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On the Mass Spectra of Hydrogen and Deuterium

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On the basis of reasonable assumptions with regard to the probabilities of electron-impact induced transitions of hydrogen and deuterium, it is calculated that the relative intensity of H^+ in the mass spectrum of hydrogen should be 2.3 times greater than that of D^+ in the mass spectrum of deuterium for ionization by electrons of less than 35-volt energy. This value is compared with experimental values 2.8 (22-v energy), 1.5 (30-v energy), 1.9 (50-v energy), and 2.2 (100-v energy).

SOME years ago it was predicted and experimentally verified¹ that the relative intensity of H^+ in the mass spectrum of hydrogen is greater than that of D^+ in the mass spectrum of deuterium. It is the object of this note to show that a relatively simple calculation leads to a quantitative prediction of this phenomenon in agreement with experiment.

When hydrogen or deuterium is exposed to the ionizing action of electrons, as in the ionization chamber of a mass spectrometer, several processes may occur. If the energy of the electrons is less than 15.4 volts, no positive ions are formed. For electrons with energies between 15.4 and 18.0 volts only molecular ions in the stable, symmetric, $^2\Sigma_g^+$ state are formed. If the energy of the electrons is greater than 18.0 volts, the molecular ions may be formed in the $^2\Sigma_g^+$ state, but above the dissociation limit of this state, so that the molecular ions immediately dissociate into an atomic ion and a free atom. For electronic energies greater than 27 volts, excitation to the repulsive, antisymmetric, $^2\Sigma_u^+$ state of the molecular ion is possible, and these molecular ions immediately dissociate into an atomic ion and a free atom. As the energy of the ionizing electrons is further increased, other excited states of the molecular ion become accessible, and since these states are repulsive they lead to the formation of atomic ions and excited free atoms. The relative probability of each of these processes becomes essentially independent of the energy of ionizing electrons when the energy of the electrons is from 25 to 50 percent greater than the minimum energy required for the process.²

Inasmuch as the electronic wave functions of hydrogen and deuterium are identical to all approximations ordinarily considered, the electronic factors of the transition probabilities of hydrogen and deuterium from a given initial to a given final state will be identical for electrons of such sufficient energy that the transition probability is essentially independent of the electron energy. For ionizing electrons of only slightly more than the minimum energy, the transition probability of hydrogen will be greater than that of deuterium, since the difference in the zero point energy of hydrogen and deuterium (0.07 ev) causes the minimum energy for transitions of hydrogen to be less than the minimum energy of the corresponding transitions of deuterium.

As was stated by Bleakney, Condon, and Smith,¹ the condition for transitions to the $^2\Sigma_g^+$ state of the molecular ions above the dissociation limit is that the interatomic distance in the molecule at the instant of ionization be less than a critical value, say r_c . The value of r_c is determined by the interatomic distance in the $^2\Sigma_g^+$ state of the molecular ion at which the energy of the molecular ion equals the dissociation energy of the molecular ion. This condition follows from the equal applicability of the Franck-Condon principle to electron-impact and optically induced transitions.¹ Thus the transition probabilities to the $^2\Sigma_g^+$ state contain a factor dependent on the electronic wave functions of molecule and molecular ion. The factors dependent on the vibrational wave function amount to nothing more than the fraction of the molecules with interatomic distances less than r_c for transitions above the dissociation limit of $^2\Sigma_g^+$, and the fraction of molecules with interatomic distances greater than r_c for transitions to the

¹ Bleakney, Condon, and Smith, *J. Phys. Chem.* **41**, 197 (1937).

² W. Bleakney, *Phys. Rev.* **35**, 1180 (1930).

TABLE I. The fraction of hydrogen and deuterium molecules with interatomic distances $\leq 0.586\text{\AA}$ and $\geq 0.586\text{\AA}$, ground vibrational state of $^2\Sigma^+_g$.

	Harmonic oscillator	Anharmonic oscillator ³
$f_H(<r_e)$	0.0429	0.0187
$f_H(<r_e)$	0.9561	0.9813
$f_D(<r_e)$	0.0193	0.0083
$f_D(>r_e)$	0.9807	0.9917
F_H/F_D ¹	2.28 ± 0.2 ²	2.29 ± 0.2 ²

¹ $F_H/F_D = [f_H(<r_e)/f_H(>r_e)]/[f_D(<r_e)/f_D(>r_e)]$.

² This uncertainty is that corresponding to the uncertainty in r_e , $\pm 0.01\text{\AA}$.

³ The Tables of incomplete gamma functions, by K. Pearson, were used to evaluate the integrals.

stable levels of $^2\Sigma^+_g$. These fractions of molecules will be designated $f(<r_e)$ and $f(>r_e)$, respectively.

If the effect of the small differences in zero point energy is neglected, and the electronic transition probabilities for transitions from the ground state of hydrogen and deuterium to the $^2\Sigma^+_g$, $^2\Sigma^+_u$, etc., states of their molecular ions are designated by $T(^2\Sigma^+_g)$, $T(^2\Sigma^+_u)$, etc., the number of atomic ions observed in the mass spectra of hydrogen and deuterium will be

$$n(a^+) = bf(<r_e)T(^2\Sigma^+_g) + bT(^2\Sigma^+_u) + \dots, \quad (1)$$

and the number of molecular ions will be

$$n(n^+) = bf(>r_e)T(^2\Sigma^+_g), \quad (2)$$

where b is a constant of proportionality.

The fractions, f , are given by

$$f(<r_e) = \int_0^{r_e} \psi_0^2(r) dr \quad (3a)$$

and

$$f(>r_e) = \int_{r_e}^{\infty} \psi_0^2(r) dr = 1 - f(<r_e), \quad (3b)$$

where $\psi_0^2(r)$ is the normalized, vibrational wave function for the ground vibrational level of hydrogen or deuterium. Only the ground level need be considered because the magnitudes of the fundamental frequencies of hydrogen and deuterium are so great that a negligible fraction of the molecules are vibrationally excited at the highest temperatures encountered in mass spectrometers (250–300°C).

Although the T 's may be taken equal for transitions of hydrogen and deuterium, the f 's of hydrogen and deuterium are different because the values of the integrals are dependent on the

numerical parameters of $\psi_0^2(r)$, and the numerical parameters are different for hydrogen and deuterium. Two approximations to the vibrational wave function, $\psi_0^2(r)$, were considered in evaluating the f 's for hydrogen and deuterium. These approximations were the solutions of the radial wave equation,³ neglecting the rotational term, for the harmonic oscillator and the Morse function approximation to the potential function. For the vibrational ground state these solutions are

$$\psi_0(r) = N_0 \exp[-\alpha(r-r_e)^2], \quad (4a)$$

$$\psi_0(r) = A_0 \exp[-\epsilon \exp\{-a(r-r_e)\}] \cdot \exp[-a(\epsilon - \frac{1}{2})(r-r_e)], \quad (4b)$$

where N_0 and A_0 are normalization constants, $\alpha = 4\pi^2\mu c\omega_e/h$, $\epsilon = D_e/hc\omega_e$, $a = 2\pi^2\mu c\omega_e^2/D_e$, and the other symbols have their usual significance.⁴ The numerical values of the various parameters were taken from the compilation by Herzberg.⁴

The value of r_e used was $0.586 \pm 0.01\text{\AA}$. This value was obtained by interpolation from the quantal calculations of Hylleraas.^{5,5} The values of the f 's are given in Table I.

The ratio of the relative abundances of H^+ and D^+ in the mass spectra of hydrogen and deuterium is

$$\frac{[n(H^+)/n(H_2^+)][n(D^+)/n(D_2^+)]}{F_H + [1/f_H(>r_e)][T(^2\Sigma^+_u)/T(^2\Sigma^+_g)] + \dots} = \frac{F_D + [1/f_D(>r_e)][T(^2\Sigma^+_u)/T(^2\Sigma^+_g)] + \dots}{F_H + [1/f_H(>r_e)][T(^2\Sigma^+_u)/T(^2\Sigma^+_g)] + \dots}, \quad (5)$$

and F_H and F_D are defined in the notes to Table I. It is known that for electrons of less than 30 to 35-volts energy $T(^2\Sigma^+_u)/T(^2\Sigma^+_g) \ll F_H$.² Thus for such electrons the ratio of the relative abundances of H^+ and D^+ in the mass spectra of hydrogen and deuterium should be equal to $F_H/F_D = 2.3 \pm 0.2$.

Two experimental investigations have been made of the ratio of the relative intensities of H^+ and D^+ . The first of these¹ leads to 2.8 for 22-volt ionizing electrons. The second⁶ gives 1.5 ± 0.2 , 1.9 ± 0.2 , and 2.2 ± 0.2 for 30, 50, and 100-volt

³ Pauling and Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), pp. 264–266.

⁴ Herzberg, *Molecular Spectra and Molecular Structure, I.* (Prentice-Hall, Inc., New York, 1939).

⁵ Hylleraas, *Zeits. f. Physik* **71**, 739 (1931).

⁶ Bauer and Beach, *J. Chem. Phys.* **15**, 150 (1947).

electrons, respectively. The calculated value, 2.3 ± 0.2 , is in satisfactory agreement with these experimental values.

It was remarked above that the higher zero point energy of hydrogen than of deuterium results in a lower appearance potential of H^+ in the mass spectrum of hydrogen than of D^+ in deuterium. Thus, as the energy of the ionizing electrons is lowered and it approaches 18 volts, the assumption of equality of $T(^2\Sigma^+_g)$ for hydrogen and deuterium fails. With decreasing electron energy, $T(^2\Sigma^+_g)$ of hydrogen becomes greater than $T(^2\Sigma^+_g)$ of deuterium and

$$[n(H^+)/n(H_2^+)]/[n(D^+)/n(D_2^+)]$$

should be greater than F_H/F_D in proportion.

For ionization by electrons of more than 50-volt energy, the probability of transitions to the repulsive state, $T(^2\Sigma^+_u)$, becomes very much greater than the probability of transition to the repulsive portion of the stable state, $f(<r_c)T(^2\Sigma^+_g)$.⁷ There are, however, two related reasons why the mass spectrometrically observed value of the ratio of the relative abundances of H^+ and D^+ will not approach unity as rapidly as might be expected from Eq. (5) and the data of Bleakney^{2,7} when the ionizing electron energy is increased. The atomic ions formed as a result of transitions to the $^2\Sigma^+_u$ state are formed with a large amount of kinetic energy. This results in an increase in the breadth of the corresponding mass spectral peaks and failure of the assumption usually made, namely, that peak height is proportional to total ion intensity. Thus using the peak height as a measure of the ion current, as is commonly done, results in underestimation of the current caused by ions with extra kinetic energy. Furthermore, the construction of ionization chambers of mass spectrometers is such that there is a disproportionate loss of ions formed with kinetic energy.⁸ This too results in the underestimation of the number of atomic ions. Of these two factors the selective loss of ions with extra kinetic energy is probably the more important in the case of the measurements of Bauer and Beach.⁶ Examination of their mass

spectra reveals asymmetry of the H^+ and D^+ peaks such as would result from contributions of fast atomic ions.

The magnitude of

$$[n(H^+)/n(H_2^+)]/[n(D^+)/n(D_2^+)]$$

is found by Bauer and Beach⁶ to increase with electron energy, rather than decrease as predicted by our theory. The failure of their mass spectrometer to record H^+ and D^+ ions with excess kinetic energy accounts for the failure of the ratio of relative intensities to decrease with increasing electron energy. That the observed ratio of relative intensities increases with electron energy, the experimental value approaching equality with the calculated value for ionization by 100-volt electrons, may be taken as indication that the assumption of equality of $T(^2\Sigma^+_g)$ for hydrogen and deuterium is not accurately valid for electrons with energies between 30 and 50 volts.

According to the assumptions that have been made, F_H and F_D should be approximately equal to the relative abundances of H^+ and D^+ in the mass spectra of hydrogen and deuterium, respectively, for ionization by electrons of less than 30 to 35-volt energy. Although the ratio of F_H/F_D is independent of the approximation to the vibrational wave function used to evaluate the integrals of Eqs. (3a) and (3b), the values of F_H and F_D are very sensitive to the nature of the wave function. Thus it is not surprising that $F_H=0.019$ and $F_D=0.008$ (anharmonic oscillator, Table I) are not in good agreement with the experimental values

$$H^+/H_2^+=0.0096, \quad D^+/D_2^+=0.0034$$

for 22-volt electrons,¹ and

$$H^+/H_2^+=0.0058, \quad D^+/D_2^+=0.038$$

for 30-volt electrons.⁶ As would be expected, the anharmonic oscillator approximation to the vibrational wave function leads to better values of F_H and F_D than does the harmonic oscillator approximation.

In conclusion, the author would like to acknowledge his indebtedness to Dr. J. Y. Beach for communicating his most recent experimental results and to Dr. E. U. Condon with whom these questions were discussed during the winter of 1940-1941.

⁷ See Fig. 5 of reference 2. Approximate values of the ratio $T(^2\Sigma^+_u)/f(<r_c)T(^2\Sigma^+_g)$ for 50-, 100-, and >150-volt electrons, estimated from the curves referred to, are 3, 6, and 7, respectively, for hydrogen.

⁸ This has been discussed by Bleakney, reference 2.