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O. K. Rice

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Predissociation and the Crossing of Molecular Potential Energy Curves

O. K. RICE, *Chemical Laboratory, Harvard University*

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The calculation of the width and shape of a line which is broadened because of predissociation has been extended so as to include perturbations of intermediate size. By "perturbations of intermediate size" we mean perturbations which are not so great that lines (of given rotational quantum number) belonging to two adjacent vibrational levels are broadened so as to overlap appreciably; they may be any size up to that limit. These calculations have been applied with certain simplifying assumptions to the case where a potential curve giving molecule formation is intersected by a repulsive curve, the curves which cross defining the unperturbed energy levels and wave functions. It is found that the discrete lines are not only broadened, but they are shifted in position, slightly distorted in shape, and there is present a series of subsidiary maxima of the

absorption coefficient. The exact amount of broadening of a line depends very greatly upon its energy relative to the energy at which the potential curves cross, and in general a line which is much broadened will also be much shifted in position. In molecules we may expect to have isolated groups of rotational levels in which the central level is sharp, and the rotational levels on either side become more and more diffuse, finally fading out. The predissociation phenomena in iodine chloride are discussed on the basis of the above theory. In particular, two groups of sharp and diffuse levels, such as described, are considered and are respectively ascribed to the isotopic molecules, ICl^{35} and ICl^{37} . There is some difficulty in describing the phenomena in iodine chloride quantitatively, but qualitatively the experimental results appear to accord with the theory.

THE question of what happens when two potential energy curves of a diatomic molecule cross has interested spectroscopists for some time. The Franck-Condon principle, so useful in explaining intensities in band spectra, says, when applied to the case of radiationless transitions such as occur for example in predissociation, that transitions are likely to occur from the electronic state corresponding to one potential energy curve to the electronic state corresponding to the other if the total energy of the system is about equal to the energy at which the two curves cross. This principle has been used by Herzberg¹ and others to explain the variation in the widths of the rotation lines in various cases of predissociation. Nevertheless, little quantitative work has been done on the subject. It is the purpose of this article to investigate quantitatively just what does happen in the neighborhood of the crossing point of two potential energy curves in a particularly simple case of predissociation.

We shall find that a given rotation level is not only broadened, but is somewhat distorted in shape, is shifted in position, and has a rather complicated secondary structure. An attempt will then be made to apply the results to the case of predissociation in iodine chloride, observed by Brown and Gibson.²

§1. GENERAL THEORY

The phenomenon of predissociation, first discovered by Henri and Teves,³ was explained as a sort of molecular Auger process by Bonhoeffer and Farkas,⁴ and considered from a quantum mechanical point of view by Kronig.⁵ I discussed it further,⁶ and gave a fairly rigorous derivation of the formula for the amount of broadening of the rotation lines as a function of the perturbation matrix component of the disturbance causing the effect. In order to handle the present situation.

¹ See Herzberg, *Zeits. f. Physik* **61**, 604 (1930); *Ergeb. d. exacten Naturwiss.* **10**, 237 (1931). Other references are given in the latter article. The question has been treated from another point of view by London, *Zeits. f. Physik* **74**, 158 (1932). In this connection see also, Neumann and Wigner, *Phys. Zeits.* **30**, 467 (1929), and Zener, *Proc. Roy. Soc. (London)* **A137**, 696 (1932).

² Brown and Gibson, *Phys. Rev.* **40**, 529 (1932).

³ Henri and Teves, *Nature* **114**, 894 (1924).

⁴ Bonhoeffer and Farkas, *Zeits. f. physik. Chemie* **134**, 337 (1928).

⁵ Kronig, *Zeits. f. Physik* **50**, 360 (1928). See also Wentzel, *Zeits. f. Physik* **43**, 524 (1927); Fues, *Zeits. f. Physik* **43**, 726 (1927); Wentzel, *Réunion Internationale de Chimie Physique*, Paris, 1928, p. 121.

⁶ Rice, *Phys. Rev.* **33**, 748 (1929); **35**, 1551 (1930).

ation, some of the approximations and specializations made in this theory need to be removed, and to this task we now address ourselves.

We consider a diatomic molecule, or a pair of atoms, and make use of an approximate wave function, ψ , which may be written in the form

$$\psi = \Theta R. \quad (1)$$

Here Θ is the wave function for the electrons and the rotation, obtained by holding the distance, r , between the two nuclei fixed. It depends therefore on the rotational and electronic coordinates, and on r only as a parameter. R is the radial part of the wave function and is a function only of r , though it depends on the quantum numbers of Θ .

A Θ belonging to a given electronic and rotational state of the molecule, distinguished by a subscript, say k , will obey an equation of the form

$$(H_0 - U_k)\Theta_k = 0, \quad (2)$$

where H_0 is the Hamiltonian operator for the electronic and rotational coordinates, and U_k (a function of r) is the energy.

A given R which goes with Θ_k , say R_{km} , may be written in the form F_{km}/r , where F_{km} obeys the equation

$$d^2 F_{km}/dr^2 + \eta^2 (E_{km} - U_k) F_{km} = 0, \quad (3)$$

where $\eta^2 = 8\pi^2 M/\hbar^2$, and M is the reduced mass of the system.

We now write, in formal fashion, the wave equation which is obeyed by the approximate wave function $\psi_{km} = \Theta_k F_{km}/r$ as

$$(H - E_{km})\psi_{km} = 0. \quad (4)$$

But this cannot be an exact equation. At the very best, in separating the electronic and rotational coordinates from the coordinate r we have made an approximation. We shall let an exact wave function ψ' obey the equation

$$(H + V - E')\psi' = 0, \quad (5)$$

where V is a perturbation term and E' the perturbed energy.

We now come more specifically to the consideration of a particular case in which predissociation may occur. We will suppose that we have two potential energy curves U_1 and U_2

with corresponding wave functions Θ_1 and Θ_2 . We further suppose that U_1 is the repulsive type curve, or else that we are interested in an energy region above its energy of dissociation, while U_2 is the type giving molecule formation and we are below its dissociation energy. Any R , let us say R_{2d} , or simply R_d , which goes with U_2 will be an eigenfunction belonging to a discrete state, while those which go with U_1 , designated in general by R_s will form a continuous set. To normalize these we shall assume that r has a largest possible value which we shall call r_∞ ; this converts the continuous set of energy levels to a very close-spaced discrete set, the energy, ϵ_s , between two adjacent "continuous" levels being given by

$$\epsilon_s = 2\pi(E_s - U_1(\infty))^{1/2}/r_\infty\eta, \quad (6)$$

where E_s is the energy of the continuous state and $U_1(\infty)$ is the asymptotic value of U_1 . We normalize R_s by setting

$$\int_0^{r_\infty} R_s^2 r^2 dr = \int_0^{r_\infty} F_s^2 dr = 1. \quad (7)$$

Now the interaction, represented by the perturbation V , causes, as is well known, an effective "broadening" of the discrete states. That is, in the exact wave function, ψ' , which can be set up as a linear function of discrete and continuous states, the coefficient of a given discrete state has an appreciable value over a certain finite energy range in the neighborhood of the original energy, E_d . By solving the perturbation problem one is able to find the "width" of these broadened discrete states. We define certain matrix components, as follows,

$$v_{11} = \int \Theta_1^* V \Theta_1 d\tau, \quad v_{22} = \int \Theta_2^* V \Theta_2 d\tau, \quad (8)$$

$$v_{12} = \int \Theta_1^* V \Theta_2 d\tau = \int \Theta_2^* V \Theta_1 d\tau, \quad (9)^*$$

$$v_{ss} = \int_0^{r_\infty} F_s v_{11} F_s dr, \quad v_{dd} = \int_0^{r_\infty} F_d v_{22} F_d dr, \quad (10)$$

$$v_{sd} = \int_0^{r_\infty} F_s v_{12} F_d dr, \quad (11)$$

* We assume v_{12} real. If it is not the necessary modification may be readily made.

the integrals (8) and (9) being taken over all possible volume elements, $d\tau$, in the coordinate space defining the Θ 's, and the asterisk denoting the conjugate complex. If we assume v_{11} and v_{22} absorbed into U_1 and U_2 , respectively, (we shall write V_1 to mean $U_1 + v_{11}$ and similarly with V_2) then it may be readily shown⁷ that the matrix components v_{ss} and v_{dd} do not enter into the problem and the only ones we have to consider are those of the type v_{sd} .

We consider the case where the discrete states are so far apart in comparison to the broadening suffered by them that we need to take into account only one of them at a time.⁸ This is, of course, a restriction on the size of the perturbations, but the only one necessary to make; such perturbations may be called "perturbations of intermediate size." We also make the assumption that there is only one set of continuous states involved. We can then write for a particular ψ' , say ψ_n ,

$$\psi_n = S_{dn}\psi_d + \sum_s S_{sn}\psi_s \quad (12)$$

ψ_d and ψ_s being written for the complete wave functions of form (1) corresponding respectively to the discrete state and to the continuous states. If E_n is the energy that goes with ψ_n , then one may show, by application of the perturbation theory, that

$$S_{dn}(E_d - E_n) + \sum_s v_{sd} S_{sn} = 0 \quad (13)$$

and, for all s ,

$$S_{sn}(E_s - E_n) + v_{sd} S_{dn} = 0. \quad (14)$$

These form an infinite set of simultaneous equations, which are to be solved for the S 's, furnishing thereby a series of values of E_n consistent with non-zero solutions for the S 's. This problem I have solved on a previous occasion⁶ on the assumption that v_{sd} did not depend on the value of the subscript s . As this assumption is too restricted for our present purposes, I will here present just a sufficient outline of the solution to show how it must be modified. From Eqs. (13) and (14) one may write

$$(E_d - E_n) - \sum_s [v_{sd}^2 / (E_s - E_n)] = 0. \quad (15)$$

Now contributions to the summation in this equation will occur in two ways. There will be contributions from regions in which E_s is very different from E_n and a contribution from the region where $E_s - E_n$ is of the order of ϵ_n . If we let α_n be the least positive value of $E_s - E_n$ and set $\beta_n = \alpha_n - \epsilon_n/2$, then it may be shown (see reference 6, especially p. 755 of the earlier article) that this latter contribution is $-v_{nd}^2(\pi/\epsilon_n) \tan(\pi\beta_n/\epsilon_n)$, where v_{nd} is the value of v_{sd} and ϵ_n the value of ϵ_s when $E_s - E_n$ is very small. If we allow r_∞ to become very large and hence ϵ_s to become very small we may write the sum as an integral, getting

$$E_d - E_n + v_{nd}^2 \frac{\pi}{\epsilon_n} \tan \frac{\pi\beta_n}{\epsilon_n} - \int_0^\infty \frac{v_{sd}^2}{E_s - E_n} \frac{d(E_s - V_1(\infty))}{\epsilon_s} = 0, \quad (16)$$

it being understood that the singularity in the integrand is handled in such a way that no contribution to the integral results from it. This gives us the values of the perturbed energy levels. For, with any given value of E_n it allows us to find the value of β_n , and thus for any particular

region we see how the perturbed levels are placed with respect to the unperturbed. It should be noted that β_n/ϵ_n approaches a definite limit for any given value of E_n as ϵ_n goes to zero.

We are really interested, however, in the absorption to the state with energy E_n , from the ground state and, indeed, for the special case in which, of the original eigenfunctions, only the one for the discrete state combines with the ground state. If this is the case, then we may take the absorption to the state E_n as proportional S_{dn}^2 and hence if we can find this quantity as a function of E_n we shall have accomplished our purpose. Now from Eq. (12), since we must have $\int \psi_n^2 d\tau = 1$ and remembering the

⁷ Zener, Phys. Rev. 37, 560 (1931). Morse and Stueckelberg, Ann. d. Physik 9, 581 (1931). This method of handling v_{ss} avoids a troublesome difficulty previously encountered in the theory.

⁸ We consider only the case in which levels of different rotational quantum number do not interact with each other and so do not need to be considered at the same time. The energy between discrete states therefore refers to the energy between two adjacent vibrational levels. See reference 6 and §3.

orthogonal properties of ψ_d and the ψ_s , we get $S_{dn}^2 + \sum_s S_{sn}^2 = 1$. Substituting for S_{sn} from (14)

$$1 = S_{dn}^2 + S_{dn}^2 \sum_s [v_{sd}^2 / (E_s - E_n)^2]. \quad (17)$$

Now starting with the state for which $E_s - E_n$ has the smallest positive value $E_s - E_n = \epsilon_s/2 + \beta_s$, the next value of $E_s - E_n$ is $3\epsilon_s/2 + \beta_s$, etc., and similarly for $E_s < E_n$ the values run $\epsilon_s/2 - \beta_s$, $3\epsilon_s/2 - \beta_s$, etc. It is seen that the series can be made to converge in as small a range of $E_s - E_n$ as we desire by making r_∞ large enough and

hence ϵ_s small enough. So we can, in the limit, take v_{sd} outside the summation, as v_{nd} . The sum can be evaluated as in our former papers, and the first term becomes negligible in the limit as r_∞ goes to infinity ($\epsilon_s \rightarrow 0$). We thus find⁶

$$S_{dn}^2 = \left[\frac{v_{nd}^2 \pi^2}{\epsilon_n^2} \left(1 + \tan^2 \frac{\pi \beta_n}{\epsilon_n} \right) \right]^{-1}. \quad (18)$$

Substituting now the value of $\tan(\pi \beta_n / \epsilon_n)$ from (16) we get, finally,⁹

$$S_{dn}^2 = \frac{\epsilon_n}{\pi} \left[\frac{v_{nd}^2 \pi}{\epsilon_n} + \frac{\epsilon_n}{v_{nd}^2 \pi} \left(E_d - E_n - \int_0^\infty \frac{v_{sd}^2}{E_s - E_n} \frac{d(E_s - V_1(\infty))}{\epsilon_s} \right)^2 \right]^{-1}. \quad (19)$$

This holds, without further restriction, for the effect of a single continuum on a discrete state, the perturbations being of "intermediate size."

§2. EVALUATION OF THE MATRIX COMPONENTS

The purpose of this paper is to discuss the case of special interest which arises when the two curves V_1 and V_2 cross each other as shown in Fig. 1. For the unperturbed state of the system we use the system which would be obtained if the two atoms forming the molecule exerted no force on each other,¹⁰ then we bring in the mutual potential energy V as the perturbation energy.

⁹ Dirac, *Zeits. f. Physik* **44**, 594 (1927) arrived at the same formula for the probability of scattering of a particle by an atom which can absorb and reemit it. It appears, in fact, that our result can be derived from Dirac's if we assume in his calculation that the particle which is reemitted is not the same one which is absorbed. Thus we could have absorption of a light particle, then predissociation (essentially equivalent to emission of another particle) the matrix component for the former process being different from the latter. If these two matrix components are different then it is no longer necessary for the matrix component for the predissociation (or reemission of the second particle) to be small (it can be of "intermediate size") which removes an apparent limitation on Dirac's derivation. I have given the other deduction here, however, in the first place because it seems interesting to look at the problem from the point of view of stationary states, in the second place because it seems worth while to have a proof which avoids the use of the Dirac δ -function. See also Weisskopf and Wigner, *Zeits. f. Physik* **63**, 54 (1930), especially the footnote, p. 64.

¹⁰ This does not prevent us from bringing in the exchange phenomena in the proper way. We can also refer the electron coordinates to axes moving with the nuclei thus getting ordinary molecular states for our unperturbed

With this scheme V_1 and V_2 consist entirely of the terms v_{11} and v_{22} .

We shall assume in making the calculation that for the important region of r near the point

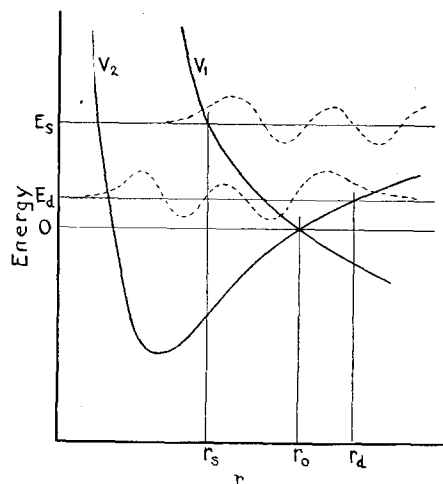


FIG. 1. Potential energy curves illustrating the situation in §2. Schematic drawings of the eigenfunction, F_d , for a discrete state of energy E_d , and the eigenfunction F_s of a continuous state with energy E_s are shown, drawn on the energy levels as zeros of ordinates. The value of v_{sd} depends on the integral of the product of F_s and F_d . It will be seen that as E_s increases and r_s thus decreases the phase relationship of F_s and F_d will change periodically and the value of v_{sd} will depend in a quasi-periodic way on $r_s - r_d$. See Eq. (23) and Fig. 2a (noting Eqs. (26) and (27)). The relation between v_{nd} and $r_n - r_d$ is, of course, the same as that between v_{sd} and $r_s - r_d$, the subscript n here really being a special case of the subscript s . The situation depicted here does not correspond very well with the simplifying assumptions made in §2, but the position of the wave functions will roughly correspond to that producing the maximum of $A \cos(\lambda\{r_n - r_d\})$ which occurs at $\lambda(r_n - r_d) = -7$ in Fig. 2a.

states. In so doing, we bring in other perturbations due to the Coriolis forces, which may or may not be of importance.

of intersection, which we shall designate as r_0 , the value of v_{12} may be taken as constant¹¹ and the curves V_1 and V_2 may be considered as intersecting straight lines. Under these circumstances it is possible to evaluate v_{nd} and the integral that appears in (16) and (19).

If the slope of the curve V_k at r_0 is V_k' , then if the approximations indicated in the above paragraph hold good we may write for an eigenfunction¹² of the Eq. (3)

$$F_{km} = N_{km} \int_0^\infty \cos \{z^3 \pm |3\eta^2 V_k'|^{1/3} (r - r_m)z\} dz, \quad (20)$$

where

$$r_m = r_0 + E_{km}/V_k' \quad (21)$$

and is the point at which $V_k = E_{km}$, as we shall

let the zero point of energy be the energy of the crossing of the potential energy curves. The plus or minus sign is to be used according as V_k' is positive or negative. N_{km} is the normalizing factor.

If v_{12} is constant, and if V_1' is negative and V_2' is positive as in Fig. 1, we have

$$v_{sd} = v_{12} \int_{-\infty}^\infty F_s F_d dr, \quad (22)$$

the integration with respect to r being extended from ∞ to $-\infty$, which is permissible as there is but little contribution to the integral, excepting from the region between the points r_s and r_d . As shown in Appendix I this may be reduced to

$$v_{sd} = \frac{N_d N_s v_{12} \pi}{[3\eta^2(|V_1'| + |V_2'|)]^{1/3}} \int_0^\infty dz \cos \left\{ z^3 + \frac{(r_s - r_d)(3\eta^2)^{1/3}}{(1/|V_1'| + 1/|V_2'|)^{1/3}} z \right\}. \quad (23)$$

The integral $\int_0^\infty dz \cos(z^3 - xz)$ has been evaluated by Airy¹³ over a considerable range of the parameter involved and the range may be extended by the Wentzel-Kramers-Brillouin approximation method.¹⁴ A discussion with a table of values is given in Appendix III.

We now turn to the evaluation of

$$\int_0^\infty \frac{v_{sd}^2}{E_s - E_n} \frac{d(E_s - V_1(\infty))}{\epsilon_s}.$$

To a good approximation we can replace this by

$$\frac{1}{\epsilon_n} \int_{-\infty}^\infty \frac{v_{sd}^2}{E_s - E_n} d(E_s - E_n).$$

As shown in Appendix II we thus get

$$\int_0^\infty \frac{v_{sd}^2}{E_s - E_n} \frac{d(E_s - V_1(\infty))}{\epsilon_s} = B_n \int_0^\infty dz \cos \{z^3 + \lambda(r_n - r_d)z\} \int_0^\infty dt \sin \{t^3 + \lambda(r_n - r_d)t\} \quad (24)$$

where

$$B_n = \pi^3 v_{12}^2 N_d^2 N_n^2 \epsilon_n^{-1} (3\eta^2)^{-1/3} (|V_1'| + |V_2'|)^{-1/3} \quad (25)$$

and

$$\lambda = (3\eta^2)^{1/3} (1/|V_1'| + 1/|V_2'|)^{-1/3}, \quad (26)$$

r_n being equal to $r_0 + E_n/V_1'$. The evaluation of the second integral in (24) is discussed in Appendix III. If we also write

$$\int_0^\infty \cos(z^3 + xz) dz = A_{\cos}(x) \quad (27)$$

¹¹ This is similar to the assumption commonly made in calculating the absorption intensities in band spectra.

¹² See Watson, *Bessel Functions*, Cambridge, 1922, p. 188. This solution of Eq. (3) has the general properties of an eigenfunction, inasmuch as it becomes small when r becomes small, and while it does not actually become zero for $r=0$, it is a sufficiently good approximation. F_{km} has the form (20), of course, only in that region where the potential curve is approximately a straight line.

For the continuous curve the energy must be determined by the boundary condition at r_∞ , and the normalizing

factor is determined by the way this form joins on to the asymptotic form of F_{km} (that is, F_s , in this case). The amplitude of the wave for large values of r is fixed by Eq. (7), and is the same for all energies. If the wave-length is short enough the value of N_s which gives the amplitude near r_0 will vary from one value of E_s to another as $(E_s - V_1(\infty))^{1/3}$. See, e.g., Nordheim, *Zeits. f. Physik* **46**, 842 (1927).

¹³ Airy, *Trans. Camb. Phil. Soc.* **8**, 598 (1848).

¹⁴ See Kramers, *Zeits. f. Physik* **39**, 828 (1926).

and

$$\int_0^\infty \sin(z^3 + xz) dz = A_{\sin}(x), \quad (28)$$

then,¹⁵ from (19), (23) and (24),

$$S_{dn}^2 = \left(\frac{\pi B_n}{\epsilon_n} \right)^{-1} \left[A_{\cos}^2(\lambda\{r_n - r_d\}) + \left(\frac{(E_d - E_n)/B_n - A_{\cos}(\lambda\{r_n - r_d\}) A_{\sin}(\lambda\{r_n - r_d\})}{A_{\cos}(\lambda\{r_n - r_d\})} \right)^2 \right]^{-1}. \quad (29)$$

This expression gives the absorption coefficient of the single broadened, shifted, and distorted predissociation line whose unperturbed energy is $E_d (= V_2'(r_d - r_0))$ by (21)) as a function of the total energy $E_n (= V_1'(r_n - r_0))$ of the energy level which is the final state in the absorption process.

The best way to appreciate the behavior of S_{dn}^2 is to study a few concrete examples. S_{dn}^2 , it

is to be remembered, is a function of E_n , since E_d is a perfectly definite energy for any discrete line; S_{dn}^2 plotted as a function of E_n will give the shape of the broadened discrete line. Let us now consider what happens when E_d has such a value that when $E_d = E_n$ we have $A_{\cos}(\lambda\{r_n - r_d\})$ at its first* zero point. To distinguish this special case we shall designate this value of E_d as E_{d_0} . In Fig. 2(b) we have plotted $S_{d_0n}^2$ as a function

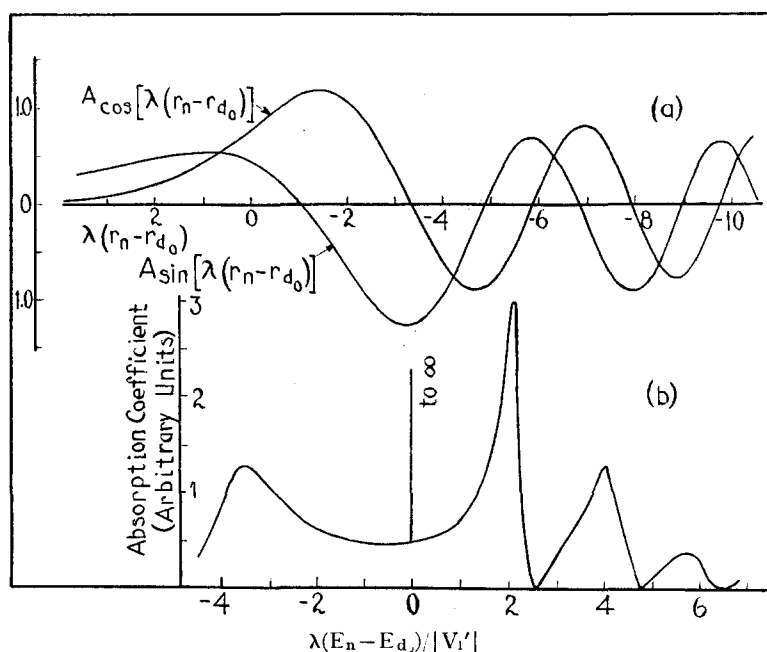


FIG. 2.

of $\lambda(E_n - E_{d_0})/|V_1'|$, the increments of which, it will be observed, are equal to the increments of $\lambda(r_n - r_d)$. We take $-5V_1'/\lambda$ as the value of B_n . The ordinates are in arbitrary units. Just above the curve for $S_{d_0n}^2$ we have plotted $A_{\cos}(\lambda\{r_n - r_{d_0}\})$ and $A_{\sin}(\lambda\{r_n - r_{d_0}\})$ against

$\lambda(r_n - r_{d_0})$ in such a position as to bring out the relationship between the various curves. Now suppose we consider another case in which E_d has a value somewhat displaced from its former value. Then the point at which $E_n = E_d$ is removed by a certain amount from the value of E_n for which $A_{\cos}(\lambda\{r_n - r_d\}) = 0$, and this is

¹⁵ In the evaluation of this expression we note that B_n is approximately independent of E_n . See Eq. (6) and reference 12.

* The general features of the phenomena will be the same for any zero point.

different than the amount by which E_d is different from E_{d_0} . The latter quantity is, of course, equal to $E_d - E_{d_0}$, while the former is equal to $(E_d - E_{d_0})(|V_1'| + |V_2'|)/|V_2'|$. For the value of E_n where $A_{\cos}(\lambda\{r_n - r_d\})$ is zero is $E_{d_0} - (E_d - E_{d_0})|V_1'|/|V_2'|$, this being the point, as is readily verified, where $r_n - r_d$ equals the original zero-point value of $r_n - r_{d_0}$. Several intensity curves, as they appear in the immediate neighborhood of the energy for which $A_{\cos}(\lambda\{r_n - r_d\}) = 0$ are exhibited in Fig. 3. These curves are based on the assumption that $|V_1'| = |V_2'|$, and again B_n is taken as $-5V_1'/\lambda$. The maximum in each case corresponds to the infinitely intense and narrow line of Fig. 2, now displaced and broadened. Thus we see that the apparent position of the discrete line will, unless the line happens to be in the special position, E_{d_0} , be displaced toward the zero-point for $A_{\cos}(\lambda\{r_n - r_d\})$ by an amount ΔE_d , where

$$\Delta E_d \leq (E_d - E_{d_0})(|V_1'| + |V_2'|)/|V_2'|, \quad (30)$$

the equality sign occurring for $B_n = \infty$. If E_d is not too greatly different from E_{d_0} the rest of the intensity curve will not differ greatly from the curve in Fig. 1 except that it will be displaced by the same amount that the zero point of $A_{\cos}(\lambda\{r_n - r_d\})$ is displaced, i.e., by an amount $-(E_d - E_{d_0})|V_1'|/|V_2'|$. As the value of $E_d - E_{d_0}$ grows greater the adjacent intensity maximum develops while the maximum near E_{d_0} grows smaller. When $E_d - E_{d_0}$ has such a value that $|A_{\cos}(\lambda\{r_n - r_d\})|$ for $E_n = E_d$ is near its maxi-

mum then both maxima in the intensity curve will be approximately of equal size.

It is interesting to consider a little further the behavior of the expression (29) when the line is so narrow (as is actually practically the case in Fig. 3) that $A_{\cos}(\lambda\{r_n - r_d\})$ and $A_{\sin}(\lambda\{r_n - r_d\})$

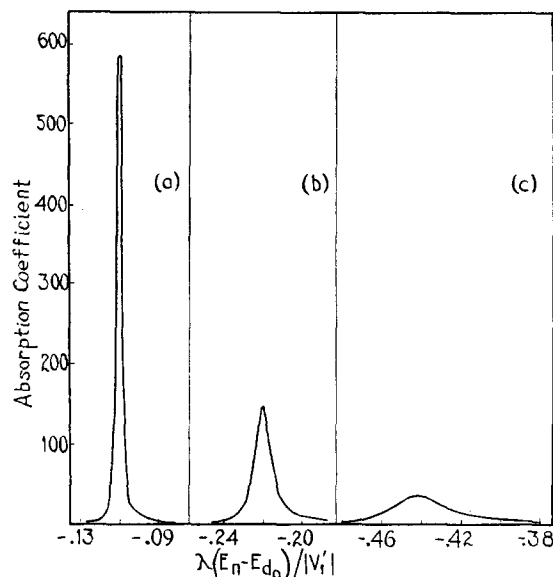


FIG. 3. The broadened predissociation line in various cases. (a) $\lambda(E_d - E_{d_0})/|V_1'| = 0.15$; (b) $\lambda(E_d - E_{d_0})/|V_1'| = 0.3$; (c) $\lambda(E_d - E_{d_0})/|V_1'| = 0.6$. Units for the absorption coefficient arbitrary but same as in Fig. 2b.

are nearly constant over the width of the line. Then the energy $E_n(\text{max})$ at which the absorption coefficient has a maximum is given very closely by

$$(E_d - E_n(\text{max}))/B_n - A_{\cos}(\lambda\{r_n(\text{max}) - r_d\})A_{\sin}(\lambda\{r_n(\text{max}) - r_d\}) = 0 \quad (31)$$

and the half absorption width ΔE_n of the line will be given by

$$\Delta E_n = 2B_n A_{\cos}^2(\lambda\{r_n(\text{max}) - r_d\}) \quad (32)$$

as may be readily seen from (29) by subtracting the one value of E_n where $S_{d_n}^2$ has half its maximum value from the other. Now we have already noted that if B_n increases (for example by increasing v_{12}) $E_n(\text{max})$ tends to go to such values that $A_{\cos}(\lambda\{r_n(\text{max}) - r_d\})$ approaches zero. It is readily seen why this happens from (31). As this happens $E_d - E_n(\text{max})$ tends to approach a constant value, in terms of which, B_n and $A_{\sin}(\lambda\{r_n(\text{max}) - r_d\})$ it is possible

to evaluate $A_{\cos}(\lambda\{r_n(\text{max}) - r_d\})$ from (31). $A_{\sin}(\lambda\{r_n(\text{max}) - r_d\})$ also tends to approach a constant value as B_n increases. From (31) and (32) we have

$$\Delta E_n = \frac{2(E_d - E_n(\text{max}))^2}{B_n A_{\sin}^2(\lambda\{r_n(\text{max}) - r_d\})}.$$

One thus arrives at the curious result that the larger B_n and hence the perturbation matrix component v_{12} the sharper is the displaced discrete line, though at the same time its intensity decreases, as is readily seen from (29). It is a little difficult to see at just what point

this breaks down. Since the width of the lines becomes smaller as B_n increases, it would at first sight seem that our criterion that two discrete lines should not be so broadened as to overlap appreciably would be automatically fulfilled. But the secondary structure of Fig. 2 must be included in the breadth of any discrete line. As B_n increases the secondary structure increases in prominence, the secondary maxima becoming stronger and narrower, and as soon as the secondary structure of an adjoining discrete line becomes as important in the neighborhood of that discrete line itself the calculation must of necessity break down. It is by no means certain, however, that this criterion for the validity of the treatment used is stringent enough.

It should be stated that the spacing between the secondary maxima will quite often or perhaps usually be of the same order of magnitude as the spacing between adjacent vibrational levels, which means that the secondary maxima will probably not be of importance in practical spectroscopy, though we conjecture they may have something to do with the phenomena in iodine chloride, as mentioned in §4.

It is interesting to note that the spacing of the maxima of the secondary structure is closely related to what the spacing of energy levels of the upper adiabatic, non-crossing curve would be if it were the unperturbed curve, but the nature of the wave functions is different, and the phenomena involved could be properly understood only if the effect of all the discrete states could be studied.

§3. VIBRATION-ROTATION LEVELS OF A MOLECULE

The actual appearance of the term diagram of a diatomic molecule, to be expected on the basis of the theory presented, can be readily deduced from the above discussion. The theory is based on the assumption that a discrete energy level interacts with only one continuum; consequently it can be applied only to molecules in which there is a selection rule operating,¹⁶ such that a

¹⁶ In general such a selection rule will operate, at least if Hund's Case *a* holds. For the value of J and its projection on a given axis must be the same for the two states which interact, the only ambiguity remaining, with given

discrete state with given rotational quantum numbers interacts only with continuous states with the same rotational quantum numbers.

If the rotational quantum number (for total angular momentum) is J , then in order to get the proper effective potential energy curve we must add to both V_1 and V_2 the quantity $J(J+1)/\eta^2 r^2$. Thus the point, r_0 , of intersection of the potential energy curves is independent of J , but the energy of intersection is increased over that for $J=0$ by an amount $J(J+1)/\eta^2 r_0^2$. For our present purposes we may ignore the change of slope of V_1 and V_2 in the neighborhood of r_0 and assume that the curves are corrected simply by adding the amount $J(J+1)/\eta^2 r_0^2$.

Suppose a given rotational line is at such a position that $A_{\cos}(\lambda\{r_n - r_d\}) = 0$ when $E_n = E_d$. Then the line with the next higher value of J will have an energy such that when $E_n = E_d$ the quantity $A_{\cos}(\lambda\{r_n - r_d\})$ is not equal to zero; for, in general, $r_e \neq r_0$, where r_e is the value of r at the minimum of the potential curve, and the energy of the line increases at a different rate than the energy for the crossing point r_0 . Thus in the molecule we will have one rotation level sharp, and it will be surrounded on either side by levels growing more and more diffuse. The diffuse levels will be displaced in position, and it may be readily verified that if $r_e < r_0$ the spacing between levels will be less than normal; in fact, one could even have reversal of the order, the levels of lower rotational quantum number having higher energy.

§4. APPLICATION TO IODINE CHLORIDE

We shall now consider, in the light of the theory just developed, the rather complex set of predissociation phenomena which has been found by Brown and Gibson² by examination of the absorption spectrum of iodine chloride.

In describing these phenomena we shall follow, as far as possible, the standard notation used by Brown and Gibson. v'' and v' will be the rotational energy curves, after J and its projection have been determined, being the orientation of the spin in one direction or the other referred to J , which gives rise to Λ -type doubling. But there will be a selection rule for the spins which prevent the two states due to Λ -type doubling from both interacting, at least appreciably, with any one state belonging to the other potential energy curve.

spective vibrational quantum numbers and J'' and J' the respective rotational quantum numbers of the initial and final states giving rise to an absorption line. $B_{v'}$ will be used for the quantity $\hbar^2/8\pi^2 I_{v'}$, where $I_{v'}$ is the moment of inertia for the v' vibrational level. Brown and Gibson have given their results in the form of wave numbers of observed lines. As we shall be chiefly interested in energy levels, all values here given, unless otherwise noted, are values of energy levels, obtained from the observed spectral lines by taking into account the energy of the initial states; the values are in wave numbers (cm^{-1}) and are referred to the state, $v''=1$, $J''=0$, as the zero of energy. $\nu_{v'}$ will denote the energy of the band head, quantum number v' , r will denote the distance between atoms, and r_e the equilibrium distance for the excited ($'$) energy level.

Brown and Gibson have found a number of bands corresponding to an absorption ${}^3\Pi_0 \leftarrow {}^1\Sigma$, which they have designated as System II. They have measured the positions of a number of band-heads, analyzed the rotational structure in so far as possible, determined v' values by use of the isotope effect and given an estimate of the convergence limit. They have found that the higher members of the band show predissociation phenomena. Their results are summarized in Table I. The data for $v'=1, 2$ and 3 are obtained

TABLE I. Constants for bands of system II.

v'	$\nu_{v'}(\text{cm}^{-1})$	$B_{v'}^*$	Remarks
1	17,093		Lines sharp
2	17,282.5	0.0829	Lines sharp
3	17,446.3	0.0800	Lines sharp $J \lesssim 50$, diffuse $J \gtrsim 50$
4	17,580	0.0748	Most lines diffuse
Convergence	17,864		See Brown and Gibson, p. 537

* $B_{v'}$ is in such units that energies will be obtained in cm^{-1} .

directly, whereas that for $v'=4$, I have obtained by indirect means to be described.

No regular band-heads or band structure are observed for $v'=4$ or greater. Instead there are isolated groups of diffuse and sharp lines, which come in pairs, the pairing being due to the fact that there are P and R branches present. Each group consists of a central sharp line, surrounded

by others of increasing diffuseness as one goes away from the sharp central lines. The lines of three such groups have been measured and by use of the combination differences their rotational quantum numbers have been obtained. In addition, there is a background consisting of a series of very faint diffuse absorption maxima which are referred to as System III. The superficial resemblance of these phenomena to those considered in §§2 and 3, is at once apparent. The groups of lines presumably correspond to lines such as shown in Fig. 3, while, though this is more doubtful, one may suppose that the faint maxima correspond to the maxima of Fig. 2b; there would possibly be enough states piled together at a band head to make these visible.¹⁷

Brown found by his analysis that the sharp energy levels of the two most prominent groups of sharp and diffuse lines, which were designated as Series I and Series II, had rotational quantum numbers J' equal to 28 and 46, respectively. Both Series I and Series II presumably have $v''=1$, $v'=4$. Now with any reasonable slopes for the two curves V_1 and V_2 it is utterly impossible to account for two sharp energy levels appearing so close together, the periodicity given by the theory being of a different order of mag-

¹⁷ Brown had a tentative explanation of these predissociation phenomena. He noted that the faint maxima seemed to be arranged as though they were an independent series of band-heads, which he called System III. The potential energy curve for these band-heads he supposed to be the adiabatic curve formed by the crossing of a repulsive curve and the curve of System II. He supposed the sharp lines to belong at the same time to System III and System II, as their placing seemed to allow that assumption. He supposed the spacing of the lines to be that characteristic of the rotational levels of System III. From this he was able to get an apparent position of the minimum of the potential curve for System III, and the approximate point at which it was crossed by the potential curve. Van Vleck, however (see Brown and Gibson, p. 542) preferred to consider the sharp lines as vestigial remains of System II, which is more in accord with the view we take here. One obvious objection to any literal acceptance of Brown's ideas and one which he apparently did not realize existed, is the fact that the crossing of the curves occurs at a point (see Brown and Gibson's Fig. 4) which is nowhere near the Morse curve for System II. (See our Fig. 4 and reference 22.) It must be admitted that our theory runs into a somewhat similar, but I believe less pronounced difficulty. In any event, Brown's suggestion, while containing a certain element of truth, had no absolute theoretical significance, as he himself well realized.

nitude. It is also apparently impossible to account for the phenomena by changing the vibrational numbering assuming, e.g., that $v''=2$ for one of the sharp lines and its surrounding group of diffuse lines, as this pushes the energy level beyond the dissociation limit of the group of bands, which appears from the analysis to be pretty well fixed. The only reasonable explanation I have been able to find lies in assuming that we have here a new and very curious kind of isotope effect, namely that Series II is due to the isotopic molecule¹⁵ ICl^{37} . If this assumption is made, it is necessary to compare the combination differences ($\Delta_2 F''$) with the combination differences for the molecule ICl^{37} . These can be found from those given in Table I of Brown and Gibson's paper by a short extrapolation, and a correction to take into account the difference in reduced mass. It is found that the agreement between the expected combination differences and those actually observed is good¹⁹ if one assigns to the sharp line the value $J'=48$ instead of 46. Since one knows that the value of $B_{v''}$ for $v''=1$ for the ICl^{35} molecule is 0.1132 and the value for $B_{v''}$ for the ICl^{37} molecule is, therefore, very approximately equal to 0.9576×0.1132 or 0.1084 (the value 0.9576 being the ratio of the reduced mass of ICl^{35} to that of ICl^{37}) one can, from the data given by Brown and Gibson, calculate the actual energies of the sharp and diffuse levels by adding to the observed frequency the proper value, $B_{v''} J''(J''+1)$, and, in the case of Series II,

¹⁵ This conclusion depends of course on all the assumptions we have made. It is not claimed that we have here made an exhaustive analysis, but certain support is lent by other observations. Thus Brown and Gibson state, p. 536, that it was impossible to observe the isotope shift of Series I and II, from which we may infer that no ordinary isotope effect is to be found. And I am indebted to Professor Gibson for the information that the intensity of the lines of Series I is stronger than that of the lines of Series II, and that judging by eye they might easily be in the isotope ratio. Of course, the Boltzmann factor would tend to make Series II weaker than Series I, but this should be about compensated by the increasing multiplicity of the lines with larger J values.

¹⁹ This is also indicated by the fact that when one calculates the energy of rotational lines from the P and R lines using the value of $B_{v''}$ for the molecule ICl^{37} one gets values which agree with each other in all cases to within 0.04 cm^{-1} .

subtracting 12.36, to allow for the isotope displacement of the lower band-head.²⁰ This will give the energy referred to the $J''=0$ level of the $v''=1$ vibrational level. In most cases two values for a given energy have been obtained, and the average of the two has been used. The results of this calculation have been tabulated in the second column of Table II. If now we assume the

TABLE II. Energy levels for series I and II and calculation of $\Delta E_d/(E_d - E_{d_0})$.

Series I, $J'=25-32$, series II, $J'=46-50$.

J'	Energy (cm^{-1})	Obs. displ. (cm^{-1})	ΔE_d (cm^{-1})	$E_d - E_{d_0}$ (cm^{-1})	$\frac{\Delta E_d}{(E_d - E_{d_0})} - 1$
25uu	17,634.26	-8.18	3.94	1.325	1.97
26uu	636.98	-5.46	2.77	0.900	2.08
27	639.62	-2.82	1.37	0.458	1.99
28s	642.44	0.			
29	645.48	3.04	-1.30	0.474	1.74
30u	648.70	6.26	-2.57	0.965	1.66
31uu	652.08	9.64	-3.82	1.47	1.60
32	655.66	13.22	-5.03	2.00	1.52
46uu	17,729.35	-8.99	5.22	1.55	2.37
47u	733.82	-4.52	2.66	0.785	2.39
48s	738.34	0.			
49u	742.99	4.65	-2.68	0.802	2.34
50uu	747.96	9.62	-5.19	1.62	2.20

s = sharp, u = broad, uu = very broad.

sharp line to be unshifted in position, we can calculate the unperturbed energy $\nu_{v'}$ for $v'=4$, provided we can make an estimate of $B_{v'}$. From the values of the latter quantity for $v'=2$ and $v'=3$, I estimate that for $v'=4$ it will be about 0.0765 for ICl^{35} and this will give 0.0733 for ICl^{37} , neglecting the effect of the isotope shift of the band-head. We thus find for $v'=4$, $J'=0$, ICl^{35} the value $17,580.3 \text{ cm}^{-1}$ and for $v'=4$, $J'=0$, ICl^{37} the value $17,566.2 \text{ cm}^{-1}$ giving an isotope shift of -14.1 . We can calculate the isotope shift from the formula $\omega_{v'}(\rho-1)(v'+\frac{1}{2})$ where $\omega_{v'}$ is the frequency of the v' vibrational level and $\rho-1 = (M_{35} - M_{37})/(M_{35} + M_{37})$ the M 's being the reduced masses. $\omega_{v'}$, judging from Table I, is about 120. This gives for the isotope shift -11.7 . The discrepancy would be increased a little by taking into account the effect of the displacement of the ICl^{37} band-head on $B_{v'}$ for this isotope, as this would tend to increase $B_{v'}$.

²⁰ I cannot check the value of 12.19 given by Brown and Gibson, but the difference is not of much significance.

a little; nevertheless, the agreement seems to be reasonably good, considering the uncertainties involved. Thus if we used the, to be sure, rather low value of $B_v = 0.073$ for ICl^{35} , to which Brown was actually led by the assumption that both groups of lines belonged to ICl^{35} , we get for the isotope shift -9.3 , already on the other side of the calculated value. The value for B_v , which I have tabulated in Table I lies between these extremes. And it must not be forgotten that the assumption, which we have made (and which Brown also made), that the sharp lines are unshifted in position, is based on the approximate calculations of §2; but it is, in any event, probably safe to assume that the two sharp levels are displaced approximately the same amount, which would leave the isotope displacement the same.

If, however, we continue to assume that the lines are unshifted, we are now in a position to calculate the value of r which we have called r_0 at which the intersection of the two potential energy curves occurs. For it seems probable that the sharp line in *each* case corresponds roughly to the *first* zero* in $A_{\cos}(\lambda\{r_n - r_d\})$, where $E_{n_d} = E_d$. If this is so, then the energy of the sharp level of Series I, minus the energy of the intersection of the potential curves should be equal to the same quantity for the sharp level of Series II. The energy of intersection will be the same for the two isotopes for $J' = 0$, but needs to be corrected for given values of J' by an amount $J'(J' + 1)B_i$ where $B_i = h^2/8\pi^2 M r_0^2$ and is different for the two isotopes. If we let B_i be the value for the molecule ICl^{35} , then the difference in the correction for the two cases will be $48 \times 49 \times 0.958 B_i - 28 \times 29 B_i$, and this must be equal to the difference in energy of the two sharp levels, which is 95.9 . We thus find that $B_i = 0.0666$ and $r_0 = 3.03$.

We can derive some further information on the assumption that the sharp levels of Series I and Series II correspond to the first zeros of $A_{\cos}(\lambda\{r_n - r_d\})$ for the respective isotopic molecules. The energy for the level $J' = 28$ is $17,642.4 \text{ cm}^{-1}$ and when corrected by the subtraction of the amount $J'(J' + 1)B_i$ or $28 \times 29 \times 0.0666$ it becomes $17,588.4$. Now Brown states that in the

$v' = 3$ band the rotation levels can be followed up to about $J' = 52$ and in this neighborhood the levels gradually become diffuse. It is difficult to get any comparison between the breadth of these levels and those of Series I and II from Brown and Gibson's paper. Likewise, it is difficult to know the values of $A_{\cos}(\lambda\{r_n(\text{max}) - r_d\})$ for the individual levels of Series I and II. If these two pieces of information were at hand we would be able, from (32), to get $A_{\cos}(\lambda\{r_n(\text{max}) - r_d\})$ and hence $\lambda\{r_n(\text{max}) - r_d\}$ for the $v' = 3$, $J' = 52$ level. I make the assumption that the broadening of the level at $v' = 3$, $J' = 52$ is about the same as that of the broadest of the lines of Series I and II yet visible, and it seems quite likely that $A_{\cos}(\lambda\{r_n(\text{max}) - r_d\})$ is still quite small for all the lines of Series I and II. The value of $A_{\cos}(\lambda\{r_n - r_d\})$ has become pretty small for $\lambda(r_n - r_d) = 4$ and we take this as the value of $\lambda\{r_n(\text{max}) - r_d\}$ for $v' = 3$, $J' = 52$. This would make the range $\Delta\lambda(r_n(\text{max}) - r_d)$ of the quantity $\lambda(r_n(\text{max}) - r_d)$ between the level $v' = 3$, $J' = 52$ and the first sharp line of Series I or II equal to about 7.5 . Now the energy of $v' = 3$, $J' = 52$ can be calculated by adding the quantity $J'(J' + 1)B_v$ to the energy of the band head; it must then be corrected by subtracting $J'(J' + 1)B_i$; the final result is $17,483.2 \text{ cm}^{-1}$. Therefore the range $\lambda(r_n(\text{max}) - r_d) = 4$ to $\lambda(r_n(\text{max}) - r_d) = -3.5$ corresponds to a range in energy of about $17,483$ to $17,588 \text{ cm}^{-1}$. Now since $r_n = r_0 + E_n/V_1'$ and $r_d = r_0 + E_d/V_2'$ we can calculate the quantity $1/|V_1'| + 1/|V_2'|$ from the relation $\Delta\lambda(r_n(\text{max}) - r_d) = 7.5$, using Eq. (26), and putting in the numerical values.²¹ We thus find $1/|V_1'| + 1/|V_2'| = 0.0086$. The units of V_1' and V_2' are cm^{-1} per A. Since the slope of the Morse curve²² for V_2 is around 1200 cm^{-1} per A in the neighborhood of the crossing point of the potential energy curves, it is seen that this gives for V_1' a value of about -125 cm^{-1} per A. Since the atomic levels of iodine and chlorine are such that

²¹ E_d can, in each case, be taken as equal to $E_n(\text{max})$ for these purposes. Remember, also, V_1' and V_2' have opposite signs.

²² Morse, Phys. Rev. **34**, 57 (1929). The Morse curve for V_2 constructed from the data of Table I is given by the expression $V_2 = 16,758 + 1106(1 - e^{-4.70(r - r_e)})^2$ and is shown in Fig. 4. The value of r_e , calculated by extrapolation of the B_v values with the aid of the work of Dunham, Phys. Rev. **41**, 721 (1932), is found to be 2.62 \AA .

* This amounts to saying that in the case of each isotope the unperturbed energy of the sharp line corresponds to the energy we have called E_{d_0} in §2.

the curve V_1 must be approaching an asymptotic value some 500 cm^{-1} less than the energy of intersection,²³ it appears that this value is rather unreasonably small.

A rather more serious difficulty appears when we attempt to use Eq. (30) to obtain the value of $|V_1'|/|V_2'|$. For the value found is inconsistent with the above conclusion. This is shown in Table II. In compiling this table we have taken the energy of the sharp level as E_{d_0} in both Series I and Series II. In Column 3 is given the observed difference of energy between the given level and the sharp level (Obs. Displ.) and in Column 4 is given ΔE_d which is obtained from Column 3 by subtracting from it $[J'(J'+1) - J_0(J_0+1)]B_{v'}$, where J_0 is the J' value for the sharp level, this being the expected difference in energy if the lines were not displaced. To get $E_d - E_{d_0}$, corrected for the change in energy of the point of intersection, we may use the obvious relation

$$E_d - E_{d_0} = [J'(J'+1) - J_0(J_0+1)](B_{v'} - B_i);$$

the value of $E_d - E_{d_0}$ is given in Column 5. Column 6 gives the value of $\Delta E_d/(E_d - E_{d_0}) - 1$ which from (30) is a minimum value for $|V_1'|/|V_2'|$. This turns out not to be quite constant, but this lack of constancy would seem to be a comparatively minor difficulty. The difference in the values of this ratio for Series I and Series II may be due to the actual difference in this ratio due to the change in slope of the curves V_1 and V_2 when the rotational term is added. In making the calculations of Table II I have used the values $B_{v'} = 0.0748$ and $B_i = 0.0666$, ICl³⁵, with the corresponding values for ICl³⁷. The value of $B_{v'}$ is chosen so as to make the isotope effect for the vibration level $v' = 4$ come out about right.

In seeking to explain the discrepancies between the values of $|V_1'|/|V_2'|$ calculated in different ways, a number of possibilities come to mind. In the first place, it may be that the curve V_2 begins to deviate somewhat from a Morse curve around $v' = 4$, and has a somewhat smaller slope. This is suggested by the low value of $B_{v'}$ for $v' = 4$, and the rather low energy of the band-head which we have found, in spite of the fact

that the values of $B_{v'}$ for $v' = 2$ and 3 have just about the relation to each other that one might expect for a Morse curve.²⁴ It should be borne in mind that rather sudden changes can occur in the law of force between two atoms in a given electronic state, and this, in fact, is known to occur in another potential energy curve²⁵ of ICl. It hardly appears, however, that we can account in this way for all of the discrepancy, though it might be part of the explanation. Another possible factor is a breaking down of the assumptions that v_{12} is independent of r , and that the curves can be taken as straight lines near the point of intersection. Thus one would expect the value of V_1' as determined in Table II to be rather the value of V_1' at an energy near E_d , while the other method of determining V_1' might be expected to give a sort of average value between the point of intersection and E_d . So if the curve V_1 were quite flat in the neighborhood of the point of intersection and then bent up rather suddenly at somewhat smaller values of r , as in Fig. 4, this might produce the effect observed. Or possibly the flat curve V_1 intersects the other

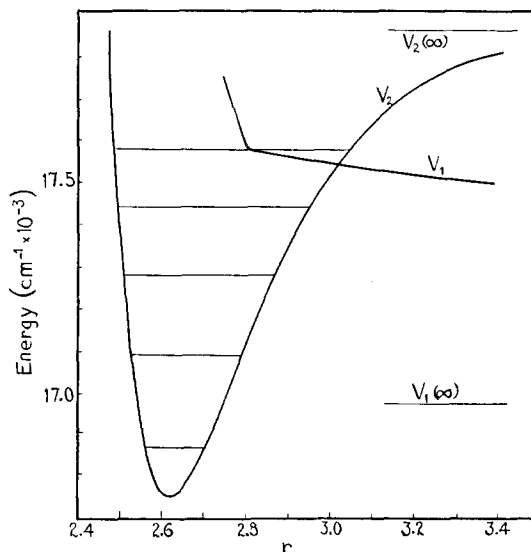


FIG. 4. Morse curve and hypothetical repulsive curve for iodine chloride.

²⁴ The value of r_0 is also about what one might expect from the Morse curve, but it may well be too small, due to the approximations we have made in calculating it.

²⁵ Curtis and Darbyshire, Trans. Faraday Soc. **27**, 85 (1931).

²³ This is shown in Fig. 4. See Brown and Gibson, p. 537.

side of the curve V_2 . This would certainly produce complications of an unpredictable sort. It is also possible that the assumption that only one discrete energy level need be considered at a time is not quite correct. Finally, it is not at all certain but that we would do better in this instance if we used the adiabatic non-crossing curves to define our unperturbed states rather than the crossing curves. An attempt will be made to find approximate solutions, using the adiabatic curves as the unperturbed curves, in order to see whether this assumption fits in better with the iodine chloride data.

Before concluding, mention should be made of certain other sharp and diffuse lines which do not go with the regular bands and which do not belong to Series I or II. Particularly noticeable is another group of lines called Series III by Brown and Gibson for which apparently $v'=5$, and which is remarkable in that it contains many more lines than Series I or Series II. It does not

seem to be worth while to attempt any detailed discussion of Series III.

We have already noted the existence of faint absorption maxima in the same region of the spectrum as Series I or Series II, and have stated that it is tempting to suppose that they have something to do with the secondary maxima of Fig. 2b. It must be said however that their spacing is much closer than would be expected. One of these diffuse maxima, which occurs at $17,577\text{ cm}^{-1}$, Brown and Gibson identify with the band-head for the $v'=4, v''=1$ band. This however, does not seem reasonable, as from Table II we may judge that the head of this band would be displaced to around $17,600$.

In conclusion, I think it may be said that while it does not seem possible to account quantitatively for the predissociation phenomena in iodine chloride, progress has been made in understanding and interpreting them, and affording a basis for their discussion.

APPENDIX I—EVALUATION OF INTEGRAL, EQ. (22)

If we denote the quantity $|3\eta^2 V_k'|^{1/2}$ by C_k , then we may write from (20) (omitting the normalizing factors)

$$\int_{-\infty}^{\infty} F_s F_d dr = \int_{-\infty}^{\infty} dr \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dt \cos [z^3 - C_1(r-r_s)z] \cos [t^3 + C_2(r-r_d)t].$$

We may extend the integrations with respect to z and t from $-\infty$ to ∞ , providing we divide through twice by 2. Doing this, and making a double application of Formula 596 of Peirce's *Short Table of Integrals*, the expression becomes

$$\frac{1}{4} \int_{-\infty}^{\infty} dr \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dt \{ \cos [(C_2 t - C_1 z)r] \cos [z^3 + t^3 + C_1 r_s z - C_2 r_d t] \\ + \frac{1}{2} \cos [z^3 - t^3 - C_1 r z + C_1 r_s z - C_2 r t + C_2 r_d t] - \frac{1}{2} \cos [z^3 + t^3 + C_1 r_s z - C_2 r_d t - C_2 r t + C_1 r z] \}.$$

It may be readily seen, by substituting $-t$ for t and $-r$ for r in one of them, that the last two terms cancel in the integration. We now perform the integration with respect to r , but instead of integrating from $-\infty$ to ∞ , which gives an indeterminate result, we integrate between very large but arbitrary limits, let us say²⁶ $-r_1$ and r_1 . This gives us

$$\frac{1}{2} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dt (C_2 t - C_1 z)^{-1} \sin [(C_2 t - C_1 z)r_1] \cos (z^3 + t^3 + C_1 r_s z - C_2 r_d t).$$

We now change over to the variables $C_2 t - C_1 z$ and $t + z$. The Jacobian of this transformation is $1/(C_1 + C_2)$. If we integrate with respect to $C_2 t - C_1 z$, holding $t + z$ constant, it will be noted that if r_1 is great enough all the contribution to the integral will come from the point where $C_2 t - C_1 z$ is zero. We can thus use the known formula $\int_{-\infty}^{\infty} x^{-1} \sin mx \, dx = \pi$, setting the variables in the cosine function equal to the values they have at $C_2 t - C_1 z = 0$. If we let $t + z = y$, then, when $C_2 t - C_1 z = 0$, we have $z^3 + t^3 + C_1 r_s z - C_2 r_d t = y^3 (C_1^3 + C_2^3) (C_1 + C_2)^{-3} + y(r_s - r_d) C_1 C_2 (C_1 + C_2)^{-1}$. If we make the further substitution $s^3 = y^3 (C_1^3 + C_2^3) (C_1 + C_2)^{-3}$, we get for the final value of the integral (remembering the integrand must be multiplied by the Jacobian of the transformation)

$$\pi 2^{-1} (C_1^3 + C_2^3)^{-1} \int_{-\infty}^{\infty} ds \cos [s^3 + s C_1 C_2 (r_s - r_d) (C_1^3 + C_2^3)^{-1}]$$

which substituted into (22) gives an expression which may readily be seen to be equivalent to (23).

²⁶ It is convenient, but by no means necessary, to have the positive and negative limits the same.

APPENDIX II—EVALUATION OF INTEGRAL, EQ. (24)

We make the substitution $r_n - r_s = x$, and use the definition of λ (Eq. 26). It is seen that $(E_s - E_n)^{-1} d(E_s - E_n) = dx/x$ and substituting from (23) into the left-hand side of (24) we have for the integral (omitting the constant factor from the portion of (23) in front of the integral sign)

$$\int_0^\infty dz \int_0^\infty dt \int_{-\infty}^\infty dx x^{-1} \cos [z^3 - \lambda xz + \lambda(r_n - r_d)z] \cos [t^3 - \lambda xt + \lambda(r_n - r_d)t].$$

A trigonometric transformation gives

$$\begin{aligned} \frac{1}{2} \int_0^\infty dz \int_0^\infty dt \int_{-\infty}^\infty dx x^{-1} \cos [z^3 + t^3 + \lambda(r_n - r_d)(z+t) - \lambda x(z+t)] + \cos [z^3 - t^3 + \lambda(r_n - r_d)(z-t) - \lambda x(z-t)] \\ = \frac{1}{2} \int_0^\infty dz \int_{-\infty}^\infty dt \int_{-\infty}^\infty dx x^{-1} \cos [z^3 + t^3 + \lambda(r_n - r_d)(z+t) - \lambda x(z+t)]. \end{aligned}$$

Another trigonometric transformation gives

$$\frac{1}{2} \int_0^\infty dz \int_{-\infty}^\infty dt \int_{-\infty}^\infty dx x^{-1} \cos [z^3 + t^3 + \lambda(r_n - r_d)(z+t)] \cos [\lambda x(z+t)] + \sin [z^3 + t^3 + \lambda(r_n - r_d)(z+t)] \sin [\lambda x(z+t)],$$

which may be readily integrated, yielding $(\pi/2) \int_0^\infty dz \int_{-\infty}^\infty dt \sin [z^3 + t^3 + \lambda(r_n - r_d)(z+t)]$. When the integrand is expanded

as the sine of the sum of two angles, $z^3 + \lambda(r_n - r_d)z$ and $t^3 + \lambda(r_n - r_d)t$, it yields one term which vanishes in the integration because the integration from 0 to ∞ cancels that from $-\infty$ to 0, while the other part gives

$$\pi \int_0^\infty dz \int_0^\infty dt \sin [z^3 + \lambda(r_n - r_d)z] \cos [t^3 + \lambda(r_n - r_d)t].$$

APPENDIX III—NUMERICAL EVALUATION OF THE INTEGRALS

Airy¹³ has tabulated values of the integral $\int_0^\infty \cos(z^3 - \chi z) dz$ (in a slightly different form) over a range of values of χ from -7.57 to 7.57 . This is ample for our purposes for negative values of χ . On the positive side we need to go further, but this can be done by means of Kramers' asymptotic formula,

$$\int_0^\infty \cos(z^3 - \chi z) dz = \pi^{1/2} (3\chi)^{-1/2} \cos[2(\chi/3)^{3/2} - \pi/4].$$

The value of $\int_0^\infty \sin(z^3 - \chi z) dz$ can be obtained for small values of χ in the same way that Airy obtained the values for the other integral, while for large values of χ an asymptotic value of it may be obtained by Kramers' method.¹⁴ Since Kramers gave but a bare outline of the way his results were obtained, we shall give the calculation for the sine integral in some detail.

We make use of contours in the complex plane as indicated in Fig. 5. The lines OP and OR make angles of $\pi/3$ and $-\pi/3$, respectively, with the real axis, and the contours W_1 , W_2 , W_3 approach asymptotically the lines OP , OR , and OQ , the real axis, as shown. We shall indicate integrals by subscripts. Thus \int_{OP} means the integral taken from 0 to ∞ along OP , \int_{W_1} means the integral taken between infinite limits along W_1 in the direction shown by the arrow, etc.

Now it is readily seen that

$$\begin{aligned} 2 \int_0^\infty \sin(z^3 - \chi z) dz = \int_0^{i\infty} \exp(z^3 + \chi z) dz \\ + \int_0^{-i\infty} \exp(z^3 + \chi z) dz. \end{aligned}$$

By the use of Jordan's lemma we may transform the integrals from 0 to $i\infty$ and from 0 to $-i\infty$ to integrals

along the lines OP and OR , respectively. Making the substitution $y = z \exp(-i\pi/3)$ or $y = z \exp(i\pi/3)$ in the result, we have

$$\begin{aligned} \int_0^{\pm i\infty} \exp(z^3 + \chi z) dz = \exp(\pm i\pi/3) \\ \times \int_0^\infty \exp[-y^3 + \chi y \exp(\pm i\pi/3)] dy. \end{aligned}$$

For small values of χ the integral on the right may be evaluated by expanding the factor $\exp(\chi y \exp(\pm i\pi/3))$ as a series in χ and integrating term by term. One gets in this way a series similar to the one used by Airy to evaluate the cosine integral. It is extremely tedious to use, however, for values of greater than 3, and for such values the asymptotic form may be used.

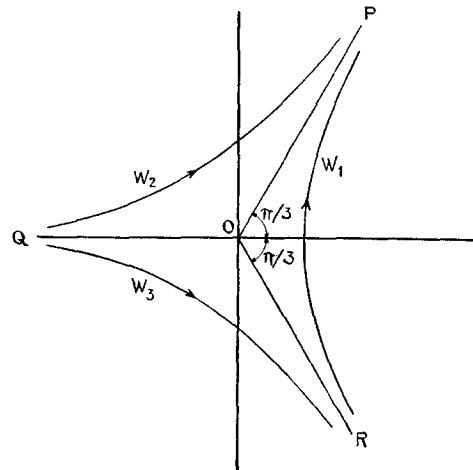


FIG. 5.

The asymptotic form will now be obtained. We note that, by Cauchy's theorem

$$\left(\int_{OP} + \int_{OR}\right) \exp(z^3 + \chi z) dz = \left(\int_{W_2} + \int_{W_3} + 2\int_{OQ}\right) \exp(z^3 + \chi z) dz.$$

The left-hand side of this equation is, as we have noted, the quantity we wish to evaluate. It may be obtained from the integrals on the right-hand side, as follows. If χ is large \int_{W_2} and \int_{W_3} may be evaluated by the method of steepest descents. Setting the derivative of $z^3 + \chi z$ equal to zero we see that a saddle point occurs at $z = i(\chi/3)^{1/3}$ for \int_{W_2} and at $z = -i(\chi/3)^{1/3}$ for \int_{W_3} . Expanding by Taylor's theorem in the neighborhood of the first of these points we see that close to the saddle point we may write

$$z^3 + \chi z = 2i(\chi/3)^{1/3} + 3i(\chi/3)^{1/3}(z - i(\chi/3)^{1/3})^2$$

and it is apparent that the curve of steepest descent for $\exp(z^3 + \chi z)$ will have a slope of $\pi/4$. Integrating along the curve we get

$$\lim_{\chi \rightarrow \infty} \int_{W_2} \exp(z^3 + \chi z) dz = \pi^{1/2} (3\chi)^{-1/2} \exp[i\{\pi/4 + 2(\chi/3)^{1/3}\}].$$

Similarly

$$\lim_{\chi \rightarrow \infty} \int_{W_3} \exp(z^3 + \chi z) dz = \pi^{1/2} (3\chi)^{-1/2} \exp[-i\{\pi/4 + 2(\chi/3)^{1/3}\}].$$

Therefore

$$\begin{aligned} \lim_{\chi \rightarrow \infty} \frac{1}{2} \left(\int_{OP} + \int_{OR}\right) \exp(z^3 + \chi z) dz \\ = \lim_{\chi \rightarrow \infty} \int_0^\infty \sin(z^3 - \chi z) dz \\ = -\pi^{1/2} (3\chi)^{-1/2} \sin[2(\chi/3)^{1/3} - \pi/4] + \int_0^\infty \exp(z^3 + \chi z) dz. \end{aligned}$$

Now to evaluate $\int_0^\infty \exp(z^3 + \chi z) dz$ for small values of χ we could expand $\exp \chi z$ as a series and integrate term by term, but this series will also be difficult to use for $\chi > 3$. If χ is very large it is obvious that the integral approaches the value $-\int_0^\infty \exp(-\chi z) dz = -1/\chi$. This suggests that we expand $\exp z^3$ as a series and integrate term by term, but if we do this we get the asymptotic non-convergent series, $-1/\chi + 3!/ \chi^4 - 6!/ / 2! \chi^7 + 9!/ / 3! \chi^{10} - \dots$. When $\chi = 3$, the value of $1/\chi$ is 0.333 and the value obtained from the first two terms is 0.259, while the value obtained from the other expansion for the integral is 0.296. When $\chi = 4$, we have $1/\chi = 0.250$ and $1/\chi - 3!/ \chi^4 = 0.227$, while when $\chi = 6$, we have $1/\chi = 0.167$ and $1/\chi - 3!/ \chi^4 = 0.162$. At $\chi = 6$, then, $-1/\chi$ will be a reasonably good value for the integral,

TABLE III. Values of $\int_0^\infty \cos(z^3 - \chi z) dz$ and $\int_0^\infty \sin(z^3 - \chi z) dz$.

χ	$\int_0^\infty \cos(z^3 - \chi z) dz$	$\int_0^\infty \sin(z^3 - \chi z) dz$	χ	$\int_0^\infty \cos(z^3 - \chi z) dz$	$\int_0^\infty \sin(z^3 - \chi z) dz$
-4.0	0.020		5.7	-0.240	0.67
-3.5	0.038		6.0	0.121	0.69
-3.0	0.067	0.354	6.3	0.463	0.55
-2.5	0.112	0.408	6.6	0.720	0.28
-2.0	0.182	0.461	6.9	0.827	-0.07
-1.5	0.280	0.507	7.2	0.767	-0.43
-1.0	0.419	0.534	7.5	0.548	-0.735
-0.5	0.581	0.521	7.8	0.202	-0.908
0.0	0.773	0.446	8.1	-0.184	-0.900
0.5	0.963	0.289	8.4	-0.528	-0.708
1.0	1.110	0.039	8.7	-0.742	-0.370
1.5	1.169	-0.296	9.0	-0.765	0.030
2.0	1.078	-0.674	9.3	-0.587	0.393
2.5	0.811	-1.021	9.6	-0.250	0.619
3.0	0.384	-1.239	9.9	0.158	0.642
3.3	0.078	-1.27	10.2	0.518	0.450
3.6	-0.237	-1.21	10.5	0.724	0.094
3.9	-0.530	-1.04	10.8	0.707	-0.320
4.2	-0.756	-0.78	11.1	0.469	-0.660
4.5	-0.889	-0.47	11.4	0.080	-0.817
4.8	-0.900	-0.12	11.7	-0.337	-0.730
5.1	-0.788	0.24	12.0	-0.637	-0.426
5.4	-0.560	0.50			

especially as it is, for large values of χ , essentially a correction term. For values of χ between 3 and 6 we have simply made an interpolation.

The asymptotic formulas for $\int_0^\infty \sin(z^3 - \chi z) dz$ and $\int_0^\infty \cos(z^3 - \chi z) dz$ hold well for values of χ greater than 3. Over the range (for $\chi > 3$) in which Airy has made his calculations we have calculated $\pi^{1/2} (3\chi)^{-1/2} \sin[2(\chi/3)^{1/3} - \pi/4]$ from his values by making use of the trigonometric relation between sine and cosine. This gives bad values when the sine is nearly zero, but one can interpolate through those points, and, in general, it seems to give better results than direct use of the asymptotic value. Outside the range of Airy's calculations the asymptotic formulas were used. I have tabulated the values of the two integrals in Table III. These values are not highly accurate, but are probably good enough for most purposes. The error may possibly be as great as 0.03 or 0.04 in the case of the sine integral for the worst part of the range where the asymptotic approximations were used; where the series or interpolation from Airy's values were used the errors in the worst cases should be under 0.01, and this is probably the upper limit of error for any part of the cosine curve.