general conclusions about trends in some properties of packed regular polypeptide structures. These generalizations are not restricted by individual constraints that would arise from a specific amino acid sequence, yet they provide explanations for many observed features in proteins. For example, all observed preferences of handedness, as well as the general trends of chain orientation in packed regular structures, have been explained in terms of interaction energies.

Insights gained from studies of the energetics of packing are important for the prediction of protein folding. Information about preferred packing arrangements makes it possible to select for a given protein a small set of probable conformations, which then can be used as starting points for detailed energy computations. This potential application is significant because it helps to alleviate the multiple-minima problem, one of the greatest difficulties that remains in the prediction of three-dimensional structures of proteins.[82] By selecting likely structures at an intermediate level (between the levels of local conformational preferences of the amino acid sequence and the overall folding of the molecule), the number of probable conformations can be lowered considerably. Thus, the analysis of packing constitutes a link between conformational analysis of small peptides and the solution of the protein-folding problem.

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Rydberg States of H_3: Application of Neutralized Ion Beam Techniques

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Introduction

The possible existence and observation of the simplest triatomic molecule, H_3, has been a subject of scientific speculation for several years. Over the past decade, a substantial body of evidence has been obtained which shows that, rather than being a scientific curiosity, the H_3 molecule represents the simplest polyatomic example of an emerging new class of compounds referred to by Herzberg[1] as "Rydberg Molecules". In this Account, we will discuss evidence for the existence of H_3 in a metastable state and many of its spectroscopic properties, which have now been obtained in several types of experimental procedures, including neutralized ion beam techniques.[2] Several excellent reviews of the neutralized ion beam technique have recently been written,[3-6] and the reader is referred to these for a detailed discussion of the technique and its application to larger species.

Historical Background

In the late 1960s, Devienne[7,8] and his associates attempted to produce H_3 molecules in an experiment involving charge neutralization of a fast beam of H_3^+ ions followed by reionization of the neutral products. The sequence of steps was

$$H_3^+ + H_2 \rightarrow H_3^* + H_2^+ \qquad \text{(neutralization)} \quad (1)$$

$$H_3^* + D_2 \rightarrow H_3^+ + e^- + D_2 \qquad \text{(reionization)} \quad (2)$$

The appearance of a mass peak ($m/e = 3$) following reionization in his mass spectrometer was taken as evidence for long-lived H_3 molecules that had to survive transit from the point of formation to the point of reionization (~microseconds). In a separate measurement, the neutralized beam was converted into negative

Gregory I. Gellene was born in Paterson, NJ, in 1957. He received his B.S. in Biochemistry from Georgetown University in 1979 and his Ph.D. from Cornell University in 1983, where he studied with Richard F. Porter, developing neutralized ion beam techniques for the study of transient species. He spent an additional year at Cornell in postdoctoral studies, applying neutralization reionization mass spectrometry to hypervalent radicals. In 1984 he joined the faculty of Notre Dame, where he is currently developing combined optical/neutralized ion beam techniques.

Richard F. Porter has been a Professor of Chemistry at Cornell since 1964. For the past decade he and his students have been utilizing neutralized ion beam techniques to generate polyatomic radicals and metastables which are difficult, if not impossible, to prepare by conventional methods. His interest in this research on novel polyatomics began in 1978 while he was a visiting scientist with Drs. Lewis Friedman and Robert Beuhler in the Chemistry Department at Brookhaven National Laboratory.

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Table I
Comparison of Experimental and Theoretical Values for H_3 Rydberg-State Energies and Lifetimes

	energy, eV			lifetime,[a] ns		
state	expt[b]	KM[c]	PTW[d]	expt	KM[c]	PTW[d]
$2s^2A_1'$	−0.156	−0.246	−0.176	$<10^{-4}$[e]	32	22
$2p^2A_2''$	0.0	0.0	0.0	$\sim10^{-2}$[f]	8×10^4	7×10^4
$3p^2E'$	1.647	1.522	1.626	1[g]	21	22
$3s^2A_1'$	2.044	1.873	2.022	<4[g]	74	58
$3p^2A_2''$	2.093	1.923	2.058	<35[h]	41	47
$3d^2E'$	2.123	1.924	2.091	<11[h]	10	9
$3d^2E''$	2.158	1.953	2.136	<11[h]	12	12
$3d^2A_1'$	2.169	1.962	2.145	<11[h]	12	13

[a] Theoretical lifetimes were calculated by using ab initio matrix elements and experimental ν_{00} transition frequencies considering radiative processes only. [b] Watson, J. K. G. In *From Atoms to Polymers*: *Isoelectronic Analogies*; Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1989. [c] Values of King and Morokuma obtained with a frozen-core methodology without electron correlation. [d] Values of Petsalakis, Theodorakopoulos, and Wright obtained with a MRD-CI methodology with all electrons correlated. [e] Reference 20. [f] Reference 20 for all states of $N > 0$. [g] Strong isotope effect observed; lifetime increases with increasing mass. Reference 45. [h] Value for low rotational levels; high rotational levels have significantly shorter lifetimes, ref 47.

ions in electron-capture collisions with peaks at $m/e = 1$ and 2 in an intensity ratio of about 2:1 and attributed to H^- and H_2^- from H and H_2 breakup products.[8] Doubt has been cast on this interpretation in recent years since H_2^- is now known to be unstable.[9] This leads to the implication that the $m/e = 2$ peak was due to D^- from an HD contaminant, which has the same nominal mass as H_3. Unfortunately, these investigators did not report their results for D_3, which would have helped to clarify the problem. Later, Gray and Tomlinson[10] investigated the processes

$$H_3^+ + Li(g) \rightarrow H_3^* + Li^+ \qquad (3)$$

and

$$H_3^* + He \rightarrow H_3^+ + e^- + He \qquad (4)$$

but found no evidence for metastable H_3^* neutrals and suggested that the $m/e = 3$ peak in Devienne's experiment was due to an HD impurity. Some positive indication for a transient metastable D_3 was obtained by Nagasaki and co-workers,[11] who investigated the D_3^+/N_2 charge-transfer reaction and observed an ion at $m/e = 6$ on reionization. However, possible states of this metastable were not discussed. Theoretical calculations have shown rather clearly that with the exception of a very weak H_2- - -H van der Waals minimum the ground state of H_3 is unstable with respect to H_2 + H for all molecular configurations from an equilateral triangle to a collinear assembly of three H's.[12-15] In 1979, Cisneros and co-workers[16] and Vogler[17,18] measured the kinetic energy release in the fragmentation products of D_3 and H_3 formed by D_3^+/Cs and H_3^+/H_2 charge exchange, respectively, but no evidence of metastable states of D_3 or H_3 was reported.

Spectroscopic Identification

In the late 1970s, while searching for the spectrum of H_3^+ in a hollow-cathode discharge, Herzberg and co-workers discovered a spectrum of H_3.[19] During the next few years, several additional band systems were identified,[20-23] with the analysis of the observed fine structure revealing intimate details of level mixing, angular momenta coupling, and Jahn–Teller interactions. Overall, however, the pattern of electronic energy levels could be readily understood in terms of two electrons forming the closed shell of the cationic H_3^+ core and the third electron residing in a molecular orbital derived from atomic orbitals with $n = 2$ or 3 resolved into D_{3h} symmetry (an equilateral triangle). This simple interpretation of the energy level structure was supported by the ab initio calculations of King and Morokuma[24] (summarized in Table I), who satisfactorily reproduced the experimental results using an electronic structure model consisting of two electrons in a "frozen" H_3^+ core with the third electron described by an extensive set of diffuse basis functions located at the center of the molecule. The more recent calculations of Petsalakis et al.,[25] including correlation of all three electrons, reproduce the experimental results to within 0.02 eV, demonstrating how well the energy levels of this system are understood.

Crucial to the identification of the H_3 lines embedded in a forest of H_2 lines were (1) their characteristic presence in the hollow cathode glow and absence in the anode glow and (2) their extensive broadening. Although for some transitions the broadening was shown to be due to efficient predissociation of the lower states, for several other band systems, the lower state was observed to emit, so that lifetime broadening could not be the explanation. It was noted[20,22] that the line widths associated with these longer lived states did show a Doppler-like scaling with wavelength and mass; however, the derived translational temperature of 3000 K for a liquid nitrogen cooled discharge made this explanation somewhat unsatisfactory.

The origin of the line broadening was identified by Miderski and Gellene,[26] who investigated the mechanism for H_3^* production in a hollow-cathode discharge

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by monitoring the rotationally resolved intensity of the 6025 Å band ($3s^2A_1' \rightarrow 2p^2A_2''$) of H_3 as a function of discharge temperature and hydrogen density. A comparison of the experimental results with the predictions of a kinetic model of the discharge using experimentally determined temperature-dependent rate constants for ion diffusion, ion/e^- recombination, and reversible hydrogen ion clustering through H_7^+ revealed that the observed temperature and hydrogen density effects on H_3^* emission intensity could be quantitatively explained if the reaction

$$H_5^+ + e^- \rightarrow H_5^{**} \rightarrow H_3^* + H_2 + KE \qquad (5)$$

was responsible for H_3^* production in the discharge. Considering this mechanism, the Doppler-like scaling of the emission line widths is quite understandable; however, the speed distribution of the radicals would be considerably narrower than that of a Maxwell–Boltzmann distribution giving rise to the same width. If the dissociation kinetic energy release (E_D) is considered to be single valued, it is possible to infer its magnitude from a detailed line-shape analysis.[27] Figure 1a shows the results of such an analysis on the $R_0(0)$ line of the 6025-Å band, where the solid curve is a photodensitometer trace of the emission line and the dotted curve is a theoretical fit from which $E_D = 0.7 \pm 0.1$ eV was derived.

Considering the enhancement of ion/e^- recombination in the relatively field free region of a hollow cathode,[28] an important role for such processes in the formation of H_3^* was anticipated. Nevertheless, the simplest such process, namely, $H_3^+ + e^-$, is not a likely possibility as this recombination to form H_3^* requires radiative stabilization, which does not compete favorably with dissociation.[29] This is probably the explanation for the failure to observe H_3^* emission following the pulsed irradiation of H_2 gas with a high-energy, high-intensity electron beam.[30] Finally, it should be noted that the recent observation of H_3^* proposed to be produced by Penning excitation,[25] mediated by the metastable $c^3\pi_u$ state of H_2 in the two-step sequence

$$Ar^*(^3P_0) + H_2(X) \rightarrow Ar(X) + H_2^*(c^3\pi_u) \qquad \Delta E \approx 0.05 \text{ eV} \quad (6)$$

$$H_2^*(c^3\pi_u) + H_2(X) \rightarrow H_3^*(n{=}3) + H \qquad \Delta E \approx 0.25 \text{ eV} \quad (7)$$

indicates that the radical can also be produced by neutral chemistry. Although reaction 7 is endothermic as written, it becomes exothermic for vibrationally excited reactants. Additionally, as ArH emission is also observed under the same conditions, the process

$$ArH(2^2\pi) + H_2 \rightarrow H_3^*(n{=}3) + Ar \qquad \Delta E \approx -0.6 \text{ eV} \quad (8)$$

can also be considered. However, the efficiency of reaction 8 will depend on the relative rates of collision and relaxation for ArH.

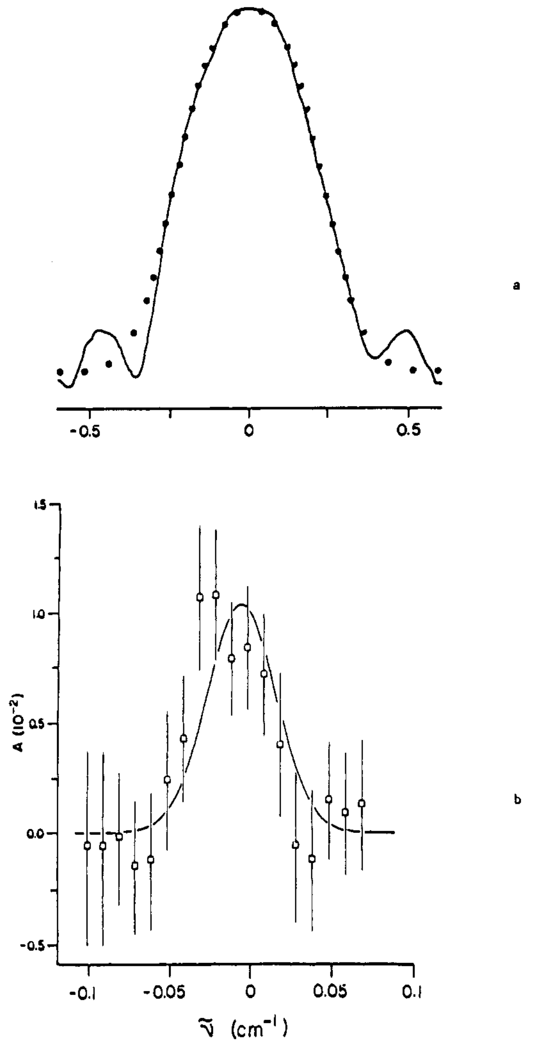

Figure 1. The $R_0(0)$ line of the 6025-Å band of H_3^* observed in (a) emission and (b) absorption. The comparatively large width of the line in emission is due to the dissociative kinetic energy released in the H_3 formation (modeled by the dotted curve). The width of the line in absorption is instrumentally limited, with the natural width being considerably narrower.

An interesting extension of the hollow-cathode studies of Herzberg et al. was provided by the laser induced emission technique of Figger et al.[31] In that work, a hollow-cathode deuterium discharge was placed coaxially inside the resonator cavity of a tunable dye laser. The cathode glow was dispersed, and D_3 emission was detected by a photomultiplier. A spectrum was recorded by tuning the monochromator to a narrow part of the D_3 spectrum and scanning the dye laser. When the laser frequency corresponded to a resonance of the upper level of the transition being monitored, the photomultiplier output would fall as a result of the laser-induced population decrease of the upper level. In principal, new spectra can be observed by this technique. However, in the reported work, all of the resonances corresponded to stimulated emission so that no new band sytsems were identified. Nevertheless, the technique was successful in extending the rotational structure and separating a number of overlapping lines (particularly in the Q branches) of the 5600- and 7100-Å bands.

Neutralized Ion Beam Spectroscopy

Neutralized ion beam spectroscopy[2-6] is a technique, similar to that described by Devienne,[7] for generating

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novel molecular species when a fast beam of ions is neutralized in a charge-transfer reaction of the type

$$X^+ + M(g) \rightarrow X^* + M^+ \qquad (9)$$

where X^+ is a molecular ion and M(g) is the target atom serving as an electron donor. If the product radical is formed in an excited state, it may undergo subsequent predissociation, radiate to a state of lower energy, or remain metastable over its beam transit time. Since the ion/target interaction time is short ($\sim 10^{-15}$ s), the internal state distribution of the product neutral molecules will be governed largely by Franck–Condon vertical overlap considerations. This causes $\Delta v = 0$ processes to be favored in the formation of neutral Rydberg states as their potential energy surfaces are generally parallel to those of the corresponding cations. By changing target atoms, and therefore donor ionization energies (IE), various states of X may be accessed in the charge-transfer reaction. Cross sections for these reactions are usually the highest when IE(X^*) = IE(M) corresponding to electronic resonance, but nonresonant processes can occur with lower probabilities. When IE(X) = IE(M), ground-state products are favored, but when IE(X) ≫ IE(M), product excitation is favored. The importance of energy resonance in fast electron-transfer processes was documented in an experimental study[32] of the H_2^+ system (M = Cs, K, Mg, and Zn). Molecules of H_3 are generated through the reaction sequence

$$H_2^+ + H_2 \rightarrow H_3^+ + H \qquad (10)$$

$$H_3^+ + M(g) \rightarrow H_3^* + M^+ \qquad (11)$$

As we will note, this is a model system for illustrating various modes of product excitation.

Several types of procedures have been employed to investigate states of H_3^* in reaction 11. These include configurations for studying the luminescence, light absorption, fragmentation behavior, and metastability of the radical. These techniques all involve a common feature, which is first to generate a fast beam of H_3^* by charge exchange. In most cases, the target M in reaction 11 is an alkali-metal atom, but in some experiments, targets of higher ionization energy such as H_2 or Ar have been used. Descriptions of experimental procedures are given in references cited below. The procedure used by Gellene and Porter[33,34] involve measurements of the angular distribution of scattered neutrals following fragmentation of H_3 and analysis of the neutral products by charge stripping to provide a reionized mass spectrum.

Dissociative States. When K or Mg is used as the electron donor in reaction 11, the majority of H_3 states formed undergo rapid dissociation (fragmentation) to H_2 + H, which scatter isotropically from the point of neutralization.[33] By analysis of the angular dependence of scattered particles (beam profiles), the fragmentation energy (FE), defined as the maximum kinetic energy released in the products, can be calculated from the relationship

$$FE = \tfrac{1}{2}m_H(1 + m_H/m_{H2})(V_{cm}\sin\theta_M)^2 \qquad (12)$$

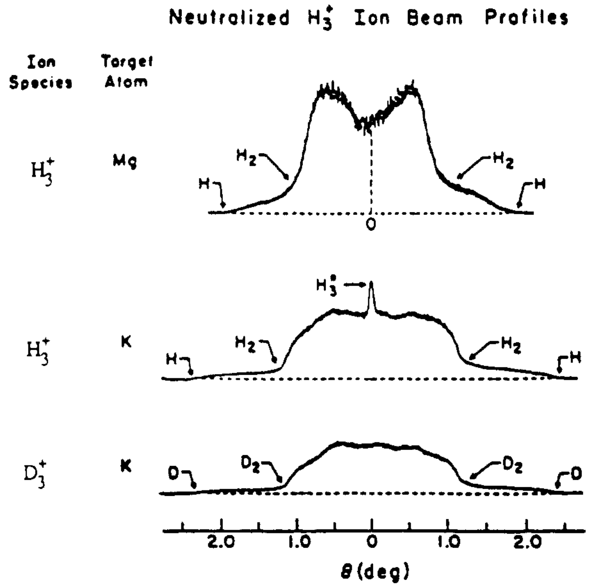

Figure 2. Neutral beam scattering profiles for products of H_3^+ charge transfer with K and Mg targets. Note that the light fragment H (or D) scatters to twice the distance of the heavy fragment H_2 (or D_2) due to linear momentum conservation. The primary ion beam energy was 6 keV.

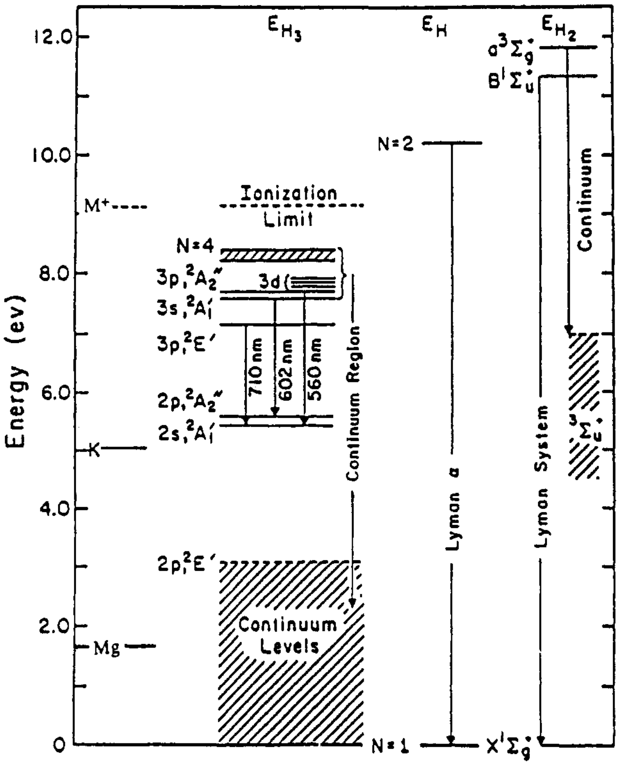

Figure 3. Energy-level diagram for H_3 showing approximate scaling of excited states relative to the zero-point level of H_3^+.

where m_H and m_{H2} are the masses of H and H_2, respectively, V_{cm} is the center of mass velocity, and θ_M is the maximum scattering angle for H atoms.[35] The widths of the beam profiles (Figure 3) show that more kinetic energy is released in the H_3^+/K reaction than in the H_3^+/Mg reactions and that different states of H_3 are accessed in the two cases at energies of 5.05 ± 0.07 (4.98 ± 0.08) eV and 3.18 ± 0.06 (3.18 ± 0.13) eV for H_3 (D_3).

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The ions used in obtaining the data in Figure 2 were generated in a high-pressure ion source operating at −160 °C and are therefore virtually completely vibrationally relaxed. Thus Rydberg states produced in reaction 11 would be expected to be in their vibrational ground states. Assuming no excitation in the products associated with θ_M, the calculated FEs allow the $2s^2A_1'$ state, which is known to undergo heterogeneous predissociation,[14] and the dissociative $2p^2E'$ ground state to be placed on a vertical energy scale with respect to the zero-point level of H_3^+ (Figure 3). The assumption seems especially justified for the $2p^2E'$ state as the experimental and theoretical values[25] are nearly identical. A consideration of differences in zero-point energies for the dissociation of the $2s^2A_1'$ state indicates that the change in fragmentation energy upon deuteration (FE(H_3)−FE(D_3)) should be slightly positive (~0.08 eV) for $v = 0$ products and slightly negative by about the same amount for $v = 1$ products. Thus the results support the assumption of $v = 0$ products; however, the question of rotational excitation is more problematical and potentially significant, considering the large rotational constants involved. Bae and Peterson[36] studied the fragmentation of D_3 from D_3^+/Cs charge exchange by measuring the kinetic energy of the scattered D atoms converted to D^- ions. Their results give a fragmentation energy distribution peaked at about 5.1 eV. However, their results cannot be compared directly with that derived from Figure 2 since their precursor D_3^+ was vibrationally excited. In that paper, no consideration was given of the electronic states of D_3 formed.

Prior to these studies, Vogler[17,18] observed the fragmentation of H_3 beams from H_3^+/H_2 charge exchange with a pair of detectors positioned to collect separately H_2 and H fragmentation products in a coincidence mode. He observed a weak structured kinetic energy spectrum, which he interpreted as dissociative scattering from the upper Jahn–Teller sheet of H_3 arising from its degenerate (in D_{3h} symmetry) ground state. Subsequent to the publication of the H_3 emission spectrum, Watson[37] reanalyzed Vogler's data and attributed the scattering to the predissociation of the $2s^2A_1'$ state of H_3 with the structure arising from different rovibrational product states of H_2. His analysis placed the 2s state at 5.52 eV, which agrees with the most recent ab initio results corrected for zero-point energies (~5.49)[19] and photoionization studies (~5.42).[38]

Metastable State ($2p^2A_2''$, $N = K = 0$ Rotational Level), Subsequently Referred to as H_3^*. Beam profiles (Figure 2) from our H_3^+/K experiment reveal a narrow, central, undissociated beam that is too intense to be due to naturally occurring HD, but the absence of a central peak in profiles from D_3^+/K experiments requires additional consideration. We also note that the central spike is absent in the H_3^+/Mg profiles. Recent charge-stripping experiments[34] clearly confirm the existence of metastable forms of H_3 and D_3 but show a disproportionately high ratio of H_3^*/D_3^* in neutralized H_3^+ and D_3^+ beams of equivalent flux (Figure 4). The identity of the metastable state of H_3 in these beam experiments was based on the following considerations: (1) line-width measurements in the emission spectrum of H_3 and quantum mechanical selection rules, (2) thermal effect on the population of rotational states of H_3^+, and (3) the unusual isotope effect on the relative abundances of H_3^* and D_3^* formed from neutralized beams of equivalent flux.

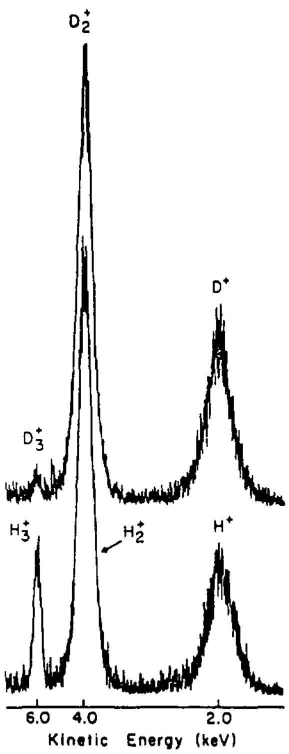

Figure 4. Reionized mass spectra of neutral products of H_3^+/K and D_3^+/K charge transfer. Initial ion beam fluxes were the same in both cases. The primary ion beam energy was 6 keV.

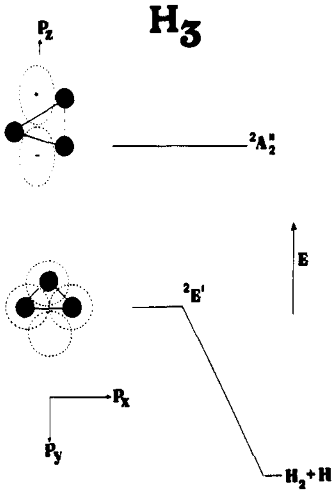

Figure 5. Simplified one electron united atom orbital representations for the $2p^2A_2''$ and $2p^2E'$ states of H_3.

In their analysis of the $3s^2A_1' \rightarrow 2p^2A_2''$ transition of H_3, Dabrowski and Herzberg[20] attributed the observed line broadening to a predissociation of the lower state by the repulsive $2p^2E'$ ground state. Coupling of the out-of-plane A_2'' orbital with the in-plane E' orbital (Figure 5) requires out-of-plane nuclear motion, which for a triatomic molecule can only occur by rotation. As pure in-plane rotation is not allowed, all excited rotational levels have an out-of-plane component to their motion. The role of Coriolis coupling in this heterogeneous predissociation was confirmed in the original

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spectroscopy[20] by noting that the line width increased proportionally to the square of the out-of-plane component of the rotational angular momentum of the lower state (i.e., $N(N+1) - K^2$ where N and K are the rotational quantum numbers of a symmetric top). The predissociation was observed to be quite efficient for H_3 with the lifetime of the first excited rotational level, $N = K = 1$, inferred to be about 3×10^{-11} s. Implicit in this analysis is the conclusion that the nonrotating $N = K = 0$ level would be much longer lived as the predissociation would be strictly forbidden. This point, however, could not be directly verified by the emission spectrum due to the residual line broadening arising from the H_5^+/e^- dissociative recombination mechanism.[26]

In general, H_3^+ ions generated by reaction 10 will carry excess rovibrational energy unless they are collisionally quenched before exiting an ion source. This effect on the production of metastable H_3 was demonstrated for thermal ion beams.[34] As the precursor ions are relaxed at high source pressures and/or low source temperatures, the intensity ratio of reionized neutrals H_3^+/H_2^+ (from H_3 and its dissociation product) reached a plateau, showing that the density of metastables in the beam has reached a maximum value which increased as the source temperature decreased. This indicated that only selected rovibrational states of H_3^+ can be efficiently converted to H_3 metastables. Excitation in H_3^+ can occur in reaction 10 by exothermicity of the reaction and by transfer of energy from vibrationally excited H_2^+ ions. The H_3^+ emerging from high-energy sources using electrical or radio frequency discharges to generate H_2^+ will usually be excited, rotationally and vibrationally. Charge neutralization will then lead to a diminished abundance of metastable H_3. Controversy surrounding some of the early literature reporting negative results on metastable H_3 may be traced to this problem.

The most compelling evidence from beam studies for the identity of a long-lived state of H_3 comes from information obtained from a comparative study of the relative abundances of metastable H_3 and D_3 observed when reaction 11 was investigated for both isotopic species under identical experimental conditions (Figure 5) as a function of the time between neutralization and reionization. For example, the H_3^*/D_3^* ratio was found to be approximately 17/1 when the ion source temperature was 135 K and the beam flight time was 0.5 μs. This ratio was found to increase at higher source temperatures and decrease for shorter flight times. These effects can be explained if the long-lived metastables in the slower beams are predominantly in the $N = K = 0$ rotational levels. To estimate the effect theoretically, we must involve the process

$$H_3^+/D_3^+(N{=}1,K{=}0) + K \rightarrow H_3^*/D_3^*(N{=}K{=}0) + K^+ \quad (13)$$

which conserves nuclear spin. In thermalized ion beams, the population of H_3^+ and D_3^+ in the necessary initial state can be calculated from rotational partition functions and the appropriate nuclear spin statistics (Fermi for H_3^+, Bose for D_3^+) for molecules of D_{3h} symmetry. For a source temperature of 135 K, the calculation predicts a ratio of H_3^* to D_3^* of approximately 20/1. This high ratio explains the lack of a metastable D_3 peak above the scattering background in the D_3 beam profile (Figure 2).

In an apparatus designed to generate intense beams of H atoms from an electrical discharge source, Garvey and Kuppermann[39,40] reported nearly equal abundances of H_3 and D_3 metastables when their gas sample contained equimolar concentrations of H_2 and D_2. From the foregoing observations, it is difficult to explain this result for their beams with flight times much greater than 0.5 μs. Their explanation of this effect requires an unusual set of conditions that permits intense beams of H_3, H_2D, D_2H, and D_3 molecules with zero angular momentum to be ejected selectively from a "hot" source.[41]

The $2p\,^2A_2''$ and $2s\,^2A_1'$ states of H_3 are both near resonant products of the H_3^+/K reaction (Figure 3), but the allowed transition $2p\,^2A_2'' \rightarrow 2s\,^2A_1'$ has a low emission coefficient. The radiative lifetime for the $2p\,^2A_2''$ state is estimated to be about 90 μs, which is relevant only to the nonrotating level since all higher rotational levels of the state undergo rapid predissociation. Nonresonant processes with targets having ionization energies much greater than 3.6 eV will lead to a diminished yield of H_3^*. These targets include H_2, N_2, and Ar with IEs in excess of 15 eV. In these cases, a more uniform distribution of Rydberg excited states in H_3 is expected.

Long-lived electronic states of molecules with energies near their ionization limits can be ionized in the presence of an electrostatic field (field ionization). The principle involves the perturbation on a state created by the electric field to generate a barrier for electron tunneling.[42] For hydrogen-like states, the basic relationship is $E_c \propto 1/n^4$, where E_c is the critical field required to ionize levels with effective principal quantum numbers $>n$. The relationship may be expressed as $n > 24(E_c)^{-1/4}$ when E_c is given in units of kilovolts/centimeter. This implies that states with $n > 24$ may be ionized with a field as low as 1 kV/cm. However, autoionization (spontaneous ionization) may also occur if the H_3^+ core is vibrationally excited. Starting with a 300-keV H_3^+ beam, Barnett and Ray[43] examined the sequence of steps

$$H_3^+ + H_2 \rightarrow H_3^* + H_2^+ \quad (1)$$

$$H_3^* \xrightarrow{E_c} H_3^+ + e^- \quad (14)$$

Their study indicated that H_3 states with principal quantum number $n > 10$ were generated in the charge-transfer step. In a similar field-ionization study, Gaillard and co-workers[44] generated metastable H_3 by H_3^+/Ar charge transfer from H_3^+ beams with 400–1500-keV kinetic energies. Their results also demonstrated the formation of H_3 states with high n and high l quantum numbers. Neither of these experiments could detect $H_3^*(n{=}2)$, which has an ionization energy above 3.7 eV.

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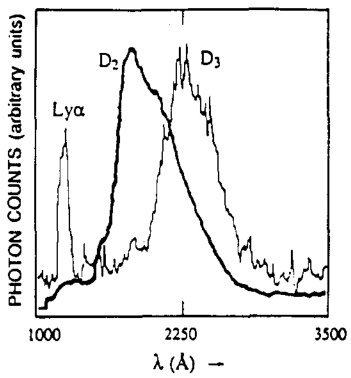

Figure 6. Emission continua following D_3^+/K and D_2^+/K charge transfer.

The ability to produce H_3^* by charge exchange with a high-velocity H_3^+ beam presents the possibility of observing new spectra by a combination of optical and neutralized ion beam techniques. Such experiments have been successful in both emission and absorption studies and will be discussed in turn.

Beam Emission Studies. Figger and co-workers have extensively studied the known emission from $n = 3$ levels of H_3 and its isotopic analogues[45-47] and very recently $n = 4$ levels[48] of D_3, produced by charge exchange of the corresponding mass resolved high velocity ion beam with Cs. The beam technique has two distinct advantages over discharge methods. First, mass separation prior to neutralization greatly simplifies identification of the spectral carrier and virtually eliminates "background" emission. This aspect of the technique was used to particular advantage in obtaining mixed isotopic spectra for which the discharge emission was prohibitively congested. Additionally, the low background signal has allowed very weak off-diagonal vibrational transitions and the continuum emission[49] from $n = 3$ levels of D_3 to the dissociative ground state to be observed. Although the D_3 continuum transition is fully allowed, Figure 6 shows that it is strongly overlapped by, but significantly red shifted from, the D_2 continuum so that its observation in the discharge dominated by D_2 emission was not possible.

The second advantage of the beam technique derives from the very narrow velocity distributions of the ions, which allow time-resolved emission studies to be performed by variation of the distance between neutralization and observation. The lifetimes of the $n = 3$ levels were thus determined by Figger and co-workers,[45-48] who found that they were generally less than the radiative lifetimes predicted by ab initio calculations (Table I). The discrepancy can be explained by predissociation of the $n = 3$ levels, which was confirmed for the $3p^2A_2''$ state by the observation of a rotational state dependent lifetime analogous to that of the $2p^2A_2''$ state.[47] Thus, it appears that efficient predissociation is a common characteristic of the low-lying Rydberg levels of H_3, and it is indeed fortunate that the radiative process was sufficiently competitive with predissociation so that the emission spectrum was observable.

Beam Absorption Studies. The quantum state identification of H_3^* with a lifetime of nearly 100 μs by Gellene and Porter in 1983 immediately presented the possibility of observing absorption spectra with H_3^* as the lower state. Three years later, such an experiment was performed by Helm,[50,51] who produced H_3^* by H_3^+/Cs charge exchange, photoexcited it to high Rydberg states ($n = 7$–40) with pulsed UV laser radiation, and detected the species by field ionization or autoionization. An analysis of the high-n Rydberg series yielded a value of the ionization potential for H_3^* that confirmed Watson's[37] placement of the states of H_3 with respect to H_2 and H. These experiments were repeated by Ketterle et al.[38,52] at higher resolution and sensitivity with their more accurate measurements in agreement with those of Helm. Interestingly, these additional measurements show that predissociation continues to be efficient for n up to 25 with $l \leq 2$. Ketterle et al. also observed off-diagonal vibrational transitions providing the first measurement of ω_1 for H_3^+. Very recently, Lembo et al.,[53,54] using a two-photon double-resonance variation of the technique, extended the measurements to $n = 4$–7 and obtained values for ω_1 in these Rydberg levels.

The marginal stability of the low Rydberg states of H_3 allows absorption of H_3^* to be observed by photofragmentation techniques, as was first done by Selgren and Gellene.[55] Figure 1b shows the $R_0(0)$ line of the $3s^2A_1' \leftarrow 2p^2A_2''$ transition observed in that study, where the instrumentally limited line width of ~0.05 cm^{-1} can be seen to be 1 order of magnitude narrower than that observed in emission. Almost immediately a similar study was reported by Cosby and Helm,[56] who additionally measured the kinetic energy release of the dissociation fragments with high resolution. In agreement with the previously established predissociation of the $n = 3$ levels,[45,46] excitation to the 3s level resulted in predissociation with a highly structural kinetic energy release corresponding to H_2 fragments with $v = 0$–12 and J peaking around 5–7. Conversely, excitation of the energetically similar 3d level resulted in H_2 fragments dominantly in $v = 5$–10 along with a continuum kinetic energy release peaking near 2.2 eV. These detailed product-state distributions of this simplest triatomic system provide a stringent test of theoretical dynamical models which are beginning to be applied to the predissociation of the excited states.[57] The energy of the continuum process, however, is too low to result directly from the predissociation of the 3d level and most probably results from a radiative transition to the ground state followed by dissociation. The energy of the emitted photon can be determined by energy balance to be 5.4 eV corresponding to a λ_{max} of 230 nm, which agrees very well with the location of the D_3 ra-

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diative continuum observed by Raksit et al.[49]

Concluding Remarks

In this Account, we have shown how neutralized ion beam techniques complement the more traditional methods of spectroscopy to obtain a substantial body of information on the simplest polyatomic radical, H_3. In particular, the combination of optical and neutralized ion beam techniques has allowed for the determination of excited-state lifetimes by time resolved emission experiments. Further, the existence of a unique metastable excited state, first identified in nonoptical neutralized ion beam experiments, has provided access to the absorption and photoionization spectra of the radical. Considering the generality of neutralized ion beam techniques, future work in this area can be expected to obtain information on an almost limitless number of chemically interesting species. Additionally, the vertical nature of the neutralization process allows regions of a neutral potential energy surface not readily accessed conventionally, such as a transition state,[58] to be probed directly by the appropriate choice of the precursor ion. In particular, emission spectra for species such as H_3O and H_2F, which have yet to be observed by conventional methods, may be obtainable by the techniques outlined in this Account. Further, as metastable states of the perdeuterated analogues, D_3O and D_2F, can be produced by ion beam neutralization,[59] their absorption and photoionization spectra should be similarly obtainable through application of the techniques that have been so successfully applied to H_3.

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Rate Processes with Dynamical Disorder

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Simple and effective methods for solving problems in nonequilibrium statistical mechanics are scarce and valuable. In the absence of elementary textbooks in this area, such methods tend to be reinvented many times. I review here one particular example: a method for treating rate processes when a rate constant is replaced by a random function of time (hence "dynamical disorder"). In particular, the rate constant is taken to be a function of some control variable which may either jump between discrete values according to exponential waiting time distributions, or else fluctuate according to a Langevin equation. Generalizations of the method are described. The method usually leads to a decay in time that is nonexponential. My emphasis will be on the method, with just enough about its applications to show how general and useful it can be.

The class of problems for which this method is effective are conveniently called "rate processes with dynamical disorder". But to set the stage it will be helpful first to discuss rate processes with *static* disorder. A typical rate equation, for the concentration C of some species undergoing chemical reaction, is

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -k(B)C \tag{1}$$

where $k(B)$ is a rate constant that depends on a barrier height B,

$$k(B) = k_0 \exp(-B/kT) \tag{2}$$

In a widely discussed example, due to Frauenfelder and co-workers,[1] the reaction is ligand binding to myoglobin. They claim that different conformational substrates have different barriers to rebinding; the probability of finding a barrier with height B in the interval $\mathrm{d}B$ is $\rho(B)\,\mathrm{d}B$. Then the average time dependence of the concentration is

$$\langle C(t)\rangle = C(0)\int \mathrm{d}B\;\rho(B)e^{-k(B)t} \tag{3}$$

In this example of static disorder, the course of the reaction clearly is no longer exponential in time.

While this illustration makes use of a particular pair of variables, the concentration C and the barrier height B, a much more general point of view is possible. C may denote any physical quantity that satisfies a rate equation, B may be any "control variable", and $k(B)$ may be any function of B. This general point of view is taken in much of what follows.

When B is a random function of time, $B(t)$, one has *dynamical* disorder. The time-dependent solution of the rate equation is

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