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Continuous Spectra of H_2 and D_2

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A complete theoretical calculation has been made of the continuous spectra of H_2 and D_2 arising from transitions from the lower vibrational levels of the $1s\sigma 2s\sigma {}^3\Sigma_g$ state to the unstable $1s\sigma 2p\sigma {}^3\Sigma_u$ state. Use of the Franck-Condon approximation has been avoided by a direct computation of the electric moment of the electronic transition, as a function of nuclear separation; this quantity is found to decrease rapidly with increasing nuclear separation. Spectra are computed for transitions from each of the vibrational levels separately, and absolute mean lives are determined for the various levels. Relative probabilities of excitation from the ground state of the molecule by electron impact are estimated, and the intensity in the spectrum due to excitation by electron impact is computed for a range of energies of the electrons. The Franck-Condon approximation is found to be more satisfactory than was indicated by a previous investigation. There is sharp disagreement of the results with the observations of Smith. This apparently arises from errors in Smith's intensity standard, and emphasizes the need for a more satisfactory intensity standard in the ultraviolet. Agreement with the results of Finkelnberg and Weizel is obtained, but its significance is weakened by uncertainties in the experimental conditions.

INTRODUCTION

In a recent paper[1] on the Franck-Condon principle we have given a detailed analysis of the problem of calculating the energy distribution in the continuous spectrum of H_2 produced by transitions from the stable $1s\sigma 2s\sigma {}^3\Sigma_g$ to the repulsive $1s\sigma 2p\sigma {}^3\Sigma_u$ state. We there presented a tentative solution based on the Franck-Condon principle, interpreted as the assumption that the electric moment of the electronic transition ($D_{ee'}(r)$ as defined by Eq. (6I)) is practically independent of the nuclear separation r over the range involved. Our results showed marked disagreement with the experimental results of Smith[2] and of Finkelnberg and Weizel,[3] and we were led to conclude that the Franck-Condon assumption is not permissible in this case, but that $D_{ee'}(r)$ must decrease strongly with increasing r.

By use of the potential curves and electronic wave functions which we have since obtained for the states involved,[4] we have been able to carry out a complete theoretical treatment of this continuous spectrum as it would be produced under certain idealized conditions. The principal improvement in the present computations arises from use of computed values of $D_{ee'}(r)$ instead of the Franck-Condon assumption; an additional but less essential improvement arises from our more precise location of the potential curve of the repulsive state. We here present the results of computations on both H_2 and D_2, together with a further discussion of the Franck-Condon assumption and the other approximations usual in computations of intensities of continuous spectra.

ELECTRIC MOMENT OF THE ELECTRONIC TRANSITION

In computing the spectral distribution of energy the first quantity to be calculated is (repeating Eq. (6I))

$$D_{ee'}(r)=\left|\int\cdots\int d\mathbf{r}_1 d\mathbf{r}_2 \mathbf{D}(\mathbf{r}_1,\mathbf{r}_2,\varphi,\theta) \times F_e(r;\mathbf{r}_1,\mathbf{r}_2)F_{e'}(r;\mathbf{r}_1,\mathbf{r}_2)\right|.$$

Here F_e and F_e' are the electronic wave functions; in our usual notation

$$F_e=\sum_{mnjkp} C_{mnjkp}[mnjkp];$$

$$F_{e'}=\sum_{m'n'j'k'p'} C'_{m'n'j'k'p'}[m'n'j'k'p'],$$

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[1] A. S. Coolidge, H. M. James and R. D. Present, J. Chem. Phys. **4**, 193 (1936). We use the notation of this paper, and refer to it as I in references to figures and equations.

[2] N. D. Smith, Phys. Rev. **49**, 345 (1936).

[3] W. Finkelnberg and W. Weizel, Zeits. f. Physik **68**, 577 (1931).

[4] A. S. Coolidge and H. M. James, J. Chem. Phys. **6**, 730 (1938).

$$[mnjkp]=\frac{1}{2\pi}\{e^{-\delta_1\lambda_1-\delta_2\lambda_2}\lambda_1{}^m\lambda_2{}^n\mu_1{}^j\mu_2{}^k-e^{-\delta_2\lambda_1-\delta_1\lambda_2}\lambda_1{}^n\lambda_2{}^m\mu_1{}^k\mu_2{}^j\}\rho^p.$$

The vector **D** is the variable part of the electric moment, but because of the $\sum$ symmetry of both states we need consider only the component along the nuclear axis, which in elliptical coordinates becomes $-er/2(\lambda_1\mu_1+\lambda_2\mu_2)$. We have, then,

$$D_{ee'}(r)=er/2\left|\sum_{mnjkp}\sum_{m'n'j'k'p'}C_{mnjkp}C'_{m'n'j'k'p'}\times\int\cdots\int d\mathbf{r}_1d\mathbf{r}_2[mnjkp](\lambda_1\mu_1+\lambda_2\mu_2)[m'n'j'k'p']\right|.$$

From the special form of the functions, it is readily seen that

$$[mnjkp](\lambda_1\mu_1+\lambda_2\mu_2)=[m+1,\,n,\,j+1,\,k,\,p]+[m,\,n+1,\,j,\,k+1,\,p].$$

All the integrals needed for the computation are accordingly of the familiar[5] type

$$\int\cdots\int d\mathbf{r}_1d\mathbf{r}_2[mnjkp][m'n'j'k'p'].$$

Using the wave functions of reference 4, we thus obtain the following values for $D_{ee'}(r)$, expressed in units of electronic charge times Bohr radius:

$r=$	1.3	1.5	1.7	1.87	2.0	2.1	2.3	2.5	2.7	2.9
$D_{ee'}(r)=$	1.719	1.503	1.289	1.128	1.012	0.975	0.845	0.742	0.673	0.611.

This quantity, determined by the electronic wave functions, is the same for H_2 and D_2, to the approximation of separated nuclear and electronic motions which we employ.

As an indication of the reliability of these calculations, we may note that when smooth curves are drawn through the first five and the last five points, respectively, and extrapolated, they fail to join by about 0.025. The two sets of points were computed entirely independently, with different series, and the errors of each set of wave functions are at their maximum in the region of joining (as shown by the corresponding energy values). Further, some of the errors are doubtless of opposite character here, since in the one case the exponential parameter is known to be too small, and in the other too large. The errors in the several computations are thus not likely to be larger than the discrepancy at the point of joining—that is, a very few percent.

POTENTIAL CURVES AND VIBRATIONAL WAVE FUNCTIONS

As the potential curve for the $^3\Sigma_g$ state we have used an empirical curve of the form suggested by Hylleraas.[6] This is the curve 9 of a previous paper[7] in which we have discussed the problem of determining potential curves from empirical data on vibrational and rotational levels; a summary of its properties will be found there. (This work was carried out before we became aware of the magnitude of the errors in the Hylleraas energy formula, with the aid of which the curve had been constructed.) As the potential curve of the repulsive $^3\Sigma_u$ state we have used the computed curve of reference 4, corrected for convergence, but without the completely negligible correction for the finite mass of the nuclei.

Vibrational wave functions for the $^3\Sigma_g$ state were obtained with the aid of the Massachusetts Institute of Technology differential analyzer, as described in I;[8] the computations for H_2 and D_2 differed only by a change in gear ratios corresponding to the change of the effective mass of the vibrator. As a check on the results we had available analytical wave functions for a Pöschl-Teller curve closely approximating curve 8 of reference 7. The locations of the nodes and maxima of the mechanical and analytic wave functions, and the relative magnitudes of the maxima, were found to agree to within the limit of error in the machine operation. This showed that the machine was giving reliable results and that we could ignore the effects of small errors in the potential curve (such as were later found to exist in curve 9).

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[5] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).

[6] E. A. Hylleraas, Zeits. f. Physik **96**, 643 (1935).

[7] A. S. Coolidge, H. M. James and E. L. Vernon, Phys. Rev. **54**, 726 (1938).

[8] We may note that in I we found, by use of a very accurate potential curve, a value of 0.170 ev for the zero-point vibrational energy in H_2, while the separations of all energy levels came out in essential agreement with observation. The value 0.170 ev is definitely too high; in the present work we find instead 0.162 ev. We do not understand the origin of this error in the previous work, but believe it can have had no effect on the other computations.

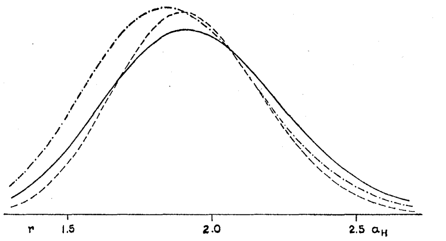

FIG. 1. Wave functions for $V=0$ of H_2 (——) and D_2 (- - - -), comparably normalized. Also product of H_2 function multiplied by $D_{ee'}(r)$ (-·-·-).

As the final stage in the computation of the integral (Cf. Eq. (9I))

$$D_{ev;\ e'E'}=\int dr R_{ev}(r)R_{e'E'}(r)D_{ee'}(r),$$

we determined the vibrational functions for the repulsive curve, $R_{e'E'}$, and simultaneously evaluated the integrals of their products with $R_{ev}(r)D_{ee'}(r)$, introduced into the differential analyzer as the function S of Fig. 3I. The technique of this work was the same as that of our previous paper, and requires no further discussion.

In Fig. 1 we show for comparison the vibrational functions of H_2 and D_2, for $v=0$,[9] and also the former function multiplied by $D_{ee'}(r)$.

MEAN LIFE OF $^3\Sigma_g$ LEVELS

Relative spectral intensity distributions for transitions from each low vibrational level of the $^3\Sigma_g$ state are given immediately by Eq. (9I), and are shown in Fig. 2 for H_2 and in Fig. 3 for D_2. Within each figure the spectra are given for the same population in the several upper levels, but there is no special relation between the vertical scales in the figures for H_2 and for D_2. (Cf. Figs. 8I, 9I.)

Knowledge of the electric moment now permits a calculation of absolute intensities and of the mean life of a molecule in each vibrational level of the $^3\Sigma_g$ state. We have for the energy radiated per second within a wave-length region $d\lambda$, caused by transitions from the vth vibrational level[10]

$$A_\lambda(v)d\lambda=[8(2\pi)^4c^2(2\mu)^{\frac{1}{2}}/3(E')^{\frac{1}{2}}\lambda^6]D^2{}_{ev;\ e'E'}d\lambda.$$

The value of $A_\lambda(v)$ is independent of the rotational quantum number K except for a slight dependence of $D_{ev;\ e'E'}$ on K, which we neglect in accordance with the discussion in I. The probability of the transitions responsible for this radiation is per second and per unit range in wave-length, $\lambda A/hc$, and the integral of this over

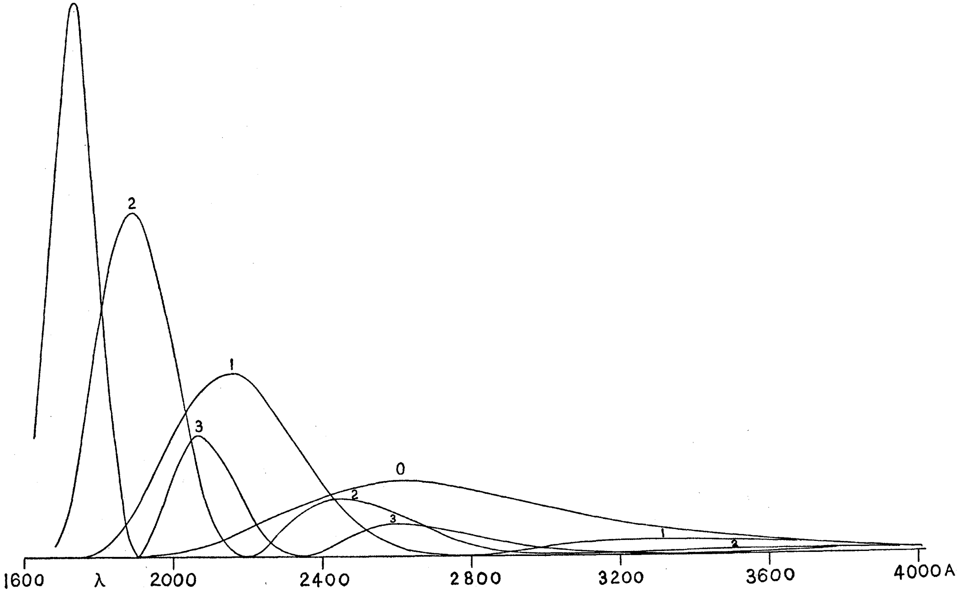

FIG. 2. I_λ for first four vibrational levels of H_2.

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[9] The other wave functions for H_2 are, within the accuracy of plotting, the same as those portrayed in Fig. 4I. For comparable normalization, these curves should be divided, not multiplied, by the factors given on page 202 I.

[10] Eq. (8I), corrected by a factor of 2. This correction applied also to Eq. (7I).

all possible wave-lengths is the reciprocal of the mean life of the vibrational state, τ_v:

$$1/\tau_v=[128\pi^4c(2\mu)^{\frac{1}{2}}/3h]$$
$$\times\int_0^\infty d\lambda[D_{ev;\,e'E'}(\lambda)]^2/\lambda^5(E'(\lambda))^{\frac{1}{2}}.$$

By graphical integration (for convenience λ^2 was used as the variable of integration) we obtain the mean lifetimes given in Table I.

TABLE I. *Mean lifetimes of molecules in various vibrational states.*

v	H_2	D_2
0	1.19×10^{-8} sec.	1.19×10^{-8} sec.
1	1.10×10^{-8}	1.12×10^{-8}
2	1.01×10^{-8}	1.05×10^{-8}
3	0.97×10^{-8}	1.02×10^{-8}
4		1.00×10^{-8}

APPROXIMATE METHODS

The calculations of our previous paper involved the approximation of replacing the true electric moment of the electronic transition, $D_{ee'}(r)$, by a constant (the Franck-Condon approximation) or a linear function of r. In addition, we considered the effects of various other simplifications, and found empirically that very good results could be obtained by method R (the reflection method of Condon[11] and of Winans and Stueckelberg[12]) in which the vibrational wave functions of the repulsive state are replaced by appropriately normalized δ functions at their classical turning points. We are now able to check these approximations against the complete calculation.

To determine the effect of the variation of $D_{ee'}(r)$ it will not be sufficient simply to compare the intensity distributions of the present with those of the previous paper, since the latter were computed with different potential curves, estimated to be upper and lower limits to the real potential curve, and indeed bearing this relation to our final curve wherever the differences are appreciable. For H_2, with $v=0$, we have estimated by several methods of interpolation the result of a F-C computation with the repulsive potential used in the present work. The result varies little with the method of interpolation, and the uncertainty in it is negligible for our purposes. Fig. 4 shows this F-C intensity distribution compared with that given by the complete computation; the F-C approximation produces a shift of the maximum I_λ toward short waves, by about 120A, together with some narrowing of the band.

Figure 4 also shows the errors introduced by use of method R, as compared to a calculation involving use of the exact form of the vibrational wave functions in the repulsive state. Whether or not one takes account of the factor $D_{ee'}(r)$, the agreement of the two methods is surprisingly good. It is clear that the full calculation may be regarded as a refinement upon method R which is unwarranted in any calculation subject to the

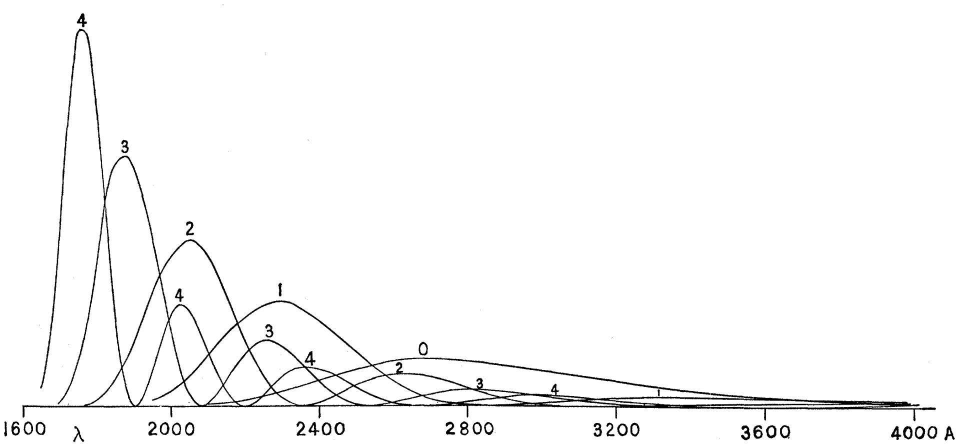

FIG. 3. I_λ for first five vibrational levels of D_2.

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[11] E. U. Condon, Phys. Rev. **32**, 858 (1928).

[12] J. G. Winans and E. C. G. Stueckelberg, Proc. Nat. Acad. Sci. **14**, 867 (1928).

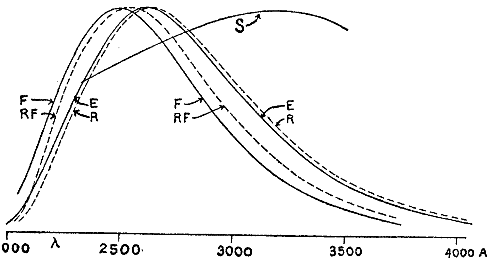

FIG. 4. I_λ for $v=0$ of H_2, by approximate methods. *E*, exact calculation. *F*, Franck-Condon method; *R*, reflection method including variable electric moment; *RF*, same ignoring electric moment; *S*, Smith's results.

much larger errors introduced by the Franck-Condon approximation.

In the case of D_2 the situation is similar. We have not made the full calculation involving only the F-C approximation, but we can estimate the error caused by neglect of $D_{ee'}(r)$ by using method *R* both with and without this factor. The resulting curves are shown in Fig. 5, together with that given by the complete theoretical treatment. As was to be expected, the error introduced by the F-C approximation is rather less than with H_2, the range of r important in the radiation process being the smaller range of the vibrational function of the stable state. (Cf. Fig. 1.)

Application of the ideas of method *R* to the consideration of the spectra caused by transitions from each of the higher vibrational levels shows at once that the intensity maxima corresponding to the loops of the vibrational functions become sharper as the loops becomes narrower, with increasing v. The F-C approximation thus produces smaller errors in the computed locations of the intensity maxima as v increases, but the ratios of intensities at the different maxima will become seriously distorted. For example, for $v=3$ in H_2 the values of $D_{ee'}(r)$ at the first and last maxima of the wave function have the ratio 1.78 to 1; neglect of this factor will exaggerate the short wave maximum with respect to the long wave one by a factor of three.

COMPARISON OF RESULTS FOR H_2 AND D_2

It may be of interest to compare the spectra of H_2 and D_2 for the case of $v=0$. The difference, as shown in Fig. 6, is the resultant of several effects arising from: (a) the smaller breadth of the upper wave functions for D_2 (there being no essential displacement of the maximum), (b) the change in form of the lower vibrational function, (c) the difference in the energies of the upper states. The success of method *R*, which does not involve the lower wave functions, in treating both systems shows that the effect of (b) is very small. Application of this method also shows the effect of (c) to be small. The difference in the spectra thus arises principally from the difference in form of the discrete vibrational functions. The effect of this factor can be analyzed into two parts, of which the more obvious is a direct dependence of the breadth of the radiation band on the breadth of the vibrational function. This breadth of the function is inversely proportional to the fourth root of the effective mass of the molecular vibrator. This effect is completely masked, however, by the distortion caused by the λ^{-6} factor in I_λ, which strongly raises the curve on the short wave side. The difference in the spectra may be interpreted as caused principally by the fact that the lighter H nuclei are able to penetrate into the nonclassical region more readily than the heavier D nuclei, so that in the case of H_2 there is a greater probability that electron transitions will occur when the nuclei are far apart.

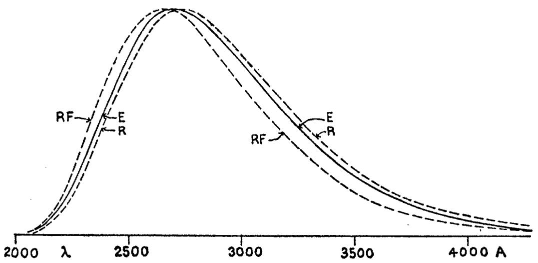

FIG. 5. I_λ for $v=0$ of D_2, by three methods explained under Fig. 4.

DEPENDENCE OF INTENSITY ON VELOCITY OF THE EXCITING ELECTRONS

We have made a new calculation of the intensity of the combined radiation from several vibrational levels when their population is maintained by inelastic collisions between electrons and molecules in the ground state. As before (Eq. (11I)) we assume that the rate of production of molecules in each vibrational state is a linear function of the excess of the energy of the electrons over the minimum excitation energy, and that the constants of proportionality for the various levels are in turn proportional to the squares of the overlap integrals of the pertinent vibrational functions with that of the lowest level of the ground state. These constants of proportionality are given in Table II. They are expressed in arbitrary units for each molecule. It will be noted that with D_2 there is a more pronounced tendency than in the case of H_2 for transitions to occur principally to those upper levels which have inner turning-points nearly coincident with the potential minimum of the ground state, in accordance with the usual crude form of the Franck-Condon argument (see Fig. 1I). This is to be expected from the more concentrated form of the wave functions.

For a given electronic energy E, the population of each vibrational level of the $^3\Sigma_g$ state should be proportional to the excitation probability as above calculated, multiplied by the mean life of that level. (The latter factor, which we find to vary by about 20 percent over the range of v considered, was treated as constant in I). From the relative populations thus deduced for each value of the electronic energy, and the radiation intensities for unit population, as given in Figs. 2 and 3, we have obtained the relations between intensity, wave-length and electron energy shown in Figs. 7 and 8. (Cf. Fig. 11I.) In these figures the solid lines are contours on the surface giving I_λ as it depends on E and λ, and show the exciting voltage necessary to produce radiation of a given I_λ at each wave-length. In order to make closer contact with experiment we have also indicated in Fig. 7 the exciting voltages needed to produce a given illumination of the plate of a typical quartz spectrograph, as it depends on λ. The values of I_λ required for constant illumination increase rapidly with decreasing λ because of the increasing spreading of the spectrum caused by variations in the refractive index of the prism and the focal length of the lens.

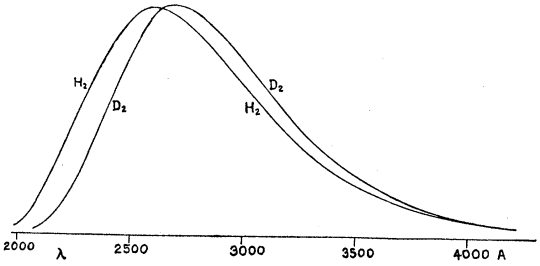

FIG. 6. I_λ for $v=0$ of H_2 and of D_2, for same population of excited state.

COMPARISONS WITH EXPERIMENT

On the basis of a comparison of the results of computations using the F-C approximation and the available experimental results, as detailed in I, we were led to conclude that inclusion in the computation of the factor $D_{ee'}(r)$ would produce a large shift in the intensity maxima toward the red. The calculations presented in this paper show only a fraction of the expected shift, and it is clear that the F-C approximation is not as bad as we were led to believe.

On the other hand, there remains a very unsatisfactory discordance of the theoretical and experimental results. The results of Smith, supposed to give I_λ for radiation entirely from the state $v=0$ of H_2, are indicated in Fig. 4. It is difficult to believe that the difference between Smith's curve and ours is due entirely to the departure of Smith's carbon arc standard from the assumed black body behavior, but a careful analysis of the situation, along the lines of I, leaves us with no other interpretation to suggest. We wish to emphasize the urgent need for an improved intensity standard in this spectral region and for a repetition of Smith's work when this standard becomes available.

The results of Finkelnberg and Weizel are shown as crosses on Fig. 7. It will be observed that only one of them falls farther than 0.06 ev from a line of constant illumination which passes through the extreme points. If, therefore, the points which they give (obtained by visual estimate) correspond to equal blackening of their

TABLE II. *Excitation constants of molecules in various vibrational states.*

v	H_2	D_2
0	1.00	1.00
1	1.13	1.82
2	0.97	2.12
3	0.62	1.89
4		1.49

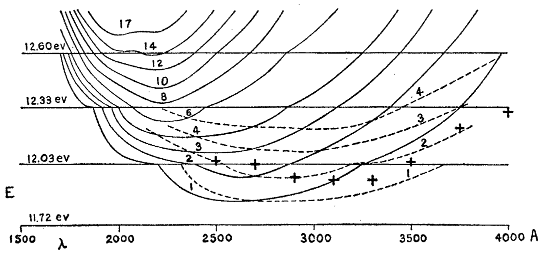

FIG. 7. Relations between I_λ, λ, and energy of exciting electrons E, for H_2. Lines of constant I_λ(——). Lines of constant illumination of plate in quartz spectrograph (- - - -). Data of Finkelnberg and Weizel (+ +). Intensities in arbitrary units.

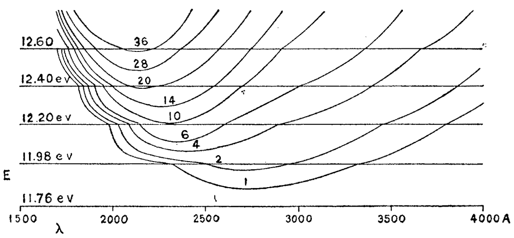

FIG. 8. Lines of constant I_λ for D_2. For explanation see Fig. 7.

plate, and this in turn corresponds to equal exposure, we may say that our calculations agree with their results to within the experimental error, estimated as 0.05 ev. Unfortunately there is no adequate reason to suppose that the assumed conditions are even approximately fulfilled. It seems more than ever desirable to obtain accurately controlled experimental results of this type also.

In conclusion, we wish to thank the Electrical Engineering Department of the Massachusetts Institute of Technology for the use of the differential analyzer. Also, one of us (H. M. J.) wishes to acknowledge gratefully a grant from the Society of Sigma Xi, which materially aided in the progress of this work.

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Capture of Neutrons by Atoms in a Crystal*

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The precise determination of the properties of nuclear resonance levels from the capture of slow neutrons is made difficult by the fact that most of the substances used for absorbers and detectors are in the solid state, so that the calculations of Bethe and Placzek for the influence of the Doppler effect are inapplicable, since these were based on the assumption of a perfect gas. In this paper, their calculations are generalized to include the effect of the lattice binding. Under the assumption that the crystal may be treated as a Debye continuum, it is shown that for sufficiently weak lattice binding, the absorption curve has the same form as it would in a gas, not at the temperature T of the crystal, however, but at a temperature which corresponds to the average energy per vibrational degree of freedom of the lattice (including zero-point energy). In cases of somewhat stronger lattice binding, the line form is found to be more complicated, and may even have a fine structure. Plots are given of the absorption line in several typical cases. An approximate formula for the cross section for self-indication is also derived.

ACCORDING to the theory of the compound nucleus proposed by Bohr and by Breit and Wigner,[1] the cross section for the capture of a slow neutron with an energy near to a resonance level of a nucleus at rest in free space is given by an equation of the form

$$\sigma = \frac{\Gamma^2}{4} \frac{\sigma_0}{(E-E_0-R)^2+\frac{1}{4}\Gamma^2}, \tag{1}$$

where σ_0, the cross section at resonance, varies inversely with v, the velocity of the neutron in the rest system, E is the kinetic energy of the neutron, and E_0 is the energy that the neutron

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[1] N. Bohr, Nature **137**, 344 (1936); G. Breit and E. Wigner, Phys. Rev. **49**, 519 (1936).