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Experimental Verification of the Theory of the Continuous Spectra of H_2 and D_2

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The continuous spectra of molecular hydrogen and deuterium have been produced and studied under conditions permitting control of the excitation processes involved, the electron beam being subjected to definite accelerating potentials. An immediate comparison of the results with those predicted on purely theoretical grounds in previous papers by the author and others was not possible because of the unavoidable thermal spread in the kinetic energies of the electrons, an effect which had not been considered in those papers. The necessary modification in the theoretical predictions has been carried out, the essential result being that no sharp separation of even the lowest vibrational level of the radiating electronic state can be expected at any accelerating potential; consequently, even at the lowest potential at which any radiation is perceptible, that coming from the lowest vibrational level will be appreciably contaminated by the contribution from the next higher. The form of functional relationship between the rate of excitation of a given level and the accelerating potential is investigated and found to be linear if the latter is higher than the critical excitation potential of the given level (but not too much higher), and exponential if it is lower. Advantage is taken of this relationship to determine the corrections due to contact potentials and possible other causes which prevent the true accelerating potential in a thermionic device from being read directly from a voltmeter connected between the source of electrons and the collector. It has been shown that at certain wave-lengths the observed radiation can come only from a single vibrational level; when the corresponding intensity is plotted as a function of the voltmeter reading, a curve of the form described is obtained, and the point at which the linear and exponential parts merge is taken as that at which the true accelerating potential is equal to the (known) critical potential. When the true potential scale has been thus established, it is found that there is good agreement between calculated and observed spectral energy distribution. Thus the original calculations, which were in painful disagreement with the only quantitative experimental data then extant, are now satisfactorily confirmed.

INTRODUCTION

THE quantitative theory of the relative energy distribution in the continuous spectrum of hydrogen and deuterium has been given in two previous papers.[1,2] This spectrum is produced by transitions from the stable $1s\sigma 2s\sigma\,{}^3\Sigma_g$ electronic state of the molecule to the unstable $1s\sigma 2p\sigma\,{}^3\Sigma_u$ state, and consists of contributions from each of the vibrational levels of the upper state. We presented a complete theoretical calculation of the composition of the contributions from the first four or five such levels, making use of no assumptions or numerical constants other than those of basic theory, and no approximations which could not be shown by internal evidence to be legitimate. In addition, we made rough estimates of the relative populations of the several levels which should be maintained when molecules in the ground state are excited by electrons with definite homogeneous kinetic energies, and of the character of the resulting composite radiation. Comparison with the existing experimental evidence was very unsatisfactory. The only work with which our accurate calculations could be compared was that of Smith,[3] who attempted to isolate the radiation from the lowest vibrational level by using a great excess of helium in his discharge tube; his results bore no resemblance to ours. The older work of Finkelnberg and Weizel[4] on the composite spectrum could be given an interpretation in harmony with our calculations, but it was not sufficiently quantitative to be regarded as definite confirmation.

In order to clear up the matter, it was decided to undertake the analysis of the spectrum radiated under simple, known conditions, with excitation produced at low pressure (0.015 mm) by thermionic electrons under controlled acceleration. It was at first hoped to be able to reproduce the conditions assumed in the calculations of II, and in particular to isolate the radiation

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[1] A. S. Coolidge, H. M. James, and R. D. Present, J. Chem. Phys. **4**, 193 (1936).

[2] H. M. James and A. S. Coolidge, Phys. Rev. **55**, 184 (1939). These two papers will hereafter be referred to as I and II, respectively.

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

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

from the level $v=0$ by keeping the electron velocities below the critical velocity for $v=1$, which lies 0.3 volt higher (for H_2). This would have been desirable because it would have provided a direct test of that part of our calculations which was wholly independent of all assumptions about the nature of the excitation process. But consideration showed that this hope could not be realized because the inevitable thermal spread in the energies of the electrons must, no matter what the accelerating voltage, produce an appreciable contamination by radiation from the next higher level. Fortunately, it is possible to modify the theoretical predictions in order to allow for this effect and thus to obtain an experimental test in which the excitation process is involved only in the determination of a correction term.

THEORY

It will be assumed, as before, that when an electron with a given kinetic energy encounters a normal hydrogen molecule, the probability of excitation to a particular vibrational level of the upper (electronic) state is zero if the electron possesses less than a certain critical energy (the excitation energy), and otherwise is directly proportional to the amount by which the electronic energy exceeds the critical value. (A discussion of this assumption will be found in I.) Actually, the relation stated is expected to break down for excess energies more than a fraction of a volt, the true excitation being less than predicted, but this will be disregarded in making the calculations.

Suppose electrons are emitted from a hot cathode and travel through an accelerating field, some of them arriving at a point of observation where the potential difference is known with respect to a point just outside the cathode surface. We wish to calculate their distribution with regard to kinetic energy and the corresponding excitation produced to various levels. Since the original velocities are small in comparison with those acquired from the field, we may ignore any differences between the paths followed by electrons of different original speeds, and assume that the same fraction of those emitted with all initial speeds arrive at the observation point. Then the final energy distribution can be found from the initial distribution simply by taking account of the fact that the increase in energy is the same for all electrons. They are emitted with a Maxwellian distribution about a mean value $2kT$. (The extra $\frac{1}{2}kT$ as compared with the mean value for the molecules in a fixed sample of gas is due to the fact that, of all the electrons of given energy present, the proportion emitted increases with the energy.) Consequently, upon arrival at the observation space, they will have a similar distribution about a mean value equal to the accelerating potential plus $2kT$, and none will have energy less than the accelerating potential. If the latter is not less than the critical potential for a given upper level, all arriving electrons can produce excitation to that level. In view of the linearity of the excitation function (the relation between the rate of excitation and the kinetic energy), the mean rate of excitation will be just that corresponding to the mean kinetic energy; the thermal energy will simply lower the apparent critical potential by $2kT$. But if the accelerating potential is lower than the critical value this reasoning fails, for the value $2kT$ represents the energy averaged over all the electrons, while the excitation rate has to be averaged only over those electrons which started with at least sufficient thermal energy to make up the deficiency between accelerating and critical potentials. The excitation rate is therefore greater than that corresponding to the mean kinetic energy, and indeed remains positive even if the latter falls below the critical value (accelerating potential more than $2kT$ below excitation potential), for there are always some exceptionally fast electrons capable of overcoming the deficiency. But this number decreases exponentially as the deficiency becomes greater. The complete prediction for the apparent excitation function (relation between rate of excitation and accelerating potential) is therefore a linear part for accelerating potentials greater than the true critical potential, joined smoothly to a curved portion which vanishes exponentially with decreasing accelerating potential.

It might appear possible to reduce the thermal spread by introducing a very slight retarding field near the cathode, so as to reflect electrons having low initial velocities and permit only the faster ones to pass. Consideration shows, however, that no diminution in spread would really occur because there would also be a reflection of fast electrons which happened to be moving obliquely. The energy distribution of the electrons passing the barrier would still be Maxwellian, and the only modification necessary in the reasoning of the previous paragraph is that the accelerating potential should be measured from the barrier instead of from the cathode surface.

To get a quantitative theory, let V be the accelerating potential and let V_0, V_1, $\cdots$, be the critical potentials for the vibrational levels $v=0$, $v=1$, $\cdots$. For convenience put $V-V_0=\Delta_0$, $V-V_1=\Delta_1$, $\cdots$. Let E' be the kinetic energy (in volts) of an electron issuing from the cathode (or crossing the potential minimum), and $E=E'+V$ its energy upon arrival at the point of observation. The distribution-in-energy of the electrons is originally that given by the equation

$$dn/dE=CE'e^{-E'\epsilon/kT},$$

where dn is the number of electrons having energies within the range dE, C is a constant which need not concern us, and ϵ is the elementary charge. [This apparently unfamiliar expression can be easily derived from any of the usual statements of the Maxwellian law. For example, Kennard[5] states that the rate at which particles cross a plane with speed in dv at v and at an angle to the normal in $d\theta$ at θ is

$$2\pi nAv^3 \exp\,(-mv^2/2kT)dv \sin\theta\cos\theta d\theta,$$

where n is the number present per unit volume and A is a constant. Upon putting $2v^3dv=v^2d(v^2)=4E'dE'/m^2$ (with m the mass of a particle) and integrating over the appropriate angle, an expression in the given form is obtained.]

The electrons arrive at the point of observation with energy distribution

$$dn/dE=C(E-V)e^{-(E-V)\epsilon/kT},\quad E>V.$$

For small positive $E-V_v$ an electron has a probability $K_v(E-V_v)$ of producing excitation to the level v, K_v being the excitation constant. (K_v is the quantity $KM^2_{ev,\,e'v'}$ of Eq. (11) of I, for which revised values are given in Table II of II.) The total rate of excitation to each level v is therefore

$$R_v=CK_v\int(E-V_v)(E-V)e^{-(E-V)\epsilon/kT}dE.$$

The upper limit of integration may be taken as infinity since the smallness of the Boltzmann factor for high electron energies prevents the failure of the assumption of a linear excitation function from producing an appreciable error. The lower limit is to be taken as V or V_v, whichever is the higher, that is, accordingly as Δ_v is positive or negative. The integration is readily performed, leading to the formulas

$$R_v=C'K_v[1+\Delta_v\epsilon/2kT],\qquad \Delta_v>0,$$
$$R_v=C'K_v[1-\Delta_v\epsilon/2kT]e^{\Delta_v\epsilon/kT},\quad \Delta_v<0.$$

Here C' stands for the new constant $2C(kT/\epsilon)^3$. The two formulas join smoothly at $\Delta_v=0$, as can be seen by expanding the exponential. For positive Δ_v, R_v is a linear function of Δ_v, while for large negative Δ_v, $\log R_v$ becomes linear in Δ_v. The functional form of R_v, plotted logarithmically against Δ_v, is shown (except for an additive

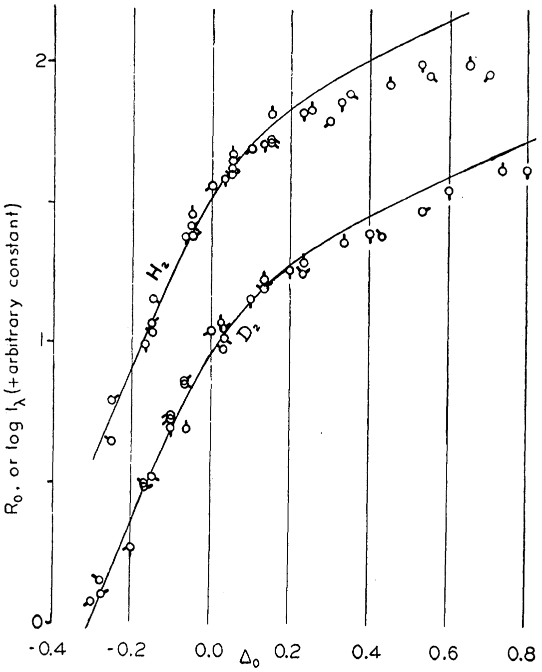

FIG. 1. Determination of absolute potential scale. Curves show calculated log R_0 plotted against Δ_0. Symbols show observed log intensity plotted against voltmeter readings and displaced so as to coincide with curves. Data for H_2 are for line 12. Data for D_2 are for line 10.

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[5] E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, New York, 1938), Eq. (71*b*).

constant) by either solid curve in Fig. 1. For large positive Δ_v its true value must be expected to fall below that given by the above formula, in view of the known breakdown of the linear relation for the true excitation function.

The remaining calculation of the radiation predicted at any potential V is made exactly as before in II, substituting R_v for $F_{ev,e'v'}$ of Eq. (11) of I. Briefly summarized, the method calculates the population of each level as the product of the appropriate R_v multiplied by the mean lifetime τ_v as taken from Table I of II. The calculated radiation from each level, as shown in Figs. 2 and 3 of II, is then multiplied by the population of that level, and the contributions are added to give the final composite result.

The degree to which the radiation from $v=0$ can be isolated depends principally on the amount of contamination from $v=1$, which is determined by the relative intensities at each wave-length of the radiations from the two pure levels and by the ratio of their populations. For $V<V_0$, this ratio is

$$\frac{\tau_1 R_1}{\tau_0 R_0}=\frac{\tau_1 K_1}{\tau_0 K_0}\,\frac{1+(V_1-V)\epsilon/2kT}{1+(V_0-V)\epsilon/2kT}\times\exp\left[-(V_1-V_0)\epsilon/kT\right].$$

As V becomes negatively infinite, the second factor approaches unity. With a cathode temperature of 1100°K, ($\epsilon/kT=10.52$ v), we may substitute the values for hydrogen:

$\tau_1=1.10\times10^{-8}$ sec., $K_1=1.13$ arbitrary units,
$\tau_0=1.19\times10^{-8}$ sec., $K_0=1.00$ arbitrary units,
$V_1=12.03$ v.
$V_0=11.72$ v.

Then the limiting value of the population ratio is 0.04, while in the range of V within which a perceptible radiation intensity may be expected, it has the following values:

V	11.42	11.52	11.62	11.72	11.82	11.92	12.02	12.12
ratio	0.066	0.073	0.083	0.106	0.159	0.252	0.382	0.495.

The resulting contamination will vary with the wave-length, being zero at 2800A where the radiation from $v=1$ vanishes, and increasing most rapidly toward shorter wave-lengths, at which the radiation from $v=1$ is much greater than that from $v=0$. It appears that for wave-lengths greater than about 2500A, and accelerating potentials in the neighborhood of the critical potential for $v=0$, the contamination should not be serious, and could be adequately accounted for by this somewhat crude method of estimating the effective excitation functions. Evidently there is nothing to be gained by attempting to push the potential far below 11.72 v, as the slightly more favorable population ratio will be more than outweighed by the loss in accuracy caused by the exponential decrease in total intensity.

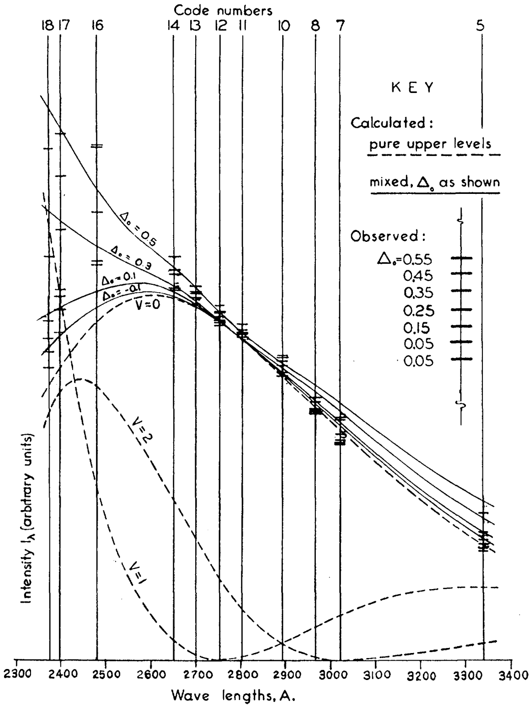

FIG. 2. Spectral energy distribution for hydrogen at various accelerating potentials. Dashed curves show theoretical distribution for pure vibrational levels. Solid curves show distributions calculated for the mixtures of levels produced at potentials $11.72+\Delta_0$ ev, with Δ_0 as indicated. Short horizontal lines show observed intensities at the wave-lengths of the standard mercury lines (indicated by code numbers) at potentials as indicated in the Key. For details see Table I. For normalization of curves, see text.

For deuterium the relations are much less favorable. This is due to the facts that the vibrational levels lie closer together, that the excitation constants for the higher levels are nearly twice as great as for hydrogen in comparison to the ground level, and that the radiation from pure $v=1$ exceeds that from $v=0$ at longer wave-lengths than for hydrogen.

TABLE I. Relative intensities I_λ (in arbitrary units) calculated and observed for H_2 at various wave-lengths and values of Δ_0 (accelerating potential relative to the critical excitation potential for $v=0$, 11.72 v).

Code number	5		7		8		10		11		12		13		14		16		17		18	
Wave-length	3341		3023		2967		2894		2804		2758		2699		2654		2481		2400		2378	
Δ_0	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
−0.1	268		518		571		639		706		745		782		806		779		714		691	
		242		490		552		640		728		745		818		837		880		730		650
0.0	272		521		573		639		707		746		784		807		789		733		714	
		248		482		550		633		735		752		820		837		890		780		685
0.1	281		526		577		642		707		747		786		811		811		778		766	
		258		485		557		640		722		756		820		840		892		823		714
0.2	296		535		584		646		709		748		790		819		851		857		859	
		267		502		560		655		720		775		807		837		890		810		755
0.3	317		548		594		652		712		751		796		830		910		970		991	
		285		540		585		665		730		765		817		860		1000		960		900
0.4	336		560		603		657		717		756		807		848		971		1078		1115	
		326		534		560		677		730		777		833		870		1150		1230		1140
0.5	351		568		610		663		725		767		824		871		1033		1172		1218	
		326		534		577		672		748		790		833		900		1145		1255		1140
0.6	—		—		—		—		—		—		—		—		—		—		—	
0.7		335		540		582		662		740		825		905		913		1330		1405		1325
1.2		340		530		593		705		805		915		985		1080		1570		1615		1505
1.9		335		524		600		720		833		920		1055		1120		1590		1700		1580

TABLE II. Relative intensities I_λ (in arbitrary units) calculated and observed for D_2 at various wave-lengths and values of Δ_0 (accelerating potential relative to the critical excitation potential for $v=0$, 11.76 v.).

Code number	5		7		8		10		11		12		13		14		16		17		18	
Wave-length	3341		3023		2967		2894		2804		2756		2699		2654		2481		2400		2378	
Δ_0	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
−0.1	350		614		663		721		792		824		853		877		910		879		860	
		299		576		640		733		808		840		885		889		900		775		725
0.0	362		619		666		725		798		834		869		901		982		981		968	
		305		580		641		743		815		842		920		918		985		845		735
0.1	388		633		677		734		815		858		906		956		1141		1204		1204	
		352		620		685		782		840		902		945		966		1150		1140		1050
0.2	428		654		694		755		845		901		970		1049		1388		1544		1564	
		387		651		720		820		885		935		999		1064		1375		1450		1350
0.3	464		677		717		778		893		968		1058		1164		1620		1846		1883	
		426		651		715		822		915		1028		1130		1218		1830		1900		1740
0.4	491		702		748		821		969		1066		1178		1304		1810		2066		2115	
0.5	—	440	—	670	—	755	—	895	—	1070	—	1190	—	1335	—	1450	—	2120	—	2170	—	2030
0.7		443		693		792		983		1160		1320		1490		1585		2180		2400		2240
1.2		440		770		897		1065		1230		1355		1495		1575		2380		2520		2420
1.9		465		795		922		1105		1280		1420		1580		1670		2500		2310		2250

The detailed structure of the radiation predicted for various accelerating potentials is shown in Tables I, II, and Figs. 2, 3. (In these tables and figures the code numbers at the top refer to the wave-lengths of certain lines in the mercury comparison spectrum which was used in the experimental part.) In computing these values, the calculated values for the pure states were first carefully interpolated at the desired wave-lengths from large drawings of the theoretical curves and were then combined as explained. At the higher potentials there is considerable structure, due to contributions from the increasingly narrow maxima in the separate terms, which would be missed if the attempt were made to interpolate from the composite curves. In the figures, the first three pure state curves are shown for comparison, being merely copied from Figs. 2 and 3 of II. In calculating the composite curves, the increase in absolute intensity with increasing potential has been neglected in order to facilitate comparison; each curve has been scaled down by a factor such that the contribution from $v=0$ is exactly the same as shown for that pure state. The height of the curve above that for $v=0$ at any wave-length is therefore a direct measure of the contamination from other states, mostly from $v=1$. The vanishing of the latter at 2800A causes the first three curves for H_2 to coincide at this wave-length.

PRODUCTION OF RADIATION

The radiation to be studied was produced in a tube shown in Fig. 4, which also indicates the essential parts of the electrical connections. Electrons were drawn from an internally heated oxide cathode *c* in the form of a flattened tube 3 cm in length, mounted in an aperture in a supporting plate *s*, to which was attached the negative lead *2* common to both heating and electronic circuits. Heating current from the battery B_h, rheostat R, and ammeter A_h was led in at *1*, the cathode being maintained at about 1100°K as determined by an optical pyrometer focused on one of the surface cracks in order to get the best approximation to blackbody radiation. The rate of electron emission, measured by the milliammeter A_e, was controlled by the accelerating grid *g*, maintained at a potential of about 7 v by means of the lead *3* from the battery B_e, potentiometer P_g, and voltmeter V_g. A portion of the electron stream entered the constant-potential box *b* by means of the double-walled slit, and passed down into the collecting trap *t*, the slit of which was wide enough to admit the total beam passed by the first slit. Box and trap were maintained at the same potential by means of leads *4* and *5*, respectively, from the potentiometer P_b and voltmeter V_b, this potential being varied from 14.6 v to 18 v (by the meter) during the course of the work. The microammeter A_t (in which the potential drop was negligible) served to measure the current to the trap, which was maintained at 25 microamperes by suitable slight adjustments of the grid potential. Within the trap were two gauze screens in order to assist in the capture of electrons.

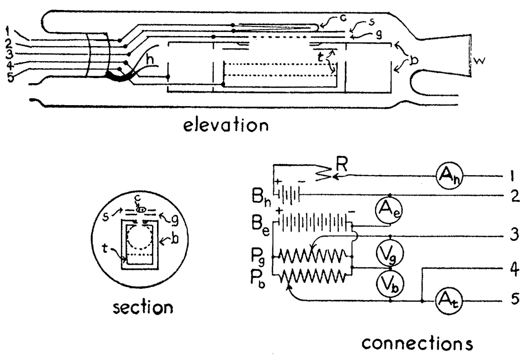

FIG. 4. Source of radiation studied.

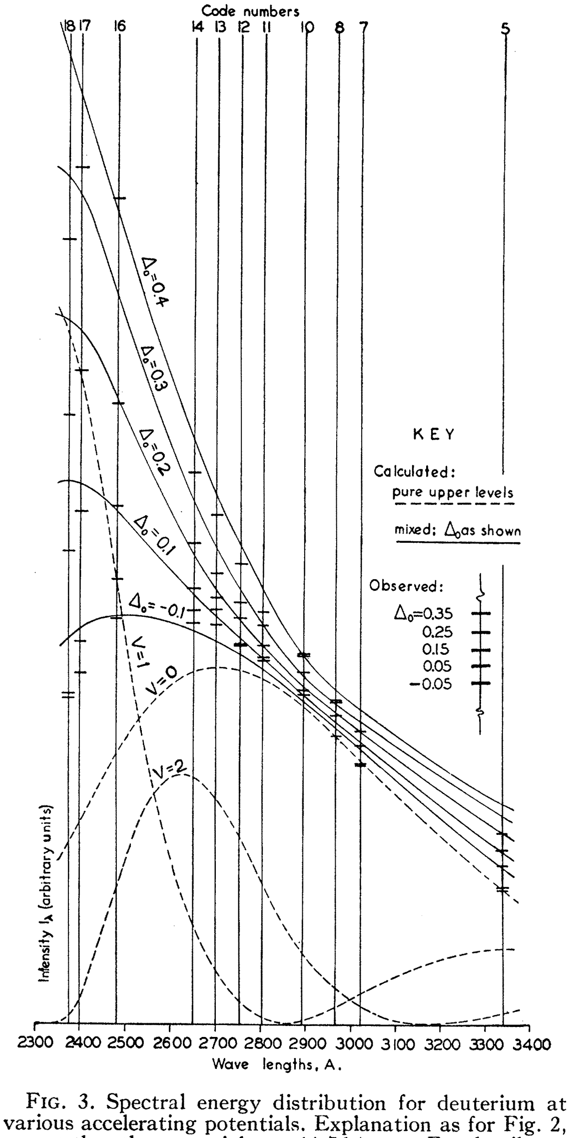

FIG. 3. Spectral energy distribution for deuterium at various accelerating potentials. Explanation as for Fig. 2, except that the potentials are $11.76+\Delta_0$ v. For details see Table II.

Box and cage were provided with holes at the ends, permitting observation through the quartz window *w*, attached by a graded seal to the Pyrex tube which housed the assembly. Reflection at the rear was prevented by the internal black glass horn *h*. Except for the lead wires in the press, all metal parts were of nickel, and were thoroughly outgassed by induction heating in vacuum before measurements were made. In spite of this treatment, it was found impossible to get clean spectra except by constructing parts *2* and *3*, which ran hot during operation, of metal which had first been heated nearly to fusion for several minutes in hydrogen at atmospheric pressure.

The tube was operated in a continuously flowing stream of gas at a pressure of 0.015 mm of mercury. To provide this, commercial hydrogen or deuterium was drawn from a cylinder to fill a mercury-sealed gasometer holding about 300 cc, enough for two days' operation. From here it passed through a parallel pair of electrically heated palladium thimbles into a small space where the pressure was kept constant at about half an atmosphere by means of a barostat controlling the heating circuit of the thimbles. Although the current was carefully limited to the least value which would supply enough gas, the thimbles repeatedly failed through the development of small holes, and had to be repaired with gold solder or replaced. From the intermediate space gas leaked into the observation tube through a long fine capillary, and was continuously removed by a diffusion pump connected through a pinhole in a diaphragm, the capillary and pinhole being so matched as to maintain the desired pressure in the tube. Both entrance and exit connections passed through dry ice traps in order to exclude mercury vapor.

When deuterium was being used, a certain amount of water invariably collected in the jackets housing the palladium thimbles. The source could not be determined. According to the label on the cylinder, the deuterium had been dried over liquid air. At first it was thought that the moisture might come from the asbestos upon which the heating coils were wound, but the effect persisted in spite of vigorous preliminary heating and pumping. In the first experiments, hydrogen had been stored over water; but in the final work only the mercury gas holder was used, and no moisture appeared except when the gas was deuterium. Of course, no moisture could penetrate the palladium, and the only cause for concern was that if ordinary water was present from any source, the exchange reaction with deuterium might contaminate the latter with hydrogen.

MEASUREMENT OF INTENSITIES

The radiation was analyzed by photographic comparison with the standard mercury arc of Krefft, Rössler, and Rüttenauer,[6] and the use of a small Hilger quartz spectrograph. When the results were computed on the basis of the calibration of this standard given by Rössler,[7] irregularities appeared which strongly suggested errors in this calibration. A new calibration was therefore carried out, and did indeed lead to revisions in the expected directions. This work is reported in a separate paper,[8] and as many details of the method there described applied also to the work on the H_2 and D_2 spectra, only the special features of the latter need discussion here. These features arose, first, from the extreme feebleness of the spectra to be measured (due to the desirability of working at the lowest possible accelerating potentials), and second, from the fact that instead of sampling light from all parts of the source, as is necessary with the mercury standard, it was essential to isolate that emitted from a small region, namely, a thin horizontal slice across the electron beam, in order to minimize the effects of possible stray fields. Because of the proximity of metal surfaces or gauzes parallel to the line of sight through the observation space, any such fields would tend to be perpendicular to that line, and such a slice should constitute a very nearly equipotential region.

These two facts made it imperative to focus the source as well as possible upon the spectrograph slit and to perform the photometric analysis upon the dispersed image produced by light passing through a single short section of the slit, and hence originating in a single zone of the luminous beam. By use of an aluminum-sputtered concave mirror in order to avoid chromatic aberration, the edgewise view of the electron beam as seen through the window of the tube was focused so as to produce the maximum illumination in the spectrograph. To facilitate making this adjustment the radiation was temporarily made visible by raising the voltage until bright lines could be seen on looking through the instrument with an eyepiece. In order to make possible accurate location of the points at which the spectrographic image was to be measured, the

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[6] H. Krefft, F. Rössler, and A. Rüttenauer, Zeits. f. tech. Physik **18**, 20 (1937).

[7] F. Rössler, Ann. d. Physik [5] **34**, 1 (1939).

[8] To appear in J. Opt. Soc. Am., hereafter cited as III.

slit was provided with an aperture plate sharply defining the portion exposed, and hence the breadth of the dispersed image. For the lowest voltages, the short wave portion was too feeble for accurate registration by this means. It was therefore arranged that by sliding the aperture plate in its ways, the portion of the slit used for the main exposure could be covered, and additional short sections just above and below could be exposed for a minute or two to strong radiation obtained by momentarily raising the voltage, thus producing two gauge marks on the plate whose relation to the main image was known once for all. To provide a wave-length scale, another short section of the slit was exposed to feeble mercury radiation, conveniently produced by holding in front of the slit an evacuated quartz tube containing mercury (actually one of the standard lamps) and operating an induction leak tester in the neighborhood. It was not necessary for an actual spark to jump.

Because of the absence of detail in the spectrum, it was permissible to operate with a slit width of 1 mm without perceptible error through loss of resolution. Satisfactory densities were obtained with exposures on Eastman 1–0 or 103–0 spectroscopic plates, ranging between one-half and two hours, according to the excitation voltage.

The comparison spectra were obtained with the standard mercury arc, essentially as described in III, except for modifications made necessary by the different character of the continuous source being measured. A very great attenuation was needed, and was obtained in part by using a narrow slit on the lamp house, and in part by providing the sector wheel with a second disk, geared to that in which the steps were cut and carrying an opening which exposed only one out of every sixteen of their transits across the slit. (In view of the prolonged exposure, the frequency of the flashes produced was still ample to prevent errors due to reciprocity failure.) No bromine filter was required, and the diffusing quartz disk could not be used because it would have prevented focusing of the hydrogen source. In order to secure a similar distribution of light entering the spectrograph, the radiation from the mercury source was reflected into the slit by the same mirror as used for hydrogen, but both source and mirror were placed so far from the slit as to form an image, acting effectively as a point source, about a meter in front of the slit. By mounting the mirror slightly askew on the end of a motor shaft, this point was spun out into a ring about 2 cm in diameter, thus providing the "narrow beam" type of illumination discussed in III.

The photometry was conducted essentially as in III, except that each hydrogen exposure yielded a single set of readings instead of a set of six. These readings were taken at wave-lengths corresponding to the mercury calibration points, and at points accurately located at a fixed fraction of the width of the image or of the distance between the gauge marks (which varied somewhat with the wave-length), in order to correspond to the same point in the slit and hence to the same portion of the luminous source. It was noticed that the intensity varied considerably along the length of the slit, particularly at the lower voltages. This could be due partly to spreading and extinction of the electron beam, but the dependence on voltage suggests the presence of some real inhomogeneity in the supposedly uniform potential space, which would naturally produce a greater relative variation in the intensity radiated near the critical potential than at higher potentials. In order to minimize errors due to faulty registration, the points chosen for analysis were selected close to the maximum of intensity with respect to the length of the slit.

Each plate carried two comparison exposures and a series of hydrogen or deuterium spectra obtained by stepping up the accelerating voltage. The comparison exposures were combined to plot a set of characteristic curves, as described in III, except that in order to accommodate the feeble intensities obtained for short wave-lengths and low voltages, it was necessary to extend the characteristic curves so as to include as much as possible of their initial non-linear portions. For this portion of the curves it was found convenient to use semi-log paper, thus in effect plotting the optical densities against the exposures themselves, as recommended by Tien Kiu,[9] rather than against their logarithms. An example of

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[9] Tien Kiu, Comptes rendus **207**, 1394 (1938). The exposure was varied by varying time, not intensity.

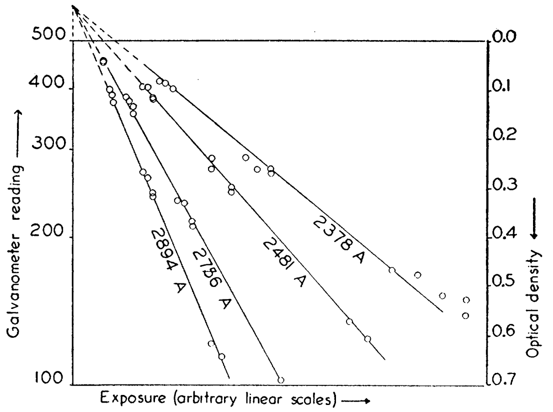

FIG. 5. Characteristic curves for small exposures at different wave-lengths. The abscissae are exposures on arbitrary scales, different for each wave-length. The scale on the left (logarithmic) shows the galvanometer reading of the densitometer, which is proportional to the light transmitted by parts of the plate receiving the exposure indicated. The reading 500 corresponds to unexposed emulsion. The optical densities (above fog) are shown by the linear scale on the right. When extrapolated back to zero exposure, the characteristic curves appear to radiate from a false zero of density.

such curves is shown in Fig. 5, and it will be seen that they are remarkably straight for densities between 0.1 and 0.5. Extrapolation to zero exposure appears to give a negative density (transmission greater than 100 percent), but this is, of course, only a convenient aid in drawing the usable portion of the curves; at very low exposures the actual curves bend over and tend to zero density. Since the ordinary logarithmic characteristic curves are practically straight at densities above 0.7, there is but a narrow range where neither form of plotting gives linear results, and since slight curvature does not interfere with accurate interpolation, there is considerable overlapping of the ranges in which the two methods are useful.

For the ordinary density range, the plates used developed to a contrast of about $\gamma = 1.7$; this showed a tendency to increase with successive batches of plates supposedly of the same type of emulsion. This high contrast was undesirable in the present work, as it limited the useful range of exposures to about a ratio of 12 to 1. Attempts to reduce it by modifying the method of development lead to irregular results and were abandoned. It did not seem feasible to use plates with softer emulsions since none were available with the requisite high sensitivity in the ultraviolet.

To judge from internal evidence, the precision of the photometry was about 4 percent at either end of the range covered, and somewhat better for intermediate values.

RESULTS AND DISCUSSION

Before comparing the results of these measurements with the theory as developed above, it is necessary to consider whether there could be any appreciable modification of the distribution-in-energy of the electrons as a result of collisions with molecules. According to Brode,[10] in hydrogen at 1-mm pressure the number of collisions of all kinds made by an electron with a velocity of a few volts is of the order of 20 per cm of path. This corresponds to about one collision every 3 cm at the prevailing pressure of 0.015 mm; hence very few electrons can have made more than one collision. Because of the disparity in mass, the energy lost in an elastic collision is negligible; the same applies to any collision producing only rotational excitation, while any vibrational or electronic excitation would remove so much energy that the electron could not take part in any further production of radiation. It seems safe to neglect the effects of previous collisions.

In order to apply the theory, some method of determining the actual accelerating potential must be found—it is notorious that the reading of a meter connected between cathode and collector may be in "error" by several volts because of the effects of contact potentials, space charges, and ohmic drops, some of which are highly inconstant and difficult to determine. It seemed best to make this determination from internal evidence in each series of exposures, and to assume that the corrections would not change appreciably during the few hours required for a single series. This was done on the basis of the theoretical apparent excitation function, giving the relation between the true accelerating potential and the intensity of radiation from a particular vibrational level at a given wave-length. It happens that in the spectrum from $v=1$ there is a region of zero intensity, falling at the

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[10] R. B. Brode, Phys. Rev. **25**, 636 (1925).

wave-length of line 12 for H_2 and near that of line 10 for D_2. (See Figs. 2, 3.) Hence, at these wave-lengths the entire radiation comes from $v=0$ until the voltage is raised sufficiently to excite $v=2$. This permits a direct test of the form of the apparent excitation function for $v=0$. On plotting the logarithm of the observed I_λ against the voltmeter reading, a curve should be obtained which can be brought into coincidence with the theoretical curve of log R_0 against Δ_0 by suitable vertical and horizontal displacements. It is thus possible to determine what voltmeter reading corresponds with $\Delta_0=0$, that is, with true potential equal to critical potential for $v=0$. Since the latter is known from spectroscopic evidence to be 11.72 v for H_2 and 11.76 v for D_2, the voltmeter correction can be determined at once.

The application of this device is shown in Fig. 1. Points indicated by the same symbol represent a single series of exposures, plotted so as to secure the best possible correspondence with the theoretical curve. The horizontal displacements used represent corrections of from -3.28 v to -3.45 v. It will be seen that below $\Delta_0=0.1$ there is satisfactory agreement with theory and that a horizontal displacement differing by 0.1 v would lead to a definitely poorer fit. The fact that the observed points lie too low for larger positive Δ_0 is entirely to be expected since it is known that the true excitation function for a triplet state rapidly drops below the linear form which was assumed in constructing the present theoretical curve, the linear form holding only for a few tenths of a volt. It seems safe to conclude that the value of the true potential was known relative to the critical potential for $v=0$ to within 0.1 v. The absolute value of this critical potential was not determined directly. But in some preliminary experiments the voltage was run up until certain identifiable lines of the molecular spectrum appeared, and it was verified that the voltmeter readings at which these lines and the continuum, respectively, first appeared were consistent, within 0.1 v, with the spectroscopically known excitation energies of the states concerned.

When interpreted in this way, each exposure furnished a set of relative values of the radiation intensity I_λ (in the notation of III) at eleven selected wave-lengths produced at a known accelerating potential. It was found that considerable variation occurred in the actual intensities obtained in different exposures even at the same accelerating potential, but this did no harm, as only the ratios are given by the theory. For comparison with theory, the results of each exposure were multiplied by an arbitrary constant so selected as to bring the average of the intensities between 2700A and 3000A into good agreement with the calculated values. Some sixty exposures were analyzed, but a complete presentation of the results would be needlessly

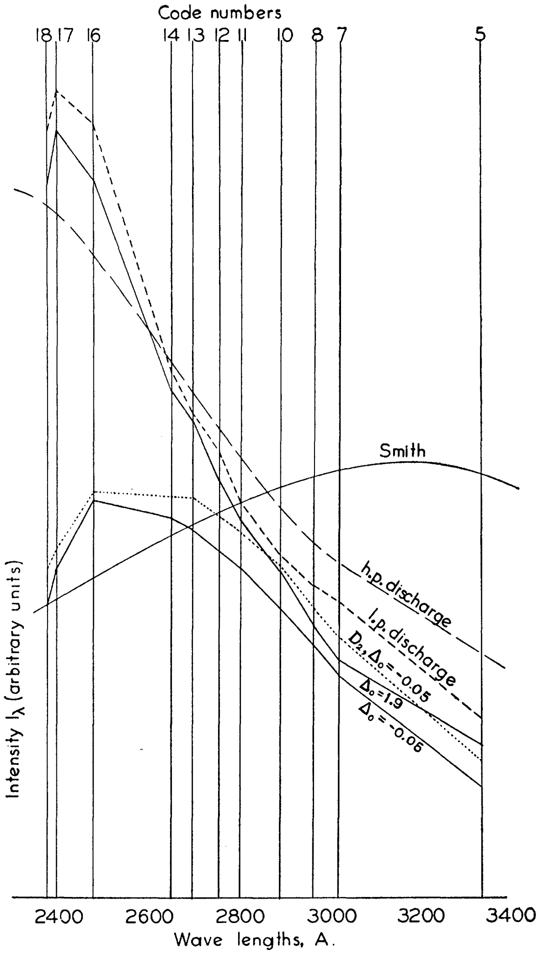

FIG. 6. Hydrogen and deuterium spectra produced under various conditions. All data are for H_2 except the curve marked D_2. The curves marked $\Delta_0=-0.05$ and $\Delta_0=1.9$ are from the data of Tables I and II. The l.p. discharge curve is from measurements on a low pressure discharge lamp. The h.p. discharge curve is given by Chalonge for a lamp with pressure 35 mm. Smith's curve is for a discharge in the presence of helium.

bulky, and some condensation by averaging is necessary. In Tables I and II the entries under "calc." are each the average of several exposures which have been individually analyzed and adjusted as described and for which the accelerating potentials have been determined to lie between the two tabulated round values indicated by the position of the entry. Thus, the first entry is the average of six exposures for which Δ_0 was determined to lie between -0.1 and 0.0. The same data are represented in Figs. 2 and 3 by short horizontal lines drawn across the vertical lines showing the selected wave-lengths. Unfortunately it did not seem possible to indicate the values of Δ_0 on the figures; in general, they increase by tenths from -0.05 for the lowest short lines to 0.55 (Fig. 2) or 0.35 (Fig. 3) for the highest, but there are some transpositions as the tables show. Above these voltages there is little reason to expect the theoretical values to be valid, because of breakdown of the assumption of a linear excitation function. No calculated values are therefore given, and the normalization of the observed values is entirely arbitrary.

For purposes of comparison, the data for H_2 and for D_2 at the lowest potential used ($\Delta_0=-0.05$) are shown together in Fig. 6, in the form of broken lines drawn between successive experimental points. There are also included the data for H_2 at the highest potential ($\Delta_0=1.9$), and a set of points obtained with a conventional hydrogen discharge lamp having a narrow capillary tube with gas at a fraction of a millimeter pressure and operating at about 50-ma current. In addition, there are included a curve given by Chalonge[11] for a discharge at 35-mm pressure, and the curve determined by Smith in the presence of helium.

On the whole, the present experimental results are in gratifying agreement with theory, both with respect to the form of the spectral distribution curves for low Δ_0, where it is almost pure radiation from $v=0$, and with respect to the magnitude and character of the contamination from higher levels when Δ_0 is increased. The differences between H_2 and D_2 are also in good accord with theory, the maximum for D_2 being at longer wave-lengths, as shown in Fig. 6 of II (the fact that the curves cross in that figure, but not in Fig. 6 of the present paper, has no significance, as the normalizations are different). The disturbing discrepancy between our calculations and Smith's results can be definitely set aside as due to some unknown source of error in the latter. It seems possible to assert that the essential correctness of the basic theory of molecular spectra has been experimentally established by a direct test.

It must, however, be admitted that the results leave something to be desired, with respect both to self-consistency and to agreement with theory. On the first score, the irregular spacing and occasional inversion of the data for a single wave-length and varying accelerating potential indicate that the conditions of production or analysis of the radiation have not been sufficiently well controlled. Particularly at the short wave end, where the effects of contamination by higher vibrational levels are most serious and most sensitive to variations in the potential, the results must be regarded with some suspicion. Above 2500A the data are more nearly self-consistent, but there appears to be a small systematic discrepancy as compared with theory, the observed curves being a little steeper than the calculated. Until more accurate data are forthcoming, it does not seem worth while to speculate as to possible explanations of the discrepancy.

It is interesting to note that the spectral distribution for $\Delta_0=1.9$ is already practically the same as for the several thousand volts in the low pressure discharge, except at the longest wave-length measured.

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[11] D. Chalonge, Comptes rendus **192**, 1551 (1931).