

## A Study of the Franck-Condon Principle

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fifteen-term function would thus in all probability have given an energy differing from  $-0.80670$  by less than this amount.

Examination of the relative importance of the terms in the following sets, where just one index varies, will show how rapidly the importance of a term falls with the increase of one of the indices, especially when this rises above 1: 2, 1, 9; 1, 3; 4, 5; 7, 6; 8, 15; 2, 10, 12; 4, 13; 3, 14; 8, 15. A very minor exception seems to be offered by the term 11, which was itself negligible.

Inspection of these results leads us to the following estimates of the improvements available on addition of remaining terms in the indicated sequences:

$[0n100] \sim 0.00005$ ;  $[n1100] + [1n100] \sim 0.00015$ ;  
 $[n0120] \sim 0.00002$ ;  $[mn120] \sim 0.00000$ ;  $[0n120] \sim 0.00010$ ;  
 $[0n300] \sim 0.00000$ ;  $[mn300] \sim 0.00005$ ;  
 $[n1010] + [1n010] \sim 0.00005$ ;  $[n0010] \sim 0.00010$ ;  
 $[m03n0] \sim 0.00000$ ;  $[003n0] \sim 0.00020$ ;  $[00n00] \sim 0.00015$ ;  
 $[mnj00] \sim 0.00005$ ;  $[001n0] \sim 0.00015$ ;  $[011n0] \sim 0.00010$ ;  
 $[mn1j0] \sim 0.00005$ .

Adding to these amounts the quantities neglected in the construction of the simple function, we obtain  $0.00186 \sim 0.050$  ev. This amount should be a very safe upper limit for the improvement obtainable from the addition of an indefinite number of terms not depending on  $\rho$ , and in

view of the usual nonadditivity of small improvements  $0.03$  ev would appear to be a safe estimate of the change to be expected.

To the seven-term function not involving  $\rho$  five terms in  $\rho$  were next added:  $[00101]$ ,  $[10101]$ ,  $[01101]$ ,  $[11101]$ ,  $[10121]$ . Of these only the first two proved to be worth keeping, the resulting nine-term function giving an energy of  $-0.80906$ , while the complete twelve-term function gave  $-0.80918$ . The improvement available from addition of further terms in  $\rho$  was estimated to be not more than  $0.01$  ev.

In the study of the basic state of  $H_2$  it was found that the convergence on addition of terms not involving  $\rho$  was much more rapid if there were already present in the function terms which did depend on  $\rho$ . (It will be noted that this is not simply a special case of "regular" convergence, since two different limits are involved.) Though in this state the  $r_{12}$  terms are much less important than in the basic state, it is to be expected that a similar effect will exist here. In view of this we have estimated that the convergence limit is probably less than  $0.03$  ev below the energy of our best function,  $-0.80906$ , and can be said to be  $-0.8100 \pm 0.0007$  with considerable assurance.

## A Study of the Franck-Condon Principle

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The validity of the Franck-Condon principle has been investigated in connection with its application to the calculation of spectral intensities in the continuous radiation due to the transitions between the  $1s2s\sigma^2\Sigma_g$  and the  $1s2p\sigma^2\Sigma_u$  states of  $H_2$ . For the latter state, a potential curve was constructed on the basis of the authors' theoretical calculations. For the former state, a curve was computed from spectral data by Dunham's method. Accurate wave functions for both states were determined by mechanical integration with the differential analyzer. Transition probabilities from the first four vibrational levels of the stable state were determined by mechanical integration, both for the case that the electric moment matrix element is constant (as assumed in the Franck-Condon method) and for the case that it is a linear function of the nuclear separation. In addition integrals were determined which permitted the calculation of the probability of excitation

of the several vibrational levels by electron impact from the ground state, upon the basis of an extension of the Franck-Condon method. The spectral intensities so obtained are compared with those given by several forms of approximate calculation, and the discrepancies critically discussed. Comparisons are also made with the experimental work of Smith and of Finkelburg and Weizel. It is concluded that the Franck-Condon principle leads to results definitely incompatible with their observations. Indications are found that other transitions than the one treated in this work are contributing appreciably to the radiation observed by Smith. An analysis of the spectrum observed by Finkelburg and Weizel leads to a critical discussion of the method used by them in deducing the potential curve of the repulsive state, from which is drawn the conclusion that this curve is without quantitative significance.

## INTRODUCTION

IN the preceding paper<sup>1</sup> a sharp disagreement was found to exist between the theoretical potential curve for the Heitler-London repulsive state of  $H_2$  and that deduced by Finkelburg and Weizel,<sup>2</sup> who applied a rough form of the Franck-Condon principle in interpreting their observations on the excitation of the continuous hydrogen spectrum. Our purpose in the present paper is to subject this principle to a careful scrutiny, investigating the fundamental assumption and comparing the crude form commonly used with more rigorous approximations. Our results will then enable us to make a critical analysis of the procedure of Finkelburg and Weizel, and to obtain a satisfactory correlation between our computed curve and their experimental results.

The continuous near ultraviolet spectrum of hydrogen is produced by transitions from the various quantized vibrational levels of the  $1s\sigma 2s\sigma^3\Sigma_g$  electronic state to the continuous levels of the  $1s\sigma 2p\sigma^3\Sigma_u$  state. (See Fig. 1.) The population of the upper state is maintained by electron-impact excitation from the ground state, of which only the lowest vibrational level is usually present in important amount, while the resulting distribution among the vibrational levels of the upper state depends upon the velocity distribution of the exciting electrons. Where the latter is known, as in the experiments of Finkelburg and Weizel, a theoretical prediction of relative spectral intensities can be carried out, provided we have knowledge of the potential curves and vibrational wave functions of the three electronic states involved, and make use of the Frank-Condon principle for both excitation and radiation probabilities. A much simpler case to treat is that where the radiation comes from a single vibrational level, so that only radiation probabilities need to be considered. An example may be furnished by the work of Smith<sup>3</sup> on the spectrum from  $H_2$  in the presence of excess He, which he believes to quench all radiation except that from the lowest vibrational level.

Of the three electronic states concerned, the

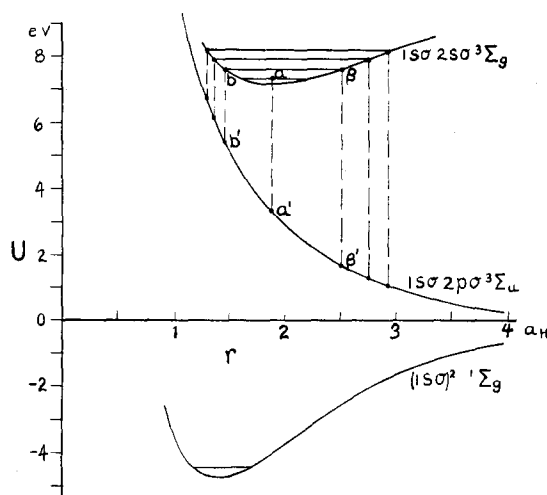


FIG. 1.  $U(r)$  curves and vibrational levels for  $H_2$ .

ground state is accurately known, both experimentally and theoretically. The upper state,  $^3\Sigma_g$ , may be determined with considerable precision, as it is the lower state of several prominent and well-known band systems. With the aid of the information about the repulsive state yielded by the calculations of the previous paper, we are in a position to make critical tests of the Franck-Condon principle, by finding out how far the spectral intensities calculated with its use agree with the observations of Finkelburg and Weizel and of Smith.

Of the electronic states involved, the ground state is the only one for whose potential curve and vibrational wave functions simple analytical expressions were used. For the excited states, the determination of the wave functions and the evaluation of the transition probabilities were effected by mechanical means. In accomplishing this, we have been fortunate in commanding the powerful assistance of the differential analyzer of Massachusetts Institute of Technology, which the engineering department kindly made available to us.

## THE FRANK-CONDON PRINCIPLE

The Franck-Condon principle applies to the calculation of transition probabilities between molecular states belonging to different electronic levels. The fundamental assumption of both the

<sup>1</sup> H. M. James, A. S. Coolidge and R. D. Present, preceding paper.

<sup>2</sup> W. Finkelburg and W. Weizel, *Zeits. f. Physik* **68**, 577 (1931).

<sup>3</sup> N. D. Smith, *Phys. Rev.* **49**, 345 (1936).

classical and the wave-mechanical forms of this principle is that in changes of electronic states the accompanying changes in the vibrational states of the nuclei depend only on the character of the nuclear motions in the two states. In classical terms, the small mass of the electrons is presumed to prevent their determining to an appreciable extent what happens to the heavy nuclei, except as they provide the potential fields in which the nuclei move in each state. In terms of wave mechanics, the transition probabilities depend upon the matrix elements between the given states of the electronic contributions to the electric moment, and the essence of the principle is the assumption that in calculating these matrix elements we need consider only an integration over the coordinates of the nuclei. It is supposed that the integration over the electronic coordinates would give a result which is independent of the positions and motions of the nuclei (at least within the range of nuclear coordinates where the nuclear part of the wave functions is appreciable) and which therefore need not be evaluated if only relative transition probabilities are desired.

In order to formulate this more specifically, let us start with the quantum-mechanical expression for the energy radiated in spontaneous transitions between two quantized states  $a, a'$  of a molecule. The energy, per second, per molecule present in the upper state, is<sup>4</sup>

$$A_{aa'} = 4(2\pi\nu)^4/3c^3 \times |\mathbf{D}_{aa'}|^2, \quad (1)$$

where  $\nu$  is the frequency radiated, and  $\mathbf{D}_{aa'} = \int \psi_a \mathbf{D} \psi_{a'} d\tau$  is the matrix element between  $a$  and  $a'$  of the variable part of the electric moment. We must assume that the complete wave function for either state may be adequately represented as the product of two factors, one describing the state of the nuclei, while the other, referring to the electrons, contains the nuclear coordinates only as parameters. This approximation amounts to treating the nuclei as though they moved in a force-field derived from a potential; it is sufficiently accurate for our purpose, even with so light a molecule as  $\text{H}_2$ . Then the electric moment with which we are concerned is that with respect to the center of the inter-

nuclear axis, and only the electrons contribute to it.

Let us consider a diatomic molecule in a  $\Sigma$  state; we represent the positions of the nuclei by their separation  $r$  and the polar angles  $\varphi, \theta$ , while the unspecified electronic coordinates (relative to the center of gravity and the figure axis) are designated  $r_1, r_2, \dots, r_n$ . We may then write<sup>5</sup>

$$\psi_a = \psi_{e, v, K, M} = F_e(r; r_1, r_2, \dots, r_n) \times R_{evK}(r) r^{-1} P_{KM}(\varphi, \theta). \quad (2)$$

Here,  $e, v, K, M$  are quantum numbers;  $F_e$  is the electronic factor, which does not involve the angles;  $P_{KM}$  is a surface harmonic.  $R_{evK}$ , the radial or vibrational function, is conveniently defined in connection with the factor  $r^{-1}$ , as this simplifies future operations; it is a solution of the Schrödinger equation

$$R'' - K(K+1)r^{-2}R + 8\pi^2\mu h^{-2}(E - U_e(r))R = 0. \quad (3)$$

where  $U_e(r)$  is the potential due to nuclear and electronic interactions, and  $E$  is a proper energy value. Now, if we multiply the product of two such  $\psi$ 's by any vector function such as  $\mathbf{D}$ , which is centrally symmetrical in the  $r_i$ , and integrate over  $r$  and the  $r_i$ , holding the angles fixed, the  $\Sigma$  symmetry insures that the resulting vector will have a component only along the figure axis. Designating the angle between this axis and the  $x$ -direction as  $\theta$ , we obtain

$$\begin{aligned} (\mathbf{D}_{evKM, e'v'K'M'})_{\theta} &= \iint \cos \theta \\ &\sin \theta d\theta d\varphi P_{KM}(\varphi, \theta) P_{K'M'}(\varphi, \theta) \\ &\times \left| \int dr R_{evK}(r) R_{e'v'K'}(r) \iint \dots \int dr_1 dr_2 \right. \\ &\dots dr_n \mathbf{D}(r_1, r_2, \dots, r_n, \varphi, \theta) \\ &\left. \times F_e(r; r_1, r_2, \dots, r_n) F_{e'}(r; r_1, \dots) \right|. \quad (4) \end{aligned}$$

The  $y$ - and  $z$ -components will differ only by angle factors in the first integral; in any case, this integral vanishes unless  $K = K' \pm 1$ .

Now it has been shown by Gibson, Rice and Bayliss<sup>6</sup> that the remainder of this integral is practically independent of  $K$ . We shall not at-

<sup>4</sup> P. A. M. Dirac, *Quantum Mechanics* (1930), p. 232.

<sup>5</sup> M. Born and R. Oppenheimer, *Ann. d. Physik* **84**, 457 (1927).

<sup>6</sup> G. E. Gibson, O. K. Rice and N. S. Bayliss, *Phys. Rev.* **44**, 193 (1933).

tempt to resolve the radiation from the different rotational levels, but shall consider only the total radiation for each vibrational transition. We shall also suppose that in the cases to be studied the distribution of radiating molecules among the rotational states is the same for each vibrational state. Then the total effect of the weighting factors arising from the angle integrations will be the same for each  $v$ , and we may write

$$I_{ev, e'v'} = N_v A_{ev, e'v'} \\ = CN_v \nu^4 \left[ \int dr R_{ev}(r) R_{e'v'}(r) D_{ee'}(r) \right]^2, \quad (5)$$

where

$$D_{ee'}(r) = \left| \iint \cdots \int dr_1 dr_2 \cdots dr_n \right. \\ \times \mathbf{D}(r_1, r_2, \cdots r_n, \phi, \theta) F_e(r; r_1 r_2 \cdots r_n) \\ \left. \times F_{e'}(r; r_1, r_2, \cdots r_n) \right|, \quad (6)$$

$N_v$  is the total population of the  $v$ th level, and  $C$  is an unknown constant.

The Franck-Condon principle rests on the assumption that  $D_{ee'}(r)$  varies so slowly,  $R_{ev}(r) R_{e'v'}(r)$  so rapidly, with  $r$ , that the former factor may be replaced by an average value, taken in front of the integral sign, and absorbed in the constant  $C$ . The problem of comparing transitions between different vibrational states of the same pair of electronic states is thus reduced to that of evaluating the overlap integral of the vibrational wave functions. In the absence of any specific information about the nature of the quantity  $D_{ee'}(r)$ , this assumption is recommended primarily by its convenience. It should be most satisfactory in cases in which at least one of the sets of vibrational wave functions concerned is concentrated into a small range of  $r$ , as with heavy molecules with strong binding and low vibrational quantum numbers. It is least likely to work in a case like  $\text{H}_2$ , where even in the lowest vibrational levels the wave function has a considerable range in  $r$ ; this is, therefore, an especially favorable opportunity to test the validity of the assumption.

Even with the aid of the Franck-Condon assumption one must have information about the vibrational wave functions in order to calculate transition probabilities. In the absence of such information, additional assumptions must be introduced. The most common one (adopted by Finkelburg and Weizel) is equivalent to replac-

ing each wave function by a constant times a  $\delta$  function at the classical turning point, or by two such functions if there are two such points (stable molecules), except that levels with  $v=0$  are represented by a single  $\delta$ -type function at the equilibrium point. Transitions are thus possible only between states having the same turning points (counting the equilibrium distance as the turning point of the ground state). Another approximation, due to Condon,<sup>7</sup> treats one wave function (specifically, that of a repulsive state) like a  $\delta$  function, while retaining the true form of the other (stable state). The overlap integral is therefore simply the value of the discrete wave function at the turning point of the state in the continuum, and the distribution of radiation intensity can be found from the square of this function by projecting it upon the vertical energy axis by means of the repulsive potential curve, and multiplying by the proper frequency factor.

Eq. (5) gives the intensity of each line in a discrete spectrum arising from transitions between two stable states. When one state lies in the continuum, we require, not the energy per line,  $I$ , but the energy per unit of spectral width, which we shall call  $I_\lambda$  when measured on the wave-length scale and  $I_\nu$  when measured on the frequency scale. We may regard this as obtained on multiplying  $I$  by the (infinite) number of adjacent states associated with radiation which lies in the band of width  $d\lambda$  or  $d\nu$ . Thus,  $I d\nu = I_\lambda d\lambda = I_\nu d\nu$ . It is easy to show by the method of artificial quantization that corresponding to Eq. (1) we have in this case

$$A_\nu = 4(2\pi\nu)^4 (2\mu)^{1/2} / 3E^{1/2} c^3 \times |D_{aa'}|^2, \quad (7)$$

$$A_\lambda = 4(2\pi)^4 c^2 (2\mu)^{1/2} / 3E^{1/2} \lambda^6 \times |D_{aa'}|^2. \quad (8)$$

Here  $E$  is the energy above dissociation of the state in the continuum, and  $D_{aa'}$  is the matrix element of  $D$  between a normalized discrete function  $a$  and a function  $a'$  in the continuum so normalized that the radial factor  $R$  reduces to a sine wave with amplitude 1 at large distances. The final expression for the energy radiated in transitions from the quantized state  $e, v$  to the band of continuous levels of the elec-

<sup>7</sup> E. U. Condon, Phys. Rev. **32**, 858 (1928).

tronic state  $e'$ , whose energies lie close to  $E'$ , so as to fill a spectral interval of width  $d\lambda$ , is found to be

$$(I_\lambda)_{ev, e'E'} = CN_v \nu^6 E'^{-\frac{1}{2}} \times [\int dr R_{ev}(r) R_{e'E'}(r) D_{ee'}(r)]^2. \quad (9)$$

The corresponding Franck-Condon expression is

$$(I_\lambda)_{ev, e'E'} = C' N_v \nu^6 E'^{-\frac{1}{2}} M_{ev, e'E'}^2, \quad (10)$$

where  $M$  is the overlap integral  $\int dr R_{ev}(r) R_{e'E'}(r)$ .

The Franck-Condon principle may be extended to the calculation of probabilities of excitation by electron impact, the reasoning being closely similar.<sup>8</sup> It would lead us to expect the changes in rotational state of a molecule with change of electronic state to be small, and to be essentially independent of the changes in vibrational state. Applying a more careful treatment to these latter transitions one finds a probability proportional to

$$[\int G_{ee'}(r) R_{ev}(r) R_{e'v'}(r) dr]^2,$$

where  $G_{ee'}$  is the matrix element of the perturbing function between the electronic states  $e$  and  $e'$ . In the case of a singlet-triplet transition, this depends on the energy of the exciting electrons,  $V$ , in a way which may be taken as proportional to the excess of this energy over a certain critical value,  $V_v$  (the excitation potential of the  $v$ th vibrational level) provided this excess is not too large.<sup>9</sup> If we now assume that  $G_{ee'}$  is so slowly varying a function of  $r$  that it may be taken outside the integral sign, we obtain an approximation corresponding to the Franck-Condon approximation in the treatment of radiative transitions. We can then write for the excitation probability

$$F_{ev, e'v'} = K(V - V_v) M_{ev, e'v'}^2. \quad (11)$$

If the interesting transitions all take place from the rotational levels of a single vibrational state, the distribution among the rotational states of each final vibrational state will be essentially the same; in treating radiative transi-

tions arising from such a distribution one might then employ Eqs. (9) or (10).

#### LOCATION OF POTENTIAL CURVES

For the  $1s\sigma 2s\sigma^3\Sigma_g$  potential curve it would possibly have been sufficiently accurate to use a Morse curve, for which the exact wave functions are known. However, since the use of the integrating machine made it possible to determine accurate wave functions for any potential, it seemed worth while to attempt to improve upon the Morse approximation, finding a curve which would give energy levels (rotational and vibrational) in somewhat better agreement with experiment.

As a starting point, we have taken the elaborate analysis of Dunham,<sup>10</sup> who has assumed a potential curve represented by  $U(\xi) = a_0\xi^2(1 + a_1\xi + a_2\xi^2 + \dots + a_6\xi^6)$ ;  $\xi = (r - r_e)/r_e$ ,  $r_e$  being the equilibrium value of  $r$ . In terms of the 8 constants in this expression Dunham derives other constants  $Y_{lj}$  such that the term value of the  $K$ th rotational,  $v$ th vibrational state can be expressed as  $F_{vK} = \sum_{lj} Y_{lj}(v + \frac{1}{2})^l K^j(K+1)^j$ . Our problem was first, to find a set of  $Y$ 's which would fit the observed term values, and second, to deduce the corresponding constants in the potential function.

Now, Richardson and Davidson<sup>11</sup> have found that the term values for this state can be satisfactorily expressed, for not too large values of  $v$  and  $K$ , by the finite series

$$F_{vK} = 2594.30v - 70.43v^2 + 0.90v^3 + 0.04v^4 + [33.386 - 1.6497v + 0.0212v^2](K + \frac{1}{2})^2.$$

This series was obtained in a form suitable for use with the old quantum theory. Upon conversion to an expression involving  $v + \frac{1}{2}$  and  $K(K+1)$  instead of  $v$  and  $(K + \frac{1}{2})^2$ , we obtain seven of the desired  $Y$ 's:  $Y_{10}$ ,  $Y_{20}$ ,  $Y_{30}$ ,  $Y_{40}$ ,  $Y_{11}$ ,  $Y_{21}$ , and  $Y_{31}$ . Since there are eight parameters in the potential function to be determined another condition is needed; this was chosen as the requirement that the ratios of successive  $a_n$ 's should not change erratically. This somewhat indefinite condition was sufficient to fix an approximate value for  $a_6$ , and it was found that

<sup>10</sup> J. L. Dunham, Phys. Rev. **41**, 721 (1932).

<sup>11</sup> O. W. Richardson and P. M. Davidson, Proc. Roy. Soc. **A125**, 23 (1929).

<sup>8</sup> N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (1933), p. 209.

<sup>9</sup> See, for instance, the computations on the excitation of the transition  $(1s\sigma)^2 1\Sigma_g - 1s\sigma 2p\sigma^3\Sigma_u$  by H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. **A135**, 258 (1932) or the observations on singlet-triplet excitations in Hg by W. Schaffernicht, Zeits. f. Physik **62**, 106 (1930).

neither the other  $a$ 's nor the value of  $U(\xi)$  in the important range was more than slightly sensitive to the choice of  $a_6$ .

By a method of successive approximations we have determined the following potential curve, which according to Dunham's formulas would give accurately the seven  $Y$ 's adapted from Richardson and Davidson:

$$\begin{aligned}\omega_e &= 2664.88 \text{ cm}^{-1}, B_e = 34.2228 \text{ cm}^{-1}, r_e = 0.986 \text{ \AA}, \\ U(\xi) &= 6.400\xi^2(1 - 1.6333\xi + 1.9397\xi^2 - 2.147\xi^3 \\ &\quad + 2.491\xi^4 - 3.076\xi^5 + 3.3\xi^6) \text{ ev.}\end{aligned}$$

It should be noted that the term values associated with this potential curve are not necessarily just those given by the 7-term equation of Richardson and Davidson, for Dunham's formulas assign small but not vanishing values to the higher  $Y$ 's.<sup>12</sup> Richardson and Davidson, using the Bohr theory formulas relating term values to the parameters appearing in  $U(\xi)$ , obtained  $U(\xi) = 6.24\xi^2[1 - 1.6375\xi + 1.943\xi^2 - 2.15\xi^3 + 2.5\xi^4]$ . The close agreement of our values with theirs is somewhat surprising when one considers the differences in the methods of quantization, especially since the quantum condition employed in deriving their formulas was  $\oint p dq = v h$  rather than  $\oint p dq = (v + \frac{1}{2})h$ , so that the zero-point vibrational energy was neglected.

A potential function in the form of a finite polynomial can be a good approximation only for small values of  $\xi$ . For large positive  $\xi$  the true function approaches a limiting value asymptotically and rapidly. An infinite series (for example, the series expansion of  $e^{-\xi}$ ) can reproduce this behavior, but any finite series must, as  $\xi$  increases, eventually become dominated by the term of highest degree, increasing or decreasing rapidly. In order to estimate the error in our function caused by omission of the higher terms, we have compared it with another series in which  $a_6$  was chosen as zero and the other coefficients selected so as to reproduce the seven

TABLE I. Potential curves for  $^3\Sigma_u$ .  $U(\xi)$  in ev.

$\xi$	$U_M$	$U_6$	$U_5$
-0.3	0.932	1.011	1.010
-0.2	0.354	0.366	0.365
-0.1	0.076	0.076	0.076
0.0	0.000	0.000	0.000
0.1	0.055	0.055	0.055
0.2	0.192	0.189	0.189
0.3	0.377	0.369	0.370
0.4	0.588	0.569	0.579
0.5	0.803	0.754	0.818
0.6	1.024	0.845	1.133

$Y$ 's when substituted in Dunham's equations. This procedure is open to the objection that a series terminating with  $a_6$ , a negative quantity, does not satisfy Dunham's boundary conditions; it is safe to assume, however, that for small values of  $\xi$  where the function is found to be but slightly sensitive to the value of  $a_6$  the error due to omitting higher terms is even slighter. In view of the regular alternating values of the coefficients, it is apparent that if the series were extended its value for small positive  $\xi$  would be found below that of the series terminating with  $\xi^6$ , and above that ending with  $\xi^5$ . The values of these series are shown in Table I for various values of  $\xi$ , under the respective headings  $U_6$  and  $U_5$ . For comparison, we have also computed  $U_M = 3.029(1 - e^{-1.471\xi})^2$ , the potential curve constructed as suggested by Morse.<sup>13</sup> It will be seen that for  $\xi$  up to 0.3 or 0.4,  $U_6$  and  $U_5$  agree with each other better than with  $U_M$ , and may be taken to be an improvement upon  $U_M$ . For larger  $\xi$ ,  $U_6$  is definitely too high,  $U_5$  too low, the mean being, however, still below  $U_M$ . As the best compromise, we have taken for our potential curve for  $\xi < 0.5$  the mean of  $U_6$  and  $U_5$ , the first being assigned three times the weight of the second. Above  $\xi = 0.5$  we have extrapolated a curve following the general course of  $U_M$  but falling gently below it. For negative  $\xi$  the sharp rise in  $U$  limits the range of interest to small values, where  $U_6$  may be confidently accepted. The fact that it does not reproduce the singularity which the true function must have at  $\xi = -1$  is of no practical importance, as the wave function is there wholly negligible in any case.

Our work with the ground state involved only

<sup>12</sup> Since this work was carried out, Sandeman [Proc. Roy. Soc. Edinburgh 55, 49 (1935)] has published an account of an essentially similar investigation. His treatment differs from ours in that he made a new analysis of the spectral term values and employed six  $Y$ 's to determine a series ending with  $a_4$ . In applying Dunham's formulas he made certain (probably good) approximations. His potential curve differs from ours in lying nearer to the Morse curve for  $\xi < 0.3$  and diverging from it for smaller  $\xi$  than does ours. He also gives an interesting discussion of the uncertainties involved in applying this method.

<sup>13</sup> P. M. Morse, Phys. Rev. 34, 57 (1929).

the lowest vibrational level. The potential curve therefore did not have to be accurately known over more than a small range, within which we assume it to be given by the Morse function

$$U = 4.723(1 - e^{-1.024\xi})^2,$$

with  $r_e = 1.4a_H$ .

For the repulsive state we constructed two potential curves (Fig. 2), between which we believe the true curve must lie for  $r > 1.5a_H$ . The upper curve passes through the three computed energies<sup>1</sup> at  $r = 1.5$ , 1.6, and  $1.87a_H$ , with the same small allowance for convergence as was carefully estimated for  $r = 1.5a_H$ . It coincides with the Heitler-London curve for  $r = 3$ , and in the intermediate portion is interpolated in as flat a curve as looks plausible. The lower curve passes through our computed points at  $r = 1.5$  and 1.6, which we believe to be quite accurate, and through the Heitler-London point at  $R = 4$ . At  $r = 3$  the curve is below the Heitler-London curve by an amount equal to 30 percent of the interaction energy. This seems a safe outside limit for the error in the Heitler-London method at this distance, in view of the fact that for the ground state it gives the interaction energy with an error of only 32 percent at the much smaller distance  $r = 1.5$ . The most probable curve, as given in the previous paper, lies between these two curves, nearer the lower one for small  $r$  and nearer the upper one for large  $r$ . For  $r < 1.5a_H$  in each case we have used the curve as given there.

#### USE OF THE DIFFERENTIAL ANALYZER

The work of finding the wave functions belonging to potential curves of the excited states, and of evaluating the normalization, overlap and other integrals, was performed with the differential analyzer. The machine (for a description of which see the paper by Bush<sup>14</sup>) is capable of turning out progressively the solution of an ordinary differential equation which follows from the arbitrary starting conditions to which the machine is initially set; at the same time it can evaluate definite integrals involving the solution being generated. In our case it was desired to find the wave functions as solutions

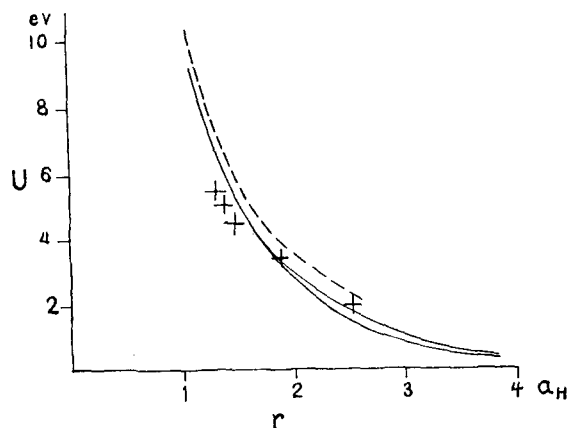


FIG. 2.  $U(r)$  curves for the Heitler-London repulsive state. Solid lines are the potential curves used in this work. + indicates a point obtained by the construction of Finkelburg and Weizel. Broken line is approximately the potential curve needed to give agreement with observation if the Franck-Condon approximation is used.

of the equation

$$R'' + (E - U(r))R = 0,$$

or

$$R' = - \int (E - U) R dr. \quad (12)$$

In this equation,  $U(r)$  is one of the potential curves already described, and was introduced into the machine in the form of a carefully prepared graph, the scale being so chosen that the constant factor in the Schrödinger equation reduced to unity. Simultaneously, it was desired to determine one or more of the integrals  $\int R^2 dr$ ,  $\int RS dr$ ,  $\int R^2 S dr$ , and  $\int RSr dr$ , over the range of  $r$  covered,  $S$  being a second function of  $r$ , introduced graphically. The machine was therefore set up as shown in Fig. 3, in the notation of Bush. (Scales, gear ratios, and directions of rotation have been omitted.)

#### INVESTIGATION OF THE $1s\sigma 2s\sigma^3\Sigma_g$ STATE

Our first concern was to control the potential curve calculated for the  $^3\Sigma_g$  state by verifying that its proper energy levels are such that their separations are in agreement with experimental data. This step also furnished the wave functions required for further work. The proper energy is the value of  $E$  such that the solution of the differential equation obtained by starting with the correct initial conditions either to the left

<sup>14</sup> V. Bush, J. Frank. Inst. **212**, 447 (1931).



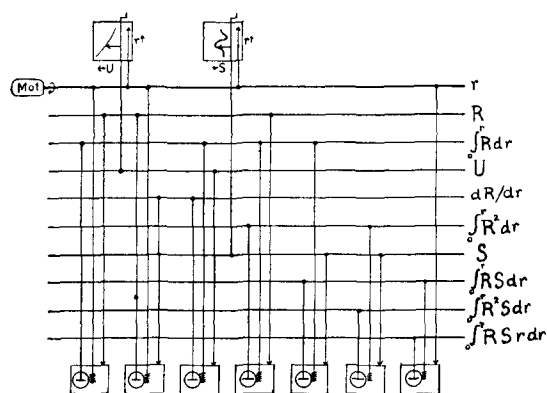


FIG. 3. Connections for the differential analyzer.

or to the right of the "classically accessible region" (i.e., the region where  $E - U$  is positive) will increase rapidly to a point of inflection at the first turning-point ( $E - U = 0$ ), oscillate through  $v+1$  maxima and minima to a second point of inflection at the second turning point, and thereafter decrease steadily, approaching the axis asymptotically if working toward the right, touching it at the origin if toward the left. This last steady decrease was never actually obtained. In the terminal region, the integration is the opposite of self-correcting, and the magnification of errors in the energy setting, in the operation of the machine itself, or in following the potential curve inevitably causes the function sooner or later to diverge violently, either above the axis or below. It was possible, however, to determine the proper energy with sufficient precision as the mean of two slightly different values, the wave functions corresponding to which were in very close agreement over the initial range and the classical range, but eventually diverged, becoming infinite in opposite senses. The same proper energy resulted from runs in the opposite direction.

Since the zero-point vibrational energy is not experimentally known we were forced to find it by a process of trial and error, obtaining  $E = 0.170$  ev for  $v=0$ . This may be confidently accepted, as that portion of the potential curve which is of importance in determining the lowest wave function lies close to the position of equilibrium, where there can hardly be any serious error in the curve. For  $v=1$ , we found  $E$  greater by an amount in very good agreement with the experi-

mental value for the separation of these two levels, but this was not the case for  $v=2$  and  $v=3$ . Since the energy separations are known directly from experiment, while the potential curve rested upon an involved process of construction, it appeared logical to attempt to modify the curve in such a way that it would more closely reproduce the observed energy levels. We found that such a curve could be produced by depressing the original curve slightly in the region  $1.25 < \xi < 1.4$ , and elevating it in the region  $1.4 < \xi < 1.65$ , the change nowhere exceeding 0.02 ev.

On comparing the wave functions laid down from the two directions (discarding, of course, the terminal portions vitiated by incipient divergence) we observed the same sort of systematic differences as were noted in preliminary tests of the machine, a gradual increase in amplitude and a slight displacement in the positions of the nodes and loops in the direction toward which the machine was operating. We were informed that the machine could in general be trusted to one percent, and that the drift in the amplitude of an oscillating function was a recognized exception. The functions finally adopted were constructed by a process which can be roughly described as averaging the results of runs in both directions over the classical region where the effects of incipient divergence were negligible, and slightly modifying the initial, nonclassical portions of the runs in each direction so as to fit them smoothly to the central portion. As the magnitude of the adjustments seldom exceeded one percent of the maximum value of the functions, it does not seem worth while to go further into details.

The correctness of a potential curve cannot be established solely by showing that it reproduces observed vibrational energy levels. Corresponding to a given set of such levels there can be an infinite series of potential curves, derived from each other by a distortion in the general nature of a horizontal shear. The correct curve can be selected only by considering rotational energy as well. As a further check on our adjusted potential curve, and on its wave functions, we have used the latter to compute values of  $B_v$ , the coefficient of  $K(K+1)$  in the term-value series, for comparison with experiment, accord-

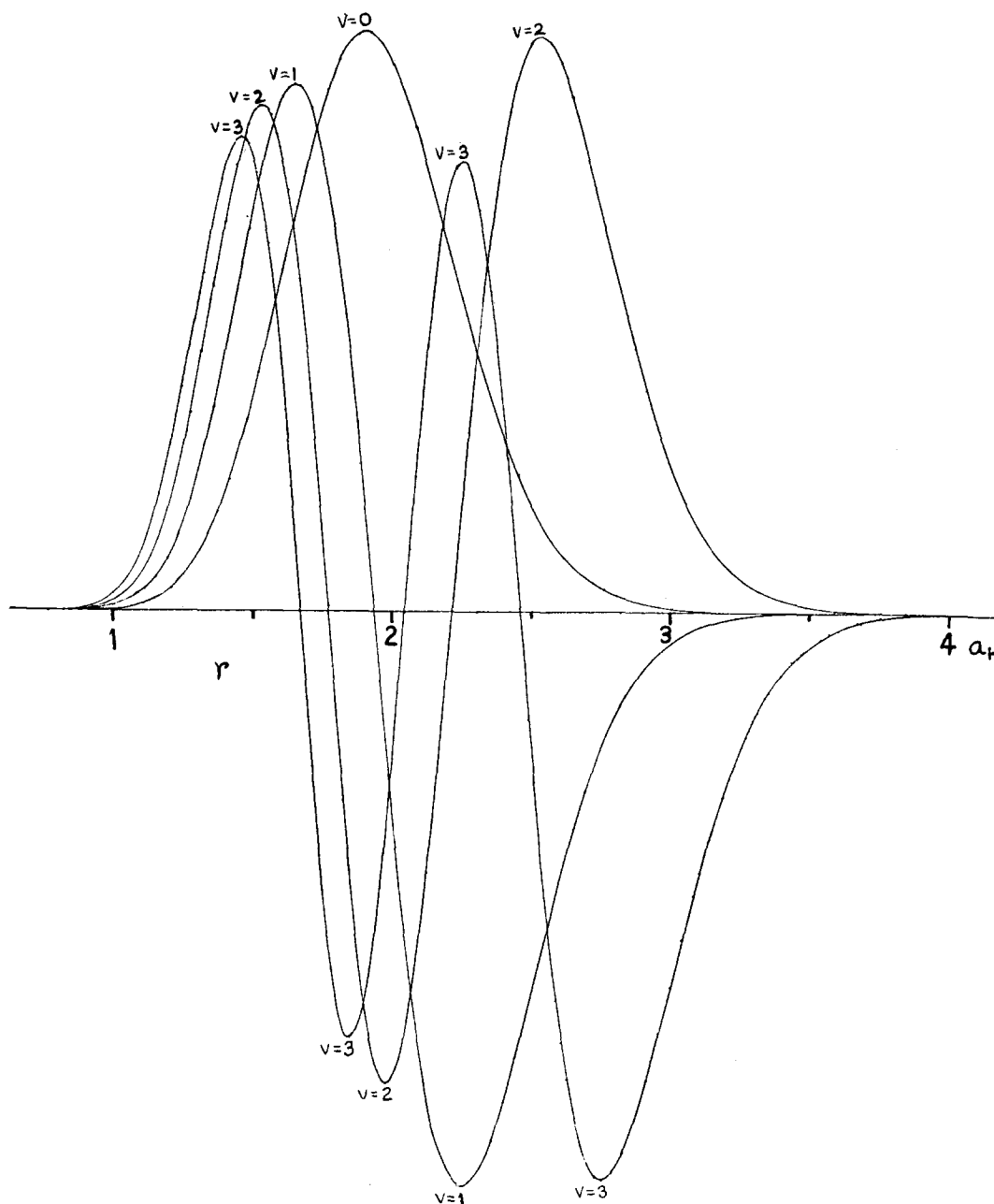


FIG. 4. Wave functions for the  $1s\sigma 2s\sigma^3\Sigma_v$  state. For normalization see the text.

ing to the formula

$$B_v = (\hbar^2/8\pi^2\mu) \int R^2 r^{-2} dr / \int R^2 dr. \quad (13)$$

(This was accomplished by setting the machine to produce  $\int R^2 S dr$  with  $S=1/r^2$ . Appropriate corrections for the slight modifications made on

the wave function were applied in computing this and other integrals.) For the three lowest levels the average error was 0.15 percent, each result being correct to within the accuracy with which the machine records. For  $v=3$ , our result was 1.2 percent too large, indicating that our

potential curve rose a little too steeply for large  $r$ . The agreement was, however, regarded as satisfactory for our purposes, and no further adjustments of the curve were attempted.

The wave functions for the four lowest levels are accurately reproduced in Fig. 4, where they have been brought to have approximately the same maximum amplitude. To normalize these functions comparably they should be multiplied by the following factors:

$$v=0, 1.000; v=1, 1.143; v=2, 1.202; v=3, 1.227.$$

In connection with the analysis of the work of Finkelburg and Weizel we have required the relative values of the overlap integrals  $\int R_v S dr$ , where  $R_v$  is the  $v$ th radial function of the  ${}^3\Sigma_g$  state and  $S$  is the radial function of the zeroth vibrational level of the  ${}^1\Sigma_g$  ground state. For  $S$  we used the solution for the Morse potential of the ground state, which was known analytically. This was plotted and introduced in the course of the integrations which gave the  ${}^3\Sigma_g$  wave functions. We found for the overlap integrals, when  $v=0, 1, 2, 3$ , the ratios  $1.00 : 1.06_3 : 0.98_5 : 0.78_8$ . The large value for  $v=0$  is at first surprising, in view of the relative positions of the potential curves (Fig. 1). The equilibrium points of the two states differ by about  $0.5a_H$ , and the classically accessible regions for the lower states overlap but little. According to the crudest form of the Franck-Condon principle one would expect excitation to the upper  $v=0$  level to be much less frequent than that to the three higher levels. The result which we have found arises in part from the rather high probability of this light molecule getting into the classically inaccessible region, and in part from the effect of the negative loops in the functions for  $v \neq 0$ , both of these being factors which are neglected in using the  $\delta$  function approximations.

#### INVESTIGATION OF THE REPULSIVE STATE

In running the machine to produce wave functions associated with the repulsive potential curve, we had naturally always to proceed toward the right, as there is no outer boundary condition to start from. This did not produce any serious errors, however, as the rapid increase in errors noticed when working with the attractive state was due to the large negative value taken

on by  $(E-U)$  beyond the second turning point, and in this case  $E-U$  remains positive, when once the classical region is entered. The systematic increase in amplitude was, of course, present; the effect was quite small, and was partially overcome by an appropriate correction. No allowance was made for the displacement of the positions of the nodes and loops.

We have already seen that it is convenient to take functions with unit limiting amplitude. In order to avoid lengthy integrations into the region where  $U$  is negligible, we have made use of the Wentzel-Brillouin-Kramers approximation, according to which the wave function may be regarded as a sine-curve with amplitude everywhere proportional to  $(E-U)^{-1/4}$ , in the region where  $E-U$  changes slowly in proportion to the wave-length. Tests showed that, beyond the third or fourth loop, the heights of successive maxima of our functions obeyed this relation within the limit of error, when proper allowance for the secular increase due to machine error was made. It was therefore easy to determine the factor required to normalize each run to unit limiting amplitude. Four typical functions, computed for the higher of our repulsive potential curves, are plotted in Fig. 5, where they have been given the same maximum amplitude.

Simultaneously with the generation of  $R$ , the wave function of the repulsive state, we evaluated the integrals  $M = \int R S dr$  and  $L = \int R S r dr$ . These integrals, in which  $S$  is one of the vibrational wave functions of the  ${}^3\Sigma_g$  state, were needed for the proposed calculation of radiative transition probabilities. For the case  $v=0$ , they were determined over a range of energies  $E$  of the lower state, and for both modifications of the potential curve, in order to study the ultimate effect of modifying this curve. For other values of  $v$  we have employed only the upper curve, for reasons to appear later. The values obtained, reduced to functions normalized as described, are given in Tables II and III.

The ratio  $L/M$ , which is a sort of average value of  $r$ , is seen to be roughly equal to the turning point of the corresponding function on the  ${}^3\Sigma_u$  curve; this relation might be useful in developing an approximate treatment of the theory of radiation in the case that  $D_{ee'}(r)$  is not constant, but can be expanded in powers of  $r$ .

## APPROXIMATE FORMS OF THE FRANCK-CONDON COMPUTATION

A study of the various current approximations to the complete Franck-Condon computation has been carried out in order to throw some light on the extent to which one may rely on the more easily applied procedures. Here we shall not be concerned with the legitimacy of the fundamental Franck-Condon approximation, but rather with the further simplifications which are so commonly made.  $H_2$  is a particularly satisfactory system on which to make such a test, because of the small mass of the nuclei.

TABLE II. Integrals  $L$  and  $M$ , upper  ${}^3\Sigma_u$  potential curve.

$E$ (ev) above dissociated atoms	$L$	$M$	$L/M$	TURNING POINT
$v=0$				
1.305	1.06	.42	2.52	2.76
1.740	3.40	1.41	2.41	2.49
2.175	6.72	2.97	2.27	2.29
2.610	10.16	4.76	2.14	2.12
3.045	11.74	5.84	2.01	1.97
3.480	11.18	5.93	1.89	1.84
3.914	9.30	5.27	1.77	1.73
4.349	6.75	4.09	1.65	1.64
4.784	4.30	2.80	1.54	1.56
$v=1$				
1.305	- 4.17	-1.57	2.66	2.76
1.740	- 9.65	-3.85	2.50	2.49
2.175	-12.47	-5.28	2.36	2.29
2.610	-10.44	-4.70	2.22	2.12
3.045	- 3.90	-1.87	2.08	1.97
3.480	+ 3.07	+1.55	1.98	1.84
3.914	+ 7.50	+4.05	1.85	1.73
4.349	+ 8.53	+4.91	1.74	1.64
4.784	+ 7.14	+4.42	1.62	1.56
5.219	+ 5.11	+3.42	1.50	1.49
$v=2$				
1.740	+13.38	+5.15	2.60	2.49
2.175	+ 7.83	+3.20	2.45	2.29
2.610	- 2.61	-1.12	2.35	2.12
3.045	- 8.83	-4.05	2.18	1.97
3.480	- 7.27	-3.54	2.05	1.84
3.914	- 1.07	- .57	1.89	1.73
4.349	+ 4.48	+2.46	1.82	1.64
4.784	+ 6.90	+4.12	1.67	1.56
5.219	+ 6.82	+4.30	1.59	1.49
$v=3$				
1.740	- 7.56	-2.82	2.68	2.49
2.175	5.68	+2.20	2.58	2.29
2.610	9.52	+3.97	2.40	2.12
3.045	1.29	.58	2.23	1.97
3.480	- 6.79	-3.17	2.14	1.84
3.914	- 7.18	-3.58	2.01	1.73
4.349	- 2.06	-1.11	1.86	1.64
4.784	3.15	1.76	1.79	1.56
5.219	6.06	3.63	1.67	1.49
5.654	6.17	4.01	1.54	1.43

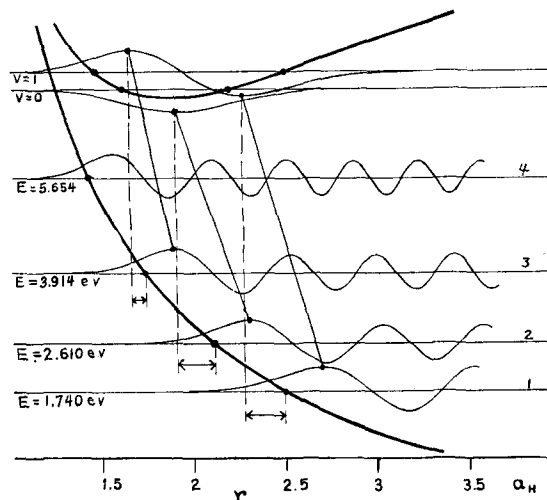


FIG. 5. Potential curves and typical wave functions for  $1s2s2\sigma^3\Sigma_g^-$  (upper) and  $1s2p\sigma^3\Sigma_u^-$  (lower). Solid lines indicate transitions giving approximately the maximum radiation intensity. Arrows indicate discrepancies between locations of turning points of lower functions and maxima of upper functions.

The vibrational quanta are large in the discrete states, and in the interesting states of the continuum the oscillations of the radial function have a relatively great wave-length. The conditions are thus particularly unfavorable for the application of the classical concepts which lead one to the simpler forms of the Franck-Condon principle, and the errors associated with them in this case may be taken as a rough upper limit for all cases.

In Table IV and Fig. 6 we have summarized the results of six methods of computing the continuous spectra associated with the four lowest vibrational levels of the  $1s2s2\sigma^3\Sigma_g^-$  state. In each case the potential function for this state was represented by our best curve, while

TABLE III. Integrals  $L$  and  $M$ , lower  ${}^3\Sigma_u$  potential curve.

$E$ (ev)	$L$	$M$	$L/M$	TURNING POINT
$v=0$				
1.305	2.48	1.02	2.44	2.76
1.740	5.31	2.31	2.30	2.49
2.175	8.12	3.72	2.18	2.29
2.610	10.32	4.98	2.07	2.12
3.045	10.87	5.54	1.96	1.97
3.480	10.13	5.48	1.85	1.84
3.914	8.25	4.73	1.74	1.73
4.349	5.73	3.53	1.63	1.64
4.784	4.06	2.64	1.54	1.56

TABLE IV. Values of  $\lambda$  for maximum  $I_\lambda$ .

*F*, complete Franck-Condon computation; *T*, correlation of turning points; *M*, correlation of maxima; *O*, maximum overlapping; *M-T*, correlation of maximum of discrete function with turning point in continuum; *R*, treatment of radial function in continuum as a  $\delta$  function at the turning point.

$v$	<i>F</i>	<i>T</i>	<i>M</i>	<i>O</i>	<i>M-T</i>	<i>R</i>
0	2620	3160*	3608	3029	3010	2700
1	3280	5600	4923	3751	3650	3230
	2180	2090	2518	2294	2290	2220
2	3710	6850	6246	4336	4270	3550
	2540		2825	2592	2500	2450
	†	1870	2110	†	1970	†
	3940	8600		4588	4820	
3	2710		2992	2786	2580	
	2150		2272	2168	2070	
		1720	1881	†	1790	

\* Corresponds to minimum in  $U(r)$ .

† Outside range computed.

the repulsive state was represented by the upper of the two approximate curves of Fig. 2. Method *F* is the complete Franck-Condon computation obtained when the integrals *M* of Table II are inserted into Eq. (10). (In Fig. 5 we have illustrated the relation of the wave functions involved in the transitions of maximum intensity, according to this method. State 2 is the corresponding end state for transitions from the  $v=0$  level, while states 1 and 3 are similarly related to the  $v=1$  level.) Method *R* is the reflection method used by Condon<sup>7</sup> and by Winans and Stueckelberg.<sup>15</sup> Method *O* results if the factor  $\nu^6$  in Eq. (10) is neglected. We have not computed the entire spectrum by this method, but have merely located the positions of maximum  $I_\lambda$ , which correspond essentially to maximum overlapping of the wave functions. The other methods give only the wave-lengths of maximum intensity. Method *T* is that of correlating turning points, as discussed in the introduction. (It will be recalled that for  $v=0$  the minimum of  $U(r)$  is used instead of the turning point. The corresponding entries in Fig. 6 and Table IV are marked with an asterisk, and the following discussion of the method does not apply to them. In Fig. 6, we have also included the two maxima which would be indicated if one were not to modify this method for  $v=0$ .) In method *M* the maximum intensity is supposed to be associated with transitions between states whose wave function have the maxima of their terminal loops

<sup>15</sup> J. G. Winans and E. C. G. Stueckelberg, Proc. Nat. Acad. Sci. **14**, 867 (1928).

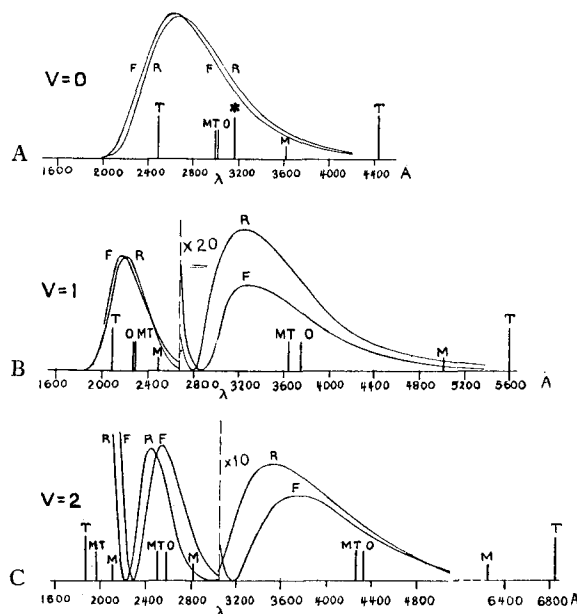


FIG. 6. Predictions of continuous spectra according to various methods. Vertical lines indicate positions of maxima of intensity. Note indicated changes of vertical scale.

at the same  $r$ . Method *M-T*, on the other hand, correlates the maximum of the discrete wave function with the turning point of the state in the continuum.

We now examine the approximations underlying the various methods, taking method *F* as the standard of perfection. Method *T* is the most commonly used and the most highly simplified. In arriving at this method it is customary to neglect the dependence of the intensity on  $\nu$ , and to consider that in evaluating the overlap integral *M* one may neglect all save the terminal loops of the wave functions. Insofar as this is permissible, the arrangement giving maximum overlapping will be very nearly that for which the maxima of the terminal loops coincide. On this basis it is the method *M* which recommends itself; the utility of method *T* will depend on the turning points having the same relation to the maxima in the two states.

Now, the distance between turning point and maximum of any function depends primarily upon the slope of the potential curve in the vicinity. To this approximation, it varies in a sense opposite to the slope, and passes through an infinity with change of sign when the slope is

reversed. Where the two potential curves have similar slope (long wave radiation in our case) method  $T$  will nearly coincide with method  $M$ . As the slopes begin to differ, the discrepancy will increase, becoming very large near the minimum of  $U(r)$  and thereafter (short wave side) being large and in the opposite direction. Thus, when method  $T$  is used to predict transitions from a stable potential curve, the results obtained from the two sides will differ considerably in character. In our case the long wave maxima come out too far to long waves, the short wave maxima too far to short waves. Method  $M$ , on the other hand, gives maxima consistently too far to the long wave side. (Note the slanting lines of Fig. 5.)

This systematic error is in part due to the neglect of the  $\nu^6$  factor, which will always bring it about that the transitions giving greatest intensity involve greater energy changes than those corresponding to the maximum of the overlap integral. Method  $O$ , which has no features to recommend its general use, has been included merely to illustrate this effect. The difference between methods  $F$  and  $O$  decreases rapidly with the slope of the repulsive potential curve, and is accordingly small for the short wave radiation.

The residual discrepancy (difference between methods  $O$  and  $M$ ) is essentially due to neglect of nonterminal loops of the wave functions. It seems to be generally believed that the shorter wave-length and smaller amplitude of these loops is so marked that they contribute negligibly to the overlap integral. Comparison of Fig. 5 with figures occurring in the literature of the Franck-Condon method will indicate that the rapidity of decrease of the amplitude is easily overestimated. (This decrease in amplitude is independent of the masses of the nuclei where the

first approximation of the W. B. K. method is valid. Note, however, that the heavier the nuclei the nearer to the turning point does this approximation hold.)

The way in which the integral  $\int_0^r R_{ev} R_{e'B} dr$  depends on the range of integration is illustrated in Table V, where there will be found the values in typical cases of these integrals taken over the first  $n$  loops of the wave function of the upper repulsive curve. In each case the upper limit of the important range of integration is fixed by the rapid decrease of the discrete wave function. In the examples given as many as five loops of  $R_{e'B}$  make important contributions to the integral, while if higher values of  $E$  or  $\nu$  had been considered even more would have been effective. For  $E=3.480$ ,  $\nu=3$  both the third and fourth loops have greater effect on the value of the integral than the first, while for  $E=4.349$ ,  $\nu=2$  the fifth loop is as important as the first. It appears from this that the effect of nonterminal loops may be very complicated.

It is clear, however, that when the terminal loops have their maxima coinciding, the overlap integral can still be increased by a shift of the function in the continuum which reduces any cancellation due to contributions from the other loops. When both functions have nodes to the right of their terminal maxima (potential curves have slopes of the same sign), this can be accomplished by a displacement in that direction which tends to bring together the nodes of the two functions, so far as is compatible with the different widths of the loops. This will be to the right or the left, according as the terminal loop of the function in the continuum is narrower or wider than that of the discrete function. When the first nodes lie on opposite sides of the main loops (potential curves have slopes of different sign), the shift should be such as to separate the nodes. In our problem, the two cases apply to the radiation bands of longest and shortest wave-length, respectively, except for  $\nu=0$ . Since the wave functions of the repulsive curve have the narrower loops, they should in both cases be shifted to larger values of  $r$ , thus producing radiation of higher energy (as predicted by method  $O$ ) than that corresponding to matching of the maxima (method  $M$ ). Evidently the same relation holds for the

TABLE V.  $\int R_{ev} R_{e'B} dr$ , integrated over  $n$  loops of  $R_{e'B}$ .

	$E=2.610$			$E=3.480$		$E=4.349$		
	$v=0$	$v=1$	$v=2$	$v=1$	$v=3$	$v=0$	$v=1$	$v=2$
$n=1$	4.96	-5.56	-1.60	-.30	-1.36	5.79	4.07	.84
2	4.74	-4.58	-1.04	2.26	-2.44	3.48	6.15	1.91
3	4.76	-4.71	-1.13	1.38	-4.21	4.26	4.29	3.48
4		-4.70	-1.13	1.58	-2.65	4.05	5.11	1.86
5				1.55	-3.33	4.10	4.86	2.69
6					-3.12	4.09	4.92	2.39
7					-3.18		4.91	2.48
8					-3.17			2.46

single band of  $v=0$  and for the intermediate bands of  $v=2, 3, \dots$ .

Increase in the slope of the potential curves, by suppressing the nonterminal loops, may diminish the difference between method  $M$  and method  $O$ . It will, however, increase the difference between method  $O$  and method  $F$ ; there is accordingly no situation in which method  $M$  may be expected to give very closely the results of method  $F$ .

Method  $M-T$  is a modification of method  $M$  which will in part correct for neglect of the  $\nu^6$  factor and the nonterminal loops. The very close agreement of method  $M-T$  with method  $O$  indicates that the result is in this case very nearly an accurate correction for the latter of these omissions. With method  $M$ , method  $M-T$  shares the advantage of giving an estimate of the position of all the maxima of intensity, while method  $T$  can deal only with the two extreme maxima of intensity. The advantage in accuracy over  $M$  has been pointed out, and the greater simplicity of application is desirable, particularly when an inverse application of the method (determination of an unknown potential curve) is to be made. It is certainly the best of the correlation methods, and even in this difficult case gives fairly satisfactory results.

Method  $R$ , in which the function in the continuum is treated like a properly normalized  $\delta$  function located at the turning point, appears to be very satisfactory, despite the difficulty of setting up a formal justification for it. Though we have not found it necessary to introduce such an approximation in discussing them, methods  $M$ ,  $T$ , and  $M-T$  give results that would be obtained if the correct wave functions were replaced by properly located  $\delta$  functions. Now it is clear from Fig. 5 that the width of the terminal loop of the function in the continuum is by no means negligible as compared with that of the loops of the discrete functions. Only when the repulsive potential curve is extraordinarily steep would it appear reasonable to replace this function by a  $\delta$  function at the turning point. The similarity in the results given by method  $O$  and method  $M-T$ , as displayed in Table IV, may be taken to indicate that under a wide range of conditions this approximation is a satisfactory one which includes a correction for

the neglect of the nonterminal loops. Then, taking the correct function for the discrete state and introducing the dependence of the radiation intensity on  $\nu$  one obtains method  $R$  as a generalization of and improvement on method  $M-T$ , which takes account approximately of all factors in the situation.

We must, however, discuss the normalization of the equivalent  $\delta$  function. Let the repulsive potential curve be treated as a straight line over the region in which  $R_1$  and  $R_2$ , solutions for the energies  $E_1$  and  $E_2$ , respectively, deviate appreciably from the W. B. K. solutions. Let  $r_1$  and  $r_2$  be equal distances from the respective turning points; then within this region  $R_1(r_1)$  will bear a constant ratio to  $R_2(r_2)$ . We now apply the first W. B. K. approximation for  $r > r_1, r_2$ . Between  $r_1$  and  $\infty$ ,  $R_1$  will decrease in amplitude by the factor  $[(E_1 - U(r_1))/(E_1 - U(\infty))]^{1/2}$ , while between  $r_2$  and  $\infty$ ,  $R_2$  will decrease by a factor  $[(E_2 - U(r_2))/(E_2 - U(\infty))]^{1/2} = [(E_1 - U(r_1))/(E_2 - U(\infty))]^{1/2}$ . If both have unit amplitude at  $\infty$ , then  $R_1(r_1)/R_2(r_2) = [(E_1 - U(\infty))/(E_2 - U(\infty))]^{1/2}$ . The areas of terminal loops will thus bear this ratio to each other, and so should the  $\delta$  functions used to replace them. Or we may use equal  $\delta$  functions, omitting the factor  $E^{-1/2}$  from Eq. (10). This is indeed what has been done by Condon and by Winans and Stueckelberg, though they give no justification for it. When the curvature of the potential curve is appreciable the terminal loops will have different breadths; one may expect that the narrower loops should be replaced by  $\delta$  functions normalized to smaller quantities.

In Fig. 6 the relative intensities predicted by methods  $F$  and  $R$  have no significance; within each figure the two intensity distributions were brought to the same maximum intensity. The positions of the maxima agree quite satisfactorily, and the general character of the intensity distributions is very similar. There is, however, a tendency of method  $R$  to give too large an intensity for large  $\lambda$ , in accordance with our remark on variation of the normalization of the equivalent  $\delta$  function with change in the slope of the potential curve. The tendency of the distributions predicted by method  $R$  to shift toward small  $\lambda$  with increasing  $v$ , as compared with those given by the complete computation, is to be

noticed. It appears to be associated with the changing effect of the nonterminal loops of the function in the continuum with decreasing breadth of the loops of the other function. In general these results seem to encourage the use of the method  $R$ , since the errors evident here are markedly smaller than those which arise from the fundamental Franck-Condon assumption in this case, as we shall show in the next division of this paper.

#### COMPARISON WITH SMITH'S WORK

We have a possible basis for a comparison between calculated and observed spectral intensities in the recent work of Smith,<sup>3</sup> who has measured the hydrogen discharge spectrum both from pure gas and in the presence of a large excess of helium.<sup>16</sup> The helium was expected to restrict the radiation to that coming from the lowest vibrational level of the upper state or states involved, removing substantially all excited vibrational energy by inelastic collisions before radiation could occur. Under similar conditions, it could be verified that the many-line spectrum was restricted to the lines associated with initial levels with  $v=0$ . The presence of helium caused a marked change in the intensity distribution of the continuous spectrum, the maximum being shifted in the long wave direction by some 700Å. This supports Smith's interpretation of the effect of the added helium, at least qualitatively, for it will be shown later that, according to our calculations, the radiations from the higher vibrational levels must have their principal maxima at shorter wave-lengths than that from the  $v=0$  level. We seem justified in concluding that Smith's technique is effective in limiting the radiation to that from the lowest vibrational levels of the various electronic states.

Now, there is no reason to suppose that Smith's spectrum was obtained wholly from the special electronic transition treated by our calculations. We must enquire whether we may expect the existence of any region in which this

<sup>16</sup> Smith's measurements were based on comparison with the carbon arc, which was assumed to have the spectrum characteristic of a black body at 3810°K. Until a better standard is available, it will be impossible to estimate the error due to this assumption, but it seems very unlikely that it can be sufficient to alter the general character of the conclusions which we shall reach.

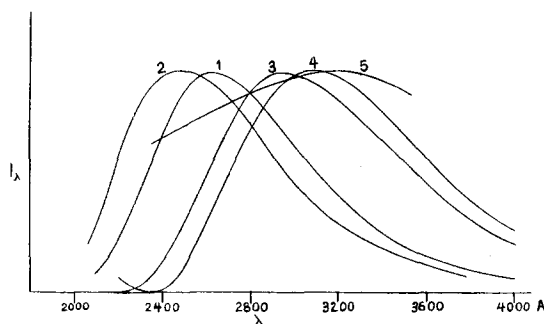


FIG. 7.  $I_\lambda$ , computed and observed. 1, upper repulsive potential curve, Franck-Condon approximation; 2, lower curve, Franck-Condon approximation; 3, upper curve,  $\xi = -0.410$ ; 4, upper curve,  $\xi = -0.434$ ; 5, Smith's observations. The relative intensities of the distributions are not significant.

particular radiation is so predominant as to justify a comparison with our calculated distribution. By reference to Fig. 7, it will be seen that the calculated  $I_\lambda$  curve for the  $1s\sigma 2s\sigma^3\Sigma_g^- \rightarrow 1s\sigma 2p\sigma^3\Sigma_u^-$  transition has a sharp maximum near 2500Å or 2600Å (according to which potential curve is used in computing). Other transitions might originate on more highly excited stable states, and go either to the same or to more highly excited repulsive states. From the latter class of transitions, no radiation of shorter wave-length than 3646Å can arise; no stable level of the system could have an energy greater than of  $H+H^+$ , while the repulsive state must have at least the energy of a normal and a two-quantum excited atom, so that the energy radiated is limited to  $Rh/4$ . Such radiations fall outside the range of Smith's observations.<sup>17</sup> Radiations due to transitions of the former class should lie well to the short wave side of the maximum for our transition. The next lowest known state which can combine with  $1s\sigma 2p\sigma^3\Sigma_u^-$  is  $1s\sigma 3d\sigma^3\Sigma_g^-$ , which lies about 2.1 eV higher. As

<sup>17</sup> The appearance of these continua may be responsible for the observations of Chalonge [Ann. de physique 1, 123 (1934)], who found that when the pressure of  $H_2$  in the discharge was made very low the radiation with  $\lambda > 3600$ Å was enhanced with respect to the rest of the spectrum. This enhancement took place under just those conditions in which the Balmer lines began to appear on his plates, indicating the production of excited  $H$ , as must be expected in connection with the radiation of these continua. Chalonge's interpretation of his observations, based on changes in the relative proportions of the radiations from the vibrational levels of the  $1s\sigma 2s\sigma^3\Sigma_g^-$  state, is clearly incompatible with Smith's observations and our calculations.



an orientating calculation, we have computed the spectrum produced by transitions from this state, using the Franck-Condon principle and representing the potential curve of the upper state by simply raising that for  $1s\sigma 2p\sigma {}^3\Sigma_g$  by 2 ev. The resulting  $I_\lambda$  has a maximum at 1900A, and at 2650A amounts to less than 5 percent of its maximum value. This distribution is probably too far toward the red; the true potential curve for  $1s\sigma 3d\sigma {}^3\Sigma_g$  has a greater equilibrium distance than that which we have used, and an allowance for this would increase the energy of the radiation. It is hardly possible that continuous radiations from  $H_2^+$  or  $He_2$  would be present, as they require too high an excitation energy.

The spectrum predicted to be observed under Smith's conditions, on the basis of the Franck-Condon principle, is therefore essentially that due to the transition here considered, slightly reenforced on the short wave side, and with slight shifting of the maximum toward higher energy. Any contamination from higher vibrational levels must operate in the same direction. It will be seen that Smith's results (curve 5, Fig. 7) are in striking disagreement with this prediction. It should be emphasized that there is no possibility of relocating the potential curve in any manner consistent with our theoretical knowledge about it, so as to remove this disagreement. We regard this as proof that in this case the Franck-Condon principle is in disagreement with experiment, and that it is necessary to take into account the way in which  $D_{ee'}$  depends upon  $r$ .

We propose to carry out a theoretical determination of this dependence. Pending the completion of this laborious task, we have been able to obtain a rough idea of the effects to be expected. With the aid of the integrals  $M$  and  $L$  of Table II, we can compute the spectrum corresponding to an electric moment function of the form  $D_{ee'}(r) = C(1 + \xi r)$ , where  $\xi$  is a constant chosen to make the position of the maximum for  $v=0$  agree with experiment. This linear moment function is nothing more than a first approximation to the real function, useful in the range of  $r$  which contributes most heavily to the overlap integral corresponding to the maximum  $I_\lambda$ , where it should have approximately the correct relative slope. Little significance must be

attached to its value in other regions, especially beyond the  $r$  where it changes sign. In Fig. 7, curves 3 and 4, we show  $I_\lambda$  for  $v=0$ , computed from the upper potential curve with two values of  $\xi$ ; that for  $\xi = -0.434$  has a maximum in fair agreement with Smith's curve. If the radiation from the higher electronic states is similarly shifted to the red, we have a plausible explanation of the form of this curve. Thus, we can again calculate the radiation from  $1s\sigma 3d\sigma {}^3\Sigma_g$ , assuming that for this transition the value of  $D_{ee'}$  is the same as for  $1s\sigma 2s\sigma {}^3\Sigma_g$ ; with  $\xi = -0.434$  we obtain a maximum at 2100A, decreasing to 10 percent at 2700A. Owing to the  $\nu^6$  factor, this more energetic radiation would be so intense that a population of the three-quantum level less than a tenth of that of the two-quantum level would explain the relative intensities found by Smith at 3200A and at 2400A.

#### THE WORK OF FINKELNBURG AND WEIZEL

The attempt to reproduce theoretically the results of Finkelburg and Weizel meets with serious difficulties, due principally to the uncertainties involved in interpreting their observations. Using the method of Lau and Reichenheim,<sup>18</sup> they have photographed the spectrum of the hydrogen discharge in such a way that a horizontal displacement on their plates corresponds to a change in wave-length, a vertical displacement to a change in the energy of the exciting electrons,  $V$ . Unfortunately for us, the purpose in hand did not require them to calibrate or photometer their plates; they merely noted the position of the fairly sharp boundary of the region of perceptible blackening, thus obtaining the apparent excitation potential of each wave-length. Actually, of course, this gives, not the theoretical critical potential for each  $\lambda$  but a threshold potential, sufficiently in excess of the critical to produce an unknown, just perceptible, finite intensity of radiation  $I_\lambda$  which depends upon the sensitivity-curve of the plates, the dispersion of the quartz prism, and the geometry of the spectrograph. A possible though improbable assumption is that the critical  $I_\lambda$  was the same at all wave-lengths. The minimum of their  $V - \lambda$

<sup>18</sup> E. Lau and O. Reichenheim, *Naturwiss.* **18**, 86 (1930).

curve would then represent the most intense radiation from  $v=0$ , which should be the first to appear when the exciting potential is raised. Finkelburg and Weizel's points are so irregular that the minimum cannot be accurately located; it seems to fall between 3000Å and 3200Å, in approximate agreement with Smith's curve, which is an argument in favor of the assumption of uniform perceptible intensity. We regard this as additional evidence that the Franck-Condon principle is invalid, since this principle requires a maximum  $I_\lambda$  between 2500Å and 2600Å. The discrepancy is much too great to be explicable as a result of any reasonable variation of the minimum perceptible intensity.

As a basis for the consideration of the continuum excited by electrons homogeneous in velocity, let us imagine a three-dimensional model, in which  $V$  and  $\lambda$  are laid out as Cartesian coordinates in a basal plane, above which a dome-shaped surface is so constructed that at each point its height is proportional to  $I_\lambda$  for the corresponding  $V$ ,  $\lambda$ . The intersection of the dome with the basal plane will trace the locus of the true critical potential. Planes parallel to the base will intersect the dome to give curves which may be projected upon the base to form a family of contour lines. Upon the assumption of uniform perceptible intensity, Finkelburg and Weizel's curve should be one of these contour lines. Upon a different assumption, it should cut across the contour lines systematically.

In order to illustrate the structure of the continuum observed under the experimental conditions of Finkelburg and Weizel we have constructed such a model, using the upper potential curve for the  $1s\sigma 2p\sigma^3\Sigma_u$  state. We have employed the linear moment function, taking  $\xi = -0.434$  in order to bring the maximum  $I_\lambda$  for  $v=0$  to  $\lambda=3100$ Å; the resulting approximation should be at least qualitatively reliable for  $\lambda > 2700$ Å. The first step was to compute the spectrum from each of the first four vibrational levels separately, using Eq. (10). These spectra are shown in Fig. 8. Fig. 9 shows, for comparison, the same spectra computed with  $\xi=0$ . The most striking effect of the assumption of linear moment is the great reduction of the relative intensity of the short wave maxima. As was indicated in the discussion of Smith's work, this reduction

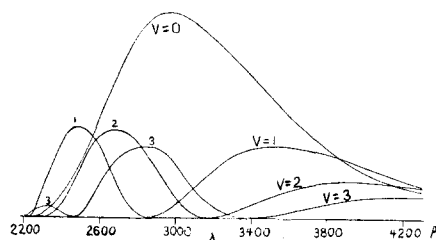


FIG. 8.  $I_\lambda$  predicted, taking  $\xi = -0.434$ .

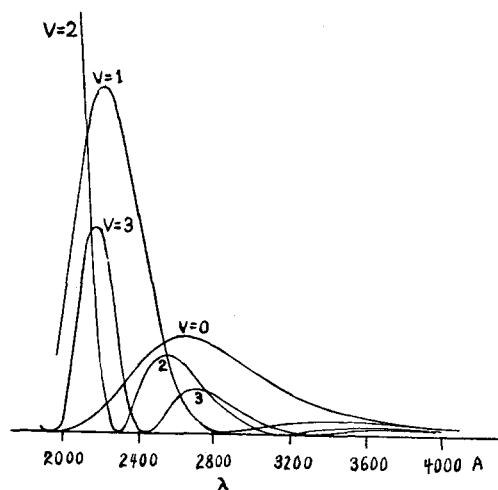


FIG. 9.  $I_\lambda$  predicted by Franck-Condon approximation.

is probably excessive, arising from the spurious vanishing of  $D_{ee'}$  at  $r=2.3a_H$ . We next computed the population of each vibrational level by Eq. (11), taking  $M_{ev, e'v'}$  between the levels in question and the lowest level of the ground state. Upon superposing the intensities of the radiations from different levels, we obtained the total intensity at each  $V$  and  $\lambda$ . Fig. 10 shows cross sections of the resulting surface, for three values of  $V$ , the contributions from each  $v$  being indicated. Fig. 11 shows the contour lines, drawn solid, while the broken lines cut across them in such a way as to pass through values of  $I_\lambda$  everywhere proportional to the dispersion of quartz, as Finkelburg and Weizel's curve should do if their perceptible intensity varied with  $\lambda$  only because of the variation in dispersion.

Although Finkelburg and Weizel's curve is a relation between  $V$  and  $\lambda$ , we cannot introduce it immediately into Fig. 11, because the absolute

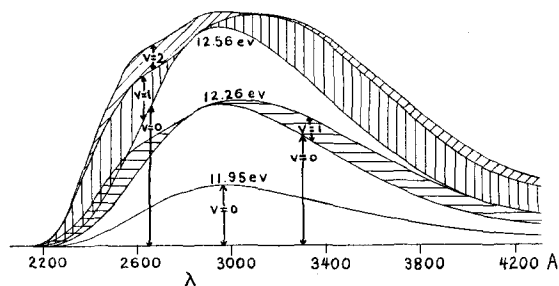


FIG. 10. Composition of radiation emitted for various exciting potentials.  $I_\lambda$  is plotted.

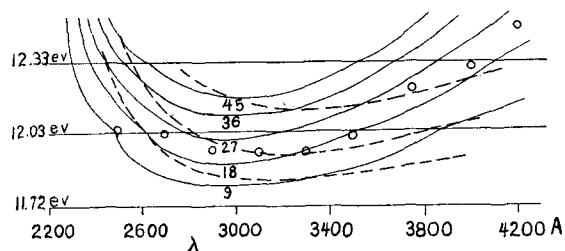


FIG. 11. Contours of  $I_\lambda$ . Solid lines are computed by using  $\xi = -0.434$ . Broken lines are contours of  $I_\lambda$  times the dispersion of quartz. Circles are observed points of Finkelburg and Weizel.

value of  $V$  in their experiments is not well known. They estimate that their minimum comes at  $V = 11.86$  eV, with a possible error of 0.2 eV, but believe that the relative position of their points is much more accurately known. We find it preferable to place their minimum at 11.95 eV, or 0.23 eV above the theoretical critical potential  $V_k = 11.72$ , the value determined by the position of our potential curves. Points representing their observations as thus interpreted are shown as circles in Fig. 11.

The assumption of linear moment, coupled with that of constant perceptible intensity, thus leads to satisfactory agreement, the circles falling nicely between the contours marked 18 and 27 except on the extreme left, where we have already stated that the calculated intensities must be expected to be too low, the contour lines therefore too high, because of the vanishing of our approximation for  $D_{ee}(r)$ . It is therefore possible to regard Finkelburg and Weizel's curve as the locus of constant  $I_\lambda$ , having that value which is excited by 0.23 eV excess potential in the region of the maximum radiation from  $v = 0$ . It is clear that other hypotheses concerning the perceptible intensity and the electric moment function could be combined in such a way as to

give perhaps equally plausible interpretations. But it seems to be definitely established that the Franck-Condon assumption of constant moment is incompatible with the experiments of Finkelburg and Weizel. We have determined roughly the relocation of the potential curve which would remove this incompatibility. We find that the broken curve of Fig. 2, in connection with the Franck-Condon assumption and method R, gives an intensity contour agreeing very well with the  $V-\lambda$  curve of Finkelburg and Weizel. Such a position of the potential curve, however, would be in definite contradiction to the Heitler-London computations, as well as our own, and cannot be regarded as a possibility.

With the above results in mind we can now pass to a discussion of the method used by Finkelburg and Weizel in locating their potential curve. If there had been observable structure in the continuous spectrum, so that a given part of the radiation could have been associated with transitions from a particular vibrational level, they could have followed the method devised by Kuhn,<sup>19</sup> which is based on the simplest form of the Franck-Condon principle, method T. Points on the repulsive curve would then have been obtained thus: The spectrum arising from transitions from the level  $v = 1$ , say, would have two principal maxima of intensity. The corresponding turning points in the known upper state,  $b$  and  $\beta$  would be first located on the energy diagram, Fig. 1. Then, measuring down from  $b$  to  $b'$  a distance corresponding to the energy of the photons at the maximum with greater  $\lambda$ , and from  $\beta$  to  $\beta'$  a distance corresponding to the energy at the other maximum, two points on the lower potential curve would be located. Since the absence of structure in the spectrum prevented such a procedure, Finkelburg and Weizel were forced to take as the most strongly radiated wavelengths those which first became observable when the energies of the exciting electrons exceeded that necessary to produce the first visible radiation (excitation of  $v = 0$ ) by the vibrational energies of the upper states. Their further procedure was then that sketched above.

A tacit assumption inherent in this method is

<sup>19</sup> H. Kuhn, *Zeits. f. Physik* **63**, 458 (1930).

that the radiation due to transitions from each level becomes observable when the exciting potential exceeds the necessary minimum by the same amount. The second, and more fundamental assumption, is that there is little overlapping of the radiation from different  $v$ 's, so that the appearance of each such radiation at the proper exciting potential will not be obscured by off-maximum radiation from the lower  $v$ 's. Figs. 8 and 9 will show how far from the truth this probably is.

It will be noted that in the interesting long-wave region the maxima for  $v=1$  and  $v=2$  are relatively weak, and occur well within the region to which  $v=0$  contributes strongly. Radiation from these levels will thus be obscured by that from  $v=0$  unless they are much more strongly excited, which is not the case. In Fig. 10 the curve for  $V=11.95$  is a cross section corresponding to the minimum energy of excitation which gives observable radiation. The minimum observable intensity is thus 23 in the arbitrary units used. To fix the wave-length associated with radiation from  $v=1$ , Finkelburg and Weizel then noted the  $\lambda$  at which radiation of this intensity appeared, when the exciting potential was raised by 0.31 ev (the difference in energy between  $v=1$  and  $v=0$ ), thus reaching 12.26 ev on our scale. According to our figure this would be 3850Å; only 30 percent of this radiation comes from the  $v=1$  level. Similarly, only about 13 percent of the radiation associated by Finkelburg and Weizel with the  $v=2$  level appears to come from that level. That the wave-lengths selected in this way are within some 400Å of the corresponding computed maxima thus appears to be merely a coincidence. Nor is this agreement a measure of the accuracy of the procedure of Finkelburg and Weizel, for as has already been shown, the form of the Franck-Condon principle used by Finkelburg and

Weizel involves even more serious approximations. It seems, then, that the construction of Finkelburg and Weizel cannot be depended on and that as yet we possess no method of determining a repulsive potential curve by observations on a continuous spectrum in which there is no analyzable structure.

Experimental studies of the  $H_2$  continuum free from those factors which complicate the interpretation of the results of Smith and of Finkelburg and Weizel are much to be desired. Controlled excitation of  $H_2$  in the presence of an excess of He should yield a spectrum arising only from transitions from a single vibrational level of the  $1s\sigma 2s\sigma^3\Sigma_g$  state, which could be compared with a theoretical prediction free from the complication of an assumed excitation function. This spectrum might be obtained by a modification of the method of Lau and Reichenheim, or by excitation with electrons emitted from a hot equipotential cathode. The Lau-Reichenheim method would also yield results of great value if the plates were properly calibrated, for the assumption of a linear excitation function seems to be a good approximation over a fair range of  $V$ . A complete theoretical treatment of the  $1s\sigma 2s\sigma^3\Sigma_g - 1s\sigma 2p\sigma^3\Sigma_u$  continuum, free from arbitrary assumptions about the quantity  $D_{ee'}(r)$ , is now under way. We hope that experimental results of comparable precision may soon become available.

In conclusion we wish again to express our indebtedness to the Electrical Engineering Department of the Massachusetts Institute of Technology for the use of the differential analyzer, and to thank Professor S. H. Caldwell and Professor P. M. Morse for advice concerning its operation. We are also indebted to Professor O. Oldenberg and Dr. N. D. Smith for helpful discussions of the experimental aspects of the problem.