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Mobility of Hydrogen Ions (H^+,H_2^+,H_3^+) in Hydrogen*

EDWARD A. MASON AND JOSEPH T. VANDERSLICE
Institute for Molecular Physics, University of Maryland, College Park, Maryland

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Force laws for H^+, H_2^+, and H_3^+ in H_2 are calculated from theory and from results on the scattering of low-velocity ion beams in H_2 gas. These results are then used to calculate the mobilities of the hydrogen ions in H_2 gas as a function of temperature. The mobilities of H^+ and H_2^+ decrease slightly with increasing temperature, but the mobility of H_3^+ increases strongly. The agreement with experiment indicates that the unidentified hydrogen ion whose mobility has been measured is probably H_2^+, rather than the usually assumed H_3^+.

INTRODUCTION

A QUANTITY of fundamental importance in phenomena involving ionized gases is ion mobility, and a number of measurements of ion mobility are available.[1,2] Unfortunately, in many cases no positive experimental identification of the ion studied has been made, nor the temperature dependence of the mobility measured. Theoretical calculations of ion mobilities are therefore of interest both to aid in ion identification and to indicate temperature dependence. The present paper reports calculations for the hydrogen ions, H^+, H_2^+, and H_3^+, in H_2 gas. The starting point for such calculations is the ion-molecule force law. In the present cases the long-range ion-molecule forces (polarization and dispersion forces) are easily obtained theoretically.[3] The more difficult short-range (exchange) forces are obtained from analysis of direct scattering measurements on low-velocity ion beams.[4,5]

The physical factors influencing the mobility are quite different in the three cases, except around $T=0°K$, where the long-range (r^{-4}) attractive polarization force is always the dominant effect. For H_3^+ in H_2, the short-range forces are repulsive, and at finite temperatures tend to "cancel" the attractive long-range forces, with the result that the mobility increases with increasing temperature. For H_2^+ in H_2, the short-range forces are essentially determined by the possibility of resonant charge exchange between H_2^+ and H_2. This charge-exchange effect tends to "reinforce" the long-range forces, and the mobility decreases with increasing temperature. For H^+ in H_2, the short-range forces are strongly attractive chemical valence forces. These also "reinforce" the long-range forces, and the mobility decreases with increasing temperature. It thus appears that the hydrogen ion whose mobility has been measured is probably H_2^+, rather than H_3^+ as has usually been assumed.[6,7]

H_3^+ IN H_2

We consider first the H_3^+ ion, since the force law for this ion is the simplest of the three cases, being a simple repulsion at small separations and the usual polarization plus dispersion at large separations. The longest range force, which determines the limiting value of the mobility at low temperatures, is the charge-induced dipole force. The potential energy function for this force is[3]

$$\varphi(r) = -\bar{\alpha}e^2/2r^4, \tag{1}$$

where $\bar{\alpha}$ is the average polarizability of the H_2 molecule, e is the electronic charge, and r is the ion-molecule separation distance. The value of $\bar{\alpha}$ can be calculated from the equation

$$\bar{\alpha} = g_{\parallel}\alpha_{\parallel} + g_{\perp}\alpha_{\perp}, \tag{2}$$

where $\alpha_{\parallel}$ is the polarizability parallel to the H_2 internuclear axis ($\alpha_{\parallel}=0.934$ A^3),[8] $\alpha_{\perp}$ the polarizability perpendicular to the axis ($\alpha_{\perp}=0.718$ A^3),[8] and $g_{\parallel}$ and $g_{\perp}$ are weight factors. If all molecular orientations have equal weight, then $g_{\parallel}$ is $\frac{1}{3}$ and $g_{\perp}$ is $\frac{2}{3}$, so that $\bar{\alpha}$ is 0.790 A^3. This value is probably somewhat too small, since the orientations with large polarizability should be favored energetically.

The next longest range energy varies as r^{-6}, and is quite small. It is made up of two terms,[3]

$$\varphi(r) = -B_1/r^6 - B_2/r^6, \tag{3}$$

where B_1 is the charge-induced quadrupole contribution, and B_2 is the London dispersion contribution. An approximate formula for B_1 has been given by Margenau,[3]

$$B_1 = \tfrac{3}{4}\bar{\alpha}^2 I/f, \tag{4}$$

where I is the ionization potential and f the oscillator strength of the gas molecule. For H_2, $B_1=4.78$ ev-A^6. The value of B_2 can be calculated from the approximate formula[3,9]

$$B_2 = \tfrac{3}{2}\bar{\alpha}\bar{\alpha}'II'/(I+I'), \tag{5}$$

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* This research was supported in part by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command.

[1] A. M. Tyndall, *The Mobility of Positive Ions in Gases* (Cambridge University Press, London and New York, 1938).

[2] L. B. Loeb, *Basic Processes of Gaseous Electronics* (University of California Press, Berkeley and Los Angeles, 1955), Chap. 1.

[3] H. Margenau, Phil. Sci. **8**, 603 (1941).

[4] Simons, Fontana, Muschlitz, and Jackson, J. Chem. Phys. **11**, 307 (1943).

[5] Simons, Fontana, Francis, and Unger, J. Chem. Phys. **11**, 312 (1943).

[6] Reference 2, pp. 75, 85, 92, 915.

[7] A. Dalgarno, Trans. Roy. Soc. (London) **A250**, 426 (1958).

[8] H. Volkmann, Ann. Physik **24**, 457 (1935).

[9] H. Margenau, Revs. Modern Phys. **11**, 1 (1939).

where the primed quantities refer to the ion and the unprimed to the molecule. The values of $\bar{\alpha}'$ and I' are not known for H_3^+, but perhaps are not too different from those for H_2. As a rough estimate, then, $B_2=7.12$ ev-A^6.[9]

The short-range potential energy is extremely difficult to calculate theoretically, even for very simple monatomic ions and molecules. The case of $H_3^+-H_2$ is quite complex, and even enormous computational efforts would lead to results of very doubtful accuracy, so that another approach is necessary. The short-range energy can be obtained from direct measurements of the elastic scattering of H_3^+ ion beams in H_2 gas under conditions such that the long-range attraction energy, given by Eqs. (1) and (3), is dominated by the short-range repulsion. Such measurements have been made some time ago by Simons, Fontana, Muschlitz, and Jackson,[4] and recent theoretical work[10] has shown how these measurements can be interpreted to give reliable estimates of the short-range energy of interaction (averaged over all orientations). For ion beam energies in the range 1.90 to 28.0 ev, the average elastic scattering cross sections can be represented by the formula

$$(\bar{S})^{\frac{1}{2}}=-1.512\log_{10}W+4.819, \qquad (6)$$

where $\bar{S}$ is in A^2 and W is the ion beam energy in ev. The parameters of an exponential repulsion energy can be derived from the constants of such an equation,[10] so that the short-range energy for $H_3^+-H_2$ is found to be

$$\varphi(r)=99.8e^{-r/0.376}\text{ ev}, \qquad (7)$$

where r is in A. This expression actually represents the total energy, and so includes some contribution from the polarization and dispersion energies. A previously discussed correction[10] for the finite width of the ion beam has been included in the calculation of Eq. (7) from Eq. (6).

The energy of interaction between H_3^+ and H_2 can thus be represented as the sum of Eqs. (1), (3), and (7),

$$\varphi(r)=[99.8\exp(-r/0.376)-(5.69/r^4)-(11.9/r^6)]\text{ ev}, \qquad (8)$$

where r is in A. This expression probably overestimates the attraction, since the exponential repulsion term already includes some contribution from the attraction energy. The complete calculation of the ion mobility as a function of temperature for an interaction energy like (8) is a formidable numerical task,[11–13] and some approximations are therefore in order. It happens for $H_3^+-H_2$ that the attraction energy is sufficiently large that at ordinary temperatures the mobility is primarily determined by the attraction and only moderately affected by the repulsion. The exponential repulsion term can thus be replaced by an empirical inverse power repulsion term, so as to be able to use tabulated cross sections. Tabulations are available[11,13] for interaction energies of the following forms:

$$\varphi(r)=\epsilon[(r_m/r)^8-2(r_m/r)^4], \qquad (9)$$

$$\varphi(r)=\tfrac{1}{2}\epsilon[(1+\gamma)(r_m/r)^{12}-3(1-\gamma)(r_m/r)^4-4\gamma(r_m/r)^6], \qquad (10)$$

where ϵ is the depth of the energy minimum, r_m is the value of r at which the minimum occurs, and γ is a dimensionless parameter which measures the relative importance of the r^{-6} term. Equation (8) was adjusted to the form of Eqs. (9) and (10) by omitting the r^{-6} term, which has a relatively small effect on the mobility, and requiring that the value of r_m and the coefficient of the r^{-4} term be correct. This procedure assures the correct mobility at low temperatures, but involves some error at high temperatures. The effect of the small r^{-6} term can be included at the end as a perturbation, as explained later. For $H_3^+-H_2$, a much better empirical fit is obtained with Eq. (9) than with Eq. (10). The parameters are $r_m=2.97$ A and $\epsilon=0.0366$ ev, which give the correct r^{-4} energy, the correct position of the minimum, and the depth of the minimum to an accuracy of 1.4%.

The mobility in cm^2-volt^{-1}-sec^{-1} referred to standard gas density at 0°C and 1 atmos (2.69×10^{19} molecules/cm^3) can be written as follows[13]:

$$K_0=\frac{1.851\times10^4}{T^{\frac{1}{2}}}\left(\frac{m+M}{mM}\right)^{\frac{1}{2}}\frac{g_0}{\bar{\Omega}^{(1,1)}}, \qquad (11)$$

where K_0 is the mobility, T the absolute temperature, m the molecular weight of an ion, M the molecular weight of a gas molecule, and $\bar{\Omega}^{(1,1)}$ is an effective average cross section ("collision integral") for diffusion in units of A^2. The collision integral $\bar{\Omega}^{(1,1)}$ depends on the temperature and the intermolecular potential. The quantity g_0 is a dimensionless correction factor which includes the higher approximations of kinetic theory, and is equal to unity within the present computational accuracy.[13] For the potential function of Eq. (9), the collision integral for diffusion has been given as[11]

$$\bar{\Omega}^{(1,1)}=2\pi r_m{}^2 s^{-\frac{1}{2}}I(s), \qquad (12)$$

where r_m is the parameter of Eq. (9) and $I(s)$ is a tabulated dimensionless function of $s=\frac{1}{2}(kT/\epsilon)^{\frac{1}{2}}$, k being Boltzmann's constant. For the potential function of Eq. (10), the collision integral has been given as[13]

$$\bar{\Omega}^{(1,1)}=\pi r_m{}^2\Omega^{(1,1)*}, \qquad (13)$$

where r_m is the parameter of Eq. (10), and $\Omega^{(1,1)*}$ is a tabulated dimensionless function of the parameter γ, and of the dimensionless temperature, $T^*=kT/\epsilon$.

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[10] E. A. Mason and J. T. Vanderslice, J. Chem. Phys. **27**, 917 (1957); **28**, 253 (1958).

[11] H. R. Hassé and W. R. Cook, Phil. Mag. **12**, 554 (1931).

[12] Dalgarno, McDowell, and Williams, Trans. Roy. Soc. (London) **A250**, 411 (1958).

[13] E. A. Mason and H. W. Schamp, Jr., Ann. Phys. N. Y. 4, 233 (1958).

The effect of the r^{-6} energy term on the mobility can be easily calculated to a first approximation from the accurately tabulated variation of $\Omega^{(1,1)*}$ with γ for the potential of Eq. (10). The value of γ is first calculated from the relation

$$\frac{\gamma}{1-\gamma}=\frac{3}{4r_m^2}\frac{B}{C}. \tag{14}$$

where $B=B_1+B_2$ is the coefficient of the r^{-6} term and $C=\frac{1}{2}\bar{\alpha}e^2$ is the coefficient of the r^{-4} term. The correction factor for the mobility is then

$$\left[\frac{\Omega^{(1,1)*}(\gamma=0)}{\Omega^{(1,1)*}(\gamma)}\right](1-\gamma)^{\frac{1}{2}}, \tag{15}$$

which is unity at $T=0$°K and less than unity at higher temperatures. A very simple approximation of Eq. (15) has been suggested by Dalgarno, McDowell, and Williams,[12] who base their argument on the cross section for orbiting collisions ("capture cross section"). We have found by empirical comparison with Eq. (15) that their result is improved by the simple replacement of the relative kinetic energy of translation with kT, so that their correction factor for the mobility becomes

$$[1+\tfrac{1}{2}(B/C)(kT/C)^{\frac{1}{2}}]^{-1}. \tag{16}$$

This approximate expression agrees with the more accurate Eq. (15) within 0.5% up to at least $T^*=1$.

The mobility of H_3^+ in H_2 up to 500°K is given in Table I, corrected for the effect of the r^{-6} energy (the maximum correction is 9% at 500°K). The increase of mobility with increasing temperature is typical of interaction energies involving only a simple repulsion at small separations.[13] Correction of the mobility for the probable overestimation of the attraction energy in Eq. (8) would cause the mobility to increase with temperature even more rapidly. The magnitude of the increase in mobility depends rather strongly on the power of the empirical repulsion term. That is, Eq. (10) with a twelfth power yields a substantially smaller increase than Eq. (9) with an eighth power, and a rigid-sphere repulsion yields an even smaller increase.[13] There is thus some reason to suspect that the magnitude of the increase given in Table I might be too large. It must be noted, however, that both Eq. (10) and the rigid-sphere model represent the energy of interaction as given by Eq. (8) much more poorly than does Eq. (9).

TABLE I. Calculated mobilities at standard gas density (0°C, 1 atmos).

T (°K)	K_0 (cm² volt⁻¹ sec⁻¹) H_3^+ in H_2	H_2^+ in H_2	H^+ in H_2
0	14.2	15.6	19.3
50	15.1	14.8	19.0
100	16.2	14.6	18.8
150	17.9	14.4	18.7
200	19.5	14.2	18.6
300	22.0	13.9	18.3
400	23.4	13.6	18.0
500	24.4	13.3	17.8

H_2^+ IN H_2

The short-range forces for H_2^+ in H_2 are more complicated than those for H_3^+ in H_2 because of the possibility of resonant charge exchange.[14] Although the internuclear distances in H_2^+ and H_2 are different, the average duration of a collision at ordinary temperature is considerably longer than the time of a molecular vibration, so that there is time for the adjustment of the internuclear separations during a collision. Thus at ordinary temperatures the behavior of $H_2^+-H_2$ should be quite similar to that of He^+-He, which is well understood.[7,14–16] The charge exchange effect complicates the force laws, but fortunately it also permits the force laws as such to be by-passed by relating the mobility to the cross section for charge exchange,[7,15–18] which can be measured independently. Simons, Fontana, Francis, and Unger[5] have used an ion-beam technique to measure the charge-exchange cross section, Q_{ex}, for $H_2^+-H_2$ at low ion-beam energies, and their results can be used to help predict the mobility of H_2^+ in H_2.

At high temperatures the charge exchange effect is completely dominant, and the cross section for diffusion is just $2Q_{ex}$,[7,18] so that the high-temperature limit of the collision integral is[13]

$$\bar{\Omega}_\infty^{(1,1)}=(kT)^{-3}\int_0^\infty Q_{ex}E^2e^{-E/kT}dE, \tag{17}$$

where E is the energy of relative motion of ion and molecule. It has been deduced theoretically[7,18,19] that $(Q_{ex})^{\frac{1}{2}}$ varies linearly with the logarithm of the relative velocity (or energy). To carry out the integration in Eq. (17), the experimental[5] values of Q_{ex} were therefore fitted by the equation

$$Q_{ex}(\mathrm{A}^2)=[3.466-0.2443\ \ln E(\mathrm{ev})]^2, \tag{18}$$

which leads to the following expression for the high-temperature collision integral:

$$\bar{\Omega}_\infty^{(1,1)}(\mathrm{A}^2)=61.15-12.44\ \log_{10}T+0.633(\log_{10}T)^2. \tag{19}$$

In this calculation, integrals of the form $\int_0^\infty x^2e^{-x}(\ln x)^n dx$

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[14] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, London, 1952), pp. 410–411.

[15] N. Lynn and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **A70**, 474 (1957).

[16] L. M. Chanin and M. A. Biondi, Phys. Rev. **106**, 473 (1957).

[17] T. Holstein, J. Phys. Chem. **56**, 832 (1952).

[18] A. Dalgarno and M. R. C. McDowell, Proc. Phys. Soc. (London) **A69**, 615 (1956).

[19] E. A. Mason and J. T. Vanderslice, J. Chem. Phys. **29**, 361 (1958).

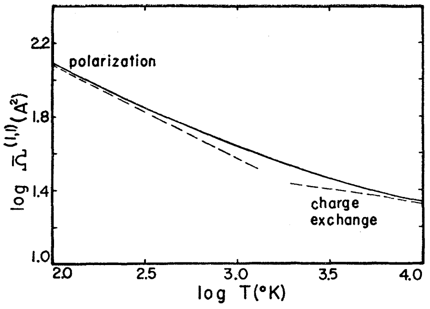

FIG. 1. Calculated collision integral (average diffusion cross section) for H_2^+ in H_2 as a function of temperature, showing the polarization and the charge exchange limits.

occur, for which a simple method of evaluation is given in the Appendix.

At low temperatures the dominant effect is just the long-range r^{-4} energy, for which the collision integral is[13]

$$\bar{\Omega}_0^{(1,1)}(\mathrm{A}^2)=1186/T^{\frac{1}{2}}. \qquad (20)$$

At intermediate temperatures the correct value of $\bar{\Omega}^{(1,1)}$ is slightly higher than either (19) or (20).[7,16] A very simple and reasonably accurate way of bridging the intermediate temperature range is by graphical interpolation on logarithmic scales, as has been done in the present case. Alternatively, semiempirical analytical schemes are available.[7,16,17]

The collision integral $\bar{\Omega}^{(1,1)}$ so obtained is shown in Fig. 1 as a function of temperature (uncorrected for the r^{-6} energy). It is interesting that the temperature must be about 1000°K before charge exchange has much effect, whereas for the lighter rare gases the effect sets in around room temperature or below.[16] The reason for this behavior is that Q_{ex} for $H_2^+-H_2$ is unexpectedly small for a case of exact resonance. Gurnee and Magee[20] have explained this smallness of Q_{ex} on the basis of low overlap between the wave functions describing the internal vibrational motion of the nuclei, which in turn results primarily from the different internuclear distances in H_2^+ and H_2.

The effect of the r^{-6} energy on the mobility is easily obtained from the approximate formula (16), which has already been shown to have good accuracy. The values of the polarization energy coefficients C and B_1 are the same as for $H_3^+-H_2$, but the dispersion energy coefficient B_2 is somewhat different. Substitution of $I'=16.4$ ev and $\bar{\alpha}'=0.42$ A^3 (obtained from Hirschfelder[21]) in Eq. (5) yields $B_2=3.83$ ev A^6. The final values of the mobility calculated up to 500°K are given in Table I. The maximum correction for the r^{-6} energy is slightly less than 7%. The decrease of mobility with increasing temperature is typical of cases involving charge exchange.

H^+ IN H_2

The general nature of the interaction energy between H^+ and H_2 is well understood from an extensive series of quantum-mechanical calculations.[22] However, for computation of the mobility of H^+ in H_2, these calculations are somewhat scanty and of necessity involve rather drastic approximations. It is therefore better for the present purpose to rely as much as possible on direct measurements for detailed information on the short-range energy, and to use the quantum-mechanical calculations only to indicate the form of the potential energy function. The measurements available are those of Simons, Fontana, Muschlitz, and Jackson[4] on the elastic scattering of beams of low-energy protons in H_2 gas.

The short-range force between H^+ and H_2 is one of strong valence attraction to form the stable species H_3^+. The maximum binding energy of a proton to H_2 is about 3 ev for the most favorable orientation (equilateral triangle), and somewhat less for the least favorable orientation (linear).[22] The equilibrium separation between the proton and the center of the molecule is about 1.5 A for all orientations.[22] These results suggest that a suitable empirical representation of the energy of interaction between H^+ and H_2 averaged over all orientations would be a Morse function,

$$\varphi(r)=D_e\{\exp[2\alpha(1-r/r_e)]-2\exp[\alpha(1-r/r_e)]\}, \qquad (21)$$

where D_e is the dissociation energy, r_e the equilibrium separation, and α is a dimensionless third parameter. The calculation of the corresponding elastic scattering cross sections for the type of apparatus geometry used by Simons *et al.* involves considerable numerical work, but has been carried through and tabulated.[19] Comparison of tabulated and measured cross sections thus permits, in principle, the determination of the three parameters of the Morse function. In practice, it turns out that as many as three parameters cannot be determined uniquely from the measurements. This difficulty can be overcome by a limited use of the quantum-mechanical calculations.[22] Most molecular quantum-mechanical calculations appear to give fairly accurate values for equilibrium separations, although calculated binding energies are often substantially in error since they are calculated as a small difference between two large numbers. We therefore take $r_e=1.5$ A from the calculations, and the scattering cross sections then determine the other two parameters as $\alpha=3$, $D_e=2.7$ ev. It is of interest that this value of D_e is also consistent with the quantum-mechanical calculations.

Calculated and measured values of the average elastic scattering cross section, $\bar{S}$, are compared in Fig. 2 as a function of the ion beam energy, W. The

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[20] E. F. Gurnee and J. L. Magee, J. Chem. Phys. **26**, 1237 (1957).

[21] J. O. Hirschfelder, J. Chem. Phys. **3**, 555 (1935).

[22] Hirschfelder, Eyring, and Rosen, J. Chem. Phys. **4**, 130 (1936); Hirschfelder, Diamond, and Eyring, J. Chem. Phys. **5**, 695 (1937); D. Stevenson and J. Hirschfelder, J. Chem. Phys. **5**, 933 (1937); J. O. Hirschfelder, J. Chem. Phys. **6**, 795 (1938).

calculations do not extend to high energies for two reasons. First, we are primarily interested in the lowest energy range for subsequent mobility calculations, and second, the cross-section calculations themselves become inaccurate at large energies because of mathematical approximations.[19] The energy range shown in Fig. 2 gives information on the potential energy $\varphi(r)$ over the range of 1.5 to 3.7 A.

The average energy of interaction between H^+ and H_2 is thus given at small distances by Eq. (21), and at large distances by Eq. (1). The effect of the r^{-6} energy of Eq. (3) on the mobility is small, and can be included at the end as a perturbation, with $B_1=4.78$ ev A^6, $B_2=0$. The simplest procedure for calculating the mobility is to approximate the calculated interaction energy by an empirical form for which the collision integrals have been tabulated. The only such empirical form available is that given by Eq. (10). The accurate $\varphi(r)$ was fitted by Eq. (10) by requiring that the position and depth of the minimum and the coefficient of the r^{-4} term be correct, so that $\epsilon=D_e=2.7$ ev, $r_m=r_e=1.5$ A, and $\gamma=0.72$. This procedure uses the r^{-12} and r^{-6} terms of Eq. (10) in a purely empirical way to simulate the behavior of a Morse function over a limited range. The calculation of the mobility according to Eq. (11) is then straightforward.

The effect of the theoretical charge-induced quadrupole energy can be calculated from the approximate Eq. (16) and applied as a correction to the mobility. The final results obtained up to 500°K are given in Table I, the maximum correction for the charge-induced quadrupole energy being less than 4%. The decrease of mobility with increasing temperature is to be expected for a system in which the important short-range energy is attractive, but it is somewhat unexpected that the rate of decrease is not faster. The slowness of the decrease in mobility suggests that the behavior of the short-range energy is rather similar to an r^{-4} energy (the mobility is temperature-independent for an r^{-4} interaction energy). Hirschfelder, Diamond, and Eyring[22] noticed this same result in their quantum-mechanical calculations, and stated, "It is surprising that the energy of H_3^+ is nearly equal to the electrostatic energy $\bar{\alpha}e^2/2r^4$ for the appropriate value of r. This equality is partly accidental since there are other types of important interactions between H_2 and H^+."

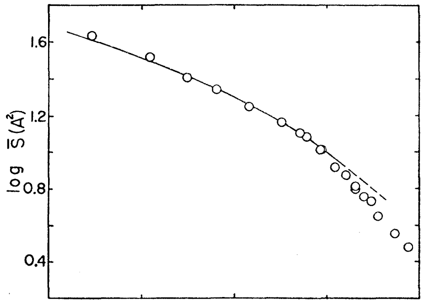

FIG. 2. Comparison of calculated and observed average elastic scattering cross sections for a proton beam in H_2 gas.

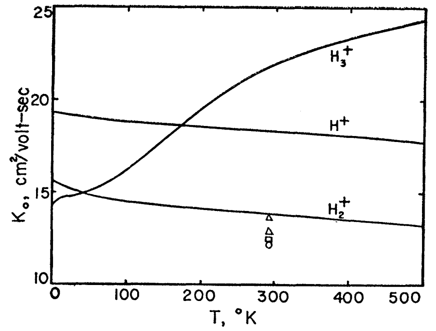

FIG. 3. Calculated and observed mobilities of hydrogen ions in hydrogen at standard gas density (0°C, 1 atmos). The experimental points were obtained by Bradbury (○), Mitchell (△), and Lauer (□).

DISCUSSION

The results of the present calculations are shown in Fig. 3 for comparison with measured values at about 20°C for hydrogen ions of an unidentified nature in hydrogen gas. The group of the three lowest points, obtained by Bradbury,[23] Mitchell,[24] and Lauer,[25] probably all refer to the same ion. A slightly higher point was also obtained by Mitchell under very rigorous conditions of gas purification, and the ion of lower mobility was then attributed to contamination.[24] Whether this is true or not, it is apparent from Fig. 3 that the present calculations definitely eliminate H^+ and H_3^+ from consideration, and indicate that the ion whose mobility was observed was probably H_2^+. If the mobility calculation is based only on the r^{-4} polarization energy, the $T=0$ limit is obtained, and the most plausible identification of the measured ion would be H_3^+. The present results show that even at room temperatures the short-range forces have a pronounced influence on the mobility, so that the heaviest ion, H_3^+, actually has the highest mobility.

Finally, it is perhaps worth pointing out that the error made in using a value of the average polarizability, $\bar{\alpha}$, obtained by giving equal weight to all molecular configurations is such as to make the calculated mobility slightly too high. Any correction for this error would thus tend to improve the agreement between the measured mobilities and those calculated for H_2^+.

APPENDIX. EVALUATION OF $\int_0^\infty x^2e^{-x}(\ln x)^n dx$

Consider the gamma function,

$$\Gamma(\beta)=\int_0^\infty x^{\beta-1}e^{-x}dx. \tag{22}$$

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[23] N. E. Bradbury, Phys. Rev. **40**, 508 (1932).

[24] J. H. Mitchell, quoted by Tyndall, reference 1, pp. 52–54.

[25] E. J. Lauer, J. Appl. Phys. **23**, 300 (1952).

By differentiation we obtain

$$\frac{d^n\Gamma(\beta)}{d\beta^n}=\int_0^\infty x^{\beta-1}e^{-x}(\ln x)^n dx, \tag{23}$$

so that the desired integrals are just the derivatives of the gamma function evaluated at $\beta=3$. To calculate the derivatives of $\Gamma(\beta)$, we use Stirling's asymptotic formula,[26]

$$\ln\Gamma(\beta)=\tfrac{1}{2}\ln(2\pi)+(\beta-\tfrac{1}{2})\ln\beta-\beta+(12\beta)^{-1} -(360\beta^3)^{-1}+(1260\beta^5)^{-1}+\cdots. \tag{24}$$

Use of Eq. (24) gives excellent accuracy except for the higher derivatives. As a check, the integral for $n=1$ can be evaluated in closed form by integration by parts to give

$$\int_0^\infty x^2e^{-x}\ln x dx=3-2\ln\gamma, \tag{25}$$

where

$$\ln\gamma=0.5772157\cdots \quad \text{(Euler's constant)}.$$

This checks the asymptotic series result to at least six figures.

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[26] P. Franklin, *Methods of Advanced Calculus* (McGraw-Hill Book Company, Inc., New York, 1944), p. 265.

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Lifetime of the 186-kev Level of Thorium-231*

D. STROMINGER
Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California

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The lifetime of the 186-kev level of Th^{231} has been studied following U^{235} alpha decay. The half-life value of this level is 0.77±0.12 mμsec.

INTRODUCTION

STROMINGER and Rasmussen[1] summarized the available lifetime data for $E1$ transitions in the actinide region. This summary showed that the $E1$ transition lifetimes varied erratically from one isotope to another. Nilsson wave functions were considered for the intrinsic states in odd-proton nuclei, and it was demonstrated that the $E1$ transitions violated selection rules[1,2] inherent in nuclei with very large spheroidal deformations. Similarly, it can be shown that all the expected low-lying $E1$ transitions between different intrinsic states in the actinide region violate the selection rules mentioned above. Hence all the low-lying $E1$ transitions are expected to have lifetimes longer by some orders of magnitude than the predictions of the single-proton lifetime formula.[3]

The alpha decay of U^{235} to the levels of Th^{231} is complex,[4] and not all the details of the decay have been worked out. Figure 1 shows a partial decay scheme of U^{235}. Stephens[5] has measured the K-conversion coefficients of the 186-kev and 143-kev transitions which depopulate the 186-kev level, and deduced that both are $E1$ transitions.

An upper limit of 1.5 mμsec for the half-life of the 186-kev level of Th^{231} has been reported.[1] Since then, improved electronic techniques have been developed which make it possible to set lower lifetime limits. This paper describes the use of these new techniques to measure the half-life of the 186-kev level of Th^{231}.

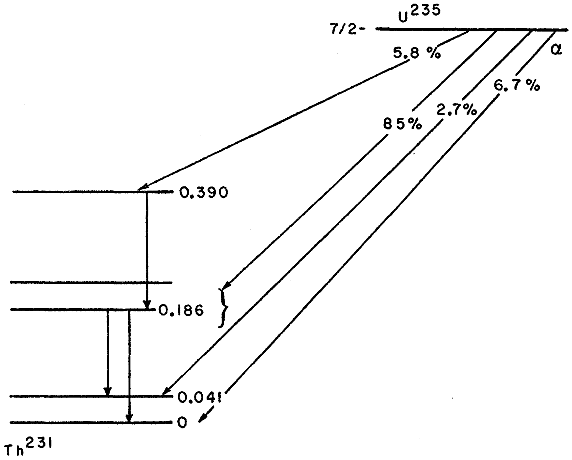

FIG. 1. Partial decay scheme of U^{235}.

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[1] D. Strominger and J. O. Rasmussen, Nuclear Phys. 3, 197 (1957).

[2] G. Alaga, Nuclear Phys. 4, 625 (1957).

[3] S. A. Moszkowski, in *Beta- and Gamma-Ray Spectroscopy*, edited by K. Siegbahn (Interscience Publishers, Inc., New York, 1955), Chap. XIII.

[4] R. C. Pilger, Jr., University of California Radiation Laboratory Report UCRL-3877, July, 1957 (unpublished); Pilger, Stephens, Asaro, and Perlman, Bull. Am. Phys. Soc. Ser. II, 2, 394 (1957).

[5] F. S. Stephens, Jr., University of California Radiation Laboratory Report UCRL-2970, June, 1955 (unpublished).