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NUCLEAR MOTIONS ASSOCIATED WITH ELECTRON TRANSITIONS IN DIATOMIC MOLECULES

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Abstract

The question of nuclear motions associated with electron transitions is discussed from the standpoint of quantum mechanics. It appears that Heisenberg's indetermination principle gives the clue to the inexactness of the earlier method based on Franck's postulate since its strict application calls for a violation of the principle. The existence of an entirely new type of band spectrum due to the wave nature of matter is predicted and the interpretation of Rayleigh's mercury band at 2476–2482 A.U. as of this type is suggested. Finally it is shown that while Franck's postulate is also true for electron jumps in atoms, it is of but trivial interest because its inexactness is much greater for the electrons than for heavy nuclei.

TWO years have elapsed since Franck proposed a mechanism for the direct dissociation of molecules by light absorption[1] and since the extension of that mechanism to a theory of intensity distribution in band systems was made.[2] In the meantime the theory has been applied with gratifying success to the discussion of a number of band systems which have been recently analyzed. It has also been possible to derive the postulate underlying Franck's idea from the new quantum mechanics and thus to bring it into closer relation with the basic principles of quantum physics.

The first publication of this connection with quantum mechanics was very brief.[3] Since the connection provides one of the more easily visualised applications of quantum mechanics and because of the rather wide applicability of the method in molecular problems it is therefore proposed here to give a fuller account of the connection. Besides providing a justification of Franck's assumption, the quantum mechanical method provides a distinct advance since it gives, in principle at least, an exact method for calculating intensities. This is illustrated particularly neatly in cases where absorption of light results in direct dissociation of the absorbing molecule (Cl_2, Br_2, ICl). It appears that the reason Franck's postulate gives only the most probable transitions and not the range of allowed transitions near the most probable is intimately connected with the so-called uncertainty principle of Heisenberg and Bohr. The quantum mechanical treatment also points to the possible existence of a new type of molecular band structure which is a direct manifestation of the de Broglie wave-length in the spectrum of a molecule.

§1. Franck's Postulate

According to the theory of band spectra the molecule exists in different electronic energy levels. Associated with each of these is an effective law of

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[1] Franck, Trans. Faraday Society **21**, part 3 (1925).
[2] Condon, Phys. Rev., **28**, 1182 (1926).
[3] Condon, Proc. Nat. Acad. Sci. **13**, 462 (1927).

force which governs the motion of the two nuclei relative to each other and which is most conveniently described by drawing the curve which gives the energy of the molecule in the non-rotating non-vibrating state as a function of the distance of the two nuclei. In Fig. 1 we have such a pair of curves drawn for the two electronic states involved in the emission of the Swan bands of carbon.[4] The curves are inferred from the energy levels of the band spectrum. Thus the moment of inertia in a given state gives the abscissa of the minimum and the frequency of vibration gives the first coefficient in the Taylor's series for the curve around the minimum, etc.

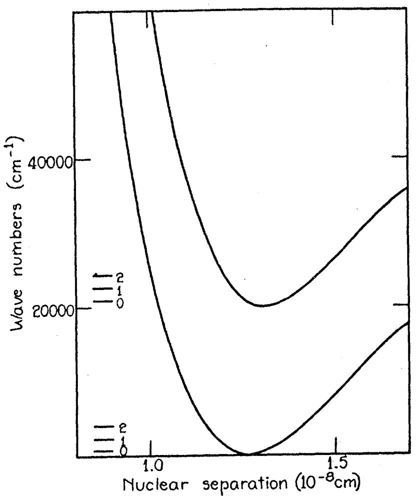

Fig. 1. Potential energy curves for the electronic states of C_2 involved in the Swan band system.

Franck postulated that in an electron transition from a state in which the molecule is not vibrating the heavy nuclei will not be affected "momentarily." Immediately after the transition the nuclei will have the same separation as before. But this will not be, in general, the equilibrium position of the law of force for the new electronic state and therefore the molecule will start to vibrate. In other words the most probable transition from the minimum of the curve for the initial state is to that point on the curve for the final state which has the same nuclear separation. This rule was then extended to make it applicable to transitions in which the molecule is vibrating initially as well as in the final state. One postulates that the electron transition affects neither the position nor the *momentum* directly. Then if the transition occurs while the nuclei are moving relatively, the most probable final state is that in which the position and momentum just after the transition is the same as that just before. This may be supplemented by supposing that the electron transition may occur with equal probability independently of the phase of the vibratory motion. This rule gives a definite probability for each of the possible final energies which can be communicated to the molecule.

It has now to be noted that it may happen that the curves lie as in Fig. 2 (which is approximately to scale for chlorine[5]). In this case absorption of light by the non-vibrating molecule would have as the transition determined by this rule that to energy level *A* which corresponds to dissociation plus a perfectly definite amount of translational energy in excess of the dissociation

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[4] Based on the analysis of Shea, Phys. Rev. **30**, 825 (1927).

[5] The frequencies of vibration and heats of dissociation are from Kuhn, Zeits. f. Physik **39**, 77 (1926). The relative position of the two curves is not known since the rotation structure of the bands has not been analyzed; their relative position as drawn here was inferred roughly from the known intensity distribution by the theory of this paper.

work, *D*. Franck first applied the method to a case of this sort—that of iodine, I_2—to explain the experiments of Dymond.[6] Experiment shows, however, that while the most favored transition is to energy level *A*, the actual absorption consists of a fairly broad continuous band. This indicates a lack of sharpness about the principle which requires explanation. Similarly in a case like Fig. 1 where the rule leads to non-dissociating transitions, its strict application leads us to predict transitions to energies in the final state which are not quantum levels. As we know that these cannot occur we are again forced to recognize a certain lack of sharpness in the rule and to suppose that the probability of transition to non-allowed levels must perhaps be assigned to the credit of the nearest allowed level.

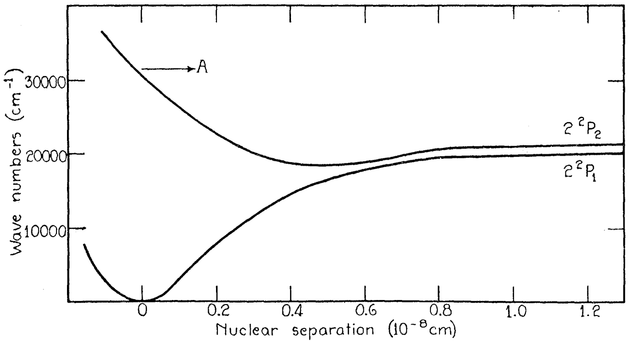

Fig. 2. Approximate potential energy curves involved in the visible absorption spectrum of Cl_2. Ordinates and abscissas as in Fig. 1.

Making such adjustments, however, the principle has proven quite useful in giving an easily visualized rule for predicting the nuclear motions set up by electron transitions. The adjustments toward looseness which have to be made in the picture are the result of a too strict application of classical ideas to the problem in hand. For a rational treatment of the problem we turn therefore to the new quantum mechanics.

§2. The Principle in Wave Mechanics

Following Schrödinger's method the behavior of a molecule is described in terms of the solution of his wave equation which involves $(3n+6)$ independent variables if n is the number of electrons in the molecule. Not much headway can be made with the equation without the application of perturbation theory. Born and Oppenheimer have shown how the problem can be handled by successive approximations amounting to an expansion in powers of $(m/M)^{1/4}$ where m is the electronic mass and M is of the order of a nuclear mass.[7] It is because of the great mass of the nuclei that one can regard their motion as determined approximately by the wave-mechanical analogue of the time-mean of the forces of all the swiftly moving electrons on the nuclei.

[6] Dymond, Zeits. f. Physik **34,** 553 (1925).

[7] Born and Oppenheimer, Ann. d. Physik **84,** 457 (1927).

Their work justifies the postulate that the coordinates of the nucleus remain approximately separable from those of the electrons in Schrödinger's theory.

We can ignore the rotation motion of the molecule. Let r be the nuclear separation and x stand for the ensemble of all the electronic coordinates. A definite state of the molecule will be characterized by e, which is the ensemble of all the electronic quantum numbers, and by n, the vibrational quantum number. The fact of approximate separability means that to a good approximation the energy of the state $E(e, n)$ is the sum of an electronic part and a vibrational part,

$$E(e,n)=E_e+E_n$$

and that the wave function for such a state $\psi_{e,n}\ (x, r)$ is the product of a function of the electronic coordinates and one of the nuclear separation,

$$\psi_{en}(x,r)=X_e(x)\cdot R_{en}(r).$$

Moreover the work of Born and Oppenheimer shows that the energies E_n and the function $R_n(r)$ are given by solving the one-dimensional wave equation in the variable r got by using an effective potential energy curve $U(r)$ representing the mean action of all the electrons in the state characterized by $X_e(x)$. Recently Heitler and London have obtained important results for the quantum theory of molecules concerning the curves $U(r)$ by approximations concerning $X_e(x)$. We may take empirically the $U(r)$ curve associated with each state as that one which is consistent with the quantum theory of the empirical energy levels of the band system in question.

Such empirical $U(r)$ curves in turn lead directly to solutions for E_n and $R_n(r)$ from a simple one-dimensional wave equation. The intensities of any given transition $(e', n')\rightarrow(e'', n'')$ have now to be considered. These are given unambiguously by the quantum mechanics in terms of the function $\psi_{en}(x, r)$. The electric moment of the molecule is given classically as the vector sum of the charges multiplied by their distances from a fixed point. Let $M(x, r)$ be this function. If the x are rectangular coordinates M is linear in all of the x and r. The electric moment which functions as a measure of the probability of the foregoing transition is

$$M(e',e'',n',n'')=\int\int M(x,r)\psi_{e'n'}(x,r)\cdot\psi_{e''n''}(x,r)dx\,dr.$$

One can carry out (in principle) the integration over the electronic coordinates and obtain an intermediate sort of electric moment function which is characteristic of the electron transition $e'\rightarrow e''$ and which depends only on r,

$$M(e',e'',n',n'')=\int M(e'e'',r)\cdot R_{e'n'}(r)R_{e''n''}(r)dr$$

Although the range of integration is $-\infty$ to $+\infty$ the only parts which make appreciable contributions are in the range of coordinates in which both $R(e', n', r)$ and $R(e'', n'', r)$ have values not too near zero. In such a range it is probably always sufficient to take $M(e', e'', r)$ as a linear form $A+Br$ where it is supposed that the origin of r has been shifted to the center of the important part of the range of integration. In what follows a little brevity is gained by neglecting all but the constant part A since the reader will have no difficulty in seeing that the argument is not much affected by omitting the linear Br term. Although $M(e', e'', r)$ is unambiguously defined, almost nothing is known about it in the present state of our ignorance of the ψ functions for molecules.

We turn now to the consideration of the relative intensity of the different $n' \rightarrow n''$ transitions, associated with a definite $e' \rightarrow e''$ transition. It is a consequence of Schrödinger's theory that $R_n(r)$ will approach zero very rapidly outside of the region of the classical vibratory motion of the same energy. Inside this region it will be an oscillatory function.

From these properties of the functions $R(e, n, r)$ we read the quantum mechanical justification of the Franck postulate; together with a definite estimate of the uncertainty involved in its application. For example the $n'=0 \rightarrow n''=0$ band by the Franck rule is most probable for zero change in moment of inertia. For large change it is an improbable transition. This follows because now the wave functions $R(e', 0, r)$ and $R(e'', 0, r)$ are both Gauss error curves, each one located symmetrically about the minimum of its own potential energy curve. The over-preciseness of the rule arises from the neglect of the fact that in the zero vibration state the particle is not precisely at the minimum of the curve but has a probability of being a short distance on either side of the minimum.

One sees then that when non-oscillatory wave functions come in question the integral has the largest value when the functions overlap most. This corresponds to Franck's rule, but extended to take into account the distribution of positions characteristic of quantum mechanics. We consider next a transition from $n'=0$ to some large value of n'' for a case in which the change in moment of inertia accompanying the electron jump is small. The wave function for the large value of n'' will now be a rapidly oscillating function of r, and for this reason the integral of the product of two wave functions will be small. This corresponds to the part of the rule of §1 which says that large changes in nuclear momentum at the instant of electron transition are improbable. This comes about because the oscillatory character of the wave function is the wave-mechanical analogue of the fact that the particle has considerable momentum at that part of its orbit. (The spacing of the zeros is given approximately by de Broglie's rule, $\lambda p=h$).

The wave functions of the higher states sink rapidly to zero outside the range of the classical motion. In the neighborhood of one of the turning points they have a broad maximum—broad because here the momentum is small so the quasi-wave-length is long, and maximum because here the particle spends a larger fraction of the time than places where it moves fast. As one goes from either of the classical turning points toward the minimum of the potential energy curve, the function oscillates more rapidly and has decreasing amplitude—both things corresponding to the greater speed of the particles at this part of the motion. We consider next a transition from the $n'=0$ state accompanied by a large change in moment of inertia. Then the vibration level which is given as most probable by the rule of §1 will be one whose wave function's broad maximum lies in a favorable position with respect to the $n'=0$ wave function and is therefore one which is favored by the wave mechanics formula. The wave functions for smaller values of n'' will not, overlap the $n'=0$ wave function, while those for larger values of n'', though they overlap, oscillate rapidly and for this reason the integral measuring the intensity is small.

Thus we see how the quantum mechanical formula agrees with the rule of §1 when that is regarded as approximate. The method of this section goes beyond that of §1 in providing exact intensity predictions and gives appreciable values to transitions in the neighborhood of those given by Franck's rule. This is an evidence of the workings of the basic uncertainty relation of Heisenberg.[4] According to this we cannot reason closely about the simultaneous values of position and momentum. One must admit uncertainties in each quantity such that their product is of the order of h. We were violating this in §1, for example where we spoke of the nuclei as having zero relative momentum when at the extremity of their classical vibratory motions. The conclusion from such a statement must, on the quantum theory, be erroneously over-precise as we have already seen is the case.

§3. THE CONTINUOUS SPECTRUM ACCOMPANYING DISSOCIATION

One can easily see that the quantum-mechanical formula gives the right order of magnitude for the breadth of the continuous band accompanying dissociation of a molecule. There are several good examples at present of molecules which, on absorbing light from their lowest state, dissociate into two atoms which rush apart from each other with translational energy. We will consider the examples of the halogens for which the data are available.

In Fig. 3 the curves are drawn to scale for I_2.[9] By Franck's rule the most probable transition on absorption from the non-vibrating state is the absorption of light of frequency 19000 cm^{-1}. What is found experimentally is a broad band of absorption which runs from λ4300 to λ5800. The part from λ4300 to λ4995 is continuous while from λ4995 to λ5800 it is banded. This observed range of absorption is indicated near the frequency scale in Fig. 3.

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[8] Heisenberg, Zeits. f. Physik **43**, 172 (1927) and Bohr, Nature **121**, 580 (1928).

[9] Some readers may recall that the outstanding blemish in the original paper[2] was the lack of agreement between theory and experiment for the absorption bands of I_2. This was due to a bad blunder on my part in using the moment of inertia for the 26th vibrational level of the excited state thinking it was the moment of inertia for the non-vibrating molecule. For calling attention to the mistake in private communications I am deeply indebted to Professors R. T. Birge and F. W. Loomis. The curves as drawn are based on the following data:

$r'_0=3.010$ $r''_0=2.663$
$\omega^{0\prime}=127.5$ $\omega^{0\prime\prime}=213.67$
$\beta'_0=0.02911$ $\beta_0''=0.03730$
$\alpha'=0.00017$ $\alpha''=0.00011$
$x'\omega'=0.85$ $x''\omega''=0.592$

What does the quantum-mechanical method predict for the breadth of this band? The wave function of the non-vibrating initial state is a Gauss error curve. The order of magnitude of the width of the band, as in §2, is given by the breadth of the frequency interval over which the integral for the electric moment has an appreciable value. An exact calculation would require knowledge of the form of the wave functions for the excited state. The order of magnitude involved one readily sees is about equal to the interval on the frequency scale given by "reflecting" the initial state wave function in the potential energy curve of the final state the result being curve (a) Fig. 3. Such a rough estimate of the quantum mechanical intensity integral has still to be multipled by ν^4 to give intensities. Curve (b) shows the result of doing this. It is seen that the theory predicts the *extent* as well as the position in the spectrum of the absorption quite nicely.

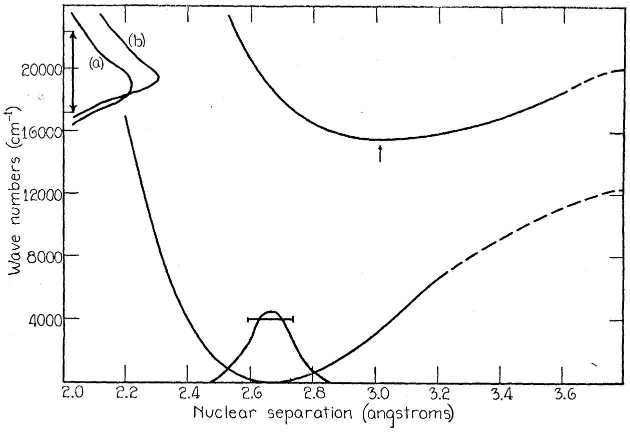

Fig. 3. Potential energy curves involved in the visible band system of I_2, together with the ψ function for zero vibration in the final state. (a) is the reflection of this ψ function in the upper state energy curve. (b) is (a) multiplied by ν^4. The two-headed arrow indicates the approximate extent of the observed absorption from the zero vibration level.

For Br_2, Cl_2, and ICl we do not at present know the moments of inertia so that we are not able to predict theoretically the exact *location* of the continuous bands accompanying dissociation. But if we put the potential energy curve for the excited state at the position which makes theory and experiment agree as to the location of the maximum then the slope comes out so in each case as to predict the observed *width* of the continuous band, at least in order of magnitude.

In Fig. 4 we have the data on the continuous absorption of Cl_2, Br_2, and ICl as a function of frequency and a line showing the theoretical width of the continuous band, as estimated in this rough way.

For Cl_2 the measurements of Halban and Siedentopf were used, for Br_2 those of Kuhn[21] for ICl those of Gibson and Ramsberger[20] while for I_2 we have only Mecke's statement[25] that the continuous begins around $\lambda 4300$. The approximate theoretical values were got by regarding the potential energy

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[25] Mecke, Ann. d. Physik 71, 104 (1923).

curve of the excited state as parabolic, the constant being determined by the known frequency of vibration. It was then assumed that this curve is truly so located relatively to that of the ground state as to give the empirical value of the maximum of the continuous correctly by the rule of §1. This determines the slope of the energy curve for the excited state at the equilibrium separation of the unexcited state. One can say that the true slope is certainly greater than the value estimated this way: This slope is then multiplied by the parameter, a, in the wave function of the harmonic oscillator for the normal state to give an estimate of the half-value width of the continuous spectrum on either side of the maximum, as indicated in Fig. 4 by the lines drawn just inside the absorption curves. Naturally such an approximation is quite crude, but it is fair to claim that it agrees well enough with the observations to serve as support of the theory.

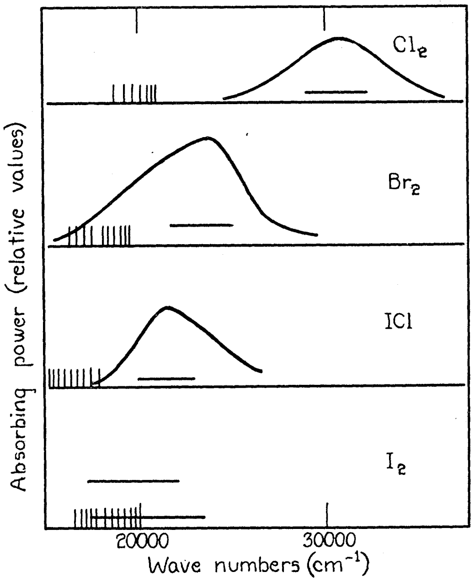

Fig. 4. The relative absorbing powers from the zero vibration state into the continuous spectrum beyond dissociation for Cl_2, Br_2, and ICl and its approximate extent for I_2 given by the lower line. The shading indicates the location of the $n''=0$ progression of bands and their high frequency convergence limits. The horizontal lines under each curve show the quantum mechanical estimate of the width of the continuous absorption. The ordinates are relative values, for each substance, so comparisons between substances are meaningless.

While this paper was in preparation Winans and Stueckelberg[11] recognized the application of these ideas to the explanation of the molecular part of the continuous spectrum of hydrogen, making use of Heitler and London's[12] quantum-mechanical potential energy curve for the 1^3S state of the molecule. Their paper serves at the same time to give not only a satisfactory account of this spectrum but also an important application of the methods of this section,

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[11] Winans and Stueckelberg, Proc. Nat. Acad. Sci. **14**, (in press) (1928).

[12] Heitler and London, Zeits. f. Physik **44**, 455 (1927).

and the first empirical evidence of the physical reality of the theoretical 1^3S state of the molecule.

§4. Diffraction Bands in the Continuous Spectrum

The argument of the preceding section from the properties of the wave functions can be translated into a justification for Franck's postulate, as we have seen. Moreover it gave a quantitative understanding of the over preciseness of the conclusions drawn from the postulate by showing how the strict use of it violates Heisenberg's uncertainty principle.

The analogy with optics is a helpful one. As is well-known, geometrical optics is the analogue of classical mechanics. In the transition to wave mechanics one can regard Heisenberg's uncertainty principle as being a semi-quantitative rule which gives the order of magnitude of diffraction deviations from geometrical optics and classical mechanics respectively. The last stage of refinement is reached in optics where the wave theory is used to predict details of diffraction patterns, and in wave mechanics where Schrödinger's equation gives the exact details of the diffraction phenomena of the de Broglie waves. In this section we shall see that cases may arise in which the quantum mechanical formulas give a rippling fluctuation in intensity in the continuous spectrum accompanying dissociation.

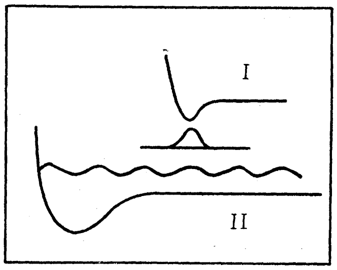

Fig. 5. Illustrating a possible relation of the two potential energy curves which would give rise to the diffraction bands.

Suppose the potential energy curves lie as in Fig. 5 where the essential point is that one curve has a very gentle slope at the abscissa values near the minimum of the other. Then by the arguments of preceding sections the most probable jump from zero vibration in electron state *I* to electron state *II* is in the continuous spectrum. By the uncertainty principle one can estimate roughly the extent of this continuous spectrum. Looking at the matter more in detail, we see that because of the gentleness of slope of curve *II* the Ψ functions associated with nuclear motion in this electronic state will have a rather long wave-length, so the distance between zeros might be about equal to the breadth of the Gauss error curve which is the ψ function of zero vibration in state *I*. We consider now the relation of the ψ_{II} functions for state *II* but different nuclear energies, W, to this error curve ψ_I function of state *I*. For values of W such that the oscillatory part of ψ lies at the same abscissa values as the maximum of the ψ_I function, the value of the integral of the product, $\psi_I\psi_{II}$ will depend very much on whether a node or a loop of the ψ_{II} function is coincident with the maximum of the ψ_I function. If a node is there, the integral will have a small value, if a loop it will be large.

We have next to consider how ψ_{II} depends on the nuclear energy W for this state. As W increases through its continuous spectrum, the ψ_{II} function will change in such a way that its wave-length gradually shortens about as $W^{1/2}$ while the positions of the zeros shift continuously past any fixed abscissa value. This has for a consequence that the intensity of transition into the continuous spectrum will undergo a rippling variation being large for those values of W which put a loop of ψ_{II} over the center of ψ_I and small for those which put a node there. All of this effect is, of course, contained within the extent of the allowed continuous spectrum as given roughly by the Heisenberg principle; just as in optics the diffraction maxima inside the geometrical shadow of a straight edge are inside the region of diffracted light given by the uncertainty principle. Finally for large values of W the wave-length of ψ_{II} will be so small compared to the breadth of ψ_I that these maxima become less and less clearly resolved while the whole intensity sinks to zero.

With the greatest reserve I will now suggest that the peculiar band recently described by Rayleigh[13] in mercury vapor may be such an intramolecular manifestation of the wave nature of matter. At least this will serve as an illustration on which to make the preceding ideas more precise. The band in question extends from λ2476 to λ2482 and is found only in emission. It has a sort of head at λ2476 and is accompanied by a weaker band with a head at λ2469 but this one does not show the banded structure. To discuss these as nuclear diffraction bands we will suppose that the head at 2476 corresponds to the transition from the zero vibration state of curve *I* (Fig. 5) to zero nuclear energy on curve *II* which will for simplicity be supposed to be absolutely horizontal under the minimum of curve *I*. On this view curve *II* is probably that of the ground state of the Hg_2 molecule and curve *I* one for which the molecule separates into one Hg atom in its normal state and one in the $^3P_2$ state, which is upper state for the forbidden atomic line λ2270—but these points are not essential to the present discussion.

The band whose head is at λ2469 may be supposed to represent transitions into the continuous range above *II* from the first vibrational level of curve *I*. This fixes the vibration frequency in curve *I* at 106.2 cm^{-1} and therefore the constant, a, giving the breadth of the wave function,

$$a=8.2/(\omega\mu)^{1/2}=0.08$$

where a is in Angstrom units, $\omega=106.2$ and μ is half the atomic weight of Hg. This formula is a convenient way of writing the general formulas

$$a^2=h/2\pi(\kappa\mu)^{1/2} \text{ and } \nu=(\kappa/\mu)^{1/2}/2\pi, \quad (C.G.S. \text{ units}),$$

from the wave mechanics of the harmonic oscillator.

On the horizontal part of *II* the function ψ_{II} will have the form

$$\psi_{\text{II}}=\lambda \sin 2\pi(x/\lambda+\delta)$$

in which λ is the de Broglie wave-length, h/p, given by the convenient formula,

$$\lambda(A.U.)=25.7/(\mu\nu)^{1/2}$$

where ν is the energy of the state in cm^{-1} reckoned up from the horizontal part of *II*. The factor λ, in front, comes from the normalization of the wave

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[13] Rayleigh Proc. Roy. Soc. **A119**, 349 (1928), especially p. 353.

functions for the continuous. As explained before δ, as well as λ, depends on ν. Assuming complete non-polarity for simplicity, the intensity of transition from state I to a level ν cm^{-1} up from the horizontal part of II is therefore proportional to the square of,

$$I_0(\nu)=\int e^{-x\ /2a}\cdot\lambda\sin 2\pi(x/\lambda+\delta)dx$$

$$=(2\pi)^{1/2}a\lambda\sin 2\pi\delta\cdot e^{-2\pi^2a^2/\lambda^2}.$$

The factor with the exponential function represents the effect of the uncertainty principle, the sine factor gives the banded diffraction structure. Inserting the numerical value of a and the relation of λ to ν the exponential factor becomes $e^{-\nu/52.3}$, so that the intensity for $\nu=100$ cm^{-1} will be about $e^{-4}=2$ percent of the value for $\nu=0$. The Rayleigh band is about 90 cm^{-1} in extent so that the order of magnitude agreement is a good one. But it does not appear to show such an exponential intensity decay.

Next we have to consider roughly the spacing of the diffraction maxima in the spectrum. A rough approximation is to suppose that curve II is simply L-shaped, that is, it extends horizontally a distance d to the left of the minimum of I and then turns up abruptly to infinity. For a range of ν of only $0-100$ cm^{-1} this is not as bad an approximation as it might at first seem. At any rate for such a curve ψ_{II} has a node at the place of infinite slope and so δ is simply given by

$$\delta=d/\lambda=d\nu^{1/2}/2.57$$

and the maxima come at $\delta(\nu)=(n+\frac{1}{2})$ with n an integer. This simple argument would then put the nth maximum at

$$\nu^{1/2}=2.57(n+\tfrac{1}{2})/d$$

This would make the maxima close together at the short-wave side and be more widely spaced toward the long-wave side. Not only is this true but $\Delta\nu^{1/2}$ is fairly constant for Rayleigh's band as Table I based on his data shows.

TABLE I. *Values of $\Delta\nu^{1/2}$ for the Hg_2 bands observed by Rayleigh.*

Wave-number	ν	$\nu^{1/2}$	$\Delta\nu^{1/2}$
40372.3	0.0	0	
354.0	18.3	4.28	
350.6	21.7	4.66	0.38
346.8	25.5	5.06	0.40
342.6	29.7	5.45	0.39
337.9	34.4	5.87	0.42
332.4	39.9	6.32	0.45
326.1	46.2	6.80	0.48
320.3	52.0	7.22	0.42
313.5	58.8	7.67	0.45
306.7	65.6	8.10	0.43
298.7	73.6	8.58	0.48
291.7	80.6	8.98	0.40
284.4	87.9	9.38	0.40

From the experimental value of $\Delta\nu^{1/2}$ one infers that d is about 6.4A which is a rather large value. But this may well be a consequence of the over simplification of the curve *II*.

Another assumption for *II* is that it is given by a straight-line of small slope, its equation in the neighborhood of the minimum of *I* being

$$U(x) = -kx$$

For this one finds for the characteristic functions

$$\psi_{II}(W, x) = (x + W/k)^{1/2} J_{1/3}\left[\left(\frac{x+W/k}{b}\right)^{3/2}\right]$$

in which $J_{1/3}(z)$ is the ordinary Bessel function of order 1/3 and

$$b = 3.345/(u_1\mu)^{1/3}$$

Here u_1 is written for k when the unit of energy is cm^{-1} and of length 10^{-8} cm, and the unit of μ is 1/16 the mass of an oxygen atom. The values of z for which $|J_{1/3}(z)|$ is a maximum are roughly (by inspection from the tables in Watson's Bessel Functions):

$m =$	1	2	3	4	5
$z_m =$	0.92	4.36	7.54	10.70	13.84
$\Delta z_m =$		3.44	3.18	3.16	3.14

For larger values of m, the ordinal number of the maximum, the interval approaches π. For larger m it is therefore sufficient to look for maxima at

$$(\nu/u_1 b)^{3/2} = (m\pi - 1.89)$$

which gives the law $\Delta\nu^{3/2} = u_1\pi b$. This assumption therefore does not fit Rayleigh's data.

The structureless band at λ2469.7 has already been supposed to be due to the transition from the first vibration level of state *I* on to the continuum of *II*. It may be apparently structureless since the ψ_I function for one vibration unit has a wider range than has ψ_I for zero vibration which tends to blur the diffraction effect. But it is hard to convince oneself that one unit of vibration energy can make so much difference.

The fact that these bands were found only in emission is consistent with the view here presented although this of course, is easily explained on more usual views by saying that their final state is an excited state of the molecule.

In conclusion it should be said that the existence of such diffraction bands either in emission or absorption (if *I* is a lower state than *II*) but not in both is a rigorous conclusion from quantum mechanics. It is not unreasonable to suppose that Rayleigh's band is a case of this but the interpretation must as yet be provisional and subject to confirmation, perhaps by the empirical determination of curves *I* and *II* through sharp bands coming from their discrete vibration levels.

§5. ADDITIONAL APPLICATIONS TO BAND SYSTEMS

Since the extension of Franck's postulate to band systems was first made the necessary data for its application to several more band systems has accumulated. This section is devoted to remarks on its application to some new band systems.

As already mentioned[9] the outstanding discrepancy between theory and experiment in the case of the visible bands of iodine has been removed by correction of a blunder in the use of the experimental data.

The iodine spectrum presents an interesting feature which was not amenable to treatment in the original Franck method, namely the somewhat irregular fluctuation of intensity in Wood's long series of resonance doublets. Such fluctuations probably are to be interpreted as arising from diffraction effects akin to those which are the subject of §4, except that we are now dealing with transitions of which both initial and final states are in the region of discrete energy levels. The main resonance doublet series, it is now known[14], arises from transitions from the $n'=26$ state of the excited molecule to various vibration states of the molecule in the normal electronic state from $n''=0$ to $n''=27$. Along this series of 28 doublets there are great intensity variations, some of the doublets being quite missing. Lenz[15] showed how this behavior is possible from correspondence principle considerations. From the criterion of the overlapping of the wave functions it is easily seen from Fig. 3 that from $n'=26$ to $n''=0$ to 27 are allowed transitions. The exact intensity of any particular one, however, will depend on the integral of the product of the wave functions of the initial and final states as in §2. And as in §4 this will depend very much on the exact phase relation of the nodes and loops of the two wave functions in question. These finer diffraction effects probably give rise to the intensity fluctuations in the resonance doublet series.

While the principle of their explanation is therefore precisely fomulated, the exact prediction unfortunately calls for a very accurate knowledge of the wave functions. This is lacking since for these large vibration quantum numbers it is quite inacceptable to treat the molecule as a harmonic oscillator or any other model for which ψ functions are at present exactly known.

The band systems which have been recently analyzed and on which the theory has been tested include especially the β bands of nitric oxide,[16] and the blue-green bands of diatomic sodium.[17] The vibrational analysis only for several more band systems has been recently published. In all of these cases the types of intensity distribution are those which this theory explains but lacking analysis of rotational analysis one is unable to use them for detailed verification of the theory. In this class at present may be mentioned the many band systems of the copper halides studied by Ritschl,[18] the absorption and

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[14] Chapter VI of National Research Council Report on Molecular Spectra in Gases.

[15] Lenz, Zeits. f. Physik **25,** 299 (1924).

[16] Barton, Jenkins and Mulliken, Phys. Rev. **30,** 175 (1927).

[17] Loomis and Wood, Phys. Rev. **32,** 223 (1928).

[18] Ritschl, Zeits. f. Physik **42,** 172 (1927).

fluorescence spectra of S_2, Se_2, Tl_2, studied by Rosen,[19] the absorption spectrum of iodine monochloride observed by Gibson and Ramsberger,[20] that of chlorine and bromine studied by Kuhn,[21] the ultra-violet system of iodine analyzed by Pringsheim and Rosen,[22] and others.

In a recent article Herzberg[23] has obtained nice measurements on the intensity distribution in the second positive group of nitrogen under different conditions of excitation, one of the systems discussed in the original paper.[2] His criticisms of the paper[2] are already covered by the explicit statement made on p. 1183 that the theory treats only of relative transition probabilities and not of distribution of the molecules in the different excited states. The latter naturally depends on the conditions of excitation and cannot come out of any theory which makes no mention of these.

§6. ELECTRON JUMPS AND THE FRANCK POSTULATE

It is natural to ask why the Franck postulate does not apply to electron transitions in atoms, that is, to questions of relative intensity of lines in atomic spectra. The classical mechanical basis for the postulate consisted in saying that the absorbed quanta and the electronic motions involved much smaller amounts of momentum than were necessary to excite the nuclear vibrations. Therefore the principle, which may be said to be one favoring as little discontinuity in the orbits as possible, should also apply to the electron orbits. This is true since one recalls that the momentum of a quantum of visible light is very small compared with the orbital momentum of electrons in the initial and final orbits concerned in the emission or absorption of such light. (Nowadays one remembers this best by recalling that the relation $p = h/\lambda$ holds equally for light and for electrons, together with the fact that λ for visible light is 10^4 times the size of an atom.)

The answer is that the postulate *is* valid to a certain extent for relative probability of electron transitions. For example, the reason why the transition $50_2 \rightarrow 1_1$ (Bohr notation) is so much less probable than a transition $2_2 \rightarrow 1_1$ in atomic hydrogen is simply because the wave functions do not overlap as much in the former case as in the latter. For atomic spectra the principle does not have so much interest as in molecular spectra, on the other hand, because here the wave-length of the electron is enough greater that the range of the Heisenberg uncertainty principle is so broad that in turn the predictions of Franck postulates become so blurred as to be of almost trivial interest. In principle, however, it is just as true for electrons as for nuclear motions.

Finally it may be said that it is in this direction that the connection of the Franck postulate with the correspondence principle is to be found, although

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[19] Rosen, Zeits. f. Physik **43,** 69 (1927).

[20] Gibson and Ramsberger, Phys. Rev. **30,** 598 (1927).

[21] Kuhn, Zeits. f. Physik **39,** 77 (1926);
Halban and Siedentopf, Zeits. f. Physik. Chem. **103,** 71 (1922).

[22] Pringsheim and Rosen, Zeits. f. Physik **50,** 1 (1928).

[23] Herzberg, Zeits. f. Physik **49,** 761 (1928).

this point today has only historical interest. The transition probabilities are related to the Franck postulate in the way here outlined and also are known to have the appropriate asymptotic connection with the Fourier coefficients of the classical motion which is demanded for the Bohr theory.[24]

In conclusion I should like to say that this paper is an outgrowth of work[3] done while abroad on a National Research fellowship and that it is a pleasure here to express my profound indebtedness to the fellowship board for its generous support of my studies.

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Princeton University.
September 10, 1928.

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[24] This fact is built into the very structure of wave mechanics and has been clearly worked out in the special case of the hydrogen atom by Eckart, Zeits. f. Physik **48**, 285 (1928).