On the Relative Proton Affinity of Argon and Deuterium[1]

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Abstract: In mixtures of Ar and D_2 at high pressures, the following ion–molecule reaction scheme is observed: $D_2^+ + D_2 \rightarrow (D_3^+)^* + D$ (1a); $(D_3^+)^* + (D_2)^2 \rightarrow (D_3^+)^\dagger + D_2$ (1b); $(D_3^+)^* + Ar \rightarrow ArD^+ + D_2$ (5); $(D_3^+)^\dagger + Ar \not\rightarrow ArD^+ + D_2$ (6); $ArD^+ + D_2 \rightarrow D_3^+ + Ar$ (4b). $(D_3^+)^*$ has of the order of 2 eV of energy according to the experiments of Leventhal and Friedman. $(D_3^+)^\dagger$ is the lowest vibrational state obtainable by collision of $(D_3^+)^*$ with D_2. The present results suggest that $(D_3^+)^\dagger$ is *not* the ground state but has at least 1 and possibly 2 quanta of vibrational energy (*i.e.*, 10–20 kcal/mol). From pressure dependence studies it is shown that a maximum of three collisions is needed to moderate all $(D_3^+)^*$ to $(D_3^+)^\dagger$. From reaction 4b, $PA(D_2) > PA(Ar)$. From threshold-double-resonance experiments on reaction 6, $PA(D_2)^+ \cong PA(Ar) + 7$ kcal/mol, with an uncertainty of ±5 kcal/mol. $PA(D_2)^\dagger$ is the energy required to remove D^+ from $(D_3^+)^\dagger$. The intrinsic proton (or deuteron) affinity of D_2, $PA(D_2)$, is felt to be 10–20 kcal/mol larger than $PA(D_2)^\dagger$.

Gas-phase proton affinities (*i.e.*, X–H$^+$ bond strengths) are a quantitative indicator of the intrinsic basicities of atoms and molecules. Considerable theoretical[2] and experimental[3–8] effort has recently been expended to determine the proton affinities of simple systems. Of particular interest are the experimental determinations of the proton affinities of the H_2 molecules and the lighter rare gas atoms, as these systems most easily lend themselves to accurate theoretical calculation. Leventhal and Friedman[7] have recently measured the proton affinity of D_2. They accomplished this by first forming and deactivating D_3^+ by the sequence

$$D_2^+ + D_2 \longrightarrow (D_3^+)^* + D \qquad (1a)$$

$$\xrightarrow{(D_2)^n} (D_3^+)^\dagger + D \qquad (1b)$$

and then by observing the threshold for the reaction

$$(D_3^+)^\dagger + M \longrightarrow D^+ + D_2 + M \qquad (2)$$

where M was He or Ne. They concluded that n in (1b) was 1 or 2. A key aspect of their determination was that $(D_3^+)^*$ had approximately 2 eV more internal energy than the final deactivated state $(D_3^+)^\dagger$.[9] They concluded that $PA(D_2)^\dagger$ [9] $\cong 4.8$ eV $= 110$ kcal/mol. No estimate of the magnitude or direction of possible errors in this number was offered.

Bowers and Elleman,[10] in contrast, have observed the reaction

$$(H_3^+)^\dagger + CH_4 \longrightarrow (CH_5^+)^* + H_2 \qquad (3a)$$

$$\longrightarrow CH_3^+ + 2H_2 \qquad (3b)$$

which indicates that $PA(H_2)^\dagger \leq 85.2$ kcal/mol. They worked under experimental conditions such that $(H_3^+)^*$ underwent up to ten deactivating collisions before encountering a CH_4 molecule. Bowers and Elleman's results[10] are in agreement with the earlier work of Aquilanti and Volpi,[11] but in considerable disagreement with the stated threshold value of Leventhal and Friedman.[7]

A large number of calculations have been done on H_3^+, with those of Schwartz and Schaad[12] and Conroy[13] being the most relevant to the work reported here. Virtually all calculations indicate that the equilateral triangle form of H_3^+ is the most stable. Using a set of floating 1s Gaussian orbitals, Schwartz and Schaad calculate a lower bound on the proton affinity of ground-state H_2, $PA(H_2) \geq 96$ kcal/mol, assuming the equilateral triangle configuration. Conroy,[13] using his unique molecular Schrödinger equation approach, estimates $PA(H_2) \cong 65$ kcal/mol for linear H_3^+, where differences in H_2 and H_3^+ zero-point energies were ignored (perhaps 5 kcal/mol should be added to $PA(H_2)$ to correct for this omission).

Peyerimhoff[14] has calculated the proton affinities of He and Ne to be $PA(He) = 1.74$ eV $= 40$ kcal/mol and $PA(Ne) = 2.03$ eV $= 48.4$ kcal/mol. These results are consistent with the photoionization data of Chupka and Russell,[8] who measured $PA(Ne) - PA(He) = 0.25 \pm 0.03$ eV. To our knowledge, no accurate calculations have been here reported for PA(Ar), although Peyerimhoff[14] indicated that preliminary

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(1) Supported in part by Contract No. NAS7-100 extended to the Jet Propulsion Laboratory by the National Aeronautics and Space Administration.

(2) For a review of LCAO-MO "nonempirical" calculations from 1960–1968, see R. G. Clark and E. T. Stewart, *Quart. Rev., Chem. Soc.*, in press.

(3) J. L. Beauchamp, Ph.D. Thesis, Harvard University, 1966, and references therein.

(4) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

(5) D. Holtz and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **91**, 5913 (1969).

(6) M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, 50, 2028 (1969).

(7) J. J. Leventhal and L. Friedman, *ibid.*, 49, 1974 (1968), and references therein.

(8) W. A. Chupka and M. E. Russell, *ibid.*, 49, 5426 (1968).

(9) $(D_3^+)^\dagger$ denotes the terminal D_3^+ state of the deactivation process 1b. This state is most likely not the ground vibrational state of D_3^+. Leventhal and Friedman[7] did not use the symbol $(D_3^+)^\dagger$ but rather assumed the D_3^+ deactivated *via* (1b) was in the ground state. We will discuss this point at length later in the paper. In order to be consistent, we are labeling the proton affinity of D_2 (or H_2) determined from reactions of $(D_3^+)^\dagger$ as $PA(D_2)^\dagger$. We feel that $PA(D_2)^\dagger$ is not the intrinsic proton affinity of D_2 but is a useful number since $(D_3^+)^\dagger$ is the easiest state of D_3^+ to obtain in large quantities.

(10) M. T. Bowers and D. D. Elleman, *J. Amer. Chem. Soc.*, **92**, 1847 (1970).

(11) V. Aquilanti and G. G. Volpi, *J. Chem. Phys.*, 44, 2307 (1966).

(12) M. E. Schwartz and L. J. Schaad, *ibid.*, 47, 5325 (1967). References are given to essentially all other H_3^+ calculations in this paper.

(13) H. Conroy, *ibid.*, 41, 1341 (1964).

(14) S. Peyerimhoff, *ibid.*, 43, 998 (1965).

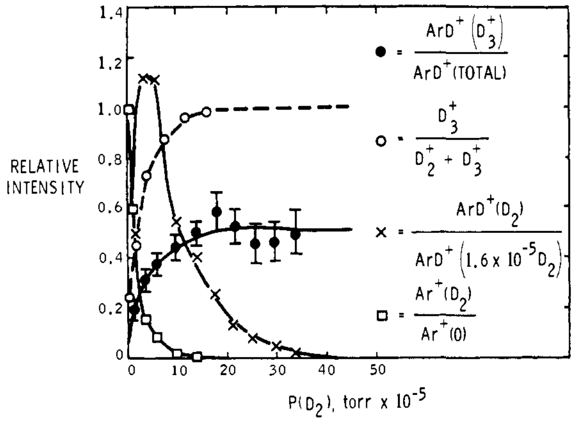

Figure 1. The relative intensity of various species as a function of D_2 pressure. The symbols are defined in the text. In all experiments the Ar pressure was 3.0×10^{-5} Torr. The ordinate for the $ArD^+ (D_2)/ArD^+ (1.6 \times 10^{-5}D_2)$ curve (*i.e.*, the X's) must be multiplied by two. All data were taken at electron energies of 50 eV.

calculations have been done. Chupka and Russell[8] experimentally place a probable lower limit of PA(Ar) ≥ 3.397 eV = 73.2 kcal/mol, however.

Owing to the considerable uncertainty in the experimental values of PA(Ar) and PA(D_2) and to the lack of accurate calculations for the potential energy surfaces of these molecules, it is useful to determine, at least semiquantitatively, the relative values of PA(D_2) and PA(Ar). In the approach presented here, PA(D_2)† is a more appropriate label[9] than PA(D_2) and the value PA(D_2)† relative to PA(Ar) is what is actually determined.

The relative proton affinities of interest can be determined by the direction and ΔH of the reactions

$$(D_3^+)\dagger + Ar \xrightarrow{?} ArD^+ + D_2 \tag{4a}$$

$$ArD^+ + D_2 \xrightarrow{?} D_3^+ + Ar \tag{4b}$$

Aquilanti, *et al.*,[15] using a tritium decay ionization source in a high-pressure mass spectrometer, presented evidence that (4b) proceeds to the right. The ambiguity in these experiments is that they used a 4-V/cm repeller field to extract the ions and hence they may have been driving (4b). Bowers and Elleman,[16] using an ion cyclotron resonance technique,[17,18] demonstrated that $(D_3^+)^*$ forms ArD^+ by a reaction similar to (4a). The ambiguity in these experiments is that no effort was made to deactivate collisionally the $(D_3^+)^*$ formed *via* (1a). Hence, the internal energy of $(D_3^+)^*$ may drive the reaction to form ArD^+. In an attempt to resolve this question, the ion-molecule reactions in Ar-D_2 mixtures are reported here as a function of both Ar and D_2 pressure. The results show that PA(D_2)† > PA(Ar). From the threshold energy dependence of (4a), PA(D_2)† ≅ PA(Ar) + 7 kcal/mol, with an uncertainty of ±5 kcal/mol.

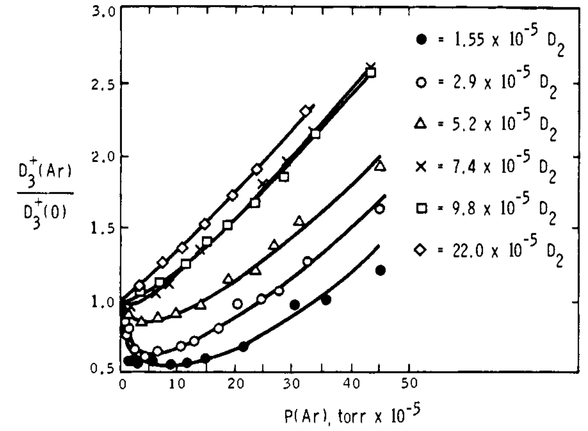

Figure 2. $D_3^+(Ar)/D_3^+(0)$ *vs.* Ar pressure for several initial values of D_2 pressure. The electron energy was 50 eV.

Experimental Section

The details of both the experimental techniques and the icr spectrometer employed in this work have been previously discussed.[10,16,19] The gases employed were Airco research grade and were used without further purification. A check of the purity of the D_2 indicated that trace quantities of N_2 were present, but it did not interfere with the experiments reported here.

Results

In a mixture of Ar and D_2, Ar^+ and D_2^+ are essentially the only ions present at low pressures with an ionizing electron energy of 50 eV. At higher pressures, D_3^+ and ArD^+ appear as product ions. ArD^+ is known to come from both Ar^+ and D_2^+ reactant ions[16,20] and D_3^+ is known to originate from D_2^+ *via* (1).[20,21] The key questions to be answered here are whether or not $(D_3^+)^+$ reacts with Ar to yield ArD^+ or whether ArD^+ reacts with D_2 to yield D_3^+ and, once the reaction is determined, what the ΔH of reaction is. In order to begin to answer these questions, the pressure dependence of each of the ions present was observed as a function of both D_2 and Ar partial pressure. The results of these studies are given in Figures 1 and 2.

If Figure 1, the dependence of various peaks on D_2 pressure at a constant Ar pressure are given. $ArD^+(D_3^+)$ is the contribution to the ArD^+ intensity from D_3^+ reactant ion and ArD^+ (total) is the total ArD^+ intensity from all sources. ArD^+ $(1.6 \times 10^{-5}D_2)$ is the intensity of ArD^+ at 1.6×10^{-5} Torr of D_2 pressure and $ArD^+(D_2)$ is the intensity of ArD^+ ion at D_2 pressures greater than 1.6×10^{-5} Torr. $Ar^+(0)$ is the Ar^+ ion intensity at zero D_2 pressure, while $Ar^+(D_2)$ is the Ar^+ intensity at D_2 pressures greater than zero. The dashed line, $D_3^+/(D_2^+ + D_3^+)$, gives the per cent of D_3^+ relative to D_2^+. At pressures above 20×10^{-5} Torr, it is clear that all of the D_2^+ has reacted to give D_3^+ (or ArD^+). Several facts are apparent. First, the intensity of Ar^+ goes rapidly to zero with a concurrent rise in the relative amount of ArD^+. This result is to be expected from the known reaction of Ar^+ with D_2. As the D_2 pressure is further raised, however, the ArD^+ relative intensity goes through a maximum and falls off to zero at D_2 pressures above 4×10^{-4}

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(15) V. Aquilanti, A. Galli, A. Giordini-Guidoni, and G. G. Volpi, *J. Chem. Phys* 43, 1969 (1965).

(16) M. T. Bowers and D. D. Elleman, *ibid.*, **51**, 4606 (1969).

(17) For a general review, see J. D. Baldeschwieler, *Science*, **159**, 254 (1968).

(18) J. L. Beauchamp and J. T. Armstrong, *Rev. Sci. Instrum.*, **40**, 123 (1969).

(19) M. T. Bowers, D. D. Elleman, and J. L. Beauchamp, *J. Phys. Chem.*, **72**, 3599 (1968).

(20) C. F. Giese and W. B. Maier, II, *J. Chem. Phys.*, **39**, 739 (1963).

(21) M. T. Bowers, D. D. Elleman, and J. King, Jr., *ibid.*, **50**, 4787 (1969), and references therein.

Torr. Thus, it appears that ArD^+ transfers a deuteron to D_2 and (4b) proceeds to the right. This conclusion is consistent with the results of Aquilanti, *et al.*[15] However, a second effect is also apparent in Figure 1. The solid circles represent the fraction of ArD^+ coming from D_3^+ reactant ions as a function of D_2 pressure. It is clear that a certain amount of ArD^+ is also being formed from D_3^+. This observation is consistent with the earlier work of Bowers and Elleman.[16]

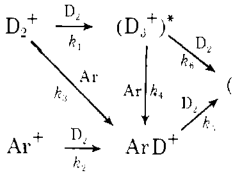
Similar results are evident in the data of Figure 2. Here, the pressure dependence of the D_3^+ peak is observed as a function of Ar pressure for several constant values of D_2. $D_3^+(0)$ is the icr intensity of the D_3^+ ion at zero Ar pressure and $D_3^+(Ar)$ is the D_3^+ pressure at an Ar pressure greater than zero. At the lower values of D_2, D_3^+ first decreases with argon pressure, reaches a minimum, and then increases. As the initial pressure of D_2 increases, this minimum moves to lower and lower argon pressure until finally at approximately 1×10^{-4} Torr of D_2 pressure the D_3^+ signal increases monotonically with Ar pressure from the onset.

Apparently, there are two distinct processes taking place. One is characterized by a form of D_3^+ that transfers a proton to Ar, while the other indicates that ArD^+ transfers a proton to D_2. The most feasible answer is that excited $(D_3^+)^*$ transfers a proton to Ar

$$(D_3^+)^* + Ar \longrightarrow ArD^+ + D_2 \qquad (5)$$

while $(D_3)^\dagger$, deactivated collisionally, does not. Such a selectivity in the reactions of $(D_3^+)^*$ and $(D_3^+)^\dagger$ has not previously been reported, although more subtle differences in reactivity of $(D_3^+)^*$ and $(D_3^+)^\dagger$ have been discussed.[7,10,22] ArD^+, on the other hand, appears to transfer a deuteron to D_2 regardless of the genesis of its formation. The conclusion is that $PA(D_2) > PA(Ar)$.

In light of the above, the complete reaction scheme for the $Ar{-}D_2$ system can be written as



(6)

It is not important whether ArD^+ forms $(D_3^+)^\dagger$ or ground-state D_3^+ as both ions are unreactive in $Ar{-}D_2$ mixtures. A straightforward kinetic analysis of reaction scheme 6 can be made and qualitatively checked with the experimental results in Figures 1 and 2.

The quotient of the total rate of formation of D_3^+ at an arbitrary value of the Ar pressure, $R(D_3^+)_T{}^{Ar}$, to the rate of formation of D_3^+ at zero argon pressure, $R(D_3^+)_T{}^0$, is directly proportional to the ratio of measured intensities, $D_3^+(Ar)/D_3^+(0)$, and is given by

$$R_G = \frac{R(D_3^+)_T{}^{Ar}}{R(D_3^+)_T{}^0} = 1 - \frac{[(D_3^+)^*][Ar]k_4}{[D_2^+][D_2]k_1} + \frac{[ArD^+]k_5}{[D_2^+]k_1}$$

where

$$R(D_3^+)_T = R(D_3^+)^\dagger + R(D_3^+)^*$$

Comparing with the data of Figure 2, R_G thus has the proper form if the second term dominates at low D_2 and Ar pressures and the third term dominates at high pressures.

In the high-pressure limit[23] we can assume Ar^+, D_2^+, ArD^+, and $(D_3^+)^*$ are all in the steady state. These assumptions yield

$$R_{high} \cong 1 + \frac{[Ar]}{[D_2]}\left(\frac{k_3}{k_1} + \frac{k_{Ar^+}}{k_{D_2^+}}\right) + \left(\frac{[Ar]}{[D_2]}\right)^2 \frac{k_{Ar^+}k_3}{k_{D_2^+}k_1}$$

where $k_{Ar^+}/k_{D_2^+}$ is the ratio of the rate constant for formation of Ar^+ to that of D_2^+ in the electron beam. For the special case of $[D_2] \gg [Ar]$, the last term can be ignored. In this limit we expect a linear increase in R_{high} with [Ar] pressure and an intercept of 1. At lower values of $[D_2]$ relative to [Ar], curvature should become apparent due to the quadratic term in $[Ar]^2$. These features are apparent in the highest pressure D_2 curves in Figure 2.

A second verification of the reaction scheme is obtained from the data in Figure 1. In Figure 1, $ArD^+(D_3^+)/ArD^+(total)$ is plotted as the filled circles as a function of D_2 pressure for a constant Ar pressure of 3×10^{-5} Torr. At high D_2 pressures, $[Ar]/[D_2] \ll 1$ and

$$R' = \frac{R(ArD^+)_{D_3^+}}{R(ArD^+)_{total}} \cong \frac{1}{2 - \dfrac{[Ar^+]k_2}{[ArD^+]k_5}}$$

where $R(ArD^+)_{D_3^+}$ is the rate of formation of ArD^+ from D_3^+ only and $R(ArD^+)_{total}$ is the rate of formation of ArD^+ from all sources. From Figure 1 it is apparent that $[Ar^+]$ decreases much faster with D_2 pressure than $[ArD^+]$ and hence $[Ar^+]/[ArD^+] \ll 1$ at high values of D_2 pressure. From the theory of Gioumousis and Stevenson,[24] $k_2/k_5 = 1.01$. Hence it is reasonable that $k_2/k_5 \lesssim 1$ since Bowers and Elleman[16] have shown that the experimental value of k_2 is one-half the theoretical and it is apparent from Figure 1 that k_5 is fairly large. Thus, reaction scheme 6 predicts that $R' \cong 0.5$. From Figure 1, $R'(\text{exptl}) \cong 0.52$. Reaction scheme 6 is again confirmed.

An upper limit on the number of collisions necessary to deexcite all of the $(D_3^+)^*$ ions to $(D_3^+)^\dagger$ can be estimated from the data of Figure 2. Reactions of $(D_3^+)^*$ with Ar result in a negative change in $D_3(Ar)/D_3^+(0)$ with Ar concentration. Only when all $(D_3^+)^*$ ions have been deactivated will the D_3^+ intensity monotonically increase from zero argon partial pressure to higher pressures. This condition has been met at D_2 pressures of approximately 1×10^{-4} Torr; that is, only deactivated $(D_3^+)^\dagger$ ions drift into the resonance region from the source region. The number of possible collisions of the $(D_3^+)^*$ ions in the source region is given by $Z = k_c N_{D_2} \tau_S$, where k_c is the collision rate constant, N_{D_2} the concentration of D_2 molecules, and τ_S the $(D_3^+)^*$ drift time in the source region. k_c can be calculated by the theory of Gioumousis and Stevenson[24] and N_{D_2} and τ_S are known system parameters. The result is $Z \cong 3$. This result is in close agreement with the previous estimates of Leventhal and Friedman.[7,22]

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[22] J. J. Leventhal and L. Friedman, *J. Chem. Phys.*, **50**, 2928 (1969).

[23] The high-pressure limit refers to the D_2 pressure. D_2 pressures above 20×10^{-6} Torr obey this limit at low values of Ar pressure.

[24] G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

A semiquantitative value for the difference in $PA(D_2)\dagger$ and PA(Ar) can be determined by observing the translational energy threshold for reaction 4a.

$$(D_3^+)\dagger + Ar \longrightarrow ArD^+ + D_2 \qquad (4a)$$

Ideally, a method similar to that of Anders[25] should be employed. For reaction 4a, however, Anders' technique cannot be used since $(D_3^+)\dagger$ is a secondary ion that has undergone several additional deactivating collisions. Standard double-resonance techniques can be utilized, however, to approximate the threshold for (4a). The averaged results of several of these experiments are presented in Figure 3, where $\Delta(ArD^+)/(ArD^+)^0$ is plotted *vs.* the square of the irradiating electric field.[26] $\Delta(ArD^+)$ is the change in ArD^+ intensity when D_3^+ is irradiated at a particular field strength, and $(ArD^+)^0$ is the icr intensity of ArD^+ in the absence of an irradiating field. The threshold comes at approximately 7.5 $(V/m)^2$. Since the linewidth of the double-resonance signal is not known at threshold, the time limited expression for the energy must be used. The result is $PA(D_2)\dagger \cong PA(Ar) + 7$ kcal/mol, with an uncertainty of ±5 kcal/mol.

Discussion

Several facts are coming into focus regarding the intrinsic proton affinity of H_2. Schwartz and Schaad,[12] through use of the variation theorem, have set an absolute lower bound at $PA(H_2) \geq 96$ kcal/mol for ground-state H_3^+ in the equilateral triangular configuration. Bowers and Elleman,[10] on the other hand, have set an absolute upper limit $PA(H_2)\dagger \leq 85.2$ kcal/mol by observing the reaction

$$(H_3^+)\dagger + CH_4 \longrightarrow CH_3^+ + 2H_2 \qquad (3b)$$

The $(H_3^+)\dagger$ utilized in (3b) was formed and stabilized *via* reaction 1. The stabilization step in reaction 1b is not merely a nonreactive, vibration–translation energy-transfer process, however. The primary mode of deactivation is most likely through proton transfer between $(H_3^+)^*$ and H_2. This process has been shown to take place by observing a rapid exchange between H_2D^+ and HD_2^+ in either pure HD or H_2, D_2 mixtures.[28] The H_3^+ that results from this kind of proton-transfer deactivation very probably retains a certain amount of vibrational energy above the ground state. Our experiments, as well as those of Leventhal and Friedman,[7,22] show that about two or three collisions are satisfactory for reducing $(H_3^+)^*$ to $(H_3^+)\dagger$. The extreme efficiency of the collisional deactivation process is in strong support of a mechanism such as proton transfer. The neutral H_2 molecules formed in the above process most likely carry off energy as vibrational excitation. What eventually happens is that $(H_3^+)^*$ rapidly moderates its vibrational energy to a point where it is not possible to transfer an additional vibrational quantum to H_2 because it has not enough energy ($\omega_e(H_2) = 4395$ cm^{-1} = 0.54 eV = 12.5 kcal/mol)[29] or because the transfer would require a significant amount of vibration–translation energy transfer. The insufficient energy requirement would leave at least 1 quantum of vibrational energy available in $(H_3^+)\dagger$ (approximately 9–10 kcal/mol), while a strong possibility exists that up to twice this energy is available from the "nonresonant" condition.[30] The subsequent moderation of this energy by vibration–rotation or vibration–translation energy transfer is slow.[31] Thus it appears probable that $(H_3^+)\dagger$, generated and deactivated *via* reaction 1, is not a good reagent for determining the intrinsic proton affinity of H_2.

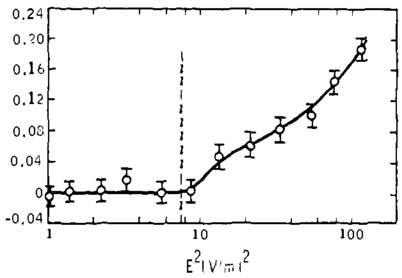

Figure 3. Plot of the relative change in ArD^+ intensity, $\Delta(ArD^+)/(ArD^+)^0$, *vs.* the square of the D_3^+ irradiating field strength. The dashed line corresponds to the assigned threshold of 7.5 $(V/m)^2 \cong$ 7 kcal/mol. The electron energy was 50 eV.

Determining the apparent proton affinity of H_2 from $(H_3^+)\dagger$ generated *via* (2) is of interest, however, since this apparent value is a measure of the residual internal energy in $(H_3^+)\dagger$ and since (1) is by far the easiest way to generate large amounts of H_3^+ which can subsequently be reacted with various species. The results presented here coupled with the previous data of Chupka and Russell[8] on PA(Ar) and Bowers and Elleman[10] on $PA(H_2)\dagger$ indicate that $79 \pm 4 \leq PA(H_2)\dagger \leq 85 \pm 4$ kcal/mol are reasonable limits to place on the proton affinity of H_2 when referenced to $(H_3^-)\dagger$ generated *via* (1).[32] The intrinsic value of $PA(H_2)$ is, of course, greater than 96 kcal/mol, as indicated by the variation calculation of Schwartz and Schaad.[12] A new approach will be needed to experimentally determine this number.

One disturbing question remains: why do our results differ so drastically from the threshold measurements of Leventhal and Friedman?[7] The answer is not immediately evident. Leventhal and Friedman generate their D_3^+ *via* (1) and are thus utilizing $(D_3^+)\dagger$ the same as we are. Yet their value for $PA(D_2)\dagger$ is 110 kcal/mol and ours is ≤85 kcal/mol. Our value is determined from the well-known heats of formation of H^+, CH_3^+, CH_4, and H_2.[33,34] A small percentage of

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(25) L. R. Anders, *J. Phys. Chem.*, 73, 469 (1969).

(26) There are two general expressions for the kinetic energy of an irradiated ion: the time-limited case,[21] $KE_{time} = q^2E^2\tau^2/8m$, and the collision-limited case,[27] $KE_{collision} = q^2E^2(m_p + M)/8\xi^2 m_p^2$. The symbols have their usual meaning. The salient point is that the kinetic energy of the irradiated ion varies as E^2, where E is the irradiating field strength.

(27) J. L. Beauchamp, *J. Chem. Phys.*, 46, 1231 (1967).

(28) J. L. Beauchamp, private communication. The exchange process has subsequently been observed in our laboratories.

(29) G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1950.

(30) The value of $\omega_e(D_2)$ = 3118 cm^{-1} = 0.39 eV = 8.9 kcal/mol (ref 29) differs significantly from that for $\omega_e(H_2)$. The corresponding vibrational frequencies for D_3^+ will also be shifted to lower values relative to H_3^+, however. Thus, it is expected the amount of vibrational energy "trapped" in $(D_3^+)\dagger$ is similar to that contained in $(H_3^+)\dagger$, although a difference of a few kilocalories between the two would not be unexpected. Experiments are being carried out to determine whether or not there are significant differences in the amounts of internal energy in D_3^+ relative to H_3^+ at the various stages of deactivation.

(31) W. H. Flygare, *Accounts Chem. Res.*, 1, 121 (1968); R. C. Millikan, Special Publication No. 20, The Chemical Society, London, 1966, pp 219–234.

(32) $PA(H_2)\dagger$ and $PA(D_2)\dagger$ may differ by 1–4 kcal/mol due to zero-point energy effects. These differences are ignored in the discussion given here.

our $(H_3^+)\dagger$ reactant ions may have up to 0.1 or 0.2 eV of translational energy from the trapping fields. It appears to us, however, that the significant difference in results must lie in the uncertainty of the threshold results. Our perusal of Leventhal and Friedman's data indicate at least a 1-eV spread in their reported data points and their assigned threshold is at the extreme upper energy limit of this uncertainty. Thus, the threshold for

$$(D_3^+)\dagger + M \longrightarrow D^+ + M + D_2 \tag{2}$$

may easily be 1 eV below their stated value of 4.8 eV. If this analysis is valid, then our results agree with Leventhal and Friedman's. If not, the discrepancy remains unexplained.[35]

Acknowledgment. The authors gratefully acknowledge support of the Directors Discretionary Fund of the Jet Propulsion Laboratory, California Institute of Technology.

(33) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, Superintendent of Documents, U. S. Government Printing Office, Washington, D. C.

(34) The heat of formation of $\cdot CH_3$ was taken to be 1.507 eV: K. M. A. Refaey and W. A. Chupka, *J. Chem. Phys.*, **48**, 5205 (1968).

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Quantum Efficiencies of Transition-Metal Complexes. I. d–d Luminescence[1a]

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Abstract: Quantum yields and lifetimes of six *cis*-$[RhX_2Y_2]^+$ (X = Cl, Br, I; Y = 2,2′-bipyridine or 1,10-phenanthroline) and *trans*-$[RhBr_2(py)_4]Br$ (py = pyridine) are reported. For each complex an intrinsic lifetime, τ_0, a radiative rate constant, k_r, and a quenching rate constant, k_q, were calculated. Evidence for a near-unity intersystem-crossing yield, ϕ_{isc}, for all the complexes is presented, and assignment of the luminescences to a spin-forbidden process is confirmed. A semiempirical spin–orbit-coupling model is shown to predict satisfactorily the intrinsic lives calculated for the complexes from the experimental measurements. Experimental evidence for rapid relaxation between states of different orbital configurations (π–$\pi^* \rightarrow$ d–$\pi^* \rightarrow$ d–d) in transition-metal complexes is presented. Two general rules governing the emission characteristics of transition-metal complexes with unfilled d shells are proposed.

Studies of the luminescence properties of transition-metal complexes with organic ligands comprise a relatively new field of endeavor. Six years ago research was focused on chromium(III) complexes which exhibited a d–d phosphorescence (analogous to that of ruby) and on a few manganese(II) systems. Several preliminary experiments on ruthenium(II) complexes and porphyrin–metal compounds had also been reported. These results were discussed in an interpretive review by Porter and Schläfer.[2] Recently, the literature on transition-metal luminescence has been reviewed by Fleischauer and Fleischauer.[3]

In the last few years large numbers of highly luminescent substances of widely different optical behaviors have been synthesized and studied spectroscopically. Included were a variety of ruthenium(II) compounds which exhibit charge-transfer (CT) luminescence,[4] several osmium(II)[5,6] and iridium(III)[7] compounds which show CT emission, a number of rhodium and iridium complexes demonstrating d–d luminescence,[7,8] and a series of metal–porphyrin complexes showing π–π^* luminescence.[9,10]

The present research was specifically confined to molecular complexes, species whose identities could, in principle, be retained both in the solid state and in a variety of solvents. Our experimental study was undertaken in an attempt to construct a coherent picture of

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