Branching ratios in the dissociative recombination of polyatomic ions: The H_3^+ case

D. Strasser,[1] J. Levin,[2] H. B. Pedersen,[1] O. Heber,[1] A. Wolf,[2] D. Schwalm,[2] and D. Zajfman[1,2]

[1]*Department of Particle Physics, Weizmann Institute of Science, Rehovot, 76100, Israel*
[2]*Max-Planck Institut für Kernphysik, D-69019 Heidelberg, Germany*

A statistical model serving to estimate the branching ratios in the dissociative recombination of polyatomic molecular ions is described. Simple phase-space assumptions are employed separately for the electronic capture step and the subsequent dissociation and yield predictions in good agreement with existing data on H_3^+. Also the vibrational state populations of molecular fragments can be obtained and for H_3^+ are found to agree well with recent measurements.

The dissociative recombination (DR) of molecular ions is a key process for the formation of complex molecules in dense interstellar clouds [1,2]. Among all species, H_3^+ attracts particular interest owing to its key role in astrochemistry [3]. Moreover, the low-energy DR rate for H_3^+ has been a controversial issue for many years, and there are still unexplained differences reaching orders of magnitude among the experimental and theoretical results [3]. In fact, for the low-energy DR of H_3^+ even the driving mechanisms have not yet been fully clarified, while at higher energy, they seem to be reasonably understood [4]. For H_3^+ the DR process with low-kinetic energy electrons can be depicted as (cf. Fig. 1)

$$H_3^+ + e^-(E) \rightarrow \begin{cases} H(1s) + H(1s) + H(1s) & (\alpha) \\ H_2(X\,^1\Sigma_g)(v) + H(1s) & (\beta) \end{cases} \quad (1)$$
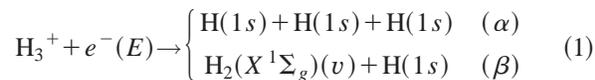
with total product kinetic energies of $E_\alpha = 4.76$ eV and $E_\beta = 9.23$ eV [the latter being given for the vibrational ground state ($v = 0$) of the H_2 fragment]. The first complete branching ratio (BR) measurement for the DR of vibrationally cold H_3^+, as a function of electron kinetic energy E, was carried out by Datz *et al.* [5]. The three-body product channel α was dominant for low E with 75% of the total reaction rate and only 25% remaining for the molecular channel β. So far, no explanations for this ratio nor for the structure of the BR observed at higher electron energies (~ 0.4–20 eV) have been given. Detailed experimental studies of the dissociation dynamics following the DR of H_3^+ have been performed recently [6], yielding also the vibrational level populations of the H_2 fragment produced in channel β. For more complex molecular ions (such as H_2O^+, CH_2^+, H_3O^+, and others [7–12]) DR measurements also showed a strongly dominant many-body fragmentation.

It has been seen as an appealing goal for more than two decades to provide a theoretical model capable of explaining these experimental results on a unified basis. The first attempt to predict the DR product branching ratios was performed by Herbst and coworkers [13,14], applying the statistical phase-space model of chemical reactions. Galloway and Herbst [15] later modified the phase-space theory, considering the effects of Franck-Condon factors and curve crossings as also emphasized by Bates [16]. However, after comparisons with experimental results for several tetratomic

systems the authors of Ref. [15] reached the conclusion that the model is lacking for such systems "general predictive power, free from parametrization."

Here we present a model describing product branching ratios for the DR of polyatomic molecular ions, based on simple statistical assumptions about the redistribution of energy among the dissociating nuclei and about the population of electronic potential surfaces. The development of this model was initially motivated by our recent experimental studies [6] of the dissociation process following electron capture on H_3^+ at the heavy-ion test storage ring (TSR), yielding the kinematic correlations in the three-body channel as well as the vibrational excitation of the H_2 product in the two-body channel; as shown below, the H_2 product vibrational populations measured in this experiment can be well described by a simple model considering the relative energy available within a pair of H nuclei, assuming a uniform distribution of the fragments in the three-body phase space. The
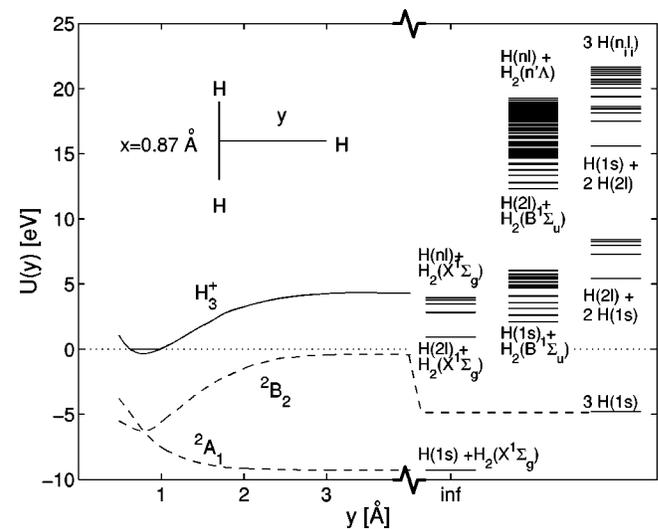
FIG. 1. Molecular potentials and final-state energies relevant for the DR of H_3^+. Indicated are the H_3^+ ground-state (solid curve) and final energies for various electronic excitations (rovibrational ground state for all H_2 fragment energies). Also shown are the H_3 potential curves (dashed) correlating to the lowest exit channels, reached at near-zero initial energy. The dependence on the Jacobi coordinate y is shown for the geometry indicated in the inset.

same energy randomization among the nuclei should also influence the product branching ratio, since a pair relative energy exceeding the H_2 dissociation energy prevents the formation of this molecular product in favor of additional contributions to the three-body exit channel. With additional simple statistical assumptions about the population of electronic configurations, the experimental low-energy value of the product branching ratio can be very well reproduced, and structures in the observed energy dependence of the branching ratio can be explained.

The DR of a molecular ion can in its main features be described as a two-step process, a basic picture which we shall adopt also here. In the first step, an electron is captured into an electronic configuration of the neutral state, corresponding to a certain potential-energy surface (PES). In the second step, this capture is followed by a rapid dissociation of the system on the PES into an exit channel. Of all electronic configurations, some (referred to as repulsive-type configurations) yield only atomic products while others (denoted as bound-type configurations) may also support molecular fragments. Let us denote by E_i the asymptotic *electronic* energy after fragmentation associated with an energy surface i. Then, at an initial energy E, a total energy $E_{k,i} = E - E_i$ is available for the relative translational motion between the fragments *plus* all rovibrational motion within those fragments which are molecules. For low-energy recombination of $H_3{}^+$ the exit channel $H + H_2$ can be reached via the $^2A_1$ PES of H_3, which represents a bound-type configuration, while the exit channel of three ground-state H atoms correlates to the $^{2,4}B_2$ surfaces, which are of the repulsive type.

In addition to the electronic pathways i, we consider *product channels* distinguished by the composition and the states of fragments. Whereas a repulsive-type configuration always yields fully dissociated fragments, a bound-type configuration may contribute not only to product channels with bound molecular fragments but, if sufficient energy $E_{k,i}$ is available, with a certain probability also to fully dissociated exit channels. Thus, for $H_3{}^+$ the bound-type configuration as represented by the $^2A_1$ surface can contribute to both product channels β and α.

For any product channel γ, we write its formation probability P_γ as a sum over contributions from various electronic pathways i,

$$P_\gamma = A \sum_i \lambda_i P_\gamma^i, \qquad (2)$$

where λ_i denotes the relative contribution of an electronic configuration i and P_γ^i the probability that fragmentation on the associated PES leads to the products γ; A is a normalization factor so that $\Sigma_\gamma P_\gamma = 1$. To estimate the probability P_γ^i, we assume that the energy release $E_{k,i}$ is randomized among *all* the nuclei which evolve on the multidimensional PES, taking into account the standard restrictions of energy and momentum conservation. If the configuration i is of the bound type and γ denotes a product channel where a subset of the nuclei can form a molecule in an electronic state j, we derive the relative kinetic-energy distribution for the specific

nuclei in this subset and then assume a bound molecule to be formed in all cases where the relative kinetic energy remains below the molecular binding energy $E_{b,j}$. Otherwise, atomic fragments are produced and the electronic configuration contributes to the fully dissociated product channel. For the cases where indeed a molecule is formed, the relative energy distribution for the subset predicts in addition the degree of rovibrational excitation for this product.

The corresponding relative kinetic-energy distribution for complete phase-space randomization can be obtained in a straightforward way for a dissociating three-body system with a total kinetic-energy E_k by using the Dalitz coordinates [17] $\eta_1 = (2E_3 - E_2 - E_1)/3E_k$ and $\eta_2 = (E_2 - E_1)/\sqrt{3}E_k$, where E_1, E_2, and E_3 are the kinetic energies of each of the three fragment atoms, respectively, and $E_k = E_1 + E_2 + E_3$ is the total kinetic energy. The relative kinetic energy in the center-of-mass system of two selected particles can be expressed in terms of the Dalitz coordinates. For example, one obtains

$$\frac{E_{12}}{E_k} = \frac{2m_1 + 2m_2 - m_3}{3(m_1 + m_2)} - \eta_1 \frac{m_1 + m_2 + m_3}{m_1 + m_2}, \qquad (3)$$

where m_1, m_2, and m_3 are the particle masses. The Dalitz coordinates are defined [17] such that a random phase-space distribution for the three particles corresponds to a uniform distribution in the (η_1, η_2) plane, confined within a region given by energy and momentum conservation. For equal masses, this region is a circle of radius 1/3, and using $\eta_1 = 1/3 - (2/3)E_{12}/E_k$ the normalized relative kinetic-energy distribution $P(E_{12})$ is obtained by integration over η_2 as

$$P(E_{12})dE_{12} = \frac{9}{\pi} \int d\eta_2 \left| \frac{d\eta_1}{dE_{12}} \right| dE_{12}$$

$$= \frac{4}{\pi E_k} \sqrt{1 - \left(1 - \frac{2E_{12}}{E_k} \right)^2} \, dE_{12}. \qquad (4)$$

For the case of $H_3{}^+$ recombination with low-energy electrons towards $H + H_2$ we have $E_k = E_{k\,^2A_1} = 9.23$ eV and $E_{b,j} = E_{b,H_2(X\,^1\Sigma)} = 4.48$ eV. As a first step, we have derived the vibrational distribution $P_\beta(v)$ of the $H_2(X\,^1\Sigma)$ products for this channel, using a simple quantization of the continuous energy distribution of Eq. (4) according to

$$P_\beta(v) = \int_{(E_{v-1} + E_v)/2}^{(E_v + E_{v+1})/2} P(E_{12}) dE_{12} \qquad (5)$$

(lower limit of 0 and upper limit of $E_{b,j}$ for $v = 0$ and $v = v_{max}$, respectively). The predicted relative vibrational populations are in very good agreement with our recent experimental data [6] (see Fig. 2).

By the same reasoning, if γ denotes a product channel where one pair of fragments atoms forms a molecule with binding-energy $E_{b,j}$ and is reached by fragmentation along the bound-type electronic pathway i, the molecular product fraction is obtained by
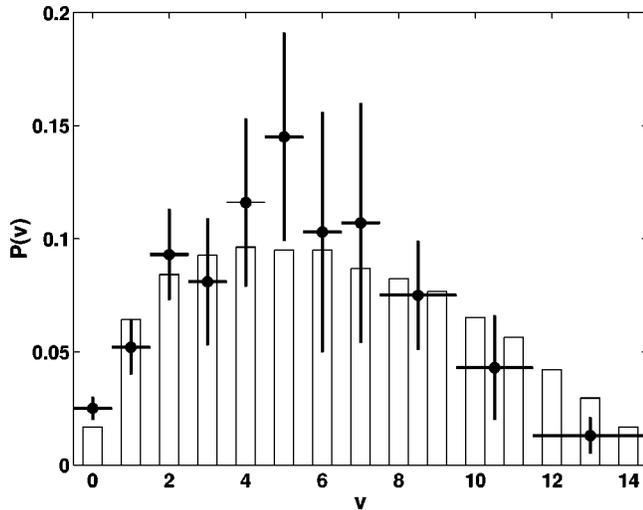
FIG. 2. Relative vibrational state populations $P(v)$ of H_2 fragments from the DR of H_3^+ at near-zero initial energy as obtained from the model (open bars), compared to the experimental results [6] (open circles).

$$P_\gamma^i = \int_0^{E_{b,j}} P(E_{12}) dE_{12}. \qquad (6)$$

For H_3^+, again Eq. (4) is applied. At near-zero electron energy, the only bound-type path is the $^2A_1$ surface, which fixes $E_k = E_{k,i}$ and $E_{b,j}$ as above. Its contribution to the two-body product channel β, from Eq. (6), is $P_\beta^{2A_1} = 0.48$, while the dissociation fraction is given by the complement ($P_\alpha^{2A_1} = 0.52$). However, the overall branching ratio between the three- and two-body product channels as represented by P_α and P_β [see Eq. (2)] also depends on the repulsive-type configurations and hence the relative probabilities λ_i at which electronic states are populated in the electron capture step. Of the two $^{2,4}B_2$ repulsive-type configurations with energetically open-exit channels at near-zero electron energy, only the doublet configuration $^2B_2$ can be formed from the initial state corresponding to the singlet ground state of H_3^+ and a free electron. We now assume that *each PES which is correlated to an energetically open asymptotic exit channel contributes to the reaction rate according to the statistical weight of the corresponding electronic configuration.* This seems to be a very rough assumption as it disregards the issue of potential-surface crossings and favorable Franck-Condon overlap factors which are usually assumed to determine the electron capture probability; however, as opposed to diatomic systems for which the latter considerations have been found important, we would expect a simple statistical assumption to become increasingly useful for polyatomic systems where often many pathways in a multidimensional coordinate space can contribute to a given reaction. For low-energy recombination of H_3^+ the statistical assumption implies $\lambda_{2_{B_2}} = \lambda_{2_{A_1}} = 2$, i.e., it is determined by the spin multiplicities $\lambda_s = 2$. Remarkably, the normalized product branching ratios of $P_\alpha = 0.76$ and $P_\beta = 0.24$, following from the model of random fragment energy distribution *and* a sta-

tistical population of the relevant electronic energy surfaces, are in perfect agreement with the experimental result [5] of $P_\alpha/P_\beta = 3$ for the BR in the low-energy DR of H_3^+.

We have tested the more general predictive power of our model based on these two statistical assumptions by calculating also the electron energy dependence of the two- and three-body product branching ratio for H_3^+ for which experimental data by Datz *et al.* [5] are available. Bound-type configurations are added with increasing final-state energy, correlating to the following exit channels (see Fig. 1): $H(nl) + H_2(X\,^1\Sigma_g)$ [atomic Rydberg states, starting with $H(2l) + H_2(X\,^1\Sigma_g)$ at 0.97 eV], $H(1s) + H_2(n'\Lambda)$ [molecular excited states, starting with $H(1s) + H_2(B\,^1\Sigma_u)$ at 1.95 eV] and combinations of both $[H(nl) + H_2(n'\Lambda)$, starting with $H(2l) + H_2(B\,^1\Sigma_u)$ at 12.15 eV].

Channels i leading to molecular singlet states $H_2(n'\,^1\Lambda)$ with $n' \leq 3$ are treated according to Eqs. (4) (with $E_k = E_{k,i}$) and (6); this implies that any decay of excited H_2 states leads to the H_2 electronic ground state. A large fraction of H_2 fragments in other electronically excited states cannot be expected to remain bound because of strong predissociation and because of radiative decay to the $^3\Sigma_u$ dissociative state. We here consider all H_2 triplet states as well as singlet states with $n' \geq 4$ to dissociate and hence to contribute to three-body fragmentation. Although somewhat simplifying, this assumption takes account of usual astrophysical conditions as well as the conditions of most experiments including Ref. [5], where the measurement of the BR was performed a few microseconds after the electron capture, leaving ample time for these decays to occur. The statistical weight of each bound-type configuration is obtained as $\lambda_i = \lambda_s(2l+1)(2-\delta_{\Lambda,0})$ for $H(nl) + H_2(^{1,3}\Lambda)$, with $\lambda_s = 2$ according to the *initial* spin multiplicity of the DR reaction. Excited repulsive-type configurations which correlate to $H(n_1l_1) + H(n_2l_2) + H(n_3l_3)$ are also included, starting with $H(2l_1) + 2H(1s)$ at 5.44 eV; their weight is set to $\lambda_i = \lambda_s\Pi_{k=1}^3(2l_k+1)$. The energy dependence of the theoretical results has been convoluted with the rotational temperature as estimated from the experimental results of Strasser *et al.* [6] and the electron temperature present in the CRYRING storage ring experiment [5].

Figure 3 shows the comparison of the model calculation with the experimental results [5]. The dashed curve includes all the electronic final states as mentioned above. It reproduces the overall shape of the BR as a function of the electron energy, although the calculated values between 0.7 and 7 eV overestimate the measured ones. The comparison between the model and the experimental data provides a rather detailed interpretation of the observed structures. In particular, the rise of the two-body product fraction at ~0.6 eV is due to the opening of the $H(2l) + H_2(X\,^1\Sigma_g)$ electronic channel. The fact that the branching ratio is observed to be approximately independent of the incident electron energy below the $H(2l) + H_2(X\,^1\Sigma_g)$ threshold (0–0.7 eV) and again below $H(3l) + H_2(X\,^1\Sigma_g)$, threshold (~1–2 eV) clearly demonstrates that, once a channel is open electronically, the growing number of rovibrational states energetically accessible for increasing electron energy does not en-
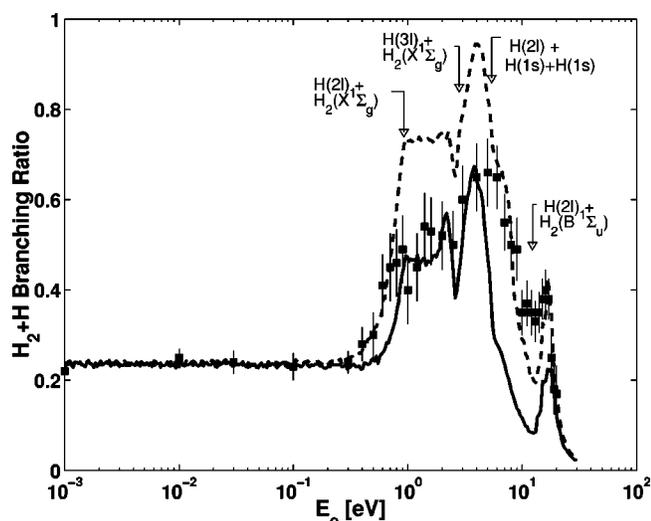
FIG. 3. Branching ratio for the two-body channel as a function of electron energy as obtained from the model including all final states (dashed curve) and final states with $l=0$ only (full curve). Some important final-state threshold energies are indicated. The model includes rotational excitation of the H_3^+ ions and the experimental electron energy distribution.

hance the reaction rate into this channel. This supports the approach of combining separate statistical assumptions for the electronic and the nuclear degrees of freedom, as opposed to considering the total weight of electronic states plus internal rovibrational states [13]. Due to the opening of further channels $H(nl) + H_2(X\,^1\Sigma_g)$ (starting at ~ 2.86 eV for $n=3$) the two-body fraction keeps increasing until ~ 4 eV. At ~ 5.5 eV, the opening of additional repulsive electronic channel leads to a strong drop in the two-body fraction. Starting from ~ 12 eV, the excited bound-type configurations $H(nl) + H_2(n'\Lambda)$ open, producing an additional peak at ~ 15

eV, and the statistical model gives the correct size of this peak once the predissociation and decay of the excited molecular hydrogen states is taken into account.

The assumption that all possible l values are actually populated in the dissociative process should be regarded as an upper limit as electron capture into states with high-electronic angular momentum is expected to be suppressed. In addition, a considerable fraction of the electronic energy surfaces correlated to high-l states of the fragments may be raised up in energy in the molecular complex as a consequence of molecular-orbital promotion, so that their Franck-Condon overlap with the initial state of the DR reaction becomes very small. To obtain the lower limit for the branching ratio in our paper, we therefore repeated our calculation counting only final electronic states with $l=0$. The result is shown by the full line in Fig. 3; the two limiting branching ratio predictions are seen to enclose the measured values over most of the energy range.

The model proposed here yields a straightforward explanation of the finding from many experiments [7–12] that a large degree of fragmentation occurs during the DR of polyatomic molecular ions as, by the energy randomization among the nuclei, exit channels where molecules can be produced also contribute to those with higher fragmentation. This will enhance fragmentation if bound- and repulsive-type configurations among themselves are populated statistically [λ_i in Eq. (2)]. The present model cannot explain the experimental results obtained for the predissociation of H_3 Rydberg states [18].

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