Properties of Hydrogen Atoms Newly Generated in Chemical Reactions and Photodissociations

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Hydrogen atoms, the most abundant of all atoms, are so reactive that they are found uncombined only at the high temperatures prevailing in flames, electric discharges, or stellar atmospheres. Elementary reactions of H atoms are nevertheless of great interest because of the enhanced possibilities of calculating a potential surface for the reaction ab initio. The $H + H_2$ reaction is the central reaction of the theory of chemical kinetics in part because such an accurate potential surface is available.

A reactive collision which usually lasts only a fraction of a picosecond leaves its imprint on the asymptotic internal state and velocity distributions of the products. Thanks to molecular beams and lasers, it is now possible to determine these nascent distributions before collisions transform them into the inevitable Boltzmann distribution. The magnitude of the kinetic energy release as compared to the total available energy is a useful guide to the reaction mechanism. So also is the anisotropy of the velocity distribution, which allows us to distinguish between direct processes and processes involving complexes lasting longer than a rotation period. In this Account, a variety of experiments are described involving a new technique for the detection of hydrogen atoms. For the first time, we can now determine the kinetic energy of nascent hydrogen atoms.

There are many techniques for detecting hydrogen atoms, crude chemical ones such as the bluing of yellow MoO_3 or scavenging by olefins, more delicate physical methods such as electron spin resonance or mass spectrometry, but still more sensitive is fluorescence. The exciting light source has usually been a resonance lamp, that is, an electric discharge in hydrogen gas that produces some H atoms in the 2p state. These emit light at 121.6 nm, which is known to astronomers as the Lyman α line. With the help of such light sources, many kinetic studies have been carried out as for instance in the recent studies of ref 1, but there remain some important difficulties. This Lyman α source is weak because relatively few 2p H atoms are present in the discharge region. The H atoms in the source emit

with a line width determined by their temperature, and one cannot therefore sweep through the Doppler-broadened absorption of the H atoms in the system under study. Because the source is so weak and inflexible, one cannot detect H atoms at very short times nor can one, in general, measure their absorption line shape. Measurements are limited to "old" H atoms, with all the precious information about the velocity distribution of the nascent H atoms having been lost.

The laser has thrown a new light on the subject. Thanks to the development of pulsed laser light at 121.6 nm,[2] H atoms can be detected at early times after they are generated by a chemical reaction or a photodissociation. Early times means that the H atoms have not had time to collide and therefore retain their initial velocity distribution. The technique depends on a phenomenon called frequency tripling in which light at frequency ω is focused in a gas, and in a small yield, light of frequency 3ω is generated. In our experiments, an intense short pulse of 364.8-nm light generated by a dye laser is focused in Kr gas, and conversion to vacuum ultraviolet light takes place with an efficiency of about 10^{-6}. In terms of total number of photons/second, the laser source is weaker than resonance lamps. On the other hand, in terms of photons emitted into a given small solid angle in a 10–20-ns time interval, it is orders of magnitude more powerful. In addition, the laser source is narrow ($\sim$0.12 cm^{-1} in our laboratory), and the shapes of fluorescence excitation curves can be measured. Figure 1 shows a block diagram of a typical experimental apparatus.

A wonderfully convenient aspect of the laser source is that it can be easily tuned from H atom to D atom wavelengths, which are only 22 cm^{-1} apart in the vacuum ultraviolet spectrum. Because the absorption coefficient of D atoms is precisely the same as that of H atoms, the ratio of the areas under their fluorescence excitation curves is the ratio of their concentrations, an important observable. Another important observable is the second moment of the fluorescence excitation curve. The shift of the absorption frequency caused by the Doppler effect is $\nu_0 v_z/c$, where v_z is the component of the velocity in the direction of the probing laser, ν_0 is the absorption frequency of the atom at rest, and c is the velocity of light. Assuming that the velocity distribution is isotropic, that is, $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \langle v^2 \rangle/3$, the average kinetic energy is just $^3/_2 M(c/\nu_0)^2$

(1) Stevens, P. S.; Bruce, W. H.; Anderson, J. G. *J. Phys. Chem.* **1989**, *93*, 4068.
(2) Wallenstein, R. *Opt. Commun.* **1980**, *33*, 119.
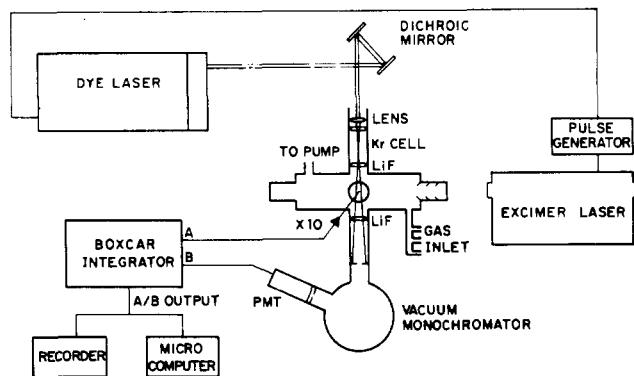
Figure 1. Block diagram of experimental system for measuring laser-induced fluorescence of H atoms.

Figure 2. LIF of H and D atoms from the H + D_2 reaction. H atoms were generated by photodissociation of HCl molecules at 157 nm. Reprinted with permission from ref 8. Copyright 1987 American Chemical Society.

times the second moment of the absorption curve. The H atom is the lightest element, and for a given translational energy, it has the highest speed and therefore the largest Doppler shifts. The Doppler shifts are therefore the easiest to measure accurately with resulting benefit.

Wallenstein[2] was the first to generate the Lyman α line by laser techniques and to use it to excite fluorescence in the H atom. This technique was soon applied by Schmiedl et al.[3] to the photodissociation of HI. Extensive studies have been carried out by Wittig[4] and his students on HI, H_2S, NH_3, PH_3, and C_2H_2. M.-Chen Chuang et al.[5] measured the H/D atom ratio from the photodissociation of CHDO as a function of wavelength. In this Account we describe mainly the results from our laboratory simply because we are more familiar with them.

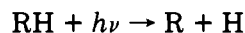The subjects of our experiments can be classified in four categories:

1. exchange reactions

$$H + RD \rightarrow RH + D$$

2. ground-state vs excited-state dissociation

$$ROH + h\nu \rightarrow ROH^* \rightarrow RO + H$$

$$RH + O(^1D) \rightarrow ROH \rightarrow RO + H$$
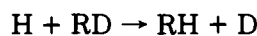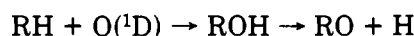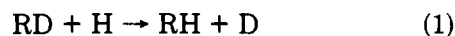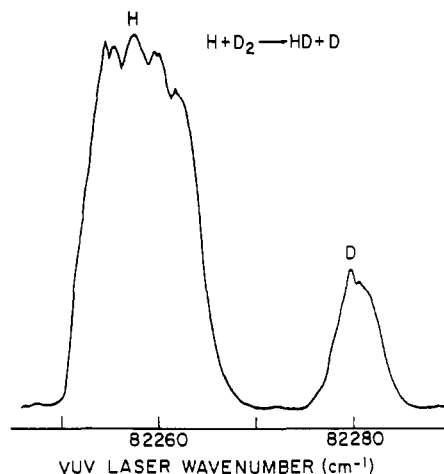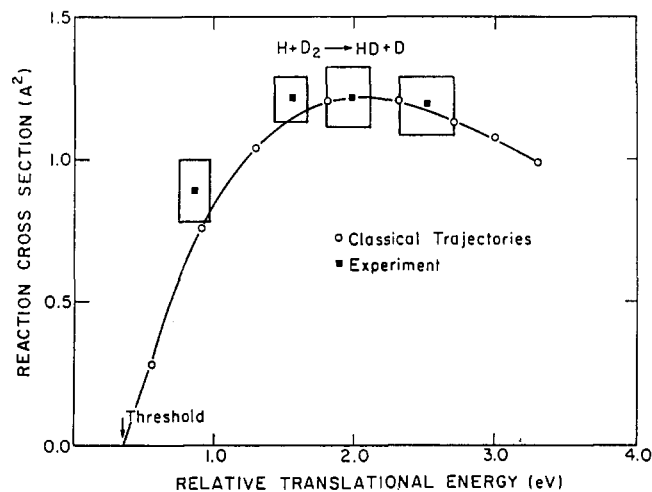
3. slow photodissociation

$$RH + h\nu \rightarrow R + H$$

4. relaxation of H atom velocity distributions

1. Exchange Reactions

In bimolecular gas-phase reactions, the accurate determination of a rate constant is generally difficult because three concentrations must be measured accurately. The isotope exchange reaction

$$RD + H \rightarrow RH + D \tag{1}$$

is uniquely simple. The rate equation

$$d[D]/dt = k[RD][H] \tag{2}$$

can be integrated at very short times to give

$$[D]/[H] = k[RD]t \tag{3}$$

One does not need to know the absolute concentrations

Figure 3. Reaction cross section vs relative translational energy for the H + D_2 reaction. Reprinted with permission from ref 8. Copyright 1987 American Chemical Society.

of either the H or the D atoms but merely the ratio of the areas under their fluorescence excitation curves, the pressure of the gas RD, and the time t between the laser pulse that generates the H atoms and the pulsed vacuum ultraviolet probing laser. If we use a target molecule HX that photodissociates to give monoenergetic H atoms, then we know the relative speed of H and RD fairly well. In this case one can write $k = v\sigma$ to obtain the reaction cross section σ.

The most important exchange reaction, in fact one of the central reactions of chemistry, is the process

$$H + D_2 \rightarrow HD + D \tag{4}$$

The reaction H + H_2 has a theoretically calculated barrier of 8 kcal/mol when the reaction is collinear, that is, when the approach of the H atom is along the axis of the molecule. For larger angles of attack, the potential energy barrier rises steeply, being about 50 kcal/mol for a sidewise approach. Recently the groups of Valentini[6] and Zare[7] have succeeded in measuring the state distribution of the HD product of the reaction H + D_2. At low energy they found little rotational exci-

(3) Schmiedl, R.; Dugan, H.; Meier, W.; Welge, K. H. *Z. Phys. A* **1980**, *304*, 137.
(4) Xu, Z.; Koplitz, B.; Wittig, C. *J. Chem. Phys.* **1989**, *90*, 2692 and references therein.
(5) Chuang, M.-C.; Foltz, M. F.; Moore, C. B. *J. Chem. Phys.* **1987**, *87*, 3815.

(6) Gerrity, D. F.; Valentini, J. *J. Chem. Phys.* **1983**, *79*, 5202; **1983**, *79*, 5202; **1984**, *81*, 1298.
(7) Blake, R. S.; Rinnen, K.; Kliner, D. A. V.; Zare, R. N. *Chem. Phys. Lett.* **1988**, *153*, 365, 371.

tation, but the higher J states became more occupied as the relative translational energy was increased.

The cross sections for reaction 4 can be determined as a function of energy by varying the photolysis wavelength or the target hydride molecule. Figure 2 shows a laser induced fluorescence (LIF) spectrum of both the H atoms dissociated from HCl at 157 nm and the D atom reaction product. Figure 3 is a plot of the cross sections for the H + D$_2$ reaction versus initial relative kinetic energy. The four experimental points[8] plotted are for H atoms dissociated from HCl and H$_2$S by photons of different wavelengths. The theoretical points were calculated by running classical trajectories on the best theoretical potential surface.[9] In general, the cross section increases with increasing relative energy because attacks at increasing angles away from collinear can lead to reaction. The agreement between experiment and theory is remarkable. The theoretical calculation uses only the fundamental constants of nature, and there are no free parameters. The great success of the classical calculation might at first sight suggest that quantum effects are not important. However, the total cross section involves no interference terms between partial waves of different orbital angular momentum.

Similar experiments for the reaction of H atoms with deuterated acetylene, methylacetylene, ethylene, and propylene have yielded cross sections of 1.69 ± 0.22, 0.50 ± 0.15, 1.85 ± 0.20, and 1.10 ± 0.14 Å^2, respectively. The relative kinetic energy of the reactants was roughly 24 kcal/mol while the fractions of this energy released as translation of the products were 0.42, 0.34, 0.40, and 0.34. Given that the product HCCD, for example, has seven vibrational modes, the data show that the energy is not redistributed throughout the molecule during a reactive collision, but remains somewhat localized at one end. Adding a methyl group to an acetylene or ethylene molecule only slightly reduces the energy released as translation. This is regarded as proof that the reaction at this energy does not involve a long-lived intermediate complex. Further confirmation comes from the observation that the velocity of the D atom product from H + C$_2$D$_2$ is correlated with the velocity of the H atom reactant.[11] These experiments provide conclusive qualitative information on the nature of the transition state during a reaction.

2. Ground-State vs Excited-State Dissociation

Suppose that a molecule is supplied with a large amount of excess energy in one of two different ways, by excitation to an excited electronic state or by activation in a chemical reaction. As examples, consider the two small molecules water and methanol. In the excited electronic state, dissociation takes place on a repulsive surface and in a time that is substantially less than a picosecond. The ground-state dissociation is only a little slower but is preceded by a certain redistribution of vibrational energy within the molecule.

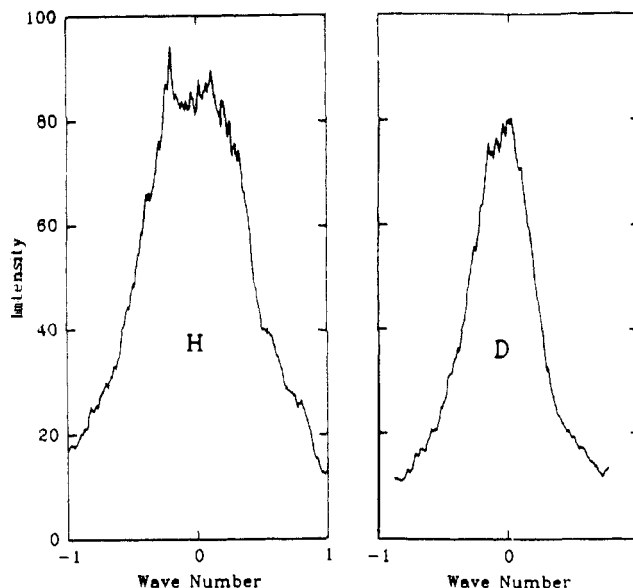In the specific case of water, excitation at 157 nm (185 kcal/mol photon energy) produces fast H atoms and

Figure 4. LIF excitation spectrum of the vapor above an equimolar mixture of H$_2$O and D$_2$O irradiated at 157 nm. Reprinted with permission from ref 14. Copyright 1989 American Institute of Physics.

OH radicals that are rotationally cold,[12] and only a small fraction are vibrationally excited. On the other hand, a vibrationally hot electronic ground state water molecule with 161 kcal/mol internal energy is produced by the attack of O(^{1}D) (photodissociated from ozone) on H$_2$.[13] The OH radical products are strongly excited both rotationally and vibrationally. This is consistent with an insertion mechanism in which the O(^{1}D) atom attacks the H$_2$ molecule from the side and forms a transient H$_2$O molecule, which vibrates violently before breaking up. The available energy of the ground-state molecule is rather democratically released into all three types of energy, translation, vibration, and rotation. In contrast, most of the available energy of the electronically excited molecule is released as translational energy.

The isotope effect[14] in the dissociation of HOD is very instructive. When excited at 157 nm, the ratio of H atoms to D atoms produced is 4 ± 1. One can understand this high ratio theoretically as follows. On the excited potential surface, the water molecule initially vibrates along a ridge. On either side of the ridge there is a steep fall, one side leading to OD + H and the other to OH + D. The potential surface is symmetric with respect to that ridge; however, the vibrations are mass dependent and therefore not symmetric. The vibrational wave function of the H atom is more diffuse than that of the D atom, and hence it is more often found in a strongly repulsive region away from the ridge. Once it is too far from the ridge, it cannot return, and a free H atom is liberated. A quantum mechanical calculation of this effect by Zhang, Imry, and Frederick[14] agrees perfectly with the experimental H/D ratio[12] of 4 ± 1 extracted from Figure 4.

The ground-state decomposition is very different. There is only a slight excess of H atoms, the experi-

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(13) Butler, J. E.; MacDonald, R. G.; Donaldson, D. J.; Sloan, J. J. *Chem. Phys. Lett.* **1983**, *95*, 183.

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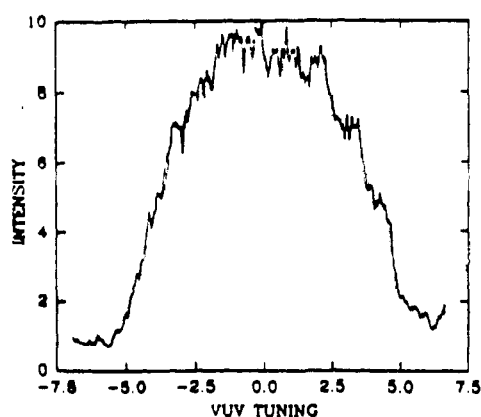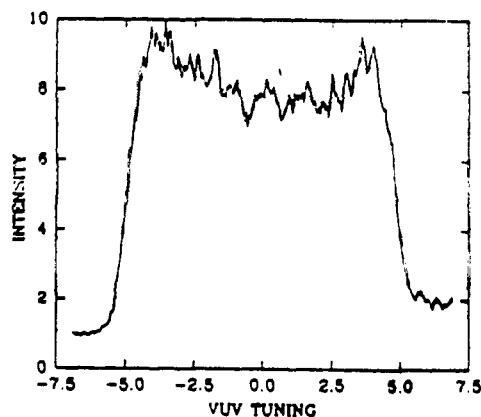
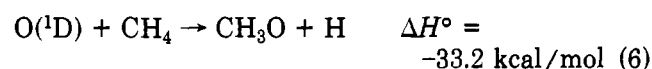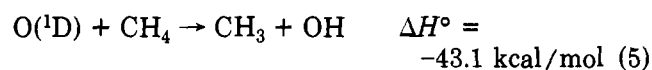H from CD_3OH: $E \parallel z$ H from CD_3OH: $E \perp z$

Figure 5. LIF excitation spectrum of H atoms photodissociated from CD_3OH by polarized 193-nm light when the propagation direction of the probe laser is parallel (left) and perpendicular (right) to the **E** vector of the dissociating light. Reprinted with permission from ref 20. Copyright 1989 American Institute of Physics.

mental H/D ratio being 1.13 ± 0.08. Here we only remark that the innocent-looking number 1.13 turns out to a crucial test of the theory. The reaction of $O(^1D)$ with H_2 has been of considerable interest to theorists because its potential surface has a deep well at the geometry of the water molecule. The reaction produces vibrationally and rotationally excited OH radicals, a property roughly reproduced by a number of theoretically deduced potential surfaces. However, as shown by Fitzcharles and Schatz,[15] different potentials give very different values of the H/D ratios, varying from 1.1 to 2.[16] The most successful potential surface is one on which the incoming hydrogen molecule is collinearly aligned by the oxygen atom, which binds to the first hydrogen atom it hits. In a typical trajectory, the second hydrogen atom revolves about the H atom before departing. Unfortunately, this surface, the Murrell–Carter surface,[18] is empirical, whereas the Schinke–Lester potential surface,[19] based on the interpolation between ab initio calculated points, yields an H/D value of about 2. The reaction is far from being understood.

Methanol is a slightly more complicated example because its potential surface is not symmetric with respect to the two possible exit channels. Breaking the O–H bond requires 103 kcal/mol, whereas breaking the C–O bond requires only 93 kcal/mol. Nevertheless, when methanol is excited by 193-nm light, it forms H atoms[20] with a yield of 0.86 ± 0.10. (The quantum yield is measured by comparing H atom signals obtained by irradiating known pressures of HCl and CD_3OH.) By using isotopic substitution, we can show that the H atom comes from the OH group exclusively and not from the methyl group. For example, CD_3OH yields H atoms but no D atoms. The demonstration of this point is a little delicate because the CD_3O radical formed readily absorbs a second photon, and D atoms are in fact produced. However, the H signal varies linearly with the laser intensity whereas the D signal varies

quadratically. The high yield for breaking the stronger bond is, we think, due to the same phenomenon seen with HDO. The lighter H more rapidly reaches the region of no return than the heavier CH_3. The dissociation is very rapid (considerably less than a rotation period of methanol perpendicular to the C–O axis, which is 0.7 ps), as shown by the strong velocity anisotropy[21,22] of the H atoms when polarized light is used for dissociation (see Figure 5). The entire process involves first the excitation of an electron from a nonbonding p state normal to the molecular plane to an in-plane antibonding σ^* orbital. The fragments then separate rapidly, sliding down a steeply repulsive potential. The proof of this latter remark is that 82% of the available energy is released as translational energy.

As with water, on the ground-state potential surface, methanol behaves quite differently. A highly energized methanol (internal energy of 142 kcal/mol) is prepared by reacting methane with $O(^1D)$. When $O(^1D)$ reacts with methane, two reactions occur:

$$O(^1D) + CH_4 \rightarrow CH_3 + OH \quad \Delta H^\circ = -43.1 \text{ kcal/mol} \quad (5)$$

$$O(^1D) + CH_4 \rightarrow CH_3O + H \quad \Delta H^\circ = -33.2 \text{ kcal/mol} \quad (6)$$

The lower energy channel producing OH and CH_3 is preferred. The H + CH_3O channel has a yield of only 0.25 ± 0.05 and an average kinetic energy of 8.7 ± 1.4 kcal/mol, and only 22% of the available energy is released into translation. The rest must be present as vibration and rotation of the CH_3O radical. (The yields are obtained by comparing H atom signals from reactions of $O(^1D)$ with known pressures of H_2 and CH_4.)

Some time ago, Cvetanovic[23] showed that when $O(^1D)$ reacts with CH_4, the methanol could be prevented from decomposing by the addition of a high pressure of buffer gas such as argon. From the pressure required, the time for dissociation was calculated to be 0.8 ps. Thus while the upper-state lifetime is shorter, both lifetimes are below a picosecond. The real difference is between the initial conditions. In the excited state,

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(18) Murrell, J. N.; Carter, S. *J. Phys. Chem.* **1984**, *88*, 4887.
(19) Schinke, R.; Lester, W. A. *J. Chem. Phys.* **1980**, *72*, 3754.
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(23) Cvetanovic, R. J. *Can. J. Chem.* **1974**, *52*, 1452.

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the initial energy is mainly potential, which is smoothly converted into translational energy, whereas in the ground state rather violent motion occurs before separation.

3. Delayed Photodissociation

One can consider a hierarchy of hydride molecules from the simplest to the complex. When a diatomic hydride such as HI is photodissociated,[3] the excess of the photon energy over the dissociation energy must necessarily go into translation unless there is the possibility of electronically exciting the other atom. In triatomic hydrides such as H_2S[4] and H_2O, largely because of the Franck–Condon principle, photodissociation in the first absorption band releases 70–95% of the available energy into translation. The upper potential surface has about the same bond angle as the ground state, and so little rotational energy results. If the molecule is just a little bit more complex, as with NH_3 and PH_3,[4] the majority of the available energy is released as vibrational energy. This does not necessarily occur in every case, as shown by the results already discussed on methanol, but its chromophore (the oxygen atom and attached bonds) and its dissociating H atom are very close. In general, as the number of atoms increase, the fraction of energy released as translational energy will decrease.

The dissociations discussed above are direct dissociations from an excited electronic state or very rapid predissociations, in any case having subpicosecond durations. What happens if the molecule is large and internal conversion is faster than dissociation? In this case, the initial electronic energy becomes converted into vibrational energy and one has a "hot" molecule. If there is enough energy to dissociate a hydrogen atom, it will eventually do so unless it hits a surface first. However, dissociation from the ground state will be orders of magnitude slower than on the excited-state surface.

Our model large hydride molecule will be toluene[24] (methylbenzene), C_7H_8. Five of the eight H atoms are attached to the ring and require an energy of 110 kcal/mol to be detached. On the other hand, only 88 kcal/mol is needed to dissociate the first H atom from the methyl group because of the enhanced resonance energy with the benzene ring of the benzyl radical as compared to toluene. Most of our experiments were done with a 193-nm laser, which adds 148 kcal/mol to the thermal internal energy of the toluene molecule. The molecule was initially excited to a high-lying electronic state, from which it passed to the ground state without any fluorescence emission. One then has to wait a mean time of 0.3 μs for at least 88 kcal/mol to appear in the dissociating coordinate (mainly a C–H stretch).

The two observables measured were the rate constant for evolution of the H atoms and the shape of their fluorescence excitation spectrum. Figure 6 shows typical growth and decay curves for the H atom signal. The decay occurs because the H atoms once formed move out of the region irradiated by the probe laser. The curve must then unfortunately be fit by two parameters, limiting somewhat the accuracy of the desired rate constants.
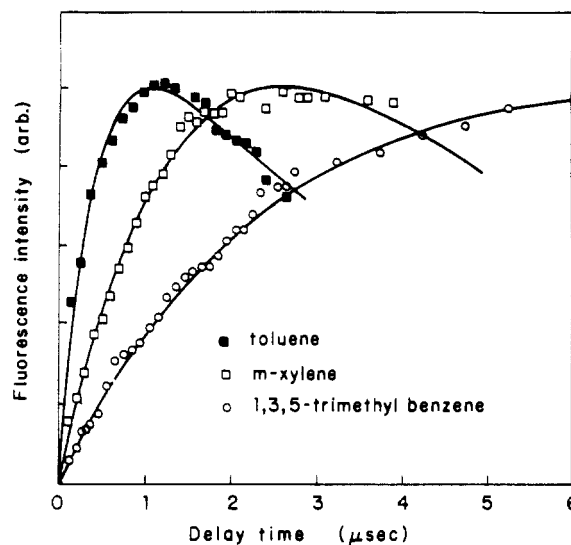
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Figure 6. Growth and decay of H atoms dissociated from toluene, *m*-xylene, and mesitylene.

A central tenet of unimolecular reaction rate theory is that within an activated molecule internal equilibrium prevails until at a random time the system reaches the region of no return, the transition state.[23] If the excitation of the various $3N - 6$ vibrational modes of the molecule with N atoms is statistical at the transition state, the rate constant depends only on the energy E and the angular momentum J, $k = k(E,J)$. This basic assumption can be severely tested on our model molecule, toluene, in a unique way.

The very simple RRK theory, which assumes that all molecular frequencies have the same value ν, predicts that

$$k = \nu \left(\frac{E - E_0}{E} \right)^s \tag{7}$$

where E_0 is the threshold energy for dissociation. In practice, if s is taken to be the number of vibrational modes in the molecule, the resulting rate constants are too small. To fit experimental results, s is usually taken to be about half the number of modes. The decrease in k with increasing molecular size is intuitively clear because the more modes over which the energy is distributed, the longer it will take until a given amount of energy E_0 randomly accumulates in a given mode. The refined RRKM theory predicts the same thing. The larger the molecule, the smaller will be the ratio of the unoccupied quantum states at the transition state to occupied quantum states in the original energized molecule.

In general, it is hard to vary the number of atoms in a molecule without changing the chemistry, that is, the transition state. The methylbenzenes furnish a unique opportunity to vary N without changing the transition state. Whatever structure and frequencies one postulates for the transition states of a methyl group, they will be unaffected by additional methyl substitution. Even an *o*-methyl group has no effect; the same rate of dissociation was found for *o*-, *m*-, and *p*-xylenes (dimethylbenzenes). The rates of dissociation of dimethyl-, 1,3,5-trimethyl-, and 1,2,4,5-tetramethylbenzene irradiated at 193 nm were measured, and the intrinsic rates were found to decrease about 1 order of magnitude for each added methyl group. (The intrinsic
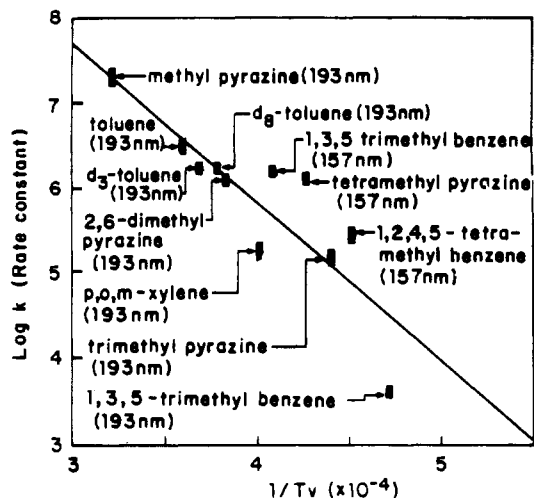
Figure 7. Logarithm of dissociation rate constant vs $1/T_V$.

rate is the observed rate divided by the number of methyl groups in the molecule.) The series of compounds methyl-, 2,6-dimethyl-, and trimethylpyrazine were investigated in the same way with similar results.

In addition to varying the number of modes in the molecule by changing its structure, one can select a given molecule and irradiate it at different photon energies. As predicted, the rate increases steeply with increasing internal energy. For example, if 1,3,5-trimethylbenzene is irradiated at 193 nm, the rate of dissociation is 4.0×10^3 s^{-1} whereas when irradiated at 157 nm the rate increases to 1.6×10^6 s^{-1}.

So far we have shown that the rate of dissociation does not depend on the specific initial state, that it decreases with increasing molecular size, and that it increases with increasing energy. In order to interpret quantitatively the dissociation rates, it is useful to recall that the laser produces an ensemble of excited molecules all with the same energy E. There are fluctuations

around this value of the order of kT where T is room temperature, but these are small relative to E, which is 148 kcal/mol. Each toluene molecule has 39 internal modes, so that in effect we have a microcanonical ensemble where all systems have the same energy and each system has a large number of degrees of freedom. In this case we can define a vibrational temperature T_V by the equation

$$E + \sum_i \hbar\omega_i[\exp(\hbar\omega_i/kT) - 1]^{-1} =$$
$$\sum_i \hbar\omega_i[\exp(\hbar\omega_i/kT_V) - 1]^{-1} \quad (8)$$

where ω_i is the frequency of the ith vibrational mode. The value of T_V for the conditions of the different experiments vary from 2000 to 3000 K. Clearly, for the same molecule, increasing E raises T_V; also, for the same E, increasing the number of modes decreases T_V. Finally and most importantly, all the rate constants are found to depend on T_V in a simple way. The logarithms of the effective rate constants are plotted in Figure 7 versus $1/T_V$.

4. Time Evolution of Velocity Distributions

The main observable discussed in this Account is the distribution of velocities of H atoms which have not had a chance to collide. We know that after enough collisions the velocity distribution will be Maxwellian, i.e., proportional to $v^2 \exp(-\frac{1}{2}mv^2/kT)$ where T is the ambient temperature. It is interesting to see how fast this relaxation process is and, if possible, to look at intermediate velocity distributions.

A series of experiments were carried out in which H atoms were generated by photodissociation of a small amount of H_2S with 193-nm light in the presence of a much larger pressure of an inert bath gas. Figure 8 shows the fluorescence excitation line shapes for H atoms generated in xenon gas at different pressures but
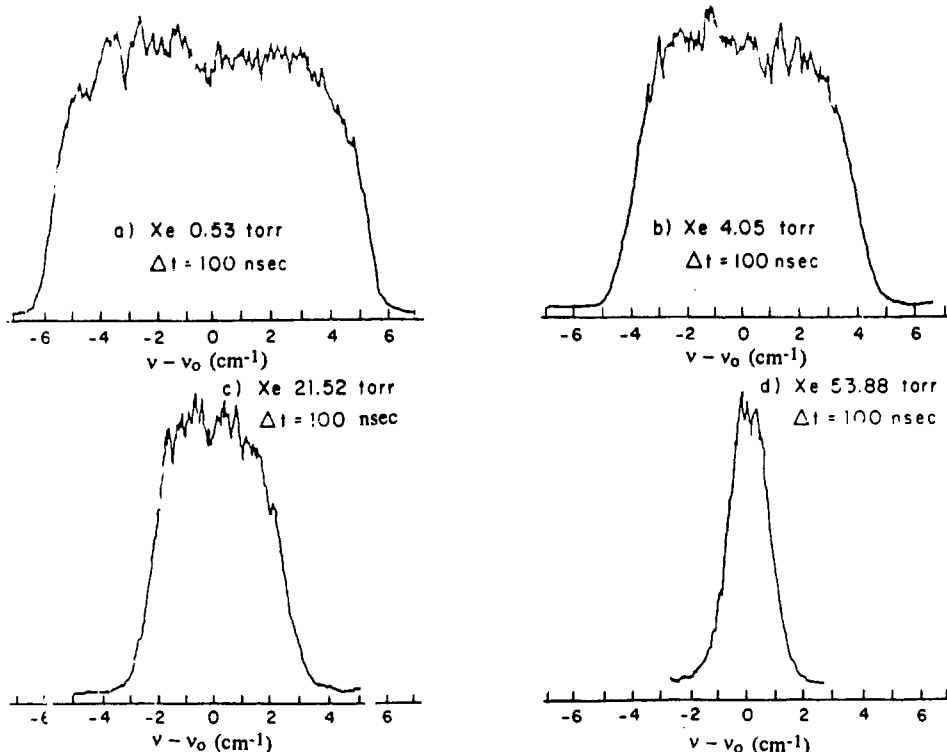

Figure 8. LIF excitation line shape of H atoms 100 ns after their dissociation from H_2S at Xe pressures of (a) 0.53, (b) 4.05, (c) 21.5, and (d) 53.9 Torr. Reprinted with permission from *J. Chem. Phys.* 1989, *91*, 7861. Copyright 1989 American Institute of Physics.

at a fixed time (100 ns) after their generation. What we are really interested in is the dependence of the velocity distribution on collision number, which is proportional to the product of the pressure and the time, so that either variable may be fixed. The average kinetic energy can be extracted quantitatively and the velocity distribution semiquantitatively from the line shapes in Figure 8.

These intermediate distributions can certainly be calculated by kinetic theory, but this is, to our knowledge, the first time that the evolution of the distribution has been measured. It is only in the last decade that fairly monochromatic intense pulsed dye lasers have been developed, thus making the measurement possible. With continuous wave lasers an equilibrium Maxwellian distribution can be measured which is irrelevant to the experiments discussed here on nascent H atoms.

The time scale of the velocity equilibration depends on the nature of the buffer gas. For monatomic gases, the very light He atom is far more efficient than the heavy Xe atom. In the latter case, the H atom bounces off the Xe as it would from an infinitely heavy wall. He atoms, on the other hand, can remove a substantial part of the kinetic energy of the H atom on each collision. The diatomic molecules O_2 and N_2 have about the same cross sections as He, presumably because the H atom

kinetic energy is easily transferred to rotational energy of the diatomic.

Conclusions

The kinetic energies of H atoms just after they are formed often reveal the nature of the reaction. We have seen that electronically excited molecules release H atoms with high kinetic energy. On the other hand, vibrationally hot ground-state molecules release relatively slow H atoms whose temperature equals that of the vibrational modes in the companion radical. The exchange reactions between fast H atoms and C_2D_2 and C_2D_4 were shown to be localized processes not involving a hot intermediate. Finally, one can follow the thermalization of a velocity distribution by measuring the Doppler width as a function of the number of collisions suffered by the H atom. The Doppler-broadened line shapes of fluorescence (or multiphoton ionization) excitation spectra are the keys to a deeper understanding of a wide range of processes involving H or D atoms.

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