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DISSOCIATION OF H<sub>2</sub><sup>+</sup> IONS BY ELECTRIC FIELDS

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Abstract

Some preliminary calculations pertinent to the dissociation of  $H_2^+$  ions by electric fields are presented. The calculations pertain to those ions which are in the various vibrational states belonging to the ground electronic state of the system. To dissociate these ions in a time on the order of one second, electric fields on the order of  $10^6$  volts per centimeter are estimated for those ions populating the highest vibrational state. Fields on the order of  $10^8$  volts per centimeter appear to be required for those ions in which the ground vibrational state is populated.

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I. Introduction

If an atomic system is placed in a steady electric field the Coulomb binding forces are supplemented by an additional force that tends to separate the charges. One might expect that a sufficiently intense external field might lead to the dissociation of the system. Oppenheimer calculated this effect for a hydrogen atom in its ground state and found that the instability of the atom was inappreciable for field intensities much less than  $10^8$  volts per centimeter.<sup>1</sup>

The physical sense of Oppenheimer's calculation is contained in the observation that the imposition of the external field brings about a qualitative change in the nature of the potential experienced by the atomic electron. The modified potential is of such a form that the electron "sees" a barrier of finite width through which it can tunnel its way to freedom.

It is a well-known property of such "tunneling" processes that the transition rate depends exponentially upon the height of the barrier. In the type of problem we are discussing, the barrier height is at least approximately defined by the energy required to excite an electron into the continuum.

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<sup>1</sup> J. Robert Oppenheimer, Phys. Rev. 31, 66 (1928). There appears to be a typographical error in the quoted field strength for atomic dissociation.

Consequently one would expect that the field magnitudes calculated by Oppenheimer to be necessary for an observable dissociation rate might be markedly reduced in a system whose pertinent binding energy is appreciably less than that of the hydrogen atom.

The conclusions just related led us to suspect that the singly ionized hydrogen molecule might furnish an example of a system that would dissociate at a reasonable rate in the presence of an appreciably smaller electric field. We reached this conclusion by recognizing that there is an essential difference in the dissociation modes of the atom and the molecular ion.

The nature of the difference in the two cases may be seen as a consequence of the fact that the only mode of dissociation of the atom leads to the transition of the electron into a free state. For the molecule, however, there are an infinite number of possible final states after disruption. Symbolically, these are indicated by



where the subscript K denotes the state of the outgoing hydrogen atom. Included in the processes (a) is the analogue of Oppenheimer's process,



One of course recognizes that different mathematical assumptions may be convenient, depending upon which particular final atomic state K is to be studied.

In this paper we study the mode of dissociation leading to a free hydrogen atom in its ground state as one of the outgoing particles. We expect this mode to be important because of the closeness in the energy of



the lowest bonding and antibonding states of the molecule. In the language of an earlier paragraph we might say that we expect the "barrier" height to be defined by the energy difference between these two last-mentioned electronic states.

Most of the remainder of this paper is devoted to a description of the computational details, which are contained in Section II. The third section contains a brief summary of the results to date.

## II. Computational Details

The nonrelativistic Schroedinger equation for a hydrogen molecular ion in the presence of a steady electric field along the z axis is

$$H\psi \equiv (H_0 + V)\psi = E\psi, \quad (1a)$$

where

$$H_0 = \frac{1}{M}(\nabla_1^2 + \nabla_2^2) + \frac{1}{m}\nabla_3^2 - \frac{2}{\hbar^2} \left( \frac{e^2}{r_{12}} - \frac{e^2}{r_{13}} - \frac{e^2}{r_{23}} \right) \quad (1b)$$

and

$$V = -\frac{2e}{\hbar^2} \mathcal{E} (z_1 + z_2 - z_3). \quad (1c)$$

Subscripts "1" and "2" denote the proton coordinates, and "3" denotes the electron coordinate.  $H_0$  is the Hamiltonian for the one-electron hydrogen molecule, and  $V$  the perturbation resulting from an external field of magnitude  $\mathcal{E}$ .  $M$  and  $m$  are, respectively, the proton and electron masses.

In order to separate the motion of the center of mass, we introduce two new coordinates:

$$\vec{r}' = \vec{r}_3 - \frac{1}{2}(\vec{r}_1 + \vec{r}_2); \quad \vec{R} = \left[ M(\vec{r}_1 + \vec{r}_2) + m\vec{r}_3 \right] (2M+m)^{-1}. \quad (2)$$

If we take  $\vec{r}'$ ,  $\vec{R}$ , and  $\vec{r}_{12}$  as the three independent coordinates of the system, we obtain instead of Eqs. (1b) and (1c) two new relations:

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$$H_0 = \left( \frac{2}{M} \nabla_{12}^2 + \frac{(2M+m)}{2Mm} \right) \nabla'^2 + \frac{1}{(2M+m)} \nabla^2 \quad (1b)$$

$$- \frac{2e^2}{\hbar^2} \left( \frac{1}{r_{12}} - \frac{1}{|\vec{r}' - \frac{1}{2}\vec{r}_{12}|} - \frac{1}{|\vec{r}' + \frac{1}{2}\vec{r}_{12}|} \right),$$

$$V = \left[ Z - \left(1 + \frac{m}{2M+m}\right) Z' \right] \frac{2e\xi}{\hbar^2}. \quad (1c)$$

That part of the wave function depending on the coordinates of the center of mass,  $R(X, Y, Z)$ , can now be separated from the internal motion, by writing

$$\Psi(R, r_{12}, r') = \Lambda(\vec{R}) \pi(r_{12}, r'); \quad E = E_R + E_{Int}. \quad (3)$$

The resulting equation for  $\Lambda$  describes a particle of mass equal to the total mass of the ion and of charge  $+e$  moving in an electric field  $\xi$ .

At this point we introduce the Born-Oppenheimer approximation and assume that the function  $\pi(r_{12}, r')$  describing the internal motion can be written as a product of an electronic eigenfunction, which is a function of the electronic coordinates and parametrically dependent on the nuclear coordinates, and a nuclear eigenfunction which is a function of the nuclear coordinates alone.

$$\pi(r_{12}, r') = \chi(r', r_{12}) \phi(r_{12}), \quad (4)$$

and where the separated motions are determined by

$$\frac{1}{m} \nabla'^2 - \frac{2}{\hbar^2} \left[ E_{el}(r_{12}) - \frac{e^2}{|\vec{r}' - \frac{1}{2}\vec{r}_{12}|} - \frac{e^2}{|\vec{r}' + \frac{1}{2}\vec{r}_{12}|} - e\xi Z' \right] \chi = 0, \quad (5)$$

we have

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$$\frac{2}{M} \nabla_{12}^2 - \frac{2}{\hbar^2} \left[ E_{\text{Int}} + \frac{e^2}{r_{12}} - E_{\text{el}}(r_{12}) \right] = 0.$$

The family of electronic eigenvalues,  $E_{\text{el}}(r_{12})$ , serves as part of the potential function for the nuclear motion. The effect of the electric field appears as a perturbation,  $e \sum Z^i$ , in the electronic Eq. (5).

We now consider the effect of the perturbation term on the  $E_{\text{el}}(r_{12})$  values. The ground-state and first-excited-state electronic wave functions for the unperturbed ion are to a good approximation respectively by<sup>2</sup>

$$\chi_g = \frac{1}{\sqrt{2(1+T)}} (\psi_1(1s) + \psi_2(1s))$$

$$\chi_u = \frac{1}{\sqrt{2(1-T)}} (\psi_1(1s) - \psi_2(1s))$$

$$T = \int \chi_g \chi_u d\vec{r} \quad (7)$$

where  $\psi_1(1s)$  and  $\psi_2(1s)$  are the ground-state atomic orbitals for the electron about proton No. 1 and about proton No. 2, respectively. If we restrict ourselves to considering only the submatrix formed from these two states, the Hamiltonian matrix to be diagonalized is

$$\begin{pmatrix} H_{gg} & H_{gu} \\ H_{ug} & H_{uu} \end{pmatrix} \quad (8)$$

The matrix elements are defined by

<sup>2</sup>Gerhard Herzberg, Spectra of Diatomic Molecules (Van Nostrand, New York, 1950) p. 384.

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$$H_{gg} = \int \chi_g \chi_g^* E_{el}(r_{12}) dr' = E_{el}^g(r_{12})$$

(unperturbed ground-state electronic eigenvalue),

$$H_{uu} = \int \chi_u \chi_u^* E_{el}(r_{12}) dr' = E_{el}^u(r_{12})$$

(9)

(unperturbed first-excited-state electronic eigenvalue), and

$$H_{ug} = H_{gu} = \int \chi_g \chi_u^* (-e \mathcal{E} z') dr' = -\frac{e \mathcal{E} r_{12} \cos \theta}{2 \sqrt{1 - T^2}},$$

where  $r_{12}$  is the proton separation, and  $\theta$  the angle between the electric field direction and the internuclear axis. Only the component of the electric field along the internuclear axis is significant; the contributions of the field components at right angles to the internuclear axis vanish in this approximation.

Diagonalization of Eq. (8) leads to the solutions

$$E_{1,2} = \frac{E_g + E_u}{2} + \frac{1}{2} (E_u - E_g) \left\{ 1 + \frac{e^2 \mathcal{E}^2 r_{12}^2 \cos^2 \theta}{(1 - T^2) (E_u - E_g)^2} \right\}^{\frac{1}{2}} \quad (10)$$

For small values of  $r_{12}$ , Eq. (10) reduces to

$$E_{1,2} = \begin{cases} E_g - \frac{1}{4} \frac{e^2 \mathcal{E}^2 r_{12}^2 \cos^2 \theta}{(1 - T^2) (E_u - E_g)} \\ E_u + \frac{1}{4} \frac{e^2 \mathcal{E}^2 r_{12}^2 \cos^2 \theta}{(1 - T^2) (E_u - E_g)} \end{cases}, \quad (11)$$

and for large values of  $r_{12}$ , to

$$E_{1,2} = \frac{E_g - \frac{e^2 r_{12} |\cos \theta|}{2}}{E_u + \frac{e^2 r_{12} |\cos \theta|}{2}} \quad (12)$$

Equations (11) and (12) indicate that the potential for the nuclear motion, which in the unperturbed case is spherically symmetric, in the perturbed case is axially symmetric, the axis of symmetry being along the electric field direction. The potential well for the ground state under the influence of the perturbation acquires a "spout" at either end, with the two spouts oriented along the field direction. As the perturbation is increased and the saddle point of the spout is lowered to a value comparable to that of the eigenvalue of the highest vibrational level, the ion tends to dissociate into a hydrogen atom and a proton in a time comparable to the vibration period. This dissociation time is of course determined by barrier penetration if the saddle point is not near an eigenvalue.

This tendency for the ion to dissociate itself into a proton and an H atom for large internuclear separations can be shown by examining the perturbed electronic eigenfunction appropriate to the diagonalized Hamiltonian. The perturbed eigenvalues Eq. (10), together with unitarity conditions on the transformation matrix and exchange-symmetry requirements on the wave function, give for the perturbed wave functions of the two electronic states

$$\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = \frac{-1}{\sqrt{(E_1 - E^u)^2 + H_{gu}^2}} \begin{pmatrix} (E_1 - E^u) \chi_g - H_{gu} \chi_u \\ H_{gu} \chi_g + (E_1 - E^u) \chi_u \end{pmatrix} \quad (13)$$

In the limit of large internuclear separations, appropriate to dissociation, Eq. (13) goes over to

$$\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} \rightarrow \begin{pmatrix} \psi_2 \\ \psi_1 \end{pmatrix} \quad (14)$$

Equation (14) is interpreted as meaning that the unperturbed ground-state wave function in the presence of the perturbation and for large internuclear separations goes over into a state in which the electron is about proton No. 2 and proton No. 1 is free, and the first excited state goes over into a state in which proton No. 2 is free and the electron is about proton No. 1. This behavior is consistent with the variation of potential as a function of internuclear separation indicated by Eq. (10).

A description of the dissociation of the ion after the perturbed potential for the nuclear motion has been determined can be given by use of the method of Oppenheimer.<sup>1</sup> This method amounts to solving the Schroedinger equation for a particle moving in a uniform electric field, which is to represent the free proton after the dissociation, and noting that this solution is almost orthogonal to the solution for the bound ion, provided the saddle point of the potential is sufficiently above the eigenvalue in question. The rate of dissociation is then given by the usual formula

$$\frac{1}{T} = \frac{2\pi}{\hbar} |H_{fi}|^2 \rho, \quad (15)$$

where

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$$H_{fi} = \int \psi_f^* \Delta V \psi_i d^3 r_{12},$$

$$\Delta V = \frac{E^u - E^g}{2} - \frac{1}{2} \left\{ (E^u - E^g)^2 + 4H_{gu}^2 \right\}^{\frac{1}{2}},$$

$\psi_f^*$  = wave function for proton moving in an electric field,

$\psi_i$  = vibrational wave function for the particular level in question,

$\rho$  = density of final states,

$T$  = mean life against dissociation.

In general it is of interest to consider all the vibrational levels of the  $H_2^+$  ground-electron state. This follows as a consequence of the fact that the vibrational states in the absence of the perturbation are stable against dipole transitions, and quadrupole transitions require times of the order of 1 sec. For  $H_2^+$  ions that originate in an ion source, all vibrational states will be populated, and because of the long lifetimes of these states, one can think of these states as being essentially stable.

There are two effects operative that tend to inhibit the dissociation. First, the effect of the perturbing term in Eq. (5) is to induce a dipole moment in the electronic configuration; this induced polarization is a function of the internuclear separation as shown in Eq. (11). As the molecule vibrates, the dipole moment changes, and from purely classical considerations one would

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expect induced dipole transitions to lower vibrational states. It is readily shown that the effect is formally equivalent to the theory of the Raman effect, and that induced dipole transitions will occur.<sup>3,4</sup> A straightforward calculation (using harmonic oscillator wave functions) for the mean life against these induced-dipole transitions yields, for the nonrotating molecule,

$$T(\text{sec}) = \frac{2\sqrt{2}}{9(1 - T^2)} \frac{e^4 E_{nm}^3 r_{12}^2}{h^3 c^3 (E^g - E^u)^2} \frac{\epsilon^2}{\sqrt{M^2 K}} M \text{ (cgs)}, \quad (16)$$

where

- $E_{nm}$  = energy separation between vibrational levels,
- $r_{12}$  = separation of the nuclei at the potential minimum,
- $M$  = ordinal number of the vibrational level,
- $K$  = effective force constant for the vibrational motion.

Here we have neglected the dependence of  $T$  and  $(E^g - E^u)$  on  $r_{12}$  and replaced them by their value at the potential minimum.

Second, the effect of the perturbation is to lower the vibrational levels. The level shift is given by first-order perturbation theory,

$$\Delta E = \int d^3 r_{12} \psi_v^* (r_{12}) \psi_v (r_{12}) \Delta V |Y_{JM}(\theta, \phi)|^2, \quad (17)$$

where  $\Delta V$  has been defined previously in connection with Eq. (15).

<sup>3</sup>Herzberg, op. cit., p. 86

<sup>4</sup>Edward U. Condon, Phys. Rev. 41, 759 (1932).



### III. Conclusions

We have made some order-of-magnitude estimates of the electric fields required for dissociating the highest and the lowest vibrational states of the  $H_2^+$  ion. To make these estimates an exact calculation of the vibrational eigenvalues and eigenfunctions of the ground electronic state of the unperturbed  $H_2^+$  ion has been carried out by use of the IBM 701 computer.<sup>5</sup> For the nonrotating molecule, the highest vibrational level is found to be approximately 0.016 electron volt below the dissociation limit. If the level shift given by Eq. (17) is ignored, a value for mean life against dissociation of 1 sec. for this level requires a field of approximately  $3 \times 10^5$  volts per centimeter (v/cm). However, the level shift appears to be sufficiently large to make the perturbation formula, Eq. (17), suspect. To meet this difficulty we are doing a variational calculation to locate the eigenvalue as a function of the perturbation. Pending the results of this variational calculation, it appears that an electric field of the order of  $10^6$  v/cm may not be unreasonable for dissociation of this highest level.

For the lowest vibrational states the perturbation formula, Eq. (17), is adequate to give the level shift, we obtain a value of the order of 1 sec for the mean dissociation time for electric fields of the order of  $10^8$  v/cm. It is interesting to note that this is similar to Oppenheimer's result for dissociation of the hydrogen atom.

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<sup>5</sup>Stanley Cohen, John R. Hiskes, Robert J. Riddell, Jr. (To be published)