MEASUREMENTS OF ENERGY PARTITIONING IN H₂ FORMATION BY PHOTOLYSIS OF AMORPHOUS WATER ICE

AKIHIRO YABUSHITA,¹ TETSUYA HAMA,¹ DAISUKE IIDA,¹ NOBORU KAWANAKA,¹ MASAHIRO KAWASAKI,^{1,2}
NAOKI WATANABE,³ MICHAEL N. R. ASHFOLD,⁴ AND HANS-PETER LOOCK⁵

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ABSTRACT

We demonstrate experimentally that photodissociation of amorphous solid water at 100 K results in formation of H₂ molecules with an ortho/para ratio of $g_{\text{OPR}} = 3$. Two distinct mechanisms can be identified: endothermic abstraction of a hydrogen atom from H₂O by a photolytically produced H atom yields vibrationally cold H₂ products, whereas exothermic recombination of two H-atom photoproducts yields translationally and internally hot H₂. These results are in accord with predictions by molecular dynamics calculations and their astrophysical implications are discussed.

Subject headings: dust, extinction — ISM: molecules — molecular data — molecular processes — ultraviolet: ISM

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1. INTRODUCTION

In cold regions of interstellar space, such as molecular clouds, the outer solar system, and circumstellar envelopes, photolysis of water ice plays an important role in astrochemistry. One of the most fundamental processes of ice photochemistry is photodissociation of the water molecule and the subsequent formation of hydrogen molecules. The efficiency of H₂ formation by photolysis of ice is expected to be smaller than that by recombination of adsorbed hydrogen atoms under conditions typical of a quiescent cloud, i.e., where the photon field is very weak and the temperature is ~ 10 K (Manicò et al. 2001). However, the efficiency of H₂ formation following photoreaction is strongly enhanced (relative to recombination) once the surface temperature exceeds ~ 20 K, because the recombination efficiency drops significantly at elevated temperatures—probably due to the small sticking coefficient and short residence time of thermal H atoms on the ice surface (Manicò et al. 2001; Watanabe et al. 2004; Perets et al. 2005). Therefore, H₂ formation by photolysis of ice becomes increasingly important as the temperature increases from 20 to 100 K. Westley et al. (1995) and Watanabe et al. (2000) have estimated the efficiencies of H₂ formation, but were not able to reveal finer details of the reactions such as the reaction mechanism or the energy partitioning.

When H₂ is produced by photolysis of water ice, the excess energy from the heat of reaction and any initial kinetic energy is partitioned into internal and kinetic energy of the H₂ product and into the surface. The energy released into the surface may be sufficient to induce desorption of molecules in the vicinity of the reaction site. The kinetic energies of primary H₂ products and the secondary (desorbed) H₂O molecules can both contribute to interstellar heating. Furthermore, the subsequent gas-phase chemistry of the H₂ products is a sensitive function of rovibrational state (Sultanov & Balakrishnan 2005). The energy partitioning associated with H₂ formation is thus crucial to the whole chemical evolution.

H₂ formation from hot H atoms produced from photolysis

of amorphous solid water (ASW) at H Ly α or within the Lyman band of H₂ (the UV wavelengths most relevant to interstellar photochemistry) involves two distinct mechanisms: hydrogen abstraction (HAB) and hydrogen recombination (HR):

Since these two routes yield H₂ products with very different rovibrational distributions, measurements of the H₂ state distributions give direct insights into the formation mechanism(s).

Since the optical penetration depth in the ultraviolet region is fairly large, many of the H atoms will be formed at sites beneath the microporous ice surface, and H₂ molecules would be formed at and very close beneath the ice surface. The desorption energy of H atoms from the surface of water ice is estimated to be 300–600 K (Al-Halabi et al. 2002; Perets et al. 2005; Al-Halabi & van Dishoeck 2007). H atoms thermalized at 100 K on the ice surface might thus be expected to desorb immediately, and the HR mechanism thus expected to occur in the bulk phase but not at the surface. In fact, thermal desorption spectra from photolyzed ASW indicate that a significant amount of photoproduct H₂ (the desorption energy of which is very similar to that of an H atom) is trapped in ASW even at temperatures greater than 100 K (Watanabe et al. 2000). As a result, the residence time (and thus the density) of thermalized H atoms in ASW at 100 K may be quite high.

In the present study, photolysis of ASW has been investigated at 100 K using pulsed 157 nm laser radiation. While the partitioning into internal and kinetic energies is likely to be dependent on excitation wavelength, we suggest that the chemical mechanisms occurring after photoabsorption at 157 nm and at the astrophysically important Ly α wavelength (i.e., within the same electronic band system of H₂O) may well be the same.

2. EXPERIMENTAL

The sample ASW films contained ~ 600 monolayers, which were deposited onto a temperature-controlled Au(111) surface and maintained at 100 K in a vacuum chamber. ASW was prepared by back-filling deposition of water vapor onto the substrate at 100 K for 60 minutes using a pulsed nozzle operating at a rate of 10

¹ Department of Molecular Engineering, Kyoto University, Kyoto 615-8510, Japan.

² Corresponding author; kawasaki@photon.mbox.media.kyoto-u.ac.jp.

³ Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan.

⁴ School of Chemistry, University of Bristol, Bristol BS8 1TS, UK.

⁵ Department of Chemistry, Queen's University, Kingston, ON K7L 3N6, Canada.

FIG. 1.—Time-of-flight spectra of $\text{H}_2(\nu = 0, J = 0)$ (top) and $\text{H}_2(\nu = 3, J = 3)$ products (bottom). The insets in the top and bottom panels are for $\text{H}_2(\nu = 0, J = 3)$ and $\text{H}_2(\nu = 3, J = 13)$ products, respectively. The solid curves are best fits to Maxwell-Boltzmann distributions with $T_{\text{trans}} = 100$ and 1500 K (top) and 110 and 1800 K (bottom). [See the electronic edition of the Journal for a color version of this figure.]

Hz and with a 20 torr stagnation pressure of water vapor. A pulsed 157 nm laser was used to photolyze ASW. It was confirmed that only single-photon absorption occurs at the laser intensity used in the present experiment. Details of the experimental apparatus have been described elsewhere (Yabushita et al. 2002). H_2 photoproducts were ionized, state selectively, 2 mm above the substrate surface by $(2 + 1)$ resonance-enhanced multiphoton ionization (REMPI) via the $E/F\ ^1\Sigma_g^+ \leftarrow X\ ^1\Sigma_g^+$ ($\nu' = 0, \nu''$) transition. Mass-selected H_2^+ signals were collected using a mass spectrometer mounted normal to the ice film surface. The measured time-of-flight (TOF) spectra of the H_2 products were fitted with one or more flux-weighted Maxwell-Boltzmann distributions, which defined the translational temperature, T_{trans} . Excitation spectra were measured at a fixed TOF as a function of REMPI probe laser wavelength, and used to obtain H_2 product rotational state distributions after scaling the measured intensities by the relevant transition probabilities reported by Pomerantz et al. (2004) and assuming an ortho/para ratio of $g_{\text{OPR}} = 3$ (see below).

3. RESULTS

H_2 photoproducts were detected in vibrational levels $\nu = 2$ –4, in all rotational states with $J \leq 17$, and in the $\nu = 0$ and 1 levels with $J \leq 5$. Weak signals due to molecules with $\nu = 5, J \leq 1$ were also observed.

Figure 1 shows typical TOF spectra of the H_2 photoproducts formed in $\nu = 0$ and 3. The solid curves are best fits to combi-

FIG. 2.—Rotational distributions of selected $\text{H}_2(\nu)$ products. P_J is the population and E_J the rotational energy. Top: $\text{H}_2(\nu = 0, J)$, where the solid lines are best fits to Boltzmann distributions characterized by rotational temperatures of $T_{\text{rot}} = 100$ and 1300 K for the slow (filled squares) and fast (open squares) TOF components, respectively. The insets show excitation spectra for $J = 0$ –5 measured at TOF = $3\ \mu\text{s}$ (slow H_2) and $0.55\ \mu\text{s}$ (fast H_2). Bottom: $\text{H}_2(\nu = 3, J)$ rotational populations for the slow (filled circles) and fast components (open circles); the curves in this case are simply to guide the eye. The insets show excitation spectra for $J = 0$ –17 measured at TOF = $3\ \mu\text{s}$ (slow H_2) and $0.55\ \mu\text{s}$ (fast H_2). [See the electronic edition of the Journal for a color version of this figure.]

nations of Maxwell-Boltzmann distributions with $T_{\text{trans}} = 100$ and 1500 K for $\nu = 0$, and $T_{\text{trans}} = 110$ and 1800 K in the case of $\nu = 3$. The relative weightings of the distributions used in the fitting are found to vary with the ν, J level. Figure 2 shows H_2 product rotational distributions; smooth fits to Boltzmann distributions are obtained only if the ortho/para ratio, g_{OPR} , was set to 3. Use of $g_{\text{OPR}} = 1.5$, appropriate for H_2 molecules in thermal equilibrium at 100 K (Sternberg & Neufeld 1999), resulted in ragged rotational distributions. The insets in Figure 2 show REMPI excitation spectra for $\text{H}_2(\nu = 0)$ and $\text{H}_2(\nu = 3)$ at TOF = $3\ \mu\text{s}$ (slow H_2) and $0.55\ \mu\text{s}$ (fast H_2), respectively. The results for $\nu = 1$ and for $\nu = 2, 4$ products were similar to those for $\nu = 0$ and $\nu = 3$, respectively. Comparison of the absolute integrated TOF signal intensities for $\nu = 2, 3, 4$ provides the vibrational population distribution shown in Table 1. The J -distributions for H_2 products in these vibrational levels are similar to one other. Table 1 also lists the calculated energetics for these products. The following de-

TABLE 1
ENERGY PARTITIONING AND RELATIVE POPULATION DISTRIBUTIONS IN THE H₂ PRODUCTS
RESULTING FROM 157 nm PHOTOLYSIS OF ASW

H ₂ (ν)	Relative Vibrational Population ^a	Vibrational Energy (eV)	Translational Energy (eV)	Rotational Energy (eV)	Energy Absorbed by Ice (eV)	Dominant Mechanism
0	^b	0	0.028	0.013	...	HAB
2	0.58	1.00 (22%)	0.032 (0.7%)	0.65 (14%)	2.82 (63%)	HR
3	1	1.48 (33%)	0.028 (0.6%)	0.54 (12%)	2.45 (54%)	HR
4	1.34	1.88 (42%)	0.044 (0.1%)	0.33 (7%)	2.25 (50%)	HR

NOTES.—HAB and HR denote the (endothermic) hydrogen abstraction and (highly exothermic) hydrogen recombination reactions, respectively. Numbers in parentheses are percentages defined relative to the excess energy associated with the HR reaction (4.5 eV).

^a Relative to $\nu = 3$ for $J = 1, 3, \dots, 13$ (ortho levels). Error bars are 15%.

^b Relative intensity was not measured.

scription focuses on the H₂($\nu = 0$) and H₂($\nu = 3$) distributions, as exemplifiers of the two different formation mechanisms.

4. DISCUSSION

H₂ formation is found to be wholly consistent with the proposed HAB and HR mechanisms. The HAB mechanism requires an energetic H atom because the associated activation energy (in the gas phase) is ~ 1 eV (Jacobs et al. 1994), while the HR process requires a comparatively high H-atom density. A search for O(¹D) atom products, by 2 + 1 REMPI at 205.4 nm, failed to reveal any evidence for a third mechanism, i.e., direct formation of H₂ via the molecular elimination channel H₂O $\rightarrow$ H₂ + O(¹D). This latter process has a much lower probability than the homolytic dissociation channels (1) and (2) in the condensed phase (Michaud et al. 2003).

Based on the optical absorption coefficient, the optical depth of water ice at 157 nm is ~ 100 nm. Excitation at 157 nm results mainly in photofragmentation, yielding H-atom products with (nascent) translational energies as high as 2.75 eV. H atoms produced below the surface will inevitably collide with surrounding H₂O molecules and progressively thermalize. Classical molecular dynamics (MD) calculations suggest that such H atoms photoproduced from ASW at 10 K will travel a (maximum) distance of ~ 6 nm (Andersson et al. 2006). At 100 K, therefore, there is ample opportunity for H₂ formation via the HAB mechanism prior to thermalization—not just at the surface, but also in the bulk ice.

The (gas phase) activation energy for the HAB reaction is ~ 1.0 eV (Jacobs et al. 1994). A simple kinematic hard-sphere model suggests that the efficiency of translational energy transfer from H to a single H₂O molecule is $\leq 20\%$ per collision (Andersson et al. 2006). Thus the HAB mechanism should still be possible even after a photolytically produced H atom has experienced a number of subsurface collisions. The dynamics of this reaction favors formation of vibrationally cold H₂ products at collision energies up to ~ 2.5 eV (Brouard et al. 2003; Zhang 2006). The population of low- ν states is understandable since reaction (1) is endothermic by 0.6 eV. Thus the H₂($\nu = 0, 1$) products observed in the present experiments are attributed to the HAB mechanism. The rough, porous surface and large surface area of ASW exposes many surface OH groups to direct attack by photoproduced H atoms. Given such surface species, the HAB mechanism can account for the translationally and rotationally excited H₂($\nu = 0$) products. Cold H₂($\nu = 0, T_{\text{rot}} = T_{\text{trans}} = 100$ K) products are likely to originate from HAB reactions occurring at greater depths within the bulk. The reactant H atoms in these cases may be slowed by collisions prior to

reaction, and the product degrees of freedom will progressively thermalize to the bulk temperature as a result of collisions. The H₂ products percolate through the micropores, and/or the extensive network of hydrogen bonded H₂O molecules that constitute the ASW surface, en route to the vacuum.

Much of the H₂ formed by 157 nm photolysis of ASW is in vibrationally excited states. The observed formation of H₂($2 \leq \nu \leq 5$) products is only compatible with the HR mechanism, whereby a photolytically produced H atom scatters onto a previously trapped hydrogen atom yielding H₂. MD simulations of HR on an ASW surface at 70 K predicted formation of translationally excited H₂ molecules in a broad range of vibrational states with $3 \leq \nu \leq 12$, peaking at $\nu = 9$ (Takahashi 1999). In related experimental work, Price and coworkers have reported similar results from HR on a cold graphite surface (Creighan et al. 2006; Islam et al. 2007; Latimer et al. 2008).

The H₂($\nu = 3$) photoproducts also exhibit two distinct translational energy distributions. The small yield of fast H₂($\nu = 3, T_{\text{trans}} = 1800$ K) products is attributed to an Eley-Rideal type mechanism, whereby a photoproduced H atom recombines with an H atom previously trapped close to the ice surface-vacuum interface. Given the optical penetration depth at 157 nm, many of the H atoms will be formed at sites beneath the microporous ice surface, and have to travel some distance in the bulk before colliding with a H atom trapped at or very close to the ASW surface (Al-Halabi et al. 2002). Since the residence time of H atoms on the ice surface at 100 K could be in the order of μs , the H atom concentration in the present experiments must decay completely in the time between laser pulses, but is nevertheless high enough during and immediately after each 20 ns laser pulse (flux $\sim 10^{14}$ photons pulse⁻¹) for HR reaction to occur. Under the much lower photon fluxes prevailing in interstellar space, however, H₂ formation via the HR mechanism at the ice surface must be a very minor process. In the case of ASW, however, it can contribute significantly, as described in § 1.

The majority of the H₂($\nu = 3$) photoproducts are detected with near-thermal translational energies, consistent with H₂ desorption after H-atom recombination on ASW (Roser et al. 2003; Hornekaer et al. 2003). The slow H₂($\nu = 3, T_{\text{trans}} = 110$ K) products are attributed to the same HR mechanism, but occurring in micropores deeper within the bulk; escape of these H₂ products will involve multiple collisions with water molecules as a result of which their translational energies thermalize to that of the bulk. The considerable energy release upon HR can also be expected to heat the immediate environment of the reaction, and thereby lead to the simultaneous release of intact gas-phase water molecules. Thus the parti-

tioning of the excess energy indirectly influences the evaporation (photoerosion) rate of the ice.

The rotational excitation of the H_2 products is also governed by collisions within the bulk ice film. Although thermalized translationally, the rotational energy distributions of the slow $\text{H}_2(\nu = 3)$ products are very nonthermal, as shown in the bottom panel of Figure 2. This can be understood as follows: vibrational quenching of H_2 is generally rather inefficient, but can show interesting resonance effects (Bodo & Gianturco 2006) that probably contribute to the unusual observed rotational population distributions. As a result, the more closely spaced, low J levels collisionally relax more efficiently than the higher J levels, with the results that (1) the higher J levels retain significant population, and (2) the population distribution among the $J = 0$ –17 states cannot be described by a single rotational temperature. MD simulations of the HR mechanism on an ASW surface at 70 K returned a translational energy for $\text{H}_2(\nu = 3)$ products of 1.3 eV (7500 K) that is significantly higher than the value observed in the present work ($T_{\text{trans}} = 1800$ K), even for just the fast $\text{H}_2(\nu = 3)$ component (Takahashi 1999). The theoretically predicted rotational energy (0.52 eV) is, however, very comparable to the observed value ($\langle E_{\text{rot}} \rangle = 0.54$ eV).

When H_2 is produced, the excess energy is partitioned into H_2 and the ice surface. Table 1 presents a summary of the deduced energy partitioning and the relative $\text{H}_2(\nu = 2, 3, 4)$ product state distributions, where the relative vibrational populations have been determined from the integrated TOF intensities of the $J = 1$ –13 (ortho) products. The vibrational population distribution derived here is consistent with the results of an MD simulation of HR on a water ice surface, which predicted formation of vibrationally excited H_2 with $\nu \geq 3$ and peaking at $\nu = 9$ (Takahashi 1999).

5. ASTROPHYSICAL IMPLICATIONS

The present experiment is relevant to H_2 formation by photolysis of the water ice mantle on dust grains in the outer solar system and in the warmer regions ($20 \text{ K} < T < 100 \text{ K}$) of the interstellar medium (e.g., in the vicinity of protostars). H_2 formation by H-H recombination on the surface of ice grains is strongly suppressed in such regions, because of the very short residence time of thermal hydrogen atoms (from the gas phase) on the ice grain surface at $T > 20 \text{ K}$. Indeed, a recent semiempirical calculation based on experimental data suggests that the ice surface only supports a high H-H recombination efficiency in a narrow temperature window between 10 and 20 K (Perets et al. 2005). The UV source in molecular clouds is cosmic-ray pumped hydrogen, so the dominant photoexcitation wavelengths available are H Ly α and within the Lyman band of H_2 .

The predicted UV flux is $>10^3 \text{ cm}^{-2} \text{ s}^{-1}$ (Prasad & Tarafdar 1983). Blackbody radiation within the envelopes of protostars includes a broad UV wavelength distribution but the spectrum is generally much softer (see, for example, Spaans 1996) and the vacuum UV region—which contains the most important photons for photochemical processing—is again dominated by Ly α and the Lyman band (Bergin et al. 2003).

The rate of H_2 formation was not measured directly in the present study, but it can be estimated using the results of previous work (Watanabe et al. 2000). Assuming typical parameters in quiescent clouds, i.e., a UV flux of $10^3 \text{ cm}^{-2} \text{ s}^{-1}$, a grain number density of 10^{-8} cm^{-3} , and a grain cross section of 10^{-10} cm^2 , the H_2 formation rate is $\sim 10^{-16} \text{ cm}^{-3} \text{ s}^{-1}$. This value is 2–3 orders of magnitude smaller than that for H-H recombination of adsorbed H atoms at $T \sim 10 \text{ K}$ (Manicò et al. 2001). In warmer regions, such as those illuminated by protostars for example, we can expect higher temperatures ($T > 20 \text{ K}$) and stronger UV radiation fields. If the H-H recombination efficiency dropped by just 2 orders of magnitude and the UV flux increased by a similar amount, then the rate of H_2 formation rate from photolysis of water ice would exceed that from recombination of adsorbed H atoms. (For reference, it is worth pointing out that the 157 nm laser used in the present study delivers a fluence of $10^{14} \text{ cm}^{-2} \text{ pulse}^{-1}$, which roughly corresponds to that in molecular clouds over 10^4 yr).

The present results provide information about the energy disposal in H_2 products arising via different formation mechanisms. Formation pumping of the H_2 rovibrational level distribution, UV pumping, and shock heating have all been invoked previously to explain the observed high rovibrational excitation of H_2 . (Lebourlot et al. 1995; Takahashi 1999; Casu & Cecchi-Pestellini 2005). However, the results of these studies differ quantitatively from one other, especially with regards to the proposed rotational distributions. Such differences can be attributed to the different surface materials assumed in the models, and to difficulties in partitioning the heat of reaction. Further, these studies do not include possible formation pumping of H_2 from the photolysis of ice. The present study is the first to show that the H_2 molecules produced photolytically from ice are both vibrationally and rotationally excited. $\text{H}_2(\nu = 5)$ molecules are the most highly vibrationally excited species detected in the present work, but this limit is dictated by experimental (Franck-Condon) limitations, and the deduced vibrational population distribution clearly suggests population of yet higher ν states. Thus photolysis of the ice mantle of dust grains could very well be one of origins of the observed highly rovibrationally excited H_2 (Burton et al. 2002). Further, the deduced g_{OPR} value of 3 implies the need for a suitable ortho-para conversion mechanism after H_2 formation, since the interstellar $g_{\text{OPR}} < 3$.

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