Destruction Rate of H_3^+ by Low-Energy Electrons Measured in a Storage-Ring Experiment

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Knowledge of the abundance of H_3^+ is needed in interstellar and planetary atmospheric chemistry. An important destruction mechanism of H_3^+ is low-energy electron impact followed by dissociation, but estimates of the reaction rate span several orders of magnitude. As an attempt to resolve this uncertainty, the cross section for dissociative recombination of vibrationally cold H_3^+ has been measured with an ion storage ring down to collision energies below 1 millielectron volt. A rate coefficient of 1.15×10^{-7} cubic centimeters per second at 300 kelvin was deduced. The cross section scaled with collision energy according to $E^{-1.15}$, giving the rate a temperature dependence of $T^{-0.65}$.

Protonized hydrogen, H_3^+, is the simplest stable polyatomic molecule and the most abundant molecular ion in any hydrogen plasma (*1*). It plays a key role as the initiator of chemical reactions in various extraterrestrial environments because of its willingness to give up one proton to other elements (*2*) and has recently been discovered in the atmospheres of Saturn (*1*), Jupiter (*3–5*), and Uranus (*6*) and possibly in the supernova 1987A (*7*). When modeling abundances of, for instance, various hydrocarbons in a hydrogen-rich environment such as a plasma or an interstellar cloud, one needs information on the rates of formation and destruction of H_3^+. The dominating loss mechanism of H_3^+ is low-energy electron recombination followed by dissociation into neutral fragments (*8*) according to the exothermic reactions $H_3^+ + e \rightarrow H + H + H$ or $H_3^+ + e \rightarrow H_2 + H$, hereafter referred to as dissociative recombination. Laboratory data on the rate coefficient for dissociative recombination of H_3^+ show a considerable uncertainty: Reported values show a spread of four orders of magnitude.

It is believed that H_3^+ is present in appreciable amounts in both dense and diffuse interstellar clouds, although extensive efforts to observe it in interstellar clouds by means of infrared absorption spectroscopy have not been successful (*1*). Spectroscopic detection of H_3^+ is crucial for the understanding of the initial ion-neutral reactions of interstellar clouds (*1*). The rate-limiting process for production of H_3^+ is the cosmic-ray ionization rate, which, however, is unknown (*1, 9, 10*). In both dense and diffuse interstellar clouds, H_3^+ initiates reaction networks that lead to the production of a variety of hydrocarbons, as well as carbon monoxide (CO) and ammonia (NH_3). Furthermore, H_3^+ is partly responsible for the formation of the hydroxyl radical ion (OH^+), which, by subsequent hydrogen abstraction and neutralization through electron recombination, produces H_2O and OH. However, OH^+ is also formed by the alternate reaction $O + H^+ \rightarrow O^+ + H$, followed by a rapid reaction of O^+ and H_2; the relative importance of these two different routes to formation of OH^+ depends critically on the rate for destruction of H_3^+. A high rate ($>10^{-9}$ cm^3 s^{-1} at low temperatures) for dissociative recombination of H_3^+ would favor the latter reaction path (*10*).

Because both the production rate and the destruction rate of H_3^+ in interstellar clouds are uncertain but are important parameters in the modeling of the chemical dynamics, knowledge of the rates for any one of the processes would considerably improve understanding of the evolution of interstellar clouds. Because of the ignorance of the accurate value for the reaction rate for dissociative recombination, these and many other questions have remained open in the chemical models of diffuse interstellar clouds (*10*). Chemical models have been developed to account for the infrared line intensities of the auroral regions of Jupiter (*3*), where the cosmic-ray ionization rate is known, and of supernova 1987A (*7*). In both models, a quite high rate (10^{-7} cm^3 s^{-1}) for dissociative recombination must be assumed to reproduce the measured spectra. Dissociative recombination of H_3^+ has recently been studied by our group at collision energies up to 30 eV (*11*). In this report, we investigate the cross section down to fractions of a millielectron volt of collision energy.

Dissociative recombination of H_3^+ has previously been analyzed experimentally by a number of different techniques, some in which the reaction rate was measured directly (*12–18*) and others in which the rate was calculated from the measured cross section (*19–22*). The former category is dominated by various microwave discharge experiments, where the concentration of H_3^+ in the afterglow of the discharge is monitored in a time-resolved manner. The latter category consists entirely of merged-beam or inclined-beam single-pass experiments. For a summary of the various experiments and a compilation of results, see (*16*). Laboratory measurements of the reaction rate show a considerable spread, from $<10^{-11}$ to 2×10^{-7} cm^3 s^{-1}. Furthermore, early theoretical attempts to calculate low-energy dissociative recombination (*23*) failed to produce the high rates found in some of the experiments. The situation has improved recently since Bates and co-workers (*24*) suggested a multistep mechanism that seems to account for a much higher destruction rate, although the theory does not yet provide quantitative predictions nor any definite information on the temperature dependence of the reaction rate. One probable reason for the large spread in laboratory data is the indeterminate mixture of internal excitation states contained in the H_3^+ ions used in the experiments (*20, 21*). In our experiment, however, it was possible to experimentally establish that ions were indeed in their ground vibrational state (*11*). At the ion storage ring CRYRING in Stockholm, stored molecular ions were allowed to collide with electrons from the electron cooler. The primary advantages of a storage-ring experiment are the very high counting rates and the possibility of preparing all the ions in the lowest vibrational level of the electronic ground-state potential. The experimental procedure has been thoroughly presented elsewhere (*11, 25*) and will not be described in very great detail here.

The environments where dissociative recombination is expected to occur range from interstellar clouds, where temperatures can be down to a few degrees, to planetary atmospheres with temperatures of hundreds of degrees (*12*). Therefore, information about the absolute cross section as a function of energy is very useful, allowing the rate to be calculated for any temperature. If a cross section is to be properly extracted from data measured in the ion

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storage ring, the velocity distribution of the electrons and ions must be appropriately described. It will not be correct in general to regard the beams as monoenergetic: This would lead to incorrect conclusions about the cross section at low collision energy. In our experiment, the electron beam was cooled by acceleration in the forward direction to a temperature that has been experimentally determined to be 6×10^{-5} eV (*26*) and is very small in comparison with the temperature of the transverse degrees of freedom (0.10 to 0.15 eV) (*26, 27*). During the first seconds after each injection into the storage ring, the ions undergo electron cooling, whereby the mutual electrostatic forces equalize the electron and ion mean velocities and reduce the transverse and longitudinal ion temperatures to match those of the colder electrons. Because of the large mass of an ion in comparison with the electron mass, the random motion of the stored ions is negligible in relation to the velocity spread of the electrons. Therefore, we need not consider the temperature of the ion beam when we describe the distribution of collision energy in the experiment, and the ions can be regarded as monoenergetic. Following the initial cooling period, the speed of the electron beam is tuned away from the velocity-matched condition so that the desired collision energy is obtained. The energy resolution of the experiment is then determined by the electron thermal motion, which is dominated by the transverse temperature, $kT_{\perp} \approx 0.1$ eV, where k is Boltzmann's constant.

We measured the number of dissociative recombination reactions per unit time (Fig. 1). The data can, following the above discussion, be modeled by a reaction probability folded by an anisotropic, or "flattened," electron velocity distribution (*28*) together with essentially cold ions (*29*) according to the expression

$$\langle v_{\mathrm{rel}}\sigma\rangle = \int v_{\mathrm{rel}}\sigma(v_{\mathrm{rel}})f(\mathbf{v}_e)d^3\mathbf{v}_e \qquad (1)$$

where $v_{\mathrm{rel}} = |\mathbf{v}_e - \mathbf{v}_i|$ is the speed of the electrons relative to the ions, $f(\mathbf{v}_e)d^3\mathbf{v}_e$ is the number of electrons in a volume element of velocity space, and the integration extends over all velocity space. The flattened electron velocity distribution, as seen in the laboratory frame, is a product of a longitudinal distribution, centered at a detuning velocity (Δ), and a transverse distribution, that is, $f(\mathbf{v}_e) = f_{\parallel}(v_{\parallel} - \Delta)\, f_{\perp}(v_{\perp})$. The detuning can be either positive or negative, meaning that the electron velocity can be tuned away from the velocity-matched cooling condition by allowing the electrons to move faster or slower than the ions. As expected (Fig. 1), the measured data show no dependence on the sign of the detuning.

In practice, the calculation of $\langle v_{\mathrm{rel}}\sigma\rangle$ can be simplified by neglecting the longitudinal electron temperature because it is low enough that it does not influence the conclusions in this work (*29*). At low collision energies, it is customary to assume a model cross section with an inverse power-energy dependence. Such a model cross section was used to compute $\langle v_{\mathrm{rel}}\sigma\rangle$, which was adjusted to the measured data; the cross section that produced the best fit was $\sigma = 1.43 \times 10^{-16}/E^{1.15}$ cm^2 (*30*) (Fig. 1).

To obtain a temperature-dependent reaction rate, which is needed in a practical situation, we folded the cross section with an isotropic electron distribution. It was necessary to justify an extrapolation of the cross section to very low energy. Wigner (*31*) has shown that cross sections for reactions between particles in the low-energy limit show the same energy dependence, independent of the structure of the particles, as long as the long-range interaction between the reacting particles is the same. For a long-range Coulomb attraction between the reacting particles, the universal energy dependence is $1/E$, no matter what the reaction mechanism is. However, the energy up to which the simple $1/E$ law is valid has, of course, to be checked experimentally in each case. McGowan and coworkers investigated 25 molecules and found experimentally that cross sections scale according to $1/E$ up to 0.1 eV in most cases (*32*), including that for H_3^+. A more recent investigation of H_3^+ by Mitchell and co-workers (*22*) showed a departure from the $1/E$ dependence. Resonant structures in the cross section may cause deviation from the $1/E$ law predicted by the asymptotic theory of Wigner. We conclude that, for the energy range investigated here, the region of very low energy where the $1/E$ law applies has not yet been reached. Thus, we use an extrapolation of the cross section to these lower energies according to the $1/E^{1.15}$ energy dependence. Possible errors in the deduced reaction rate attributable to deviation from $1/E^{1.15}$ at energies less than 10^{-4} eV will be negligible for the temperature range of interest. The rate coefficient, $\alpha(T)$, was calculated with a uniform Maxwellian electron distribution of temperature according to

$$\alpha(T) = \frac{8\pi m_e}{(2\pi m_e kT)^{3/2}} \int_0^{\infty} \sigma(E)e^{-E/kT}E\,dE \qquad (2)$$

where m_e is the electron mass. Because other structures appear in the cross section at $E = 0.1$ eV, we should not use the $1/E^{1.15}$ law above 0.1 eV; for practical purposes, it suffices to limit the integration at 0.1 eV. Performing the integration, one arrives at a closed form expression for the dissociative recombination rate as a function of temperature. We thus find $\alpha(T) = 4.6 \times 10^{-6}/T^{0.65}$ cm^3 s^{-1}, which implies a rate of 1.15×10^{-7} cm^3 s^{-1} at 300 K. The uncertainty in the reaction rate is about 20%, originating from uncertainties in the transverse electron temperature, in the measurement of the circulating ion current, and in the length of the interaction section. For comparison, earlier experiments in which the ions were claimed to be in the lowest vibrational state gave rates for dissociative recombination of 1.7×10^{-7} cm^3 s^{-1} at 300 K (*14*), 1.1×10^{-7} cm^3 s^{-1} at 650 K (*15*), and 1.5×10^{-7} cm^3 s^{-1} at 300 K (*18*).

There are no quantitative theoretical predictions of either the rate coefficient or the cross section at low collision energy. However, our measured cross section at high energy, $E \approx 10$ eV (*11*), is in very good agreement with recent theoretical calculations (*33*), which also preliminarily indicate that a completely vibrationally relaxed population of H_3^+ best describes the

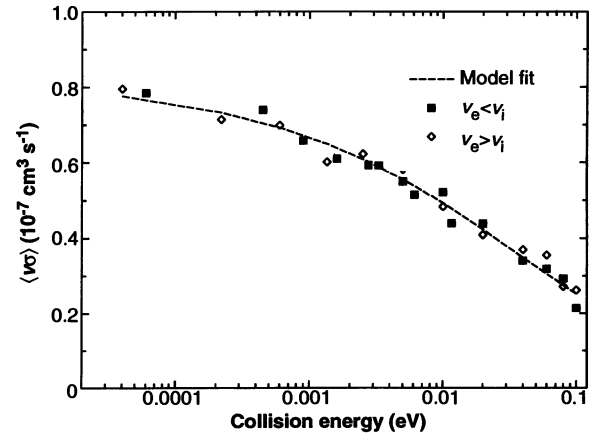

Fig. 1. The measured rate as a function of collision energy for the reactions $H_3^+ + e \rightarrow H + H + H$ or $H_3^+ + e \rightarrow H_2 + H$. The experimental data are symmetric with respect to whether the electrons move faster or slower than the ions. The dashed line is a convolution of a model cross section of the type $1.43 \times 10^{-16}/E^{1.15}$ cm^2, which was folded with the flattened electron velocity distribution with a transverse temperature of 0.125 eV and zero longitudinal temperature. The data illustrate that sensible results can be obtained for collision energies down to $\sim 10^{-4}$ eV despite the fact that the resolution is limited by the transverse temperature of the electron beam: Although the limited resolution tends to smear the curve, there still remains some slope even at very low energy.

measured data (*11*). Finally, a possible complication of the results derived in this work may be that the cross section possesses a pronounced dependence on rotation of the molecule. However, Amano (*14*) has investigated the dependence of the reaction rate on rotation between 110 and 273 K and concluded that the rotational dependence is very small or negligible. This does not, of course, exclude a speculative possibility of a stronger rotational dependence for rate coefficients at very low temperatures.

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30. This result corresponds to $kT_\perp = 0.125$ eV. When we take into account the uncertainty in electron temperature, we find $\sigma = (1.43 \pm 0.02) \times 10^{-16} / E^{(1.15 \pm 0.02)}$ cm^2, where the minus sign refers to $kT_\perp = 0.1$ eV and the plus sign to $kT_\perp = 0.15$ eV. In a previous paper (*11*), we represented the cross section at a higher energy range ($E > 0.0025$ eV) by a curve with an energy dependence according to $1/E^{1.44}$. However, the $1/E^{1.44}$ curve should merely be regarded as an attempt to describe the cross section up to 1 eV of collision energy and should not be used to deduce a reaction rate. To avoid confusion, we emphasize that figure 4 in (*11*) represents average cross section, $\langle v\sigma \rangle / v$, which practically equals the cross section σ for $E > 0.1$ eV.
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34. The authors thank A. E. Orel and K. C. Kulander for communicating results from calculations of the cross section before publication and D. Belkic for valuable discussions regarding the energy dependence of cross sections, in particular concerning the paper by Wigner (*31*). This work was supported by the Göran Gustafsson Foundation and the Swedish Natural Science Research Council. J.R.M. was supported by NSF, and S.D. was sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

7 September 1993; accepted 23 November 1993

Hubble Space Telescope Observations of Comet P/Shoemaker-Levy 9 (1993e)

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The Hubble Space Telescope observed the fragmented comet P/Shoemaker-Levy 9 (1993e) (P indicates that it is a periodic comet) on 1 July 1993. Approximately 20 individual nuclei and their comae were observed in images taken with the Planetary Camera. After subtraction of the comae light, the 11 brightest nuclei have magnitudes between ~23.7 and 24.8. Assuming that the geometric albedo is 0.04, these magnitudes imply that the nuclear diameters are in the range ~2.5 to 4.3 kilometers. If the density of each nucleus is 1 gram per cubic centimeter, the total energy deposited by the impact of these 11 nuclei into Jupiter's atmosphere next July will be ~4 × 10^{30} ergs (~10^8 megatons of TNT). This latter number should be regarded as an upper limit because the nuclear magnitudes probably contain a small residual coma contribution. The Faint Object Spectrograph was used to search for fluorescence from OH, which is usually an excellent indicator of cometary activity. No OH emission was detected, and this can be translated into an upper limit on the water production rate of ~2 × 10^{27} molecules per second.

In late March of 1993, a string of comet-like bodies was discovered near Jupiter (*1*). Subsequent observations showed convincingly that this object, comet P/Shoemaker-Levy 9 (1993e), made a close approach (~1.4 R_J; R_J is Jupiter's radius) to Jupiter in July 1992, at which time tidal forces broke the parent body into numerous fragments, which now follow slightly different orbits (*2*). Integration of these orbits forward in time shows that all of the major fragments in the comet will almost certainly impact Jupiter's atmosphere over an approximately 6-day period centered on 20 July 1994. Because the fragments will be traveling rapidly (~60 km s^{-1}) as they enter Jupiter's atmosphere, the impact could be spectacular. Although the impacts are predicted to occur on the hemisphere that is unobservable from Earth, the effects on the atmosphere will probably still be visible as the impact zone rotates into Earth's view (Jupiter's rotation period is 9.84 hours).

The energy deposited into Jupiter's atmosphere by each impacting body is proportional to the cube of its size, so it is important to obtain the best possible size estimates. The Hubble Space Telescope (HST) has the highest spatial resolution of

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