DISSOCIATION OF H_2^+ BY ELECTRON IMPACT*

Gordon H. Dunn, Bert Van Zyl, and Richard N. Zare†

Joint Institute for Laboratory Astrophysics,‡ Boulder, Colorado

(Received 30 August 1965)

The absolute cross section as a function of electron energy has been measured for the sum of the processes represented by

$$H_2^+(1s\sigma_g)+e \rightarrow H_2^+(2p\sigma_u)+e \rightarrow H+H^++e, \quad (1a)$$

$$H_2^+(1s\sigma_g)+e \rightarrow H_2^+(2p\pi_u, 2s\sigma_g, \text{ others})$$
$$+e \rightarrow H^*+H^++e, \quad (1b)$$

$$H_2^+(1s\sigma_g)+e \rightarrow H^++H^++2e. \quad (1c)$$

The strong motivation for this work comes from several sources:

(A) The hydrogen molecular ion as the simplest of all molecules is the only molecular species for which reliable quantum mechanical calculations of collision cross sections exist. In particular, several calculations have been made[1-5] for dissociation by electron impact.

(B) There have apparently been no real measurements of cross sections for dissociative excitation [as in (1a) and (1b)] by electron impact on any molecule, despite some ingenious attempts in H_2.[6,7]

(C) The calculations of Peek[4,5] indicate that the cross section for the process (1a) is a strong function of internuclear separation and thus of vibrational state of the target H_2^+ molecule. Such a dependence has not before been experimentally observed in an interpretable manner.

(D) Various high-energy plasma devices depend for their success upon the cross sections for processes such as those in Eq. (1).

A schematic diagram of the experiment is shown in Fig. 1. Ions are formed by bombardment of H_2 gas at about 0.4 μ by 200-eV electrons. The 10-keV ion beam is mass-analyzed and is passed through various differentially pumped chambers before entering the collision region. Here the ion beam of about 1 μA and 0.15-cm^2 cross section is crossed by a variable-energy modulated electron beam of order 1 mA and 2-cm^2 cross section.

Protons resulting from the dissociation of H_2^+, and thus having one-half the kinetic energy of the H_2^+, are separated from the parent ion beam with a 45° parallel-plate electrostatic analyzer.[8,9] The two different ion species are collected in separate Faraday cups and their currents measured.

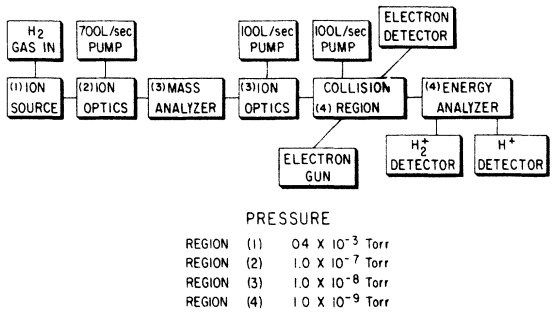

FIG. 1. Block diagram of experimental arrangement.

The electron beam is modulated at 37 cps, and a lock-in detector together with a high-impedance preamplifier is used to measure the proton current. Electron and H_2^+ currents are measured with standard electrometers. Electron, H_2^+, and proton currents are integrated for preset times, and the integrated values are punched in digital form on paper tape. Both primary beams are probed using a 0.005-in. slit which can be scanned through the beams. These data are used to determine the beam profiles and their degree of overlap.

Cross sections are calculated from the equation

$$\sigma=\frac{eI_{H^+}}{I_{H_2^+}+I_e}\frac{V_iV_e}{(V_i^2+V_e^2)^{1/2}}\frac{1}{\Omega}, \quad (2)$$

where σ is the cross section, I_{H^+} the measured H^+ signal current, I_e the electron current, $I_{H_2^+}$ the primary ion current, V_i and V_e the velocities of the ions and electrons, e the electronic charge, and Ω the beam overlap factor given by

$$\Omega=\frac{\int R(z)G(z)dz}{\int R(z)dz\int G(z)dz}. \quad (3)$$

Here $R(z)$ and $G(z)$ are one-dimensional, spatial distribution functions of the electron and ion beams determined by the probe measurements discussed above. The factor $V_e/(V_i^2+V_e^2)^{1/2}$ is necessary because the target ions

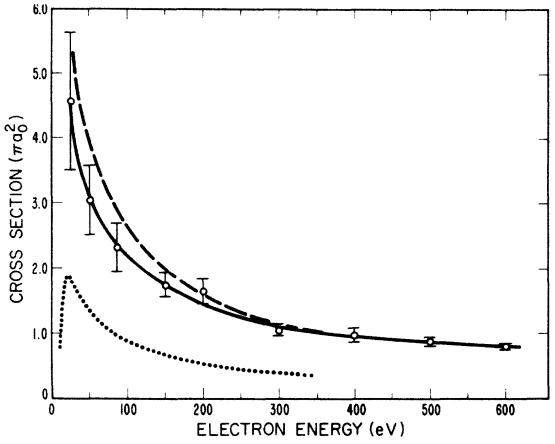

FIG. 2. Cross section versus electron energy for the process $H_2^+ + e \rightarrow$ protons. The points are experimental with the flags representing standard deviations, and the solid curve is a reasonable fit through the points. The dashed curve is a composite theoretical curve σ_t, as described in the text. The dotted curve is theory for $H_2^+(1s\sigma_g, v=0) + e \rightarrow H_2^+(2p\sigma_u) + e$.

are not at rest.

Measured values of the cross section are shown in Fig. 2, where the flags represent standard deviations from the mean. The points at energies above 50 eV were taken with integration times of 250 sec, while the 25- and 50-eV points were integrated for 1250 sec. The solid curve is drawn smoothly through the experimental points.

Theoretical estimates with which to compare these measurements must include all of the processes (1a) through (1c). The Born-approximation calculations of Peek[4,5] are used for the transitions $1s\sigma_g \rightarrow 2p\sigma_u$, $1s\sigma_g \rightarrow 2p\pi_u$, and $1s\sigma_g \rightarrow 2s\sigma_g$. Transitions to other excited states are probably not important.[10] A Gryziński calculation by Alsmiller[3] has been used for the ionization processes (1c). The composite expected curve is then computed from

$$\sigma_t = \sigma_{1a} + \sigma_{1b} + 2\sigma_{1c}, \tag{4}$$

the factor of 2 being included since each event in (1c) contributes two protons.

Peek[4,5] has shown that σ_{1a} is a strong function of internuclear separation and thus of the vibrational population of $H_2^+(1s\sigma_g)$. This cross section has thus been obtained from the relation

$$\sigma_{1a} = \sum_v p_v \sigma_{1a}^v, \tag{5}$$

where the p_v are normalized populations of the vibrational levels of the $1s\sigma_g$ state and σ_{1a}^v are the cross sections calculated for individual vibrational levels by Peek.[5] Due to the possibility of autoionization, there has been considerable doubt expressed recently[11,12] about what values the p_v should take; but since more established values are lacking, we have used the Franck-Condon factors between ground state H_2 and H_2^+ as the p_v in (5). Ion source conditions noted above were such that the H_2^+ should[13] have remained in the states formed initially. No allowance for variance with internuclear separation has been made for the $1s\sigma_g \rightarrow 2p\pi_u$, $2s\sigma_g$, or double ion transitions. There is some evidence[10,14-16] that any such variation for these transitions is much less important than for the transition $1s\sigma_g \rightarrow 2p\sigma_u$.

The resultant curve for σ_t is shown as the dashed line in Fig. 2. The contributions to σ_t from the different processes at 340 eV are shown in Table I, where we see that the transition $1s\sigma_g \rightarrow 2p\sigma_u$ contributes about 70% of the total predicted. The dotted curve in Fig. 2 is Peek's[4,5] calculation for σ_{1a}^0, i.e., the transition $1s\sigma_g \rightarrow 2p\sigma_u$ if all ions are in ground vibrational level.

The close agreement between our experimental results and the calculated σ_t allows us to conclude that the cross section varies with internuclear separation, as predicted by Peek,[4,5] and that there exist vibrationally excited H_2^+ ions in the primary ion beam. Both of these conditions are necessary in order to cause the cross section to vary appreciably from the dotted curve in Fig. 2. The degree to which the controversial p_v are approximated by the Franck-Condon factors cannot be assessed here.

Many tests were made demonstrating the proper functional relationships of I_e, $I_{H_2^+}$, V_i, and Ω in Eq. (1). The signal was shown to be independent of the large dc proton current arising from breakup of H_2^+ on background gas. Within the statistics, it was shown that all signal ions were collected. The primary source of possible systematic error arises from a modulated proton current coming from collisional breakup of H_2^+ on gas which is desorbed from the electron-gun surfaces by the modulated elec-

Table I. The relative contributions to σ_t in Eq. (4) at 340-eV electron energy. Units are πa_0^2.

σ_{1a}	$\sigma_{1b}(2p\pi_u)$	$\sigma_{1b}(2s\sigma_g)$	$2\sigma_{1c}$	σ_t
0.709	0.17	0.012	0.16	1.05

tron beam. Within the statistics, this source of error was eliminated by properly degassing the electron gun. An estimate of systematic errors such as instrument inaccuracies, nonlinearities, etc., gives between +10 and −2% from these sources.

It is a pleasure to acknowledge the assistance of Mr. Edwin Williams.

---

*This research was supported in part by the Controlled Thermonuclear Branch of the U. S. Atomic Energy Commission.

†Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

‡Of the National Bureau of Standards and the University of Colorado.

[1]E. H. Kerner, Phys. Rev. 92, 1441 (1953).

[2]E. V. Ivash, Phys. Rev. 112, 155 (1958).

[3]R. G. Alsmiller, Oak Ridge National Laboratory Report No. ORNL-3232 (unpublished).

[4]J. M. Peek, Phys. Rev. 134, A877 (1964).

[5]J. M. Peek, Phys. Rev. 140, A11 (1965).

[6]H. S. W. Massey and E. H. S. Burhop, Electronic and Ionic Impact Phenomena (Clarendon Press, Oxford, England, 1952), p. 233.

[7]S. J. B. Corrigan, Bull. Am. Phys. Soc. 10, 158 (1965).

[8]G. D. Yarnold and H. C. Bolton, J. Sci. Instr. 26, 38 (1949).

[9]W. C. Lineberger, J. W. Hooper, and E. W. McDaniel, to be published.

[10]D. R. Bates and A. R. Holt, Proc. Phys. Soc. (London) 85, 691 (1965).

[11]D. D. Briglia and D. Rapp, Phys. Rev. Letters 14, 245 (1965).

[12]J. W. McGowan and M. A. Fineman, Phys. Rev. Letters 15, 175 (1965).

[13]G. H. Dunn, in Atomic Collision Processes, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 997.

[14]J. M. Peek, private communication.

[15]D. R. Bates, U. Öpik, and G. Poots, Proc. Phys. Soc. (London) A66, 1113 (1953).

[16]D. R. Bates, R. T. S. Darling, S. C. Hawe, and A. L. Stewart, Proc. Phys. Soc. (London) A66, 1124 (1953).

PHOTOELECTRON SPECTROSCOPY WITH A SPHERICAL ANALYZER. THE VIBRATIONAL ENERGY LEVELS OF H_2^+

D. C. Frost, C. A. McDowell, and D. A. Vroom

Chemistry Department, University of British Columbia, Vancouver, Canada

(Received 30 August 1965)

This Letter reports the use of a spherical energy analyzer to study the photoelectron-energy distribution in an ionized gas. This has enabled us to measure the separations of the first five vibrational energy levels of $H_2^+(^2\Sigma_g^+)$ and the relative probabilities of ionization to them.

The photon source is a microwave discharge in helium, which emits essentially 584 Å (21.21 eV) in the energy range above the hydrogen ionization potential. To a very close approximation, the photoelectrons will have kinetic energies equal to 21.21 eV minus the ionization potential of hydrogen. If H_2^+ can be formed in more than one vibrational state, we expect a group of photoelectrons corresponding to each. The differences between the group energies should give the vibrational level spacing, and the relative intensities will be proportional to the transition probabilities from $H_2(^1\Sigma_g^+)$ for 584Å radiation.

In this work we have restricted ourselves to observations on the $^2\Sigma_g^+$ ground electronic state.

All previously reported work on photoelectron kinetic-energy distributions in gases has been done using cylindrical-grid energy analyzers.[1-4] Although vibrational structure can be clearly seen in some differential retarding curves,[4] the resolution has not been sufficient to permit accurate measurements on vibrational energy-level spacings or transition probabilities.

The low resolution stems primarily from the photoelectron spatial distribution being close[3] to that predicted theoretically,[5] i.e. dependent on $\sin^2\theta$ (θ = angle between photon and electron). Since retarding fields using cylindrical grids affect only the radial component of kinetic energy, electrons expelled over a considerable range of angles will cause a smoothing out of what would be a stepped retarding curve for electrons ejected in one direction only.

To overcome this difficulty we have built an analyzer wherein photoelectrons are produced in a small volume at the center of a spherical grid system, so that initial ejection is always