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The Franck-Condon Principle and the Ionization and Dissociation of Hydrogen by Electron Impact

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RECEIVED MARCH 25, 1960

Various old and new data on the ionization and dissociation of hydrogen and deuterium by single electron impact are reviewed. It is shown that neither the average appearance potentials of H_2^+ and D_2^+, nor the distribution in kinetic energy of the protons or deuterons are those expected from the conventional application of the Franck–Condon principle to the potential energy diagrams of hydrogen and its molecule-ions. The experimental findings can be rationalized with the presumably accurately known potential energy curve information on the hypothesis that 15 to 100 volt electrons can form transient complexes with hydrogen molecules [H_2-], with lives in the range 10^{-14} to 10^{-13} second.

Introduction

In all discussions of the ionization of molecules by single electron impact, it has been explicitly assumed that the distribution in conformation with which the ions are formed can be deduced from the distribution in conformation of the isolated molecules by the application of the Franck–Condon principle to the appropriate potential energy curves or hypersurfaces.[1–4] It is the purpose of the present communication to describe certain data on the ionization of hydrogen and deuterium by single impact of slow (15–100 volt) electrons that are not in accord with the above-mentioned assumption, *i.e.*, data that indicate in this case (hydrogen) at least, it is not possible to factor the wave functions so as to treat separately electronic and nuclear motions during an ionizing collision. The particular experimental data with which we will be concerned are: (1) the average appearance potentials of H_2^+ and D_2^+ in the mass spectra of hydrogen and deuterium as deduced by the linear extrapolation of the ionization efficiency curves for the formation of H_2^+ and D_2^+ and (2) the distribution in kinetic energy of protons (H^+) and deuterons (D^+) formed as a result of ionization of hydrogen and deuterium to the antibonding $^2\Sigma_u$ state of the molecule-ions.

The Average Appearance Potentials of H_2^+ and D_2^+.—There are shown in Figs. 1 and 2 the precisely known potential energy curves, $E(r)$ *vs.* internuclear distance r, for the $^1\Sigma_g^+$ state of H_2 (D_2) and the $^2\Sigma_g$ and $^2\Sigma_u$ states of the molecule-ions, H_2^+ (D_2^+).[5,6] There is also shown in Fig. 2 the internuclear distance distribution function for H_2 for the harmonic oscillator approximation. The conventional application of the Franck–Condon principle to such diagrams leads to the expectation that the most probable $^1\Sigma_g(H_2) \rightarrow {}^2\Sigma_g(H_2^+)$ transition should result in the molecule-ion being formed in the vibrational state with $v = 3$, about 0.75 ev. above the ground vibrational state of H_2^+. For this transition of deuterium the most probable state of D_2^+ would be $v = 5$, again about 0.75 ev. above the ground state. Evaluation of the overlap

$$\int \psi_0(\text{H-H})\ \psi_v(\text{H-H}^+),\ v = 0,1,2,3,\cdots$$

integrals for the harmonic oscillator approximation

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[1] W. Bleakney, *Phys. Rev.*, **35**, 1180 (1930).

[2] W. Bleakney, E. U. Condon and L. G. Smith, *J. Phys. Chem.*, **41**, 197 (1937).

[3] H. D. Hagstrum and J. T. Tate, *Phys. Rev.*, **59**, 354 (1941). A discussion of the implications of the Franck–Condon principle for the "shape" of ion peaks in mass spectra.

[4] H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford, 1952, p. 229–249, give a thorough discussion of implications of the Franck-Condon principle for the effect of the ionizing electron energy on the excitation products of single impact on H_2. It should be noted that the potential energy curve for the $^2\Sigma u$ state of H_2^+ shown in Fig. 113 is not in agreement with the results of the best calculations now available, see later ref. 6 of this paper.

[5] For the $^1\Sigma_g$ state of H_2, the data given in Tables 14.1-1 and 14.1-2, p. 1060 and 1061 of "Molecular Theory of Gases and Liquids," by J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, John Wiley and Sons, Inc., New York, N. Y., 1954, were used.

[6] D. R. Bates, K. Ledsham and A. L. Stewart, *Phil. Trans. Roy. Soc. London*, **A246**, 215 (1953). This reference gives detailed tables from which $E(r)$ for the $^2\Sigma_g$ and $^2\Sigma_u$ states of H_2^+ can be constructed.

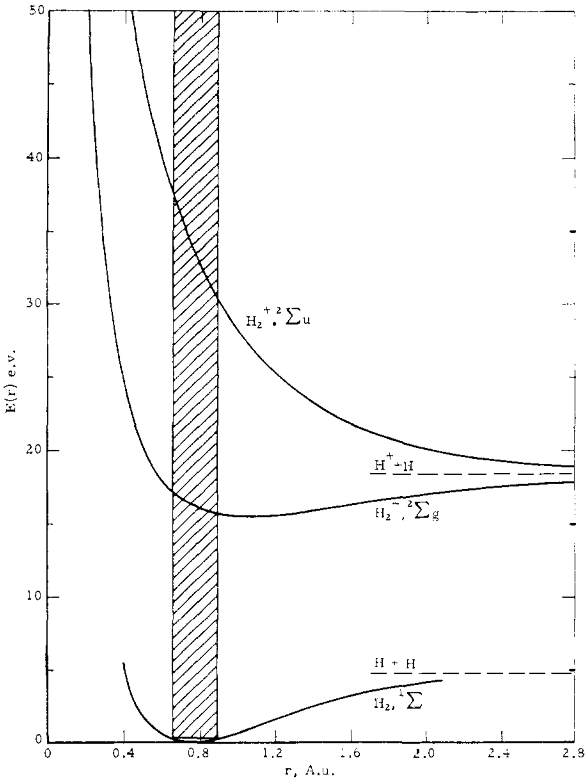

Fig. 1.—The potential energy curves for ${}^1\Sigma_g$ of H_2 and ${}^2\Sigma_g$ and ${}^2\Sigma_u$ of H_2^+; the "classical Franck-Condon area" of H_2 is shown cross-hatched. The energies of the two states of the molecule-ion are from the recent accurate calculations of Bates, Ledsham and Stewart.[6] Note that the energy zero is taken at r_e at 0.742 Å. of ${}^1\Sigma_g$ of H_2, the zero point energies of H_2 and H_2^+ are 0.26 and 0.14 ev., respectively.

to both vibrational wave functions leads to the expectation that the average vibrational excitation energy of the molecule-ion in the ${}^2\Sigma_g$ state should be about equal to the most probable excitation energy. It should be noted that the error introduced by the neglect of anharmonicity in calculating the overlap integrals with the harmonic oscillator wave functions gives extra weight to the vibrational states of H_2^+ with small v. Hence this means of calculating the expected excitation energy leads to a lower limit to this excitation energy. From the accurately known differences in energy between $v = 0$ of the molecule and ion, 15.427 ev. (H_2), 15.457 ev. (D_2),[7] one thus concludes that the average appearance potentials of both H_2 and D_2 should be $\geq 16.2 \pm 0.1$ ev.

As has been discussed by Mariner and Bleakney,[8] the intercept on the ionizing electron energy axis obtained by extrapolation of the linear portion of the ionization efficiency curve of an ion in a mass spectrum is to be associated with the average appearance potential of the ion in the mass spectrum. When the ion is the parent molecule-ion as is the case of H_2^+ or D_2^+, this average appearance potential is to be associated with the average ionization potential.

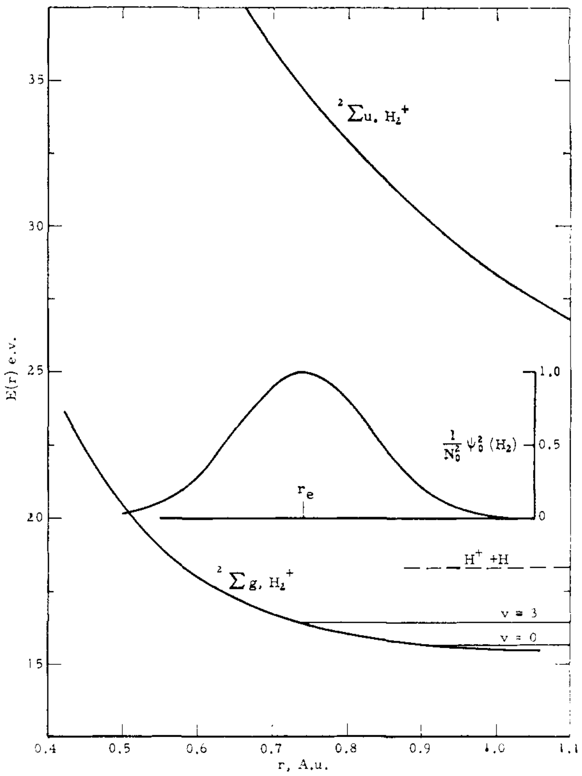

Fig. 2.—An expanded view of the Franck-Condon region of the ${}^2\Sigma_g$ and ${}^2\Sigma_u$ states of H_2^+. In the inset there is shown the internuclear distance probability distribution for $v = 0$ of ${}^1\Sigma_g$ of H_2 for the harmonic oscillator approximation

$$N_0^{-2}\psi_0^2(r) = \exp(-61.6\,\xi^2)$$
$$\xi = (r - 0.742)\ \text{Å}.$$
$$N_0^2 = (61.6 \times 10^{16}/\pi)^{1/2}$$

The energy levels of ${}^2\Sigma_g$ of H_2^+ were taken to be given by $E_v = 0.2770\,(v + 1/2) - 0.00768\,(v + 1/2)^2$ ev. from Herzberg.[7]

We have determined the average appearance potentials of H_2^+ and D_2^+ in the hydrogen and deuterium mass spectra from the extrapolated intercepts of the linear portions of their respective ionization efficiency curves. Measurements on the ionization efficiency curves of Ne^+ and He^+ of the neon and helium (admitted simultaneously with the hydrogen and/or deuterium) mass spectra were employed to calibrate the ionizing electron energy scale. Typical examples of the observed ionization efficiency curves are shown in Fig. 3. The details of the experimental conditions are summarized in the legend to Fig. 3. The results of our measurements are summarized in Table I.

Our results for $\bar{A}(H_2^+)$ and $\bar{A}(D_2^+)$, shown in Table I, are in excellent accord with the value reported by Bleakney for $\bar{A}(H_2^+) = 15.4 \pm 0.1$ ev. In this important pioneering study Bleakney employed data on the ionization efficiency curve of Hg^+ (taking $\bar{A}(Hg^+) = 10.4$ ev.) to calibrate the ionizing electron energy scale. The important point is that these values of $\bar{A}(H_2^+)$ and $\bar{A}(D_2^+)$ agree within the conservative estimates of the limit of error with the lowest appearance potentials

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[7] G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1950, p. 456 and 534. 1 ev. = 8068.3 cm.$^{-1}$.

[8] T. Mariner and W. Bleakney, *Phys. Rev.*, **72**, 807 (1947). See also D. P. Stevenson, *Rad. Research*, **10**, 610 (1959).

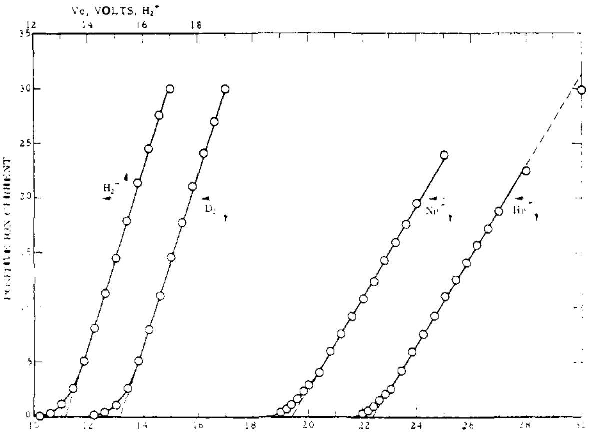

Fig. 3.—Typical ionization efficiency curves, initial portions of $M^+(V_c)$ for H_2^+, D_2^+, Ne^+ and He^+. The abscissa, V_c, is the cathode-ionization chamber potential difference in volts uncorrected for contact and ion drawn out field potentials. Westinghouse, Type LV, $\pi/2$-sector analyzer mass spectrometer. Ion peaks magnetically scanned with ion repeller potential +4.0 v., ion analyzer potential −2000 volts and ion chamber and ion collector at ground potential. Measurements were made on H_2–Ne and D_2–He mixtures.

deduced from the ionization efficiency curves by the initial break method by Bleakney[9] and Hagstrum and Tate[3] in which studies argon was employed to calibrate the ionizing electron energy scale. Furthermore, all the electron impact measurements of $A(H_2^+)$ and $A(D_2^+)$ agree within the experimental error with the accurately known $I^z_{0,0}$ = 15.427 or 15.457 ev., energy separation

TABLE I

AVERAGE APPEARANCE POTENTIALS OF H_2 AND D_2^+

Molecule	Ion	V^0c volts[a] June 58	Oct. 58	φ or A [c]	Remarks
Helium	He^+	22.1_8	22.3_3	2.3_2	$I^z = 24.58$[d]
Neon	Ne^+	19.0_7	19.3_7	2.3_7	$I^z = 21.59$[d,e]
Hydrogen	He^+		13.2_0	$15.5_4 \pm 0.1$	
Deuterium	D_2^+	13.1_2[b]	13.1_7	$15.4_9 \pm 0.1$	

[a] Extrapolated linear intercept of ionization efficiency curve on cathode potential (V_0) axis. Measurements with Westinghouse Type LV mass spectrometer, magnetic scan with ion repeller potential, + 4.0 volts and ion analyzing potential of −2000 volts. [b] Measurements with a C.E.C. 21–103 mass spectrometer at Brookhaven National Laboratory in July 1958 by Dr. L. Friedman and the present author gave $V^0_c(He^+) - V^0_c(D_2^+) = 9.0$ ev. in excellent agreement with results shown in this table. [c] φ = sum of contact and field potentials contributing to actual energy of ionizing electrons. This quantity taken equal to I^z (rare gas ion) − V^0_c (rare gas ion). [d] Atomic energy levels, N.B.S. Circular 467, Vol. I (1949). [e] For neon $I^z(^2P_{3/2}) = 21.559$, and $I^z(^2P_{1/2}) = 21.656$.

between $v = 0$ of H_2 (D_2) of $^1\Sigma_g$ and $v = 0$ of H_2^+ (D_2^+) in the $^2\Sigma_g$ state. There is clearly very much greater probability of the 0 → 0 transition than can be accounted for in terms of the overlap of the corresponding vibrational wave functions for $v = 0$ of H_2 and H_2^+.

Kinetic Energy Distribution of Protons and Deuterons.—From his measurement of the ionization efficiency curve for the ion H^+ of the hydrogen mass spectrum, Bleakney[1] was able to show that two different processes contribute to the formation of protons from hydrogen as a result of single electron impact ionization. From the magnitudes of the two appearance potentials that he found for H^+, Bleakney concluded that the proton giving rise to $A(H^+)$ = 18.0 ev. resulted from H_2^+ formed in the $^2\Sigma_g$ state above the dissociation limit, *i.e.*, H_2^+ in the $^2\Sigma_g$ state formed with internuclear separation less than 0.586 Å. (see Fig. 1). He further found that the protons giving rise to a second appearance potential of ~30 ev. were formed with considerable initial kinetic energy, and thus concluded these to be formed as a result of ionization of H_2 to the $^2\Sigma_u$ state of H_2^+.

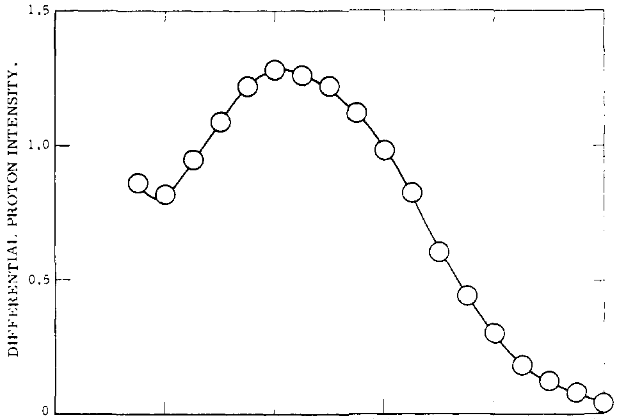

Fig. 4.—Distribution of protons in initial kinetic energy corresponding to excitation by 46.5 volt electrons. The differential proton intensity *vs.* proton kinetic energy curve shown in this figure was reconstructed from data given in Fig. 3 of Lozier.[10] The abscissa has been corrected (Lozier's eq. 5) for the effect of the electron beam collimating magnetic field on the proton kinetic energy.

Lozier[10] made a very careful study of the formation of ions with initial kinetic energies greater than 2 ev. as the result of single electron impact ionization in hydrogen. He reported the distribution in initial kinetic energy of the ions, most certainly protons, as a function of the energy of the ionizing electrons from 20 to 250 volts. There is shown as an example, in Fig. 4, the proton kinetic energy distribution found by Lozier for ionization by 46.5 volt electrons.

From observations on the ionization efficiency curves for protons with particular kinetic energies > ~ 5 ev. Lozier found a third appearance potential for H^+ at about 45 ev. that he assigned to excitations of H_2 to H_2^{++} as predicted by Condon and Smyth.[11] Because of the difficulty in separating the individual contributions of the two processes

$$H_2 \longrightarrow H_2^+(^2\Sigma_u) + e^- \longrightarrow H^+(K^0) + H(K^0) + e^-$$

$$H_2 \longrightarrow H_2^{++} + 2e^- \longrightarrow 2H^+(K^0) + 2e^-$$

to the kinetic energy distribution function of the protons, we will restrict our discussion of Lozier's

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(9) W. Bleakney, *Phys. Rev.*, **40**, 496 (1932). $A(H_2^+) = 15.4_6 \pm 0.03$ ev. after correcting the ionization potential of argon from 15.69 taken by Bleakney to the modern value 15.76 ev.

(10) W. W. Lozier, *Phys. Rev.*, **36**, 1285 (1930).

(11) E. U. Condon and H. D. Smyth, *Natl. Acad. Sci. U. S.*, **14**, 871 (1928).

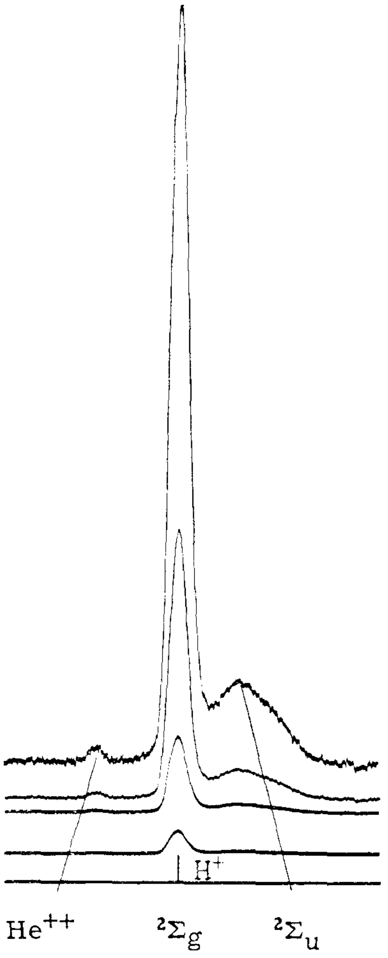

Fig. 5.—Mass "2" peaks of the mass spectrum of deuterium–helium mixtures excited by 100 volt ionizing electrons. C.E.C. 21-102 mass spectrometer, $D^+(K^0 \sim 0)$ V_a = 1020 volts. The linear separation of the He^{++} peak from the $D^+(K^0 \sim 0)$ peak along with the helium–deuterium mass defect, $m/q(D^+) - m/q(He^{++}) = 0.64_3 \times 10^{-3}$ a.w.u. and the ion analyzing potential serves to determine the equivalent kinetic energy dispersion on the chart paper by the relation $\Delta K^0/\Delta X = V_a \Delta M/M\Delta X$. The recorder paper is driven at constant speed and the analyzing accelerating potential driven in such a manner that $d \ln M/dt$ = constant.

observations to those made with ionizing electrons with energies $\leq A_3(H^+)$.

From the position of the maximum of $D(K^0)$, $K^0 = 5.8 \pm 0.3$ ev., of the kinetic energy (K^0) distribution function shown in Fig. 4, one concludes that the most probable excitation of H_2 to H_2^+ $^2\Sigma_u$ must take place to a point 11.6 ev. above the dissociation limit. Since the dissociation limit for both $^2\Sigma_g$ and $^2\Sigma_u$ of H_2^+ is at $E(r)$ = 18.34 ev., this point would be at $E(r)$ = 30.0 ev. on the diagrams shown in Figs. 1 and 2. $E(r)$ = 30.0 on the $^2\Sigma_u$ curve is at the extreme right hand edge of the classical Franck–Condon area of the H_2 diagram. The conventional application of the Franck–Condon principle would lead to the expectation that the most probable transition to $^2\Sigma_u$ would be at $E(r)$ = 34.5 ev.

Hagstrum and Tate[3] and Hagstrum[12] made independent investigations of the kinetic energy distribution of protons in the mass spectrum of hydrogen. In the first of these studies it was found that the m/q = 1 peak of the hydrogen mass spectrum shows a bimodal distribution in intensity. In this peak they found a sharp component centered at m/q = 1 and a broad component whose maximum was on the high "mass" side of m/q = 1, displaced a distance corresponding to 5.0 ± 0.5 ev. initial kinetic energy of the H$^+$'s. The second of these studies[12] consisted of a differential retarding potential analysis of the kinetic energy of protons reaching the ion collector of the mass spectrometer with results in exact agreement with the earlier work.[3]

We have examined the shape of the m/q = 2 peak of the deuterium mass spectrum with both $\pi/2$-sector analyzer and 180° deflection Dempster type mass spectrometers. A reproduction of a typical record so obtained is shown in Fig. 5. The distribution in kinetic energy of the deuterons produced from deuterium by ~100 volt ionizing electrons deduced from our mass spectrometric records lies between those for protons obtained by Hagstrum[3] by the mass spectrometric technique and Lozier[10] in his special instrument. Our value for the most probable K^0 of deuterons is 5.5 ± 0.5 ev., whereas for excitation by 100 volt electrons Lozier found 6.2 ± 0.5 ev. as the most probable proton energy.

The sign of the small discrepancy between the results of Lozier and those obtained by the mass spectrometric technique is that to be expected from the kinetic energy discrimination characteristic of mass spectrometer ion sources as has been discussed by Hagstrum and Tate.[3]

Discussion and Conclusions

In the preceding two sections of this paper, we have found that neither the average appearance potentials of H_2^+ and D_2^+ in the hydrogen and deuterium mass spectra, nor the most probable initial kinetic energy of protons and deuterons in these mass spectra are quantitatively in accord with expectations based on the conventional application of the Franck–Condon principle to the potential energy diagrams of hydrogen and its molecule-ion. The results of the two different experiments are in agreement in indicating that H_2^+ (or D_2^+) formed in either the bonding $^2\Sigma_g$ or antibonding $^2\Sigma_u$ states as the result of single impact with 15 to 100 volt electrons have as their most probable initial internuclear separation the distance $0.9_5 \pm 0.10$ Å. The conventional theory calls for this most probable distance to be about r_e = 0.74 Å. of the $^1\Sigma_g$ state of H_2 (or D_2).

In order to account for the experimental observations, it appears to be necessary to predicate the existence of virtual states of a transient complex, $[H_2^-]$ or $[D_2^-]$, with a distribution of lifetimes in the range 10^{-14} to 10^{-13} second, formed by the electron–molecule collisions. The magnitude of the required lifetimes of the complex are those necessary for the massive, slowly moving nuclei to

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(12) H. D. Hagstrum, *Rev. Mod. Phys.*, **23**, 185 (1951); compare Fig. 5 of this with Fig. 10 of ref. 3.

assume a new distribution in internuclear distance in the field of the three electrons.[13] In order to conserve momentum, it is not possible for the nuclei to increase their speed significantly as a result of the electron–molecule collision.

An alternate hypothesis that could be advanced to explain the experimental observations would be that there are large systematic errors in the calculated potential energy curves of both the $^2\Sigma_g$ and $^2\Sigma_u$ states of H_2^+. In view of the care that has been taken in solving the H_2^+ problem[6] and the excellent agreement between the results of different calculations, this does not appear to be a tenable hypothesis.

The results of experiments that are not in accord with accepted and seemingly well founded theory are always suspect. In the present case, however, we find concordance between the results of quite different experiments, *i.e.*, appearance potential measurements and kinetic energy distribution measurements, as well as good agreement between the work of different investigators with different types of apparatus, at various times over a period spanning thirty years. Thus we are strongly inclined to accept the experimental results and therewith the hypothesis of the existence of the transient complexes, $[H_2^-]$ and $[D_2^-]$, with lives that are comparable to those of the activated complexes of the bimolecular reactions of more conventional chemistry.

On the other hand, it should be noted that the relative intensities of protons, deuterons and tritons formed without kinetic energy in the mass spectra of hydrogen, deuterium and tritium, respectively, are very nicely accounted for by the assumption of the applicability of the Franck–Condon principle to transitions from the $^1\Sigma_g$ state of the hydrogens to the $^2\Sigma_g$ state of the molecule-ions.[2,14,15] In these cases the relative intensities of the H^+, D^+ and T^+ are essentially equal to the fractions of H_2, D_2 and T_2, respectively, that are calculated to have internuclear distances less than $r_c = 0.586$ A.U. by simple integration of the square of the ground state oscillator wave function from $r = 0$ to $r = r_c$.

Finally, it should be further noted that Condon[16] has indicated that there are theoretical reasons for expecting that the approximate rules he formulated in 1926 for the use of the principle can be expected to be not exactly quantitative and thus that the literal application of these rules can be expected in some cases to lead to apparent failure of the principle. Hence it may well be that the suggestion of a transient H_2^- is simply an admission that the present author is incapable of properly applying the Franck–Condon principle in its rigorous form to the problem at hand, *i.e.*, discussing in detail the electron impact induced transitions of H_2 from its $^1\Sigma_g$ state to the $^2\Sigma_g$ and $^2\Sigma_u$ states of H_2^+.

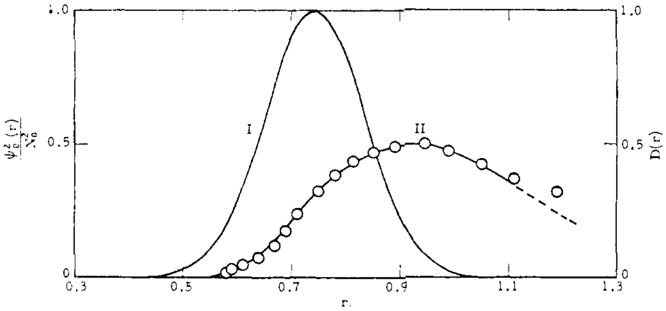

Fig. 6.—Internuclear distance distribution function for H_2(I) and the hypothetical $[H_2^-]$(II). For H_2, $N_0^{-2}\psi_0^2(r) = \exp[-61.6(r - 0.742)^2]$ and for $[H_2^-]$, D(r) was derived from D(K^0) of Fig. 4 and the $E(r)$ for $^2\Sigma_u$ of H_2^+. Areas under the two curves are approximately equal.

To the extent that we accept the existence of the hypothesized $[H_2^-]$ and $[D_2^-]$ complexes, it is of interest to compare the distribution in internuclear distances these complexes must have with those of H_2 and/or D_2 in their ground states. The internuclear distance distribution may be obtained by reversing the procedure previously employed by Hagstrum and Tate[3] in the prediction of kinetic energy distribution to be expected of fragment ions in mass spectra. The procedure consists of reflecting the distribution in kinetic energy shared by the proton–hydrogen atom pair from the potential energy curve onto the internuclear separation axis. This procedure, of course, only leads to information on those hypothetical complexes that form the antibonding $^2\Sigma_u$ state when they dissociate two electrons to form H_2^+.

Employing the data shown as Fig. 4 there was constructed the D(r) curve for the $[H_2^-]$ formed from H_2 and 46.5 volt electrons shown in Fig. 6. For comparison purposes there is again (from Fig. 3) shown $\psi_0^2(r)$ for $^1\Sigma_g$ of H_2.

NOTE ADDED IN PROOF.—Since this paper was accepted for publication, Marmet and Kerwin, *Canadian Journal of Physics*, 38, 972 (1960), have published the results of measurements of the initial portions of the H_2^+ ionization efficiency curve made with electrons they believe to have an energy spread of but 0.03 ev. They find the initial portions of the H_2^+ yield *vs.* electron energy curve so measured to be made up of linear segments 0.27 to 0.21 ev. in length, and they attribute the "breaks" to the appearance of progressively higher vibrationally excited states of H_2^+ since $\omega_e(H_2^+) = 2297$ cm.$^{-1} \cong 0.28$ ev. From the relative slopes of the successive linear segments they estimate the relative transition probabilities for the first four vibrational states of H_2^+ to be in the ratio 0.4:0.6:1.0:0.7, about what one would expect from the conventional application of the Franck–Condon Principle to the transition $H_2(^1\Sigma g)v'' = 0$ to $H_2^+(^2\Sigma g)v' = 0, 1, 2, 3$, respectively. These results of Marmet and Kerwin are not compatible with the interpretation given in the foregoing text of the measurements of the initial portions of the H_2^+ and D_2^+ ionization efficiency curves made with electrons with an energy spread of the order of 0.5 to 1.0 ev. If these results of Marmet and Kerwin are substantiated by further measurements in which the additive constant in energy scale of their electrons is established, it will indicate that there are hitherto unexpected difficulties in the interpretation of ionization efficiency curves measured with polyenergetic electrons and that the discussion of the $H_2(^1\Sigma g) \rightarrow H_2^+(^2\Sigma g)$ transition given in the text is *not* valid.

Acknowledgments.—The author takes great pleasure in acknowledging his indebtedness to Drs. W. Heller, J. D. Swalen and T. F. Schatzki for

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[13] The recent calculations of I. Fischer-Hjalmars, *Arkiv. för Fysik*, 16, 33 (1959), indicate the equilibrium internuclear distances in the low lying states of H_3^- to be in the range 0.8 to 1.0 A.

[14] D. P. Stevenson, *J. Chem. Phys.*, 15, 409 (1947).

[15] O. A. Schaeffer and J. M. Hastings, *ibid.*, 18, 1048 (1950).

[16] E. U. Condon, *Am. J. Phys.*, 15, 365 (1947).

stimulating discussions in connection with the preparation of this paper. Messrs. L. G. Coykendall and P. A. Wadsworth assisted materially with the experimental work herein reported.

CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, UNIVERSITY OF CHICAGO, CHICAGO 37, ILLINOIS]

Molecular Complexes and their Spectra. XII. Ultraviolet Absorption Spectra Caused by the Interaction of Oxygen with Organic Molecules[1]

BY H. TSUBOMURA[2] AND R. S. MULLIKEN

RECEIVED APRIL 8, 1960

D. F. Evans and others have found that extra absorption spectra appear when oxygen is dissolved in some organic solvents. In the present research, extra absorption spectra caused by oxygen have been measured by bubbling oxygen into ethyl alcohol, dioxane, *n*-butylamine, benzene, mesitylene, pyrrole, triethylamine, aniline, N,N-dimethylaniline, etc. It has been found that the smaller the ionization potential of the organic solvent molecule, the longer the wave length at which the oxygen-induced band lies. This and other experimental results seem to indicate that the extra absorption bands are caused by charge-transfer interaction between oxygen as an electron acceptor and the organic solvents as electron donors, although no stable complexes are formed between them. Wave functions for various excited states of the O_2-donor pair including the charge-transfer states have been set up and the matrix elements of the Hamiltonian between these states estimated. It is concluded that the charge-transfer interaction between oxygen and an organic donor molecule can indeed give rise to charge-transfer absorption, with an intensity which is enhanced by interaction between the charge-transfer state and a singlet excited state or states of the donor. It is found that the charge-transfer state can also interact with triplet excited states of the donor and thereby cause the observed enhancements by oxygen of the singlet-triplet absorption bands.

Introduction

Evans reported that oxygen dissolved in aromatic substances gives rise to absorption at wave lengths longer than for the aromatic compounds alone.[3a] Also Munck and Scott[4] found that saturated hydrocarbons and aliphatic alcohols and ethers show absorption in the near ultraviolet when oxygen is dissolved in them. They also reported that the absorption intensity in the case of cyclohexane is proportional to the partial pressure of oxygen in equilibrium with the solvent. Later, Evans[3b] remarked that the *maxima* which he obtained for the absorption of oxygen–aromatic compound systems might be due to instrumental error, although the existence of extra absorption at longer wave lengths was not in doubt. More recently, Evans[3c] measured the absorption spectra of aromatic compounds both in solution and in vapor with oxygen under high pressure dissolved in the solution or mixed with the vapor. He found additional small peaks at the long wave length tail of the diffuse and stronger absorption which he had observed before. He concluded that these weak bands are singlet-triplet absorption bands enhanced by oxygen. With regard to the stronger bands, he considered it more probable that they are due to charge-transfer absorption[5] caused by the interaction between oxygen and the aromatic compounds, with oxygen as an electron acceptor, rather than to transition from the ground to higher triplet states of the aromatic molecules.

Heidt and others[6] observed that oxygen dissolved in water showed absorption below 220 $m\mu$, which they explained as due to hydrogen bonding between oxygen and water. However, from the close similarity of the absorption of the oxygen–water system to the oxygen-donor systems just discussed, the reason for the appearance of absorption would seem to be the same in both cases.

In this paper, further experimental and theoretical work has been done on the effect of oxygen upon the electronic absorption spectra of various organic compounds.

Experimental

A Warren Spectracord was used for the measurements of the ultraviolet and visible absorption intensities. The substance to be studied (mostly organic pure liquid, sometimes solution in an organic solvent) was filled into a 1 cm. quartz cell with ground glass stopper, nitrogen was bubbled through for at least 1 minute, the stopper was immediately put in, a wax seal was applied and the absorption spectrum was recorded. Then oxygen was bubbled into the substance for at least 1 minute, the cell was sealed and the spectrum was again recorded. After that, nitrogen was bubbled again into the sample, and the absorption spectrum was once more recorded. For all substances except *n*-butylamine, the absorption spectra of the samples through which nitrogen was passed for the first and the second time agreed well with each other. This is evidence that the extra absorption bands found are not due to oxidation products. In the case of *n*-butylamine, a slight change was observed between the two spectra, indicating a slow irreversible reaction during the measurements.

Materials.—The oxygen used was the Extra Dry Grade of the Matheson Co., with minimum purity of 99.6%. The purification of iodine, *n*-heptane, N,N-dimethylaniline and its *o*- and *p*-methyl derivatives was the same as described elsewhere.[7] Ethyl alcohol was the pure absolute alcohol of the U. S. Industrial Chemicals Co., which seemed to contain about $2 \times 10^{-4}M$ of benzene as concluded from its ultraviolet absorption spectrum. This was used without further purification. Anilinium hydrochloride was prepared from purified aniline and hydrochloric acid. All other samples were Eastman organic chemicals. Aniline was dried with sodium hydroxide and distilled under reduced pressure with a column about one foot high. Mesitylene was distilled under reduced pressure with the same column. Dioxane, *n*-butylamine, pyridine and triethyl-

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