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Product distributions in the reactions of excited noble-gas atoms with hydrogen-containing compounds

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Dissociation and ionization of small H-containing molecules following energy transfer from electronically excited ($^3P_{0,2}$) states of Ar, Kr, and Xe have been studied in discharge–flow systems, using the atomic resonance fluorescence and the saturation ion–current techniques. Chemi-ionization is observed in all reactions in which Penning ionization is exothermic, but molecular dissociation is the major channel in all cases. Elimination of H atoms is strongly favored over both loss of H_2 and cleavage of central bonds of larger molecules, in contrast to the known vacuum–UV photochemistry of several of the molecules. When strongly exothermic, elimination of two H atoms in a single reactive event is a major and, in some cases, the dominant channel.

I. INTRODUCTION

The reactions of electronically excited atoms and small molecules are very important in such diverse areas as atmospheric chemistry, visible and UV lasers and combustion chemistry, but, in most cases, only rate constants have been measured, with much less known about the product distributions. Recently, experimental studies[1-8] of the major products of the reactions of excited alkali, alkaline earth (and Cd and Hg), and noble gas atoms have been commenced, using molecular beam and spectroscopic techniques. The ultimate aim of such studies is increased insight into the mechanism of the quenching process, which may include reaction on an adiabatic surface, long-range near-resonant energy transfer, curve crossing, possibly via a charge–transfer intermediate, and complex formation.

For the lowest metastable states of the noble gases Ar*($^3P_0$, $^3P_2$) (energies 11.72 and 11.55 eV, respectively), Kr*($^3P_2$) (energy 9.92 eV), and Xe*($^3P_2$) (energy 8.32 eV), the rate constants for quenching by almost all molecular reagents are close to the collision number,[9] largely due to the many accessible reaction channels. In order to gain information on the competition between these channels, we are using atomic resonance fluorescence and saturation ion–current measurements to obtain absolute branching fractions for dissociation and total chemi-ionization channels. Recent results[7,8] for some diatomic and triatomic oxygen-containing reagent molecules showed molecular dissociation to be the major reaction channel, with chemi-ionization an important minor channel, when energetically accessible, but dissociative excitation usually accounting for only a small fraction of the dissociation channel. A tantalizing result was the observation of atomization of H_2O to $2H + O$ in approximately one-half of the quenching collisions with Ar*; this inspired the present study of reactions with several H-containing compounds to search for similar multifragmentation processes. A parallel study of some halogen-containing reagents, in which the competition with noble-gas halide excimer formation is probed, will be published separately.[10] An important aspect of the discussion of the results is comparison with available data on the photochemistry of the molecules studied.

II. EXPERIMENTAL

Two discharge–flow systems, operating at total pressures of 1–5 Torr, have been used, one[7] for the resonance fluorescence measurements and the other[8] for the saturation ion–current measurements. Emission measurements can be made in either system. The metastable atoms are generated by passing Ar, or very dilute mixtures of Kr or Xe in Ar, through a dc discharge into a Pyrex reaction vessel, mounted, in each system, in the entrance port of a vacuum monochromator. Typical concentrations of Ar($^3P_2$) metastables are $(1-2) \times 10^{10}$ cm^{-3}, with those of Ar($^3P_0$) approximately an order of magnitude smaller, and those of Kr($^3P_2$) and Xe($^3P_2$) about a factor of 2 lower than those of Ar($^3P_2$). The excited gas flows into the vessel with a linear velocity of ~50 ms^{-1} and passes through the reaction and observation regions as a well-defined jet, little broadened by diffusion.

In the resonance fluorescence system, small flows of the reagent are added through a concentric inlet tube and quench the excited atoms within a reaction zone, typically of 1–3 cm. By appropriate positioning of the movable gas inlets, the monochromator field of view can be centered either on the reaction flame (for emission measurements) or a few centimeters downstream (for resonance fluorescence measurements). For the resonance fluorescence, water, at a mole fraction of ~3×10^{-4} in flowing He carrier gas, was excited by a microwave discharge, as a source of H Lyman-α emission at 121.6 nm and O($^3S - ^3P$) lines at 130.2–130.6 nm. Both the emission and resonance fluorescence signals were dispersed by the monochromator and detected by photomultipliers. For the low concentrations of O and H atoms in this study $\lesssim 4 \times 10^{10}$ cm^{-3}, the resonance fluorescence intensity was accurately proportional to atom concentration.

As discussed previously,[7] each experiment consisted of measuring the resonance fluorescence signal from the products of a given reaction, relative to that obtained when the same excited noble gas was reacted with a reference reagent, such as H_2 or O_2. This procedure eliminated the effects of day-to-day variations in the resonance lamp output or the metastable atom concentration.

Further, by knowing the absolute yield of H or O atoms from the reference reaction (see the Discussion section and Ref. 7), the *absolute* atom yield from the reaction of interest was obtained directly.

The vessel for the saturation ion–current measurements contains two sets of stainless-steel electrodes downstream of the dc discharge. The first set serves to remove any charged particles produced in the discharge. Further downstream, just past a Teflon loop reagent injector, is the second set, composed of a split cylindrical shell and, downstream, a wire grid perpendicular to the gas flow, at which the chemi-ions are collected, yielding saturation ion currents of 0.1 to 10 μA. Absolute branching fractions for chemi-ionization are determined, with an uncertainty of $\pm 35\%$, using a calibration of the flux of metastable Ar* atoms.[8] Each experiment consisted of measuring the saturation ion currents from the reaction of interest and from a reference reaction, for which the absolute branching fraction for ionization had been determined.[8] NO and CF_2Br_2 were used as reference reagents.

The reagent concentrations were varied typically over the range 2×10^{13}–2×10^{14} cm^{-3}. Addition of the reagents to the vessel was carried out in several ways. HCl, NH_3, and C_2H_6 (all Matheson) were pumped on at 77 K and stored in bulbs; CH_4, CF_3H, D_2 (Matheson), and H_2 (Airco) were used directly from lecture bottles. CH_3OH (Baker), C_2H_5OH (U. S. I.), CH_3OD, and C_2H_5OD (Aldrich) were taken from cooled storage traps. The reagent line was predeuterated using D_2O. In several experiments, the deuterated alcohols were stored in a cold trap immediately upstream of the reagent inlet point and swept into the vessel by Ar carrier gas. The D atom yields were found to be the same for both methods of addition. The H_2CO monomer was prepared according to established procedures[11] from paraformaldehyde (Aldrich) and distilled into a cold trap on the vacuum system where it was normally stored at 77 K. For experiments, the monomer was kept at 148 K, where it has a vapor pressure of ~1 Torr, and the vapor swept into the vessel with Ar carrier gas.

III. RESULTS

A. Resonance fluorescence

Resonance fluorescence data were obtained by subtracting the scattered light (dc discharge off) and background emission (resonance lamp off) from the signal with both the dc discharge and resonance lamp on. For the reagents used in this study, the reaction was readily pushed to completion by employing reagent concentrations greater than ~5×10^{13} cm^{-3}; under these conditions, the background emission was negligibly weak. The lamp was operated to give a scattered light signal at the photomultiplier of 2–5 counts s^{-1}, under which conditions the largest resonance fluorescence intensities (from reactions with O_2 and H_2) were an order of magnitude larger. Integration times of 100–200 s were employed to obtain satisfactory signal-to-noise ratios.

Data were obtained over a range of reagent concentration. Typical behavior is shown in Fig. 1 for the re-
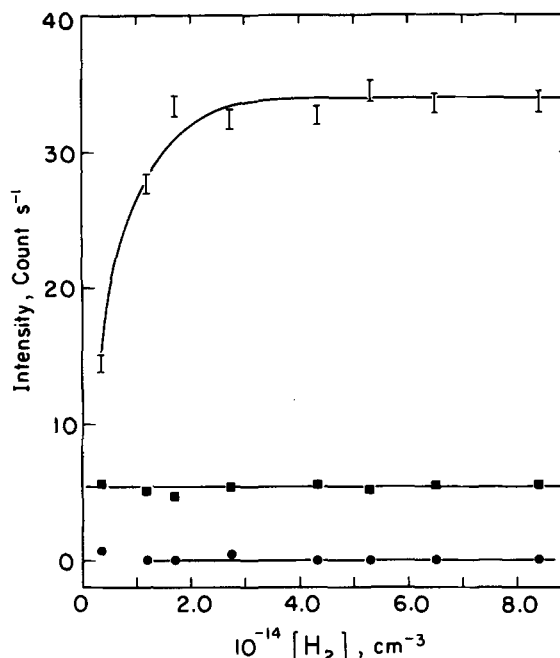

FIG. 1. The dependence of emission intensities at 121.6 nm on $[H_2]$ in the reaction of Xe* with H_2. ● Background emission; ■ scattered light from the resonance lamp; I the resonance fluorescence signal.

action of Xe* with H_2. At low H_2 concentrations, the reaction zone extends downstream of the observation zone, resulting in a low resonance fluorescence signal. At sufficiently high concentrations (H_2 is an anomalously slow quencher[9]), the reaction is completed upstream of the observation zone and the signal becomes independent of reagent concentration.

Data obtained in this plateau region were compared with H and O yields from the reference reactions with H_2 and O_2, respectively. On the assumption that the reference reagents are dissociated in all quenching collisions,[7] the absolute H and O yields per quenching collision were derived for the reagent of interest. This procedure proved satisfactory for all the reactions of Kr* and Xe* investigated and for the reactions of Ar* with H_2, CH_4, C_2H_6, H_2O, and HCl; the absolute H and O yields are listed in Table I. Each entry represents the average of at least three and more commonly five or more measurements at different reagent concentrations; the quoted uncertainty represents the standard deviation of these measurements.

B. Effect of SF_6 on the atom yields

The reactions of Ar* with C_2H_2, NH_3, and CH_3OH gave less satisfactory H-atom resonance fluorescence data, which showed considerably larger scatter and, in the case of C_2H_2, a clear dependence on reagent concentration. It was found that addition of a very small flow of SF_6 with each of these reagents eliminated these spurious effects, but also caused a significant decrease in the resonance fluorescence signal. Data for the reaction with NH_3 are shown in Fig. 2. A concentration of 2 $\times 10^{12}$ cm^{-3} of SF_6 caused a 30% decrease in the signal,

TABLE I. Ionization branching fractions f_{ion} and absolute H- and O-atom yields from the reactions of excited Ar, Kr, and Xe atoms.

Reagent	f_{ion} (Ar*)	Atom	Atom yields		
			(Ar*)	(Kr*)	(Xe*)
HCl	...	H	1.00 ± 0.05	1.01 ± 0.06	0.99 ± 0.05
H$_2$O	...	H	1.52 ± 0.10	1.08 ± 0.06	1.00 ± 0.06
		O	0.46 ± 0.04	0.14 ± 0.04	0 ± 0.02
NH$_3$	0.42 ± 0.04	H	0.62 ± 0.04	1.10 ± 0.05	1.04 ± 0.06
CH$_4$	...	H	1.53 ± 0.08[a]	1.10 ± 0.04[a]	0.98 ± 0.02[a]
CH$_2$O	0.33[b]	H	0.80 ± 0.04	1.68 ± 0.08	1.90 ± 0.08
		O	0.21 ± 0.03	0.09 ± 0.02	0.03 ± 0.01
CH$_3$OH	0.20 ± 0.01	H	1.45 ± 0.03	1.70 ± 0.04	1.49 ± 0.03
		O	0.05 ± 0.03	0 ± 0.02	0 ± 0.02
CH$_3$OD	n.m.[c]	H	1.01 ± 0.03	1.12 ± 0.04	0.81 ± 0.02
		D	0.46 ± 0.04	n.m.	0.68 ± 0.02
C$_2$H$_5$OH	0.16 ± 0.01	H	1.34 ± 0.06	1.42 ± 0.06	1.22 ± 0.06
		O	0 ± 0.02	0 ± 0.02	0 ± 0.02
C$_2$H$_5$OD	n.m.	H	0.94 ± 0.06	0.98 ± 0.04	0.72 ± 0.04
		D	0.32 ± 0.02	n.m.	0.52 ± 0.02
CH$_3$OCH$_3$	0.21 ± 0.01	H	1.06 ± 0.04	n.m.	0.86 ± 0.04
		O	0 ± 0.02	n.m.	0 ± 0.02
C$_2$H$_6$	0.01	H	1.82 ± 0.04	1.68 ± 0.08	1.08 ± 0.04

[a]Measured data corrected for minor absorption by CH$_4$ at 121.6 nm.
[b]One measurement only.
[c]n.m.—not measured.

while larger flows of SF$_6$ had only a very small additional effect, consistent with slight competition with NH$_3$ for removal of Ar*. As shown in Fig. 3, the H-atom resonance fluorescence intensity is clearly independent of NH$_3$ concentration when SF$_6$ is present.

Small additions of SF$_6$ were found to cause analogous decreases in the H-atom yields in the reactions of Ar* with CH$_3$OH, C$_2$H$_5$OH, CH$_2$O, and CH$_3$OCH$_3$ and typical data are included in Table II. (In the reactions with C$_2$H$_2$, carbonaceous deposits were formed on the lamp window and no reliable data could be obtained.) No effect of SF$_6$ was observed in the reactions of Xe* or Kr* with these reagents, nor in the reactions of Ar* with H$_2$, CH$_4$, and C$_2$H$_6$. A comparison of the resonance fluo-

rescence and ion–current data reveals that this effect is only observed for those reactions which undergo an appreciable extent of chemi-ionization. It was concluded that the spurious effects in the absence of SF$_6$ were due to secondary reactions between Penning electrons and either the reagent or Penning ions, and that SF$_6$ eliminated the effects through extremely efficient scavenging of the electrons.[12] It is thus expected that the data obtained in the presence of small concentrations of SF$_6$ are valid and these are included in Table I.

The discovery of this effect prompted a reexamination of the O-atom yields[7] in the reactions of Ar* with NO and OCS, which have been found to occur, in part, by chemi-ionization. No significant change in the O-atom yield in the former reaction was found when SF$_6$ was added.
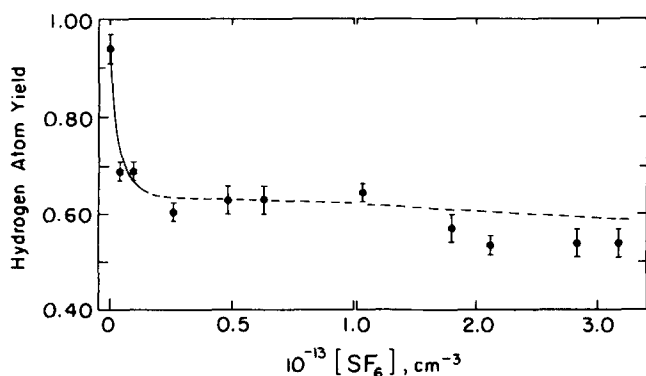

FIG. 2. The dependence of hydrogen atom yield on SF$_6$ concentration in the reaction of Ar* with NH$_3$. Note scale change at [SF$_6$]$=1 \times 10^{13}$ cm^{-3}. [NH$_3$]$=1.1 \times 10^{14}$ cm^{-3}. Dashed line: theoretical dependence, using quenching rate constants, Ar* + NH$_3$: 5.4×10^{-10} cm^3 s^{-1}: Ar* + SF$_6$: 1.6×10^{-10} cm^3 s^{-1}.
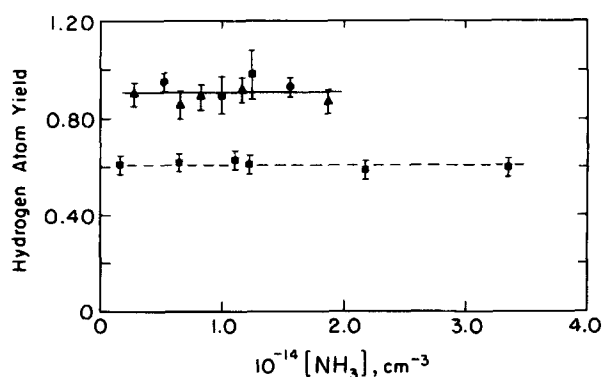

FIG. 3. The dependence of hydrogen atom yield on NH$_3$ concentration in the reaction of Ar* with NH$_3$. Solid line: no SF$_6$ present; dashed line: [SF$_6$]$=(3-5) \times 10^{12}$ cm^{-3}. The various symbols refer to separate experiments.

TABLE II. Saturation ion–currents and atom yields (relative to 2.0 for O_2 and H_2) in the reactions of Ar* in the absence and presence of SF_6. Ar flow rate: 3×10^{-4} mol s^{-1}, total pressure: 1.0–1.2 Torr, $[SF_6] = (3-6) \times 10^{12}$ cm^{-3}.

Reagent	Ionization Potential (eV)	Saturation ion current (μA)		Atom	Atom yields	
		No SF_6[a]	SF_6 present		No SF_6	SF_6 present
NH_3	10.2	3.8	7.40	H	0.91 ± 0.05	0.62 ± 0.04
CH_2O	10.9	4.6	6.56	H	0.90 ± 0.06	0.80 ± 0.04
				O	0.18 ± 0.04	0.21 ± 0.03
CH_3OH	10.8	1.7	3.97	H	1.64 ± 0.08	1.45 ± 0.03
				O	0.06 ± 0.02	0.05 ± 0.03
C_2H_5OH	10.5	1.5	3.16	H	1.58 ± 0.08	1.34 ± 0.06
CH_3OCH_3	10.0	2.5	4.40	H	1.22 ± 0.04	1.06 ± 0.04

[a]Applied voltage at ion-collection electrodes 150 V.

In the reaction of Ar* with OCS, the atom yield was reduced from 0.10 ± 0.02 per reactive collision[7] to 0.06 ± 0.02 in the presence of SF_6; this latter value is therefore preferred and emphasizes the lack of importance of dissociation of OCS to O + CS, the more exothermic dissociation to S + CO being presumably strongly favored.

C. Saturation ion–current measurements

Ions were detected in the reactions of Ar* with those reagents NH_3, CH_3OH, C_2H_5OH, CH_2O, and CH_3OCH_3, which have ionization potentials below 11.5 eV. The dependence of the measured ion current on the potential applied to the cylindrical electrode was as expected[8]; a region of increasing current at low voltages and a near-constant "saturation current" at higher voltages, typically 50–130 V, see Fig. 4. However, in all cases, addition of a trace of SF_6 with the reagent caused a large increase in ion current. As shown in Fig. 4, the saturation currents were even more clearly defined than in the absence of SF_6, the value being independent of SF_6 concentration in the range $(1-6) \times 10^{12}$ cm^{-3} (the reagent concentration was at least two orders of magnitude larger). The saturation currents obtained in the absence and presence of SF_6 are included in Table II.

The low ion currents in the absence of SF_6 were ascribed to ion–electron recombination (or possibly to ambipolar diffusion of the positive ion and electron to the electrodes); it was thus expected that the effect should be reduced at smaller concentrations of the charged species. This was tested in two ways: first, a 10 cm long tube was inserted downstream of the dc discharge, leading to a fourfold decrease in the Ar* concentration at the reagent inlet. Second, mixtures of the reagent of interest and N_2 were added, in the presence and absence of SF_6. The N_2 scavenged part of the Ar* metastables, the extent of scavenging being monitored via the emission intensity of the resulting $N_2(C\,^3\Pi_u - B\,^3\Pi_g)$ (0, 0) band.[13] In both cases, the size of the SF_6 effect was greatly reduced at the lower ion concentrations; consistent branching fractions for ionization, determined by comparison of ion currents with that from the reference reaction of Ar* with NO,[8] were obtained only by use of the data obtained *in the presence of* SF_6. These values are included in Table I, the quoted uncertainties being the scatter (standard deviation) in the values ob-

tained by the various techniques.

Branching fractions for chemi-ionization of several reagents by Ar* have been published recently.[8] Under the experimental conditions used, the ion currents obtained from the reactions with NO, Cl_2, PCl_3, CCl_4, $CHCl_3$, $CHBr_3$, CH_2Br_2, CH_2I_2, CH_3I, $CFBr_3$, and CF_2Br_2 were unaffected by addition of SF_6; most of these reagents are themselves expected to be fairly efficient electron scavengers. However, with OCS, CH_2Cl_2, CH_3Cl, and CH_3Br, SF_6 addition caused a significant increase in the saturation ion currents. The data published for the latter three reagents were obtained in the presence of SF_6 and need no adjustment; the branching
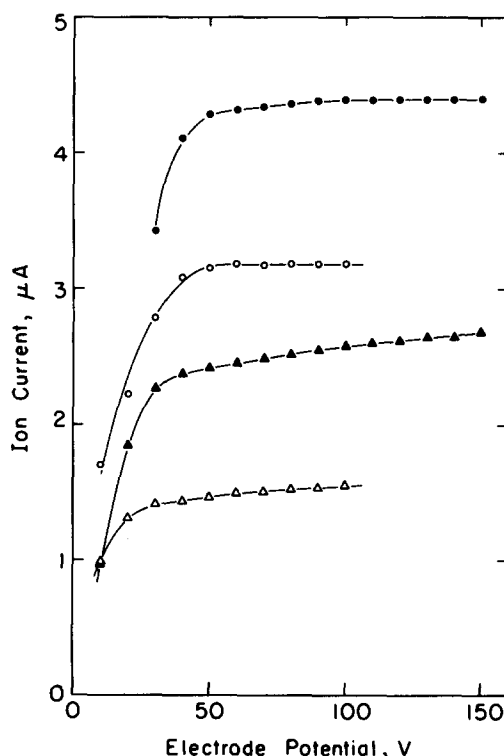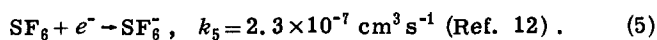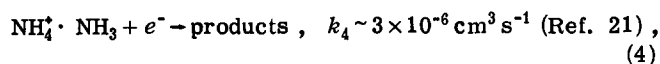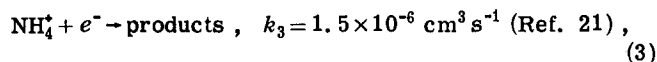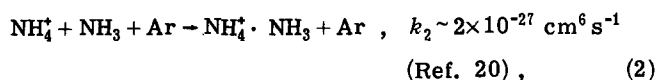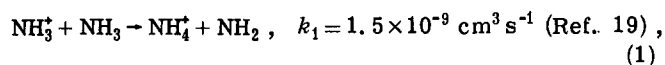

FIG. 4. Dependence of ion current on applied electrode potential. Triangles: no SF_6. $\triangle$ Ar* + C_2H_5OH, $\blacktriangle$ Ar* + CH_3OCH_3. Circles: SF_6 present. O Ar* + C_2H_5OH, $[SF_6] = 8 \times 10^{12}$ cm^{-3}. $\bullet$ Ar* + CH_3OCH_3, $[SF_6] = 2 \times 10^{12}$ cm^{-3}.

fraction for chemi-ionization of OCS by Ar* has been remeasured as 0.47, which supersedes the value of 0.30 quoted earlier,[8] which was obtained in the absence of SF_6.

IV. DISCUSSION

The data in Table I reveal that dissociation of the molecular reagents to produce H atoms is a very important channel for the quenching of metastable Ar, Kr, and Xe atoms. Indeed, many reactions appear to produce more than one H atom per collision event. It is important to establish the validity of the absolute H yields and that the atom yields refer solely to the primary quenching process. For the reactions with H_2, competition with dissociation to $H(^2S)$ atoms can arise from electronic-to-vibrational energy transfer and, for the reaction with Ar*, electronic-to-electronic energy transfer to yield $H_2(B^1\Sigma_u^+)$ or $(c^3\Pi_u)$. Fluorescence from $B^1\Sigma_u^+$ is extremely weak and has been ascribed to reaction of $Ar(^3P_1)$[14,15] [formed by collisions of Ar with $Ar(^3P_2)$ and $Ar(^3P_0)$]; however, no information concerning $H_2(c^3\Pi_u)$ and vibrationally excited H_2 could be obtained in the present system. Because of the crucial need to establish a firm reference, HCl was used as a second reference reagent. As shown in Table I, the H-atom resonance fluorescence data (relative to H_2 as reference reagent) from the reactions of Ar*, Kr*, and Xe* with HCl are consistent with dissociation of HCl as the dominant channel (emission from HCl* accounts for about 1% of the reaction of Ar* with HCl[16]). This finding is wholly consistent with Cl atom yields from these reactions (relative to Cl_2 and CF_3Cl as reference reagents)[10] and thus adds independent support to our assumption that dissociation of H_2 is the dominant reaction channel.

It has been shown in the previous section that electron-ion recombination provides an additional source of H atoms in some reactions of Ar*, but also that this secondary process can be essentially eliminated by adding a small amount of SF_6. A complete explanation of these effects is hindered by the fragmentary information concerning relevant ion–molecule reactions and the rates and products of the electron–ion recombination reactions. However, using NH_3 as an example, it is possible to confirm that the postulated processes will occur to a significant extent during a typical residence time of the gases in the reaction zone of about 1 ms. The potentially important secondary processes are

$$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2 , \quad k_1 = 1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \text{ (Ref. 19)}, \tag{1}$$

$$NH_4^+ + NH_3 + Ar \rightarrow NH_4^+ \cdot NH_3 + Ar , \quad k_2 \sim 2 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1} \text{ (Ref. 20)}, \tag{2}$$

$$NH_4^+ + e^- \rightarrow \text{products} , \quad k_3 = 1.5 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1} \text{ (Ref. 21)}, \tag{3}$$

$$NH_4^+ \cdot NH_3 + e^- \rightarrow \text{products} , \quad k_4 \sim 3 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1} \text{ (Ref. 21)}, \tag{4}$$

$$SF_6 + e^- \rightarrow SF_6^- , \quad k_5 = 2.3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \text{ (Ref. 12)} . \tag{5}$$

With a typical NH_3 concentration of 5×10^{14} cm^{-3}, reaction (1) is expected to be driven to completion. At a total pressure of 1 mm Hg of Ar and a typical Penning electron concentration of about 10^{10} cm^{-3}, processes (2) and (3) may both occur to a significant extent. However, irrespective of the amount of additional clustering of NH_4^+ with NH_3, rapid ion–electron recombination must finally occur, depleting the ion concentration and almost certainly generating H atoms, as observed. At a concentration of $> 1 \times 10^{12}$ cm^{-3}, SF_6 can scavenge the electrons successfully $k_5[SF_6] \gg k_4[NH_4^+ \cdot NH_3]$, and thus eliminate ion–electron recombination. The ion–electron recombination coefficients in the NH_3 system appear typical of those for a wide range of ions,[22] so that the above analysis should be valid for the other reagents used in this study.

The experimental results imply that, in the presence of SF_6, ion–ion recombination, such as of NH_4^+ with SF_6^-, is not an important ion-removal process under the experimental conditions used. In agreement, the measured rate constants[23] for the recombination of a range of simple and cluster positive ions with several negative ions are typically $(5-8) \times 10^{-8}$ cm^3 s^{-1} at pressures similar to those used here, much smaller than the rate constants for ion–electron recombination. Therefore, in the presence of SF_6, saturation ion–current and H-atom resonance fluorescence measurements should give valid information concerning chemi-ionization and neutral dissociation channels, respectively; it should be noted that, first, residual occurrence of reactions such as (1) and (2) does not affect the *total* ion yield, and second, in the absence of ion–electron and ion–ion recombination, no H atoms are expected to be produced via the chemi-ionization channel, as dissociative ionization,

$$Ar^* + RH \rightarrow Ar + R^+ + H \tag{6}$$

is endothermic for all the reagents RH studied here.

Because of the very small concentrations of reaction products ($\sim 10^{10}$ cm^{-3}), the only other possible secondary reactions are of neutral dissociation fragments with the reagent molecule, which could contribute only if occurring at close to the collision rate. In general, this would lead to a dependence of the resonance fluorescence signal on reagent concentration, as observed previously[7] in the reaction of Ar* with NO_2, where $O + NO_2$ occurs as a nonnegligible secondary reaction; no such dependence was seen for the reagents used in this study. This finding agrees with expectation, based on literature values of rate constants of simple dissociation products with the relevant parent molecules; hot atom effects are not expected to be important because of the thermalization provided by the large excess of Ar buffer gas. The data will thus be interpreted in terms of primary processes only.

Interpretation of the atomic yields of specific dissociation channels is most difficult for those reactions of Ar*, which also cause chemi-ionization. The uncertainty in the ion branching fractions arises principally from the calibration process[8] and has been estimated as ±35%. From a comparison of ionization and atomic yields, it is believed that the accuracy is considerably better than this quoted figure suggests. First, it is very unlikely that the true ionization branching fraction for Ar* + NH_3

TABLE III. Energetics and branching fractions for dissociation channels.

Reagent	Products	Threshold energy (eV)	Branching fractions		
			Ar*	Kr*	Xe*
H_2O	$O+H+H$	9.5	0.46 ± 0.05	0.11 ± 0.05	$\cdots$[a]
	$OH+H$	5.1	0.54 ± 0.04	0.86 ± 0.04	1.00 ± 0.06
	$O+H_2$	5.0	0	0.03 ± 0.03	0 ± 0.06
NH_3	$NH+2H$	8.5			$\cdots$[a]
	$N+H_2+H$	7.6			$\left.\begin{array}{c} \\ \\ \end{array}\right\} 1.00 \pm 0.06$
	NH_2+H	4.6			
	$NH+H_2$	4.0			0 ± 0.06
CH_4	CH_2+2H	9.3	0.65 ± 0.12		$\cdots$[a]
	$CH+H_2+H$	9.2	$\left.\begin{array}{c} \\ \\ \end{array}\right\} 0.35 \pm 0.12$		$\cdots$[a]
	CH_3+H	4.5			0.98 ± 0.02
	CH_2+H_2	4.8			0.02 ± 0.02
CH_2O	CH_2+O	7.7	0.21 ± 0.03[b]	0.09 ± 0.02	0.03 ± 0.01
	$CO+2H$	4.5	0.37 ± 0.05[b]	0.81 ± 0.07	0.94 ± 0.04
	$CHO+H$	3.8	0.06 ± 0.07[b]	0.07 ± 0.10	$\lessgtr 0.04 \pm 0.04$
	$CH+OH$	7.7 $\left.\begin{array}{c} \\ \end{array}\right\}$	0.03 ± 0.05[b]	0.03 ± 0.06	$\lessgtr 0.02 \pm 0.04$
	$CO+H_2$	0.0			
CH_3OH	CH_3+O+H	8.4			0 ± 0.02
	CH_2O+2H	5.4			0.58 ± 0.10
	CH_3O+H	4.5			0.10 ± 0.10
	CH_2OH+H	4.0			0.22 ± 0.11
	CH_3+OH	4.0			0.10 ± 0.11
C_2H_6	C_2H_4+2H	5.9	0.86 ± 0.05[c]	0.76 ± 0.08	
	C_2H_5+H	4.2	0.09 ± 0.09[c]	0.16 ± 0.16	
	CH_3+CH_3	3.9 $\left.\begin{array}{c} \\ \end{array}\right\}$	0.04 ± 0.04[c]	0.08 ± 0.08	
	$C_2H_4+H_2$	1.4			

[a]Endothermic channels.
[b]The uncertainties do not take account of the uncertainties in f_{ion}.
[c]Assuming that dissociation to $C_2H_3 + 3H$ is unimportant.

is significantly lower than the quoted figure of 0.42, else the yield of H atoms from competing channels would be less than one per dissociative event, inconsistent with virtually all the other resonance fluorescence data. Second, for $Ar^* + CH_2O$, the *maximum possible* ionization branching fraction, which is consistent with the atom yields, is 0.39 ± 0.04, in which case the competing processes are constrained to be

$$Ar^* + CH_2O \rightarrow Ar + CO + 2H + 7.0 \text{ eV} , \quad (7)$$

$$\rightarrow Ar + O + CH_2 + 3.8 \text{ eV} , \quad (8)$$
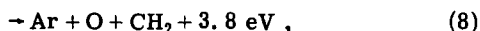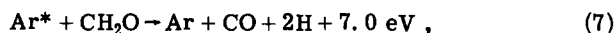
with branching fractions, respectively: $f_7 = 0.40 \pm 0.02$ and $f_8 = 0.21 \pm 0.03$. It is concluded that a more realistic maximum uncertainty in the ion yields, based on the uncertainties in the measured atom yields, is $+20\%$, -15%.

In the remainder of the discussion, the resonance fluorescence data are interpreted in terms of the energetically accessible dissociation channels and comparisons are made with photodissociation data and models for energy transfer. A major stimulus for the present study was our discovery of complete atomization of H_2O in approximately one-half of its quenching collisions with Ar^*, while dissociation to $O + H_2$ could be completely ruled out. It was anticipated that the reactions with CH_3OH and $(CH_3)_2O$ would yield comparably large amounts of O atoms, but this expectation was not realized, as

shown by the data in Table I. Instead, attention became focused on the remarkably efficient production of H atoms. These high yields allow branching fractions for specific dissociation channels to be deduced with low uncertainty in several reactions; these are listed in Table III. Several general conclusions can be drawn from these data.

A. Elimination of H_2

Elimination of molecular H_2 is completely unimportant in the reactions of the three metastables with H_2O and of Xe^* with NH_3 and CH_4 (dissociation of NH_3 to $N + H_2 + H$, which is only weakly exothermic and requires three bonds to be broken, is not expected to be important). The cracking patterns for the reactions of CH_2O are more complex, but the yields of $CO + H_2$ are likewise very small. The only evidence for this channel was the observation of very weak $CO(A^1\Pi - X^1\Sigma^+)$ emission from the reaction with Ar^*; the vibrational distribution in the $CO(A^1\Pi)$ state precluded a secondary reaction of CO with Ar^* as the source of this emission. The reactions of Ar^* and Kr^* with C_2H_6 further illustrate the lack of importance of H_2 elimination.

B. Rupture of central bonds of the reagent molecule

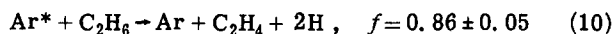The large H-atom yields suggest that modes of dissociation, such as of CH_3OH to $CH_3 + OH$ and of C_2H_6 to

$CH_3 + CH_3$, are not of major importance. An upper limit of $f = 0.21$ for this channel in the reaction of Xe* with CH_3OH was deduced. For Ar* + C_2H_6, the branching fraction for formation of $CH_3 + CH_3$ is less than 0.08 (unless the weakly exothermic channel to $C_2H_3 + 3H$ occurs significantly).

C. Loss of two (or more) H atoms

Yields of more than one H atom in Table I provide direct evidence for channels in which two atoms are lost. The most striking example is the reaction of Xe* with CH_2O, for which the branching fraction for formation of CO + 2H is greater than 0.9. Such two-atom elimination also occurs in more than one-half of each of the reactions: Kr* + CH_2O, Ar* + CH_4, Xe* (and probably Kr*) + CH_3OH and Kr* (and probably Ar*) + C_2H_6. Where this channel is observed to be most dominant, it is also very favorable energetically. For instance,

$$Xe^* + CH_2O \rightarrow Xe + CO + 2H \qquad (9)$$

is exothermic by 3.8 eV, while

$$Ar^* + C_2H_6 \rightarrow Ar + C_2H_4 + 2H , \quad f = 0.86 \pm 0.05 \qquad (10)$$

is exothermic by 5.6 eV. In contrast this channel occurs only weakly near threshold, e.g.,

$$Kr^* + H_2O \rightarrow Kr + 2H + O + 0.5 \text{ eV} , \quad f = 0.11 \pm 0.05 . \qquad (11)$$
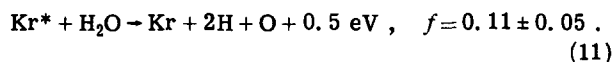
Individual reagents are discussed below, in the light of the above comments.

1. H_2O, CH_4, and NH_3

CH_4 and H_2O appear to show comparable behavior: simple dissociation to R + H on Xe* impact and increasing branching towards H + H elimination with increasing metastable energy. For the reactions with Ar*, this channel is 2.0 and 2.2 eV exothermic for H_2O and CH_4, respectively, and the branching fractions are appreciable, but well below unity. Although dissociative excitation of H_2O to $OH(A^2\Sigma^+) + H$ is an important channel,[7] emission from the reaction of Ar* + CH_4 is very weak. Unlike the analogous reaction of H_2O, the branching fractions for the reaction of CH_4 with Kr* cannot be deduced and the possibility of significant dissociation to $CH_2 + H_2$ cannot be excluded.

The H yields from Kr* and Xe* + NH_3 parallel those from the reactions with H_2O and CH_4. The low H-atom yield from Ar* + NH_3, 0.62 per reactive collision, is in part due to the efficiency of the ionization channel (ionization potential = 10.2 eV). Taking $f_{ion} = 0.42^{+20\%}_{-15\%}$ (see above), the yield of H atoms from channels other than ionization is $1.07^{+0.17}_{-0.10}$, much lower than the values for the analogous reactions of H_2O and CH_4. This result is surprising, since dissociation of NH_3 to NH + 2H requires only 8.6 eV, less energy than for the other two molecules. If dissociation to NH + 2H does indeed occur, it must be balanced by a similar yield of $NH + H_2$, which in turn is surprising, since this channel is absent in the reaction with Xe*.

2. CH_2O

The cracking pattern is revealed almost completely by the measurements of H, O, and ion yields. Dissociation to CO + 2H is dominant for Xe* + CH_2O but becomes *less* important in the Kr* and Ar* reactions, as less exothermic channels, dissociation to O + CH_2 and chemi-ionization, become accessible. The data very clearly illustrate the characteristic behavior found in this study, namely the very sharp onset of chemi-ionization near threshold, compared to the very slow increase in the yield of the dissociative channels, such as to O + CH_2, above threshold.

3. CH_3OH and C_2H_6

These molecules are related in being derived from H_2O and CH_4, respectively, by replacement of an H atom by CH_3. Both CH_3OH and C_2H_6 yield significantly more H atoms (from nonionization channels) than do H_2O and CH_4 and, for the reactions with Ar* and Kr*, the yields for CH_3OH and C_2H_6 are very similar. The ease of two-atom loss can be ascribed to the energetically favorable formation of $CH_2O + 2H$ and $C_2H_4 + 2H$; for instance, the energy required for the former process is only 5.4 eV, compared to the 9.5 eV required for dissociation of H_2O to H + H + O. As mentioned above, it is clear that dissociation to $CH_3 + OH$ or $CH_3 + CH_3$ are not major competing channels. However, precise branching fractions cannot be obtained for the Ar* and Kr* reactions with CH_3OH because of the unknown importance of dissociation to CHO + 3H.

The use of CH_3OD has given additional insight into the dissociation channels. The close similarity of total hydrogen atom yields from CH_3OH and CH_3OD, tested for Ar* and Xe*, precludes large isotope effects. The large yields of D atoms and the small yields of O atoms emphasize the preference for atom (D) rather than radical (OD) elimination. Surprisingly, although the total H-atom yield (from nonionization channels) increases from 1.49 to 1.70 to 1.81 over the series Xe*, Kr*, Ar* + CH_3OH, the yields of D atoms actually decrease: 0.68, ~0.58, and 0.58 (of which 0.05 is probably due to formation of O + D). If this reflects the importance of competing channels, closed for the Xe* reaction, but open for those of Ar* and Kr*, this suggests that initial fragmentation to CH_2OD is followed, in the latter reactions, by some fragmentation to CHOD + H (threshold energy ~9 eV) or to CH_2 + OD (threshold energy 8.7 eV).

4. C_2H_5OH and CH_3OCH_3

For these molecules, which contain one more C atom than CH_3OH, significantly smaller H-atom yields are observed and no O atoms are detected. In other respects, C_2H_5OH and C_2H_5OD resemble CH_3OH in behavior and it is suggested that two-atom loss to CH_3CHO is a favorable channel. It is not clear whether the lower H yields are due to an increased importance of breaking the C–C or C–O bond or whether dissociation to $C_2H_4 + H + OD$ (requiring 5.6 eV) is significant. The H-atom yields from the reactions of CH_3OCH_3 are lower even than those from CH_4. For neither CH_3OCH_3 nor CH_4 can a stable double-bonded species be formed by H-atom loss.

The low yield, 0.86 ± 0.04 H atoms, from the reaction with Xe* provides the first relatively direct evidence for dissociation processes other than terminal-bond rupture.

D. Comparison with photochemical studies

Fragmentary data exist on the vacuum–UV photochemistry of several of the molecules included in this study. The most popular photolysis sources are the noble-gas resonance lines at 147, 123.6, and 104.7/106.5 nm, allowing direct comparison with the reactions of Xe*, Kr*, and Ar* metastables, respectively. However, most investigations, in which quantitative yields of photoproducts were obtained, involved analysis of stable products and thus gave information on different channels from those observed in this study. Despite this difference in perspective, there are several clear-cut instances, in which metastables and isoenergetic photons induce widely different chemistry. This behavior has been confirmed by a recent quantitative study of the H atoms produced by photodissociation of H_2O, NH_3, and CH_4.[24]

The most striking feature of the photochemistry is the importance of H_2 elimination. For CH_4 photolysis at 123.6 nm, the branching fraction for this channel has been measured[25] as 0.58 and for C_2H_6, the analogous values[26] are 0.85, 0.40, and 0.26 at 147, 123.6, and 105–107 nm, respectively. In contrast, the branching fractions for elimination of H_2 from NH_3 have been found to increase with photon energy,[27,28] with values of ~0.06–0.12, ~0.24, and 0.31 at 147, 123.6, and 105–107 nm, respectively. Finally, for CH_2O, about 50% of photodissociation at 147 and 123.6 nm has been found[29] to produce $CO + H_2$. The data for C_2H_6 and CH_2O cannot be reconciled with the present results and clearly indicate different pathways in the photon- and metastable-induced excitation. The data for CH_4 can be reconciled, if Kr* induces dissociation to $CH_2 + H_2$ and to $CH_2 + 2H$ to roughly equal extents; the H-atom yields from photolysis of CH_4 at 121.6 nm are consistent with this view. However, it should be reemphasized that our data for the reaction of Xe* with CH_4 show H_2 elimination to be entirely negligible. Finally, for NH_3, the low H yields from the reactions of Kr* and Ar* are not incompatible with H_2 production. However, photolysis at 121.6 nm[24] reveals NH + 2H as the dominant products (these data suggest a branching fraction for NH + H_2 production of less than 0.10), implying a further marked discrepancy with the results from Kr* + NH_3.

It is possible that spin conservation is partly responsible for the differences noted above, if photoexcitation favors population of excited singlet states, but the metastable ^3P_J reactions cause excitation to triplet states. However, as both NH and CH_2, for instance, have low-lying singlet and triplet states, NH + H_2 and $CH_2 + H_2$ can be formed via both singlet and triplet states of the parent molecules. It has recently been argued[30] that photodissociation of CH_4 to $CH_2 + H_2$ should be expected to be favored over production of $CH_3 + H$, at threshold at least, on symmetry grounds and it may be that the lower symmetry induced by the noble gas atom is in part

responsible for the differences. However, the possibility that the difference arises because the noble gas generally transfers its energy with low efficiency can be ruled out; the results for CH_2O and C_2H_6 show the metastables to induce *high-energy* channels more readily than the isoenergetic photons.

It is appropriate to conclude this discussion by speculating on the possible nature of the $A^* - Q$ interactions which lead to the observed large quenching cross sections and the highly efficient transfer of energy into dissociative or ionizing states of the reagent molecule. A long-range dipole–dipole interaction[31] is not expected to be important, because of the metastability of the excited noble gas states and the contrasts with photochemistry. A charge-transfer mechanism[7] is likewise ruled out, as none of the reagents used have appreciable electron affinities. Complex formation is difficult to rule out completely, especially because of the apparently smooth variation of product distributions with metastable energy; however, the breakup of the complex would be expected to impart translational energy to the separating $A - Q^*$ pair, which may not be consistent with the observed efficient transfer of energy to internal degrees of freedom of Q^*.

A clue may be provided by very recent *ab initio* calculations of the Ar* + H_2 system.[32] The entrance channel lies close in energy to a possible exit channel Ar + $H_2^*(a\,^3\Sigma_g^+)$ and strong coupling of the states of common symmetry is found, up to Ar–H_2 separations of about 5 Å, where overlap of the Rydberg orbitals is appreciable, but direct overlap of the $H_2(1s\sigma)$ and Ar(3p) core orbitals is expected to be slight. As shown by their absorption spectra, all the reagents investigated in this study have available states at the energies of the metastable atoms and thus all have opportunities for comparably strong interactions. The coupling to a *bound* state of H_2 is not, of itself, conducive to efficient quenching, as any energy transfer, induced by this coupling, is reversible; however, for the larger molecules studied here, the interactions will be, in general, with (pre-) dissociative or ionizing states of the molecule, allowing efficient, irreversible energy transfer. In accordance with this model, quenching of the excited noble gases by molecules which lack accessible acceptor states (notably Xe* + CF_4 and CF_3H) is characterized by much smaller quenching cross sections and by unusual reaction channels, which compete significantly with molecular dissociation.[10]

The following model appears consistent with the dissociation data. Energy is transferred efficiently to the reagent molecule from the noble gas, which takes little part in the subsequent energy disposal. The dissociation of the energized molecule is believed to occur sequentially, the first step being nonstatistical and favoring the cleavage of terminal bonds. The initial dissociation transfers typically 1–3 eV of energy into relative translation or into rotation of the molecular fragment. The molecular fragment contains only moderate amounts of vibrational energy and its further dissociation, if energetically possible, is likely to occur more statistically.

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