

Dynamics of Three-Body Breakup in Dissociative Recombination: H_2O^+

S. Datz,¹ R. Thomas,^{3,2} S. Rosén,³ M. Larsson,³ A. M. Derkatch,³ F. Hellberg,³ and W. van der Zande²

¹*Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6377*

²*FOM Instituut AMOLF, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands*

³*Department of Physics, Stockholm University, P.O. Box 6730, S-113 85 Stockholm, Sweden*

(Received 5 September 2000)

To better understand the propensity for the three-body breakup in dissociative recombination (DR) of dihydrides (H_3^+ , NH_2^+ , CH_2^+ , and H_2O^+), we undertook a study of the dynamics of this process. A study of DR of H_2O^+ to give $\text{O} + \text{H} + \text{H}$ was carried out at the CRYRING Heavy-Ion Storage Ring in Stockholm. With the stored beam energy of 4.5 MeV, we separated the O signal from the H signals with a differential absorber, thus reducing the problem to a sum of two two-body problems. Results included (1) the ratio of $\text{O}(^3P)$ to $\text{O}(^1D)$ product, (2) the distribution of recoil-kinetic energy between the two hydrogen atoms, (3) the angular distribution between the hydrogen atoms in the $\text{O}(^3P)$ channel and in the $\text{O}(^1D)$ channel.

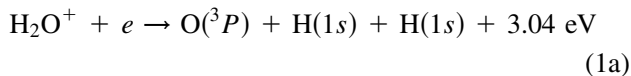
PACS numbers: 34.50.Gb, 34.50.Lf

Dissociative recombination (DR) is the process in which a free electron combines with a molecular ion and the added energy, essentially the negative of the molecule's ionization potential, causes dissociation into neutral fragments.

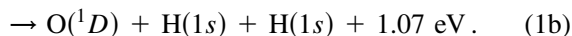
The DR process is important in the dynamics of, e.g., low temperature plasmas, ionospheres, and interstellar clouds. With the advent of heavy-ion storage rings, the DR process has come under intensive investigation. Studies have included collision energy dependent total cross sections, breakup into atomic and molecular fragments, and, in the case of diatomic molecular ions, populations of internal atomic energy states [1].

DR of simple triatomic dihydrides has shown a strong propensity for fragmentation into three separate atoms. For, e.g., H_3^+ [2], CH_2^+ [3], NH_2^+ [4], and OH_2^+ [5–7], the three-body channel constitutes 60%–80%. Thus far, no theoretical explanation of this phenomenon has been forthcoming. To help clarify this situation, we undertook a study of the dynamics of three-body breakup, i.e., internal excitation of the atomic products, distribution of kinetic energy between fragments, and angular distribution between the product atoms. Here, we report on the dynamics of the H_2O^+ DR breakup (absolute total cross sections for the DR of H_2O^+ are reported in Refs. [5–7]). The DR product fractions measured here at approximately zero collision energy are 0.19 for $\text{OH} + \text{H}$, 0.08 for $\text{O} + \text{H}_2$, and 0.73 for $\text{O} + \text{H} + \text{H}$.

At zero collision energy, only two three-body channels are energetically possible:



and



Almost all of the energy released must be divided between the two (light) hydrogen atoms. For the $\text{O}(^3P)$

channel, equal distribution for the two hydrogen atoms gives ~ 1.5 eV per atom; also the *minimum* energy for the faster of two hydrogen atoms released is ~ 1.5 eV. Similarly, for the $\text{O}(^1D)$, equal distribution gives 0.54 eV per atom and a *maximum* energy of 1.07 eV. Hence any H atom with energy $\lesssim 1.1$ eV must come from decay to the $\text{O}(^3P)$ state. In the experiment, the recoil velocities are determined by measuring the distances and angles of the recoiling H atoms from the O atom after DR takes place in an energetic circulating beam of H_2O^+ .

The experiment was performed at the CRYRING Heavy-Ion Storage Ring in Stockholm. The H_2O^+ ions are injected into the ring and accelerated to 4.5 MeV (250 keV/amu). After acceleration, the ions “coast” in the ring vacuum for 5 s which is sufficient to radiatively relax into the ground vibrational state. The beam is phase space cooled by passing through a merged electron beam 85 cm in length, which is matched to the velocity of the stored beam. The “cooling” process reduces the beam size to ~ 4 mm. The cooler also acts as the electron target in which DR can occur. At velocity matching, the relative collision energy is ~ 0 eV; however, the transverse temperature of the electron beam introduces a 2-meV spread.

Neutral fragments pass through the dipole magnet following the electron target and strike an imaging detector (Fig. 1). The imaging detector used in this experiment consists of three stacked microchannel plates (MCPs) and a phosphor screen (size $\Phi = 77$ mm) and is similar in design to that of Amitay and Zajfman [8] and Rosén *et al.* [9]. Fragment atoms from the DR of H_2O^+ strike the MCPs detector and generate flashes on a phosphor screen. The screen is imaged onto a CCD camera and onto a multichannel photomultiplier tube (PMT, 16 lines). The former records the separation of the fragments, and the latter is used to report the difference in arrival times and it also acts as a trigger to the image intensifier (II). Each of the 16 lines of the PMT is connected to

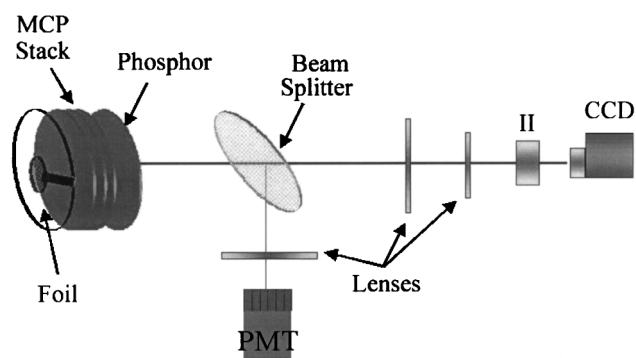


FIG. 1. Detector system, multichannel plates, fluorescent screen, image intensifier, CCD camera, and multichannel photomultiplier.

a single channel in a 16-channel constant fraction discriminator. To remove signals arising from spurious events and thermal electrons in the MCP array, the detector is operated in a gated mode.

The problem is that both the H atoms and the O atoms give identical signals on a MCP detector. The solution was to place a thin ($2.5 \mu\text{m}$) Al disk (5 mm in diameter) at the center of the MCP (see Fig. 1). At 250 keV/amu, the range of protons in Al is $2.2 \mu\text{m}$ and the range of oxygen is $3.2 \mu\text{m}$. With a 4.5-MeV H_2O^+ beam, the $2.5\text{-}\mu\text{m}$ Al foil completely stops at 250-keV H atom, but a 4.0-MeV ^{16}O atom exits the foil with ~ 400 keV and strikes the MCP. Thus any pulse occurring from a strike behind the foil area must be due to an oxygen atom.

The distance from the center of the 85-cm-long merging region to the detector is 6.4 m, so that the recoil distances are $\pm 7\%$. When the H-O-H plane is parallel to the detector plane, the maximum recoil separation on the MCP for the $\text{O}(^3P)$ is (3.04 eV) 22.5 mm, the minimum for the faster of the two H atoms is 15.7 mm (one-half the maximum recoil energy). Similarly, for the $\text{O}(^1D)$ channel, the maximum spacing (1.07 eV) is 13.2 mm, and the minimum for the faster H is 9.3 mm. Therefore, any recoil separation of ≥ 15.7 mm must arise from the $\text{O}(^3P)$ channel, and the pulses occurring at larger distances represent the energy spectrum of the more energetic H atom fragment accompanying an $\text{O}(^3P)$ atom.

The procedure is to record all events in which three particles make an MCP hit within ~ 10 ns. Keying on a hit made within the area behind the Al foil (i.e., oxygen atoms), the distances between the O atom hit and the associated H atom hits are recorded as is the H-O-H angle. The system of three particles can, of course, have any orientation with respect to the MCP detector plane (MCPDP). It is only when the plane containing the three particles is parallel with the MCPDP and hence at a maximum projected distance that the interatomic distances represent the true recoil energies. The timing between pulses is also a measure of the orientation of the H-O-H plane with respect to the detector plane, i.e., the closer the H-O-H plane is parallel to the detector plane, the shorter will be the sepa-

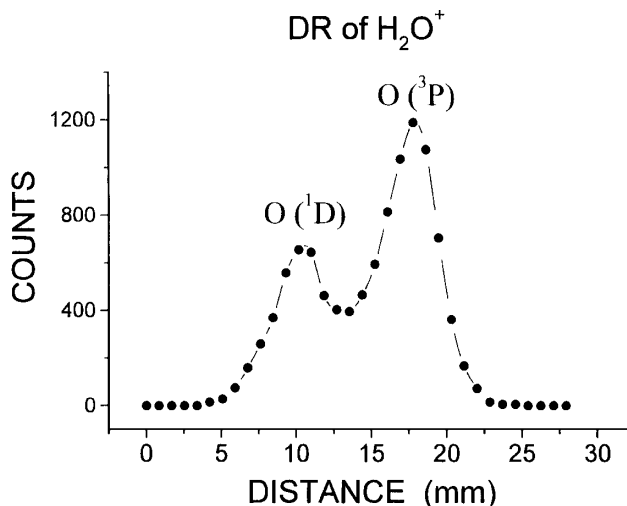


FIG. 2. Measured distribution of total recoil distances (taken from the square root of the sum of the squares of the two O-H distances). The time window was < 800 ps.

ration between pulse arrival times. Introducing timing constraints can do much to clear up the spectrum by rejecting latecomers.

From the square root of the sum of the squares of the two O-H distances, one derives the total recoil distance in the DR process. The recoil distance spectrum taken from the three particles in coincidence within an 800-ps time window is shown in Fig. 2. The upper peak corresponds to DR resulting in an $\text{O}(^3P)$ state [Eq. (1a)] and the lower to the $\text{O}(^1D)$ state [Eq. (1b)]. Integration yields $\text{O}(^3P):\text{O}(^1D) = 3.5 \pm 0.5:1$.

To obtain the distribution of the kinetic energy released (KER) between the two hydrogen atoms for the $\text{O}(^3P)$ channel, we use those events whose total recoil distance (RD) is measured to be greater than 20 mm. The selection of the uppermost edge is to limit consideration to events most parallel to the detector plane. For each H atom in a given H_2O molecular DR, we separately measure its recoil distance and plot the number of events at that distance divided by the distance, versus distance. This is a particularly convenient formulation for comparison with Monte Carlo calculations using different models. The data is plotted in Fig. 3 for the $\text{O}(^3P)$ case. Also shown are the results for three models. The narrow calculated peak assumes that the two hydrogen atoms share the total KER exactly (50-50 distribution). For a nonequal but sharply defined energy distribution (i.e., 90-10), we obtain the bimodal distributions shown. However, the best fit to the data is given by a random distribution of energies.

This lack of structure indicates the lack of a well-defined intermediate state, i.e., the existence of an intermediate excited state of OH or H_2 . The vibrational distribution in a postulated OH^* or H_2^* would surely smear any sharp binary distribution, but it is unlikely to completely eliminate it.

The distribution of angles between the two departing H atoms is plotted in Fig. 4 for the $\text{O}(^3P)$ channel and the

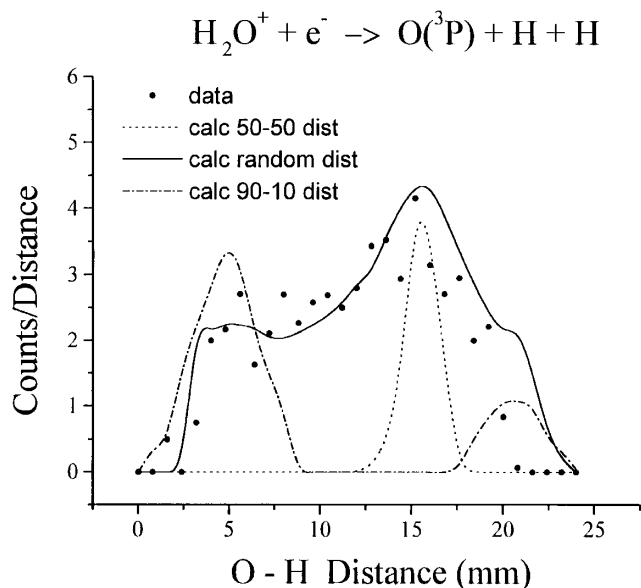


FIG. 3. Distribution of recoil H atom distances in the $O(^3P)$ channel divided by distance. Three models chosen for Monte Carlo analysis are chosen; the dashed line assumes 50:50 distribution between the two hydrogen atoms; the dash-dotted line assumes a 90:10 division; the solid line is obtained using a random distribution.

$O(^1D)$ channel. Here again, to ensure the best fragment plane orientation, we use only the data from an upper slice of the measured recoil distances (Fig. 2). For the $O(^3P)$ case, we use $RD \approx 20$ mm and for the $O(^1D)$ case, we use $10 < RD < 14$ mm. The line drawn in Fig. 4 for the $O(^3P)$ is a two point smooth line and, in the $O(^1D)$ case, we use a Lorentzian fit. Both curves, however, are just meant to “guide the eye.”

The H-O-H bond angle in the ground states of both H_2O and H_2O^+ is $\sim 110^\circ$. In the case of $O(^3P)$, there is no hint of preference in this angular region. The distribution rises sharply at 40° and continues to rise at the lowest measurable H-O-H angle. This strongly indicates rearrangement of the H_2O^* complex prior to dissociation. However, the random distribution of velocities between the two H atoms (above) mitigates against any formation of an H_2 intermediate. A possibly relevant observation in regard to the peaking at low angle is that in the two-body DR channels, i.e., $OH + H$ and $O + H_2$, the ratio $(OH + H)/(O + H_2)$ is only a factor of 2, i.e., as though statistically distributed even though the $O + H_2$ channel would require considerable rearrangement to bring the two H atoms into close contact. This “statistical” distribution was noted in a DR fragmentation study of H_2D^+ , where the HD/H_2 product ratio was 2:1 [10]. Similar observations were made in the DR of CH_2^{+3} . The angular distribution from DR to $O(^1D)$ gives a broad peak in the region of 90° , i.e., qualitatively different from the $O(^3P)$ and close to what might be expected from dissociation along the bond angle directions.

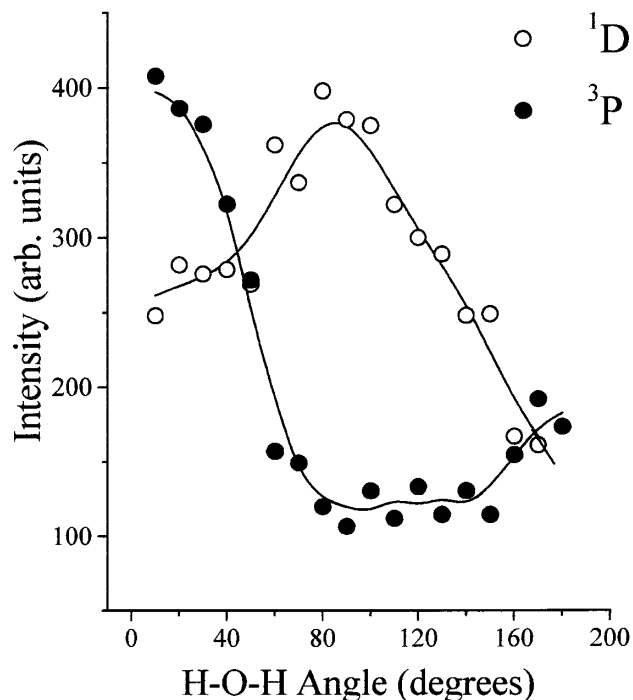


FIG. 4. Angular distribution of the H atoms departing from H-O-H. For the $O(^3P)$ channel (\bullet), the data used is from recoil distances >20 mm (Fig. 2). The line is a two point smoothing to guide the eye. For the $O(^1D)$ channel (\circ), the data used is from recoil distance regions 10–14 mm. The line is a Lorentzian fit to guide the eye.

Summing up, we have investigated for the first time the dynamics of three-body breakup in dissociative recombination. The case in point being dissociative recombination of H_2O^+ at approximately zero collision energy.

(i) The yield in the $O(^3P)$ channel exceeds the yield in the $O(^1D)$ channel in a ratio of $3.5 \pm 0.5:1$.

(ii) The distribution of kinetic energies between the two recoiling hydrogen atoms appears to be quite random, indicating single step three-body dissociation without a well-defined intermediate state (e.g., OH^* or H_2^*).

(iii) In the case of the $O(^3P)$ channel, the measured angular distribution of the recoiling hydrogen in the 2P channel decreases rapidly from 0° to 70° with a slight rise at 180° . There is no trace of any preference for the region of the H-O-H bond angle, indicating major rearrangement prior to breakup.

(iv) In the case of the $O(^1D)$ channel, a broad peak at $\sim 90^\circ$ is observed, i.e., not too distant from the ground state H_2O and/or the H_2O^+ bond angle.

Although there has been no direct theoretical treatment of three-body DR dynamics, several publications may have a bearing on our observations. For example, Dixon and co-workers [11] did trajectory calculations on photodissociation of H_2O and showed that, along excited surfaces, there was a lot of three-body decay and angular smearing. Child [12] speculated that dissociation proceeds via Rydberg states associated with the second excited

superbent state B_2B_2 of H_2O^+ . At least one Rydberg state, $(\tilde{A}^2A_1)3pb_2^1B_2$, has been shown to be linear [13] and may be associated with the rise near 180° . The net result of this paper is to give detailed information on the dynamics of DR of H_2O^+ . The theoretical reasons for this behavior remain to be elucidated.

We thank the CRYRING staff at the Manne Siegbahn Laboratory for their superb collaboration. We also thank C. R. Vane (ORNL) for many helpful discussions. One of us (S.D.) acknowledges research sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under Contract No. DE-AC05-00OR22725 with UT-Battelle, LLC. This work was also supported by the Swedish Natural Science Research Council, the Goran Gustafsson Foundation, and the Swedish Foundation for International Cooperation in Research and Higher Education.

-
- [1] For a review of DR measurements in storage rings, see M. Larsson, *Ann. Rev. Phys. Chem.* **48**, 151 (1997); M. Larsson, *Photoionization and Photodetachment*, edited by C. Y. Ng (World Scientific, Singapore, 2000), p. 693.
- [2] S. Datz, G. Sundström, C.H. Biedermann, L. Broström, H. Danared, S. Mannervik, J.R. Mowat, and M. Larsson, *Phys. Rev. Lett.* **74**, 896 (1995).

- [3] Å. Larsson, A. Le Padellec, J. Semaniak, M. Larsson, S. Rosén, R. Peverall, H. Danared, N. Djuric, G. Dunn, and S. Datz, *Astrophys. J.* **505**, 459 (1998).
- [4] L. Vikor, A. Al-Khalili, H. Danared, N. Djuric, G. H. Dunn, M. Larsson, A. Le Padellec, S. Rosén, and M. af Uglass, *Astron. Astrophys.* **344**, 1027 (1999).
- [5] L. Vejby-Christensen, L. H. Andersen, O. Heber, D. Kella, H. B. Pedersen, H. T. Schmidt, and D. Zajfman, *Astrophys. J.* **483**, 531 (1997).
- [6] S. Rosén, A. Derkatch, J. Semaniak, A. Neau, A. Al-Khalili, A. LePadellec, L. Vikor, R. Thomas, H. Danared, M. af Ugglas, and M. Larsson, *Faraday Discuss.* **115**, 295 (2000).
- [7] M.J. Jensen, R. C. Bilodeau, O. Heber, H. B. Pedersen, C. P. Safvan, X. Urbain, D. Zaifman, and L. H. Andersen, *Phys. Rev. A* **60**, 2970 (1999).
- [8] Z. Amitay and D. Zajfman, *Rev. Sci. Instrum.* **68**, 1387 (1997).
- [9] S. Rosén, R. Peverall, H. ter Horst, G. Sundström, J. Semaniak, O. Sundqvist, M. Larsson, M. de Wilde, and W.J. van der Zande, *Hyperfine Interact.* **115**, 201 (1998).
- [10] S. Datz, M. Larsson, C. Strömholm, G. Sundström, V. Zengin, H. Danared, A. Källberg, and M. af Ugglas, *Phys. Rev. A* **52**, 2901 (1995).
- [11] R. N. Dixon, D. W. Hwang, X. F. Yang, S. Harich, J. J. Lin, and X. Yang, *Science* **285**, 1249 (1999).
- [12] M. S. Child, *Faraday Discuss.* **115**, 303 (2000).
- [13] S. T. Pratt, J. L. Dehmer, and P. M. Dehmer, *Chem. Phys. Lett.* **196**, 469 (1992).