fulcher bands and interacts feebly with it. $(2p\sigma)(2s\sigma)^3\Sigma_u$ would be a possibility if it is continuous, as it would be expected to combine strongly with the lower state $(1s\sigma)(2s\sigma)^3\Sigma_g$. There is, however, at present no experimental evidence either for or against such a possibility.

§5. VIBRATIONAL (TYPE B) PERTURBATIONS

The perturbation function for vibrational perturbations is given by

$$H^{(4)}\psi = B\left[(M_\xi^2 + M_\eta^2)\Phi - 2r\frac{\partial\Phi}{\partial r} - r^2\frac{\partial^2\Phi}{\partial r^2} - \frac{2r^2}{R}\frac{\partial R}{\partial r}\frac{\partial\Phi}{\partial r}\right] RU,$$

in which r is the internuclear distance and Φ, R, U are the electronic, vibrational and rotational wave functions, respectively. As all the essential quantities are real, the matrix elements are real in this case and the phase in the interference term must be either 0 or π. The formulae for the intensities become then

$$I_a = \frac{R^2}{R^2+\epsilon^2}\left((I_1)^{\frac{1}{2}} \mp \frac{\epsilon}{R}(I_2)^{\frac{1}{2}}\right)^2, \qquad (14a)$$

$$I_b = \frac{R^2}{R^2+\epsilon^2}\left((I_2)^{\frac{1}{2}} \pm \frac{\epsilon}{R}(I_1)^{\frac{1}{2}}\right)^2. \qquad (14b)$$

The upper signs hold if the interaction element is positive, the lower ones if it is negative.

We have now intensity relations completely different from those of the rotational perturbations. We can have now, for instance, a case when $I_1 \sim (\epsilon^2/R^2) I_2$ that one of the perturbed lines is completely absent and the other one has the sum of the intensities of both unperturbed lines, a state of affairs which never can occur in class A perturbations. In a typical perturbation case we have two sets of rotational levels $W_1(K)$ and $W_2(K)$ such that

$$W_1(K) < W_2(K) \quad \text{if} \quad K < K_0,$$
$$W_1(K) > W_2(K) \quad \text{if} \quad K > K_0.$$

$K = K_0$ is the place of maximum perturbation.

If we regard now the intensities of the set $W_a(K)$ which are the perturbed values of W_1, then we see that below the maximum perturbation the amplitudes are subtracted (if S is positive) and we may get very low intensities, whereas above the maximum perturbation the amplitudes are added and we get abnormally large intensities. This sudden jump in the intensities is characteristic for class B perturbations. We have seen that the intensities behave quite smoothly in class A perturbations. In general we can expect much more irregular intensities for vibrational than for rotational perturbations.

The ratios $R(K-1)/P(K+1)$ are not affected by vibrational perturbations, as only levels with the same Λ interact, and we have therefore $f_a = f_1 = f_2$. (This would be true *independently* for any kind of interaction between levels with the same Λ.)

The only case of a vibrational perturbation in which the intensities have been measured is that of the interaction of the $2s\,{}^1\Sigma$ and $(2p\sigma)^2\,{}^1\Sigma$ states and the bands which are produced by the transitions from these levels to $2p\,{}^1\Sigma$. The intensities which appear at first sight highly erratic are shown in another paper to behave exactly as predicted by the preceding formulae.

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An Anomalous Crystal Photo-Effect in *d*-Tartaric Acid Single Crystals*

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Brady and Moore observed that certain crystals which appeared to have flaws and were not very transparent gave a current response which started out in one direction just after the light was turned on, decreased rapidly with time of illumination, and then flowed in the opposite direction. This phenomenon has been investigated in detail. All clear, well-formed, single crystals exhibit this current-reversal phenomenon when light falls on certain points of the crystal surface. These points always lie between two regions which respond with normal current flows in opposite directions. The superposition of the two normal current-response curves gives a resultant which agrees with the observed current-reversal curve within the experimental error. The various current response curves for different illuminated faces of the crystal, including the current-reversal effect, are correlated by assuming a particular direction in the unit cell of the crystal for which the electrical conductivity is a maximum.

It has been shown by Brady and Moore[1] that tartaric acid crystals exhibit a crystal photo-effect (actinoelectric effect). Just after the light is turned on, the galvanometer used to measure the amplified photo-current exhibits a deflection which rises very suddenly to a maximum, then decreases, and finally reaches a steady value. This behavior will be referred to as the "normal effect." Brady and Moore observed, also, that certain crystals which appeared to have flaws and were not very transparent behaved differently from the normal response curve. When light was turned on such a crystal, the galvanometer deflected first in one direction, then quickly reversed passing through zero to reach a maximum in the opposite direction. It then decreased slowly and finally approached a steady value as shown by curve E, Fig. 2. This phenomenon was investigated in detail in the present experiment. It will be referred to as the "abnormal effect."

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* Published with the approval of the Monographs Publication Committee, Oregon State College. Research paper No. 50, School of Science, Department of Physics.

[1] J. J. Brady and W. H. Moore, Phys. Rev. **55**, 308 (1939).