FAR ULTRA-VIOLET PHOTOLYSIS OF AMMONIA
QUANTUM YIELD DETERMINATION FOR THE PRIMARY PROCESS:
NH_3 (ND_3) + hv → NH (ND) + H_2 (D_2)

R. L. LILLY, R. E. REBBERT and P. AUSLOOS

National Bureau of Standards, Radiation Chemistry Section, Washington, D.C. 20234 (U.S.A.)

SUMMARY

The gas phase photolysis of NH_3–C_2D_4 and ND_3–C_2H_4 mixtures has been investigated at 147 nm (8.4 eV), 123.6 nm (10 eV) and 104.8–106.7 nm (11.6–11.8 eV). The quantum yield of D_2 in the irradiation of ND_3–C_2H_4 mixtures is independent of the concentration of C_2H_4 and of the pressure of ND_3 (10 to 180 Torr). It is concluded that in these mixtures D_2 is entirely formed by molecular elimination from excited ND_3. The quantum yields of such a process are as follows at these energies: 147 nm, 0.032 ± 0.005; 123.6 nm, 0.244 ± 0.01; and 104.8–106.7 nm, 0.306 ± 0.007 (M/N_{ex} = 0.52 ± 0.02). Although the NH_3–C_2D_4 photolysis data exhibit less reliability, it can be concluded that the quantum yield of molecular H_2 at 147 nm is twice that of molecular D_2. Isotope effects are much less pronounced at higher photon energies.

At 147 and 123.6 nm, D_2 is eliminated *via* the primary process:

ND_3 + hv → ND ($a^1\Delta$) + D_2 threshold: 5.54 eV

and/or:

ND_3 + hv → ND ($b^1\Sigma^+$) + D_2 threshold: 6.61 eV

On the basis of the spectroscopic observation of Okabe and Lenzi it can be concluded that at 104.8–106.7 nm the primary process:

ND_3 + hv → ND ($c^1\pi$) + D_2 threshold: 9.35 eV

must also contribute significantly to the formation of molecular hydrogen. It is suggested that the ND_3^+ ions which are formed at these energies do not contribute to the formation of molecular D_2, but that the occurrence of an overall process:
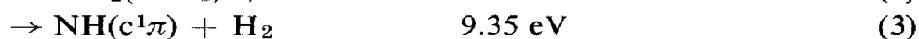
ND_3 + hv → N + D_2 + D   threshold: 7.63 eV

cannot be ruled out. The extinction coefficients of NH_3 and ND_3, at the rare gas lines have been redetermined and were found to differ significantly from those derived from published absorption curves.

INTRODUCTION

The photolysis of ammonia which plays an important role in the Jovian atmosphere[1] and is also thought to be responsible for the formation of biomolecules in the primitive earth atmospheres[2] has been investigated extensively[3]. A considerable amount of information has been obtained concerning the primary decomposition processes and the energy partitioning among the primary fragments[3]. It is well established[3-8] that at longer wavelengths ($>$ 165 nm) the photolysis of ammonia can be adequately accounted for by the primary process:

$$NH_3 + h\nu \rightarrow NH_2(X_2\ ^2B_1) + H \qquad\qquad 4.43\ eV \qquad\qquad (1)$$

At shorter wavelengths[5, 7, 9] as well as in radiolysis[10] the situation is more complex in that a multitude of primary processes are energetically possible. Some of these (processes 2 and 3) have been detected through the radiative decay of the NH_2 ($\tilde{A}^2A_1$) and NH ($c^1\pi$) species formed in the processes:

$$NH_3 + h\nu \rightarrow NH_2(\tilde{A}^2A_1) + H \qquad\qquad 5.7\ eV \qquad\qquad (2)$$
$$\rightarrow NH(c^1\pi) + H_2 \qquad\qquad 9.35\ eV \qquad\qquad (3)$$

while one other primary process[5, 9a]:

$$NH_3 + h\nu \rightarrow NH(X^3\Sigma^-) + H + H \qquad 8.44\ eV \qquad\qquad (4)$$

was evidenced by the observation of absorption $NH(A^3\pi \leftarrow X^3\Sigma^-)$ in the flash photolysis of NH_3 (125–160 nm). It has also been argued[7] that the process:

$$NH_3 + h\nu \rightarrow NH(a^1\Delta) + H_2 \qquad\qquad 5.54\ eV \qquad\qquad (5)$$

must occur at 147 and 123.6 nm because "molecular" hydrogen is produced at both these wavelengths in yields considerably higher than those of the other H_2 producing process (3). It is to be noted, however, that the absorption NH ($c^1\pi \leftarrow a^1\Delta$) has not been observed in the flash photolysis of NH_3[9c]. In addition, it is conceivable that the process:

$$NH_3 + h\nu \rightarrow NH(b^1\Sigma^+) + H_2 \qquad\qquad 6.61\ eV \qquad\qquad (6)$$

may also contribute to the formation of "molecular" H_2.

The present study describes measurements of the total quantum yield of molecular hydrogen formed by processes such as (3), (5), and (6) at 147, 123.6, and 104.8–106.7 nm, using xenon, krypton and argon resonance radiation. In previous investigations[6, 9d] at 184.9, 147, and 123.6 nm the yield of molecular hydrogen relative to the total hydrogen yield formed in pure NH_3 was determined by comparing the yields of hydrogen formed in the presence and absence of added C_2D_4. However, since it is known[3] that in pure NH_3, the quantum yield of H_2 is not necessarily equal to unity (the quantum yield is generally lower than unity and

strongly dependent on experimental conditions), these relative measurements do not give information about the quantum yield of molecular hydrogen. Also, as will be shown, some of these relative measurements have to be revised in the light of a redetermination of the extinction coefficients of NH$_3$ at the relevant resonance lines.

EXPERIMENTAL

Apparatus and absorption measurements

The fabrication of the rare gas resonance lamps and reaction vessels used in this study have been described previously[11]. The xenon and argon resonance lamps were provided with LiF windows, while the krypton resonance light source was fitted with a CaF$_2$ window transmitting only the 10 eV resonance line. The number of photons transmitted through the LiF window (diameter 2.1 cm) of the resonance lamps were as follows: xenon, 3 × 10^{13} photon/s (97%, 147 nm; 3%, 129.5 nm); krypton, 1 to 4 × 10^{14} photon/s; argon, 1 to 4 × 10^{13} photon/s (45%, 104.8 nm; 55%, 106.7 nm). The pressure of the various compounds in the reaction vessel was measured by means of a calibrated quartz spiral manometer. Prior to a series of photolysis experiments on ND$_3$ the microwave discharge was applied to the reaction vessel filled with 5 Torr ND$_3$. This had the effect of conditioning the wall of the reaction vessel with D atoms. The hydrogen formed in the photolysis of pure ND$_3$ after conditioning of the reaction vessel still contained approximately 10 to 20% HD. After treatment, isotopic exchange of ND$_3$ on the wall is of minor importance in view of the fact that the hydrogen formed by applying a microwave discharge on ND$_3$ gas (5 Torr) which has been standing in the reaction vessel for a time comparable to the duration of an actual photolysis experiment contained less than 5% HD. The higher HD content observed in the actual photolysis experiment can be ascribed to reaction of D atoms with H containing active centers on the wall.

The extinction coefficients and photoionization quantum yields given in Table 1 were determined using two reaction vessels in series[11, 12]. Both are provided with parallel plate electrodes and are separated from each other by a LiF window. The back cell, the purpose of which is to record the light transmitted through the front cell, was filled with trimethylamine (ionization potential 7.82 eV) which photoionizes over the entire wavelength range covered in this study. Measurement of the saturation ion current in trimethylamine induced by absorption of the photons transmitted through the LiF window separating the two reaction chambers, provides an accurate measure of the fraction of light absorbed by ammonia in the front cell[12]. Typical plots of the ion current measured in the second compartment *versus* the pressure of NH$_3$ and ND$_3$ obtained by this method at 147 nm are shown in Fig. 1. The ordinate represents log I_0—log $I_{transmitted}$ and ε(atm^{-1} cm^{-1}) is given by the expression:

$$\frac{(\log I_0 - \log I_t)}{P(\text{Torr})} \cdot \frac{[760 \, (\text{Torr/atm})] \, (2.3)}{d(\text{cm})} \tag{I}$$

where d is the distance between the lamp window and the window separating the two compartments of the apparatus.

The photoionization quantum yield determinations given in Table 1 were obtained by comparing the saturation ion current in NO with that in ammonia under conditions where all the incident light is absorbed. Such measurements carried out at 1048–1067 Å gave $\Phi_+(NH_3)/\Phi_+(NO) = 0.56 \pm 0.02$ and $\Phi_+(ND_3)/$

TABLE 1

ABSORPTION COEFFICIENTS AND IONIZATION QUANTUM YIELDS

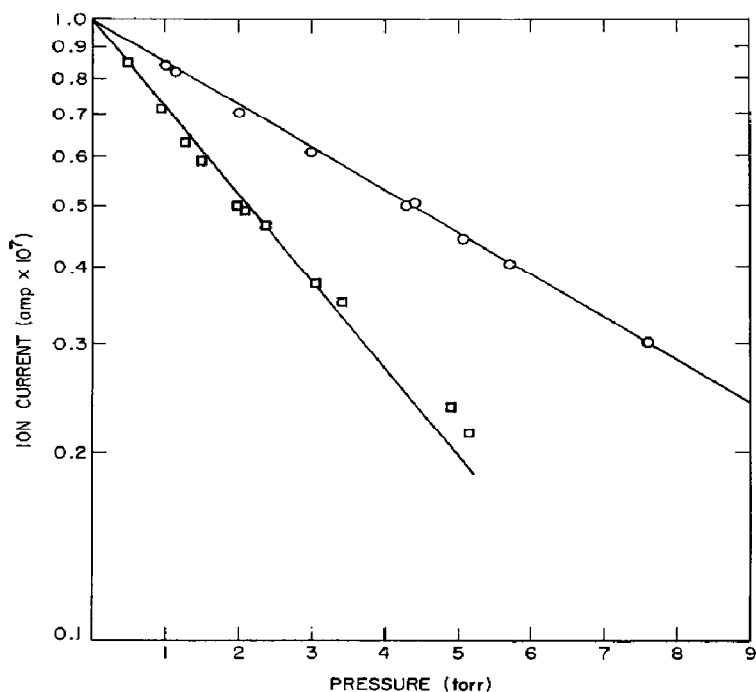| λ (nm)	NH$_3$		ND$_3$		ε (atm^{-1} cm^{-1})	
	ε (atm^{-1} cm^{-1})	Φ_+	ε (atm^{-1} cm^{-1})	Φ_+	C$_2$H$_4$	C$_2$D$_4$
147	48.1 $\pm$ 5	0.00	23.6 $\pm$ 2	0.00	412 $\pm$ 6	400 $\pm$ 6
123.6	302 $\pm$ 30	0.00	175 $\pm$ 20	0.00	647 $\pm$ 12	636 $\pm$ 12
104.8–106.7	673 $\pm$ 20	0.40 $\pm$ 0.01*	659 $\pm$ 30	0.42 $\pm$ 0.01*	966 $\pm$ 30	863 $\pm$ 30

* Taking $\Phi_+(NO) = 0.70$.

Fig. 1. Saturation ion current measurements *versus* pressure of NH$_3$ (ND$_3$) made in actinometry cell filled with 5 Torr of trimethylamine (see experimental). Light source: xenon resonance lamp. O, ND$_3$; □, NH$_3$.

$\Phi_+(\mathrm{NO}) = 0.59 \pm 0.02$. There is some uncertainty as to the value of $\Phi_+(\mathrm{NO})$ at the wavelengths corresponding to the argon resonance lines. For an argon lamp emitting the two resonance lines in approximately equal intensities a value of 0.7 based on the measurements of Watanabe *et al.*[13] has generally been adopted by this laboratory but a much lower value of 0.56 has recently been reported by Klots[14].

Quantum yield determinations

Quantum yields are based on the measurement of the yield of $^{13}\mathrm{CO}$ formed in the photolysis of $^{13}\mathrm{CO_2}$. $^{13}\mathrm{CO_2}$ rather than $^{12}\mathrm{CO_2}$ was used in order to distinguish between the carbon monoxide $^{13}\mathrm{CO}$, formed in the primary dissociative process of carbon dioxide and the $^{12}\mathrm{CO}$ formed by reaction of intermediates (presumably O or $\mathrm{CO_3}$) with $^{12}\mathrm{C}$ contamination on the wall of the reaction vessel or the window assembly[15]. It has been found that the formation of extraneous $^{12}\mathrm{CO}$ is particularly important (20–40% of total carbon monoxide) at 104.8–106.7 nm. The use of $^{13}\mathrm{CO_2}$ offers the added advantage that traces of $\mathrm{N_2}$ (from air) in the CO fraction can be accurately determined by mass spectrometric analysis. The $^{13}\mathrm{CO_2}$ actinometry was carried out after each set of 4 to 6 photolysis experiments and $\Phi(^{13}\mathrm{CO})$ was taken to be equal to unity at all wavelengths[15]. Prior to filling the reaction vessel, the incident intensity of the light source was adjusted by monitoring the saturation ion current in the actinometry cell containing trimethylamine. After the experiment, the $^{13}\mathrm{CO}$ or hydrogen product is distilled from the bulk compound which is maintained at 77 K. These products are then measured by means of a calibrated gas burette. Analysis of the gas mixture was performed on a mass spectrometer. As will be discussed later, at 147 nm, quantum yields could also be derived from the isotopic analysis of the hydrogen formed in the $\mathrm{NH_3\text{--}C_2D_4}$ or $\mathrm{ND_3\text{--}C_2H_4}$ without any knowledge of the total amount of hydrogen produced in the photolysis.

The quantum yields of hydrogen formed per photon absorbed by ammonia will be designated as $\Phi(\mathrm{H_2})_{\mathrm{NH_3}}$ or $\Phi(\mathrm{D_2})_{\mathrm{ND_3}}$. $\Phi(\mathrm{H_2})_{\mathrm{NH_3}}$ is simply the measured quantum yield of $\mathrm{H_2}$/photon absorbed by the mixture divided by the fraction $(f_{\mathrm{NH_3}})$ of the radiation absorbed by $\mathrm{NH_3}$. In $\mathrm{NH_3\text{--}C_2D_4}$ mixtures the latter is given by:

$$\frac{\varepsilon(\mathrm{NH_3}) \cdot P(\mathrm{NH_3})}{\varepsilon(\mathrm{NH_3})P(\mathrm{NH_3}) + \varepsilon(\mathrm{C_2D_4}) \cdot P(\mathrm{C_2D_4})} = f_{\mathrm{NH_3}} \qquad \text{(II)}$$

where $\varepsilon(\mathrm{NH_3})$ and $\varepsilon(\mathrm{C_2D_4})$ represent the extinction coefficients of $\mathrm{NH_3}$ and $\mathrm{C_2D_4}$, and $P(\mathrm{NH_3})$ and $P(\mathrm{C_2D_4})$ represent their pressures, respectively.

RESULTS AND DISCUSSION

As in earlier studies[6, 9d], the yield of "molecular" hydrogen is based on the residual yield of $\mathrm{D_2}$ and $\mathrm{H_2}$ produced in the photolysis of $\mathrm{ND_3\text{--}C_2H_4}$ and

$NH_3-C_2D_4$ mixtures respectively. It is assumed that H or D atoms will be effectively scavenged by ethylene to form ethyl radicals which subsequently disappear from the system mainly by recombination with other radicals. It would follow that in the photolysis of $C_2H_4-ND_3$ mixtures only D_2 or H_2 should be observed as hydrogen products and that these can be entirely ascribed to the occurrence of the primary processes:

$$C_2H_4 + h\nu \rightarrow C_2H_2 + H_2 \tag{7}$$

$$ND_3 + h\nu \rightarrow ND + D_2 \tag{8}$$

Because the probability of the formation of extraneous D_2 was considered much less likely than that of producing H_2 most of the experiments were performed on ND_3 rather than NH_3. After conditioning the reaction vessel with ND_3 (see experimental) H_2 was still a non-negligible fraction (2–4%) of the hydrogen formed in the photolysis of pure ND_3 (see Tables 2, 4 and 5). It is disturbing that (as also reported by other investigators, see Table 3) HD is a significant product both in the presence and absence of C_2H_4. The mode of formation of this product is not known. It can be noted that in most $ND_3-C_2H_4$ experiments HD/D_2 is fairly invariant with the concentration of C_2H_4. This is particularly apparent from the 147 nm data given in Table 2 which show that for mixtures containing more than 1% C_2H_4 at a pressure of 17.8 Torr, the ratio of HD/D_2 is 0.42 $\pm$ 0.05 [$\Phi(HD)_{ND_3}$ = ~ 0.015]. At lower C_2H_4 concentrations there is, however, a distinct increase in HD/D_2. The fact that in this low C_2H_4 concentration region, $\Phi(D_2)_{ND_3}$ remains unchanged implies that the formation of HD and D_2 are unrelated. This is also indicated by the fact that $\Phi(HD)_{ND_3}$ at 123.6 nm (Table 4) is at most a factor of two higher (~ 0.03 $\pm$ 0.005) than at 147 nm, even though the value of $\Phi(D_2)_{ND_3}$ differs by nearly a factor of 10. One of the factors which may contribute to the formation of HD would be a reaction of the D atoms produced in the photolysis of ND_3 with accumulated products containing C_2H_4 entities absorbed on the surface of the vessel or the LiF window. It is of some interest to note that there is a distinct increase of $\Phi(HD)_{ND_3}$ with an increase of the extinction coefficients of ammonia and ethylene. At 104.8–106.7 nm, where $\varepsilon(ND_3) = 659 \pm 30$ atm^{-1} cm^{-1}, $\Phi(HD)_{ND_3}$ varies from one experiment to another, but is never less than 0.03 (Table 5). Again the rather erratic changes in $\Phi(HD)$ occurring in this wavelength region are not accompanied by any noticeable variation in $\Phi(D_2)$.

In the $NH_3-C_2D_4$ experiments (Tables 3 and 6) $\Phi(HD)$ is distinctly lower than in the $ND_3-C_2H_4$ photolysis experiments. This can, however, be accounted for by the premise that any H(D) atoms originating from NH_3 (ND_3) predominantly pick up an H atom to form H_2(HD). It would then follow that $\Phi(H_2)_{NH_3}$ values which can be derived from the $NH_3-C_2D_4$ experiments given in Tables 3 and 6 are slightly higher than the actual quantum yields of molecular hydrogen.

TABLE 2

PHOTOLYSIS OF ND₃ AT 147 NM

P (ND₃) (Torr)	C₂H₄ (%)	Distribution (%)			Φ (D₂)ND₃*	Φ (D₂)ND₃**
		H₂	HD	D₂		
8.5	—	2.0	21.5	76.5	—	—
8.5	1.05	58.4	16.6	25.0	0.0313	0.031
17.8	0.37	26.8	43.9	29.3	0.0283	0.030
17.8	0.55	44.5	20.9	34.6	0.0340	—
17.8	1.00	62.5	11.6	25.9	0.0280	0.039
17.8	2.3	76.7	6.5	16.8	0.0353	—
17.8	4.2	88.2	3.8	8.0	0.0265	—
17.8	8.0	92.1	2.5	5.4	0.0328	—
40.0	5.3	90.1	2.8	7.1	0.0290	0.039
80.0	1.0	66.0	9.8	24.2	0.0258	0.032
80.0	4.9	90.3	2.7	7.0	0.0263	0.035
160.0	1.1	69.7	6.7	23.6	0.0262	0.031

* Based on Φ (H₂) = 0.4 in pure C₂H₄. Average 0.0294 ± 0.003.
** Based on ¹³CO₂ actinometry. Average 0.034 ± 0.003.

TABLE 3

PHOTOLYSIS OF NH₃ AT 147 NM

P (NH₃) (Torr)	C₂D₄ (%)	Distribution (%)			Φ(H₂)NH₃*	Reference
		H₂	HD	D₂		
86.5	1.9	52.4	4.5	43.1	0.076	This work
86.5	7.6	21.8	2.7	75.5	0.073	This work
86.5	14.2	14.5	2.2	83.3	0.066	This work
86.5	33.4	5.5	2.1	92.4	0.082	This work
42	5.0	36.0	12.5	51.5	0.123	9d
45	12.5	19.4	6.8	73.8	0.125	9d

* Based on Φ(D₂) = 0.4 in pure C₂D₄.

147 nm photolysis

At 147 nm the extinction coefficient of ethylene is nearly a factor of 10 higher than that of ammonia (Table 1). It follows, therefore, that even at relatively low percentages of ethylene added to ammonia, photolysis of ethylene will be important. This feature of the experiment gives the advantage that the quantum yield of molecular hydrogen elimination from ammonia can simply be derived from the percentage distribution of hydrogen as given in Tables 2 and 3 and no actinometry is required. For instance, in the case of the ND₃–C₂H₄ experiments the values given in the next to last column are simply derived from the expression:

$$\Phi(D_2)_{ND_3} = \frac{[D_2]\, P(C_2H_4)\, \varepsilon(C_2H_4)}{[H_2]\, P(ND_3)\, \varepsilon(ND_3)} \cdot \Phi(H_2)_{C_2H_4} \tag{III}$$

TABLE 4

PHOTOLYSIS OF ND_3 AT 123.6 NM

P (ND_3) (Torr)	C_2H_4 (%)	Distribution (%)			$\Phi(D_2)_{ND_3}$*
		H_2	HD	D_2	
10.0	—	2.4	19.0	78.6	0.79
10.0**	4.95	20.7	12.2	67.1	0.231
26.8	0.12	4.1	15.9	80.0	0.235
26.8	0.19	4.2	16.8	79.0	0.233
26.8	1.3	9.0	10.5	80.5	0.250
26.8	1.6	12.1	10.8	77.1	0.249
26.8	2.5	16.0	13.5	70.5	0.247
26.8	4.8	20.6	11.4	68.0	0.244
60.0	0.14	3.8	12.2	84.0	0.252
60.0	1.1	7.8	10.2	82.0	0.253
60.0	4.0	14.0	9.0	77.0	0.243
150.3	1.1	7.0	7.0	86.0	0.268
180	0.14	3.2	9.7	87.0	0.248
180	0.34	3.5	9.2	87.3	0.252
180	1.1	5.8	7.0	87.2	0.253
180	2.1	10.9	9.3	79.8	0.252

* Based on $^{13}CO_2$ actinometry.
** 700 Torr of argon added.

TABLE 5

PHOTOLYSIS OF ND_3 AT 104.8–106.7 NM

P (ND_3) (Torr)	C_2H_4 (%)	Distribution (%)			$\Phi(D_2)_{ND_3}$*	$M(D_2)/N_{ex}^{**}$
		H_2	HD	D_2		
10	—	3.8	10.8	85.4	0.690	1.19
10	0.52	3.7	8.0	88.3	0.309	0.531
10	1.11	6.5	17.0	76.0	0.300	0.516
10	1.23	3.9	8.1	88.0	0.307	0.528
100	1.26	3.7	16.9	79.4	0.300	0.516
10	2.18	6.4	8.9	84.7	0.314	0.540
100	2.20	5.0	19.2	75.8	0.302	0.519
10	4.90	9.6	13.8	76.6	0.309	0.531

* Based on $^{13}CO_2$ actinometry.
** Taking $\Phi_+ (ND_3) = 0.42$.

where $\Phi(H_2)_{C_2H_4}$ stands for the quantum yield of the molecular elimination process (7), while $[D_2]/[H_2]$ represents the ratio of the hydrogens as derived from Table 2. A value of 0.4 was used for $\Phi(H_2)_{C_2H_4}$. Glasgow and Potzinger[16] recently reported values ranging from 0.35 to 0.40 for the quantum yield of process (7) $[P(C_2H_4)$: 5 to 70 Torr]. A pressure independent ($P = 5$ to 100 Torr) value of 0.40 ± 0.03 was obtained in the course of the present study. Using the ε values given in Table 1, a value of 0.0294 ± 0.003 is obtained for $\Phi(D_2)_{ND_3}$ on the basis

TABLE 6

PHOTOLYSIS OF NH$_3$ AT 104.8–106.7 NM

P (NH$_3$)	C$_2$D$_4$	Distribution (%)			Φ(H$_2$)$_{NH_3}$*	M(H$_2$)/N$_{ex}^{**}$
(Torr)	(%)	H$_2$	HD	D$_2$		
10	—	99.2	0.8	0.0	0.70	1.17
10	0.52	97.2	1.8	0.9	0.573	0.955
10	1.39	95.1	2.4	2.5	0.396	0.660
10	2.10	95.2	2.1	2.7	0.378	0.630
10	5.12	92.7	2.2	5.1	0.353	0.588
10	8.33	90.7	2.0	7.3	0.338	0.563

* Based on $^{13}CO_2$ actinometry.
** Taking Φ_+ (NH$_3$) = 0.40.

of eqn. (III). It is significant that this value is in good agreement with the average quantum yield value of 0.034 ± 0.003 which is based on the quantitative measurement of the D$_2$ production as related to the production of ^{13}CO in separate $^{13}CO_2$ photolysis experiments (see experimental). The quantum yield of ^{13}CO was taken to be equal to unity at $^{13}CO_2$ conversion of less than 0.05%[17, 18]. Both sets of quantum yield data show clearly that Φ(D$_2$)$_{ND_3}$ shows no dependence on the concentration of C$_2$H$_4$ added to ND$_3$. Furthermore they show that an increase in ND$_3$ pressure from 8.5 to 160 Torr has within experimental error no effect on Φ(D$_2$)$_{ND_3}$. In view of the foregoing we suggest that the quantum yield of D$_2$ [Φ(D$_2$)$_{ND_3}$ = 0.032 ± 0.005] can be considered as the quantum yield of process (8).

The NH$_3$–C$_2$D$_4$ experiments represented in Table 3, do not provide as clearcut an answer concerning the quantum yield of the analogous process:

$$NH_3 + h\nu \rightarrow NH + H_2 \tag{9}$$

An increase in the percentage of C$_2$D$_4$ (from 1.9 to 14.2%) added to NH$_3$ lowers Φ(H$_2$)$_{NH_3}$ as calculated from expression (III). [The quantum yield of molecular D$_2$ formation in the photolysis of C$_2$D$_4$ was taken to be the same as that measured in C$_2$H$_4$. Photolysis of equimolar C$_2$H$_4$–C$_2$D$_4$ mixtures gives Φ(H$_2$) = Φ(D$_2$)]. The apparent reversal of this trend at 33.4% C$_2$D$_4$ can probably be ascribed to the contribution of extraneous sources to the H$_2$ production, the total yield of which is only 5.5% of the hydrogen fraction.

From the data of Table 3 we conclude that Φ(H$_2$)$_{NH_3}$ which can be ascribed to process (9) is equal to or less than 0.066. This is a factor of two lower than the value derived from the hydrogen analysis reported by Groth et al.[9d] (Table 3). [In ref. 9d it was concluded that the yield of H$_2$ produced in the presence of C$_2$D$_4$ is 12% of that produced in the absence of C$_2$D$_4$. It should, however, be noted that a value of 76 atm^{-1} cm^{-1} was taken for ε(NH$_3$) from the absorption spectrum reported by Zelikoff and K. Watanabé [J. Opt. Soc. Am., 43 (1953) 756]. In view of the pronounced structure in this absorption spectrum, our value [ε(NH$_3$) = 48.1 ± 5] measured using the xenon resonance radiation can be considered as

being more reliable. Using the latter value for ε the yield of H_2 in NH_3–C_2D_4 experiments of Groth *et al.*[9d] is only 7.5% of that in pure NH_3. It is to be noted, however, that the quantum yield of H_2 in pure NH_3 is probably less than unity. In the two experiments reported in that study, the unusually high HD content in the hydrogen distribution points to the formation of H_2 from sources other than process (9).

Because the threshold of process (3) is nearly 1 eV above the energy corresponding to the xenon resonance line (8.4 eV), the formation of molecular hydrogen must be ascribed to process (5) and/or process (6). The energetically more favorable process:

$$NH_3 + h\nu \rightarrow NH(X^3\Sigma^-) + H_2 \qquad\qquad 3.91 \text{ eV} \qquad\qquad (10)$$
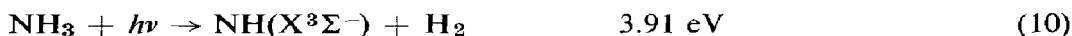
can be excluded because it is spin forbidden. Also, there is no evidence for the formation of molecular H_2 at 1849 Å[6] where process (10) would also be energetically feasible.

Even though the reliability of the quantum yield estimate of process (9) is lower than that of process (8) it would seem that there is a distinct isotope effect favoring process (9) over process (8).

123.6 nm photolysis

At 123.6 nm all quantum yield data given in Table 4 were based on $^{13}CO_2$ actinometry. Use of eqn. (III) was not feasible at the low C_2H_4 concentration used, because the disparity between the extinction coefficients of ethylene and ammonia at this wavelength is not as large as at 147 nm. Furthermore, the quantum yield of process (7) in pure C_2H_4 was found to be nearly a factor of two lower at 123.6 nm than at 147 nm. Actually, application of eqn. (III) to the data given in Table 4 yields values of $\Phi(D_2)_{ND_3}$ which increase sharply with increasing concentration of C_2H_4. In contrast the values of $\Phi(D_2)_{ND_3}$ which are based on $^{13}CO_2$ actinometry (see experimental) show remarkably good consistency, independent of the concentration of C_2H_4 as well as of the pressure of ND_3 (from 10 to 180 Torr). The value of $\Phi(D_2)_{ND_3}$ thus obtained is equal to 0.244 ± 0.01. Addition of 700 Torr of argon to a 10 Torr ND_3–C_2H_4 (1:0.02) mixture did not affect the value of $\Phi(D_2)_{ND_3}$, from which we conclude that abstraction of a D atom from ND_3 by a translationally hot D atom does not occur when 2% or more of C_2H_4 is added to ND_3. It follows from the foregoing that the measured values of $\Phi(D_2)_{ND_3}$ given in Table 4 can be equated to the quantum yield of process (8) at 123.6 nm.
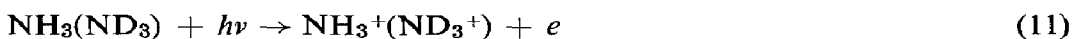
The quantum yield of molecular H_2 in the photolysis of NH_3 is apparently more difficult to determine. Earlier experiments[6] carried out at 123.6 nm have shown that the production of H_2 in NH_3–C_2D_4 experiments is approximately 15–22% of that observed in pure NH_3. [Based on $\varepsilon(NH_3) = 302$ atm^{-1} cm^{-1} (Table 1) rather than $\varepsilon(NH_3) = 400$ used in ref. 9d.] However, the quantum yield of H_2 in the photolysis of pure NH_3 under similar experimental conditions was

not determined. A number of NH_3–C_2D_4 experiments carried out under our experimental conditions yielded values for $\Phi(H_2)_{NH_3}$ based on $^{13}CO_2$ actinometry which fluctuated from 0.25 to 0.30 for mixtures containing between 5 and 10% C_2D_4.
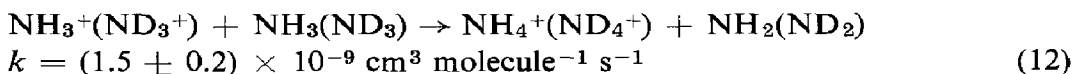
In conclusion, the 123.6 nm results indicate that there is a rather sharp increase in the quantum yield of the elimination of molecular hydrogen from ammonia for an increase in photon energy of only 1.6 eV and that the isotope effect is less pronounced than at the onset of this process. Although at 123.6 nm besides processes (5) and (6) an additional H_2-producing process occurs (process 3), the emission data of Okabe and Lenzi[7] show that the quantum yield of this process is quite low ($\Phi < 0.01$) in this wavelength range. It follows that the important contribution to molecular hydrogen formation at 123.6 nm must be ascribed to a greater role of processes (5) and/or (6).

104.8–106.7 nm photolysis

In this wavelength range, absorption of a photon by ammonia leads to the production of positive ions:
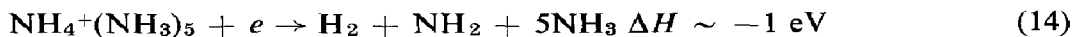
$$NH_3(ND_3) + h\nu \rightarrow NH_3{}^+(ND_3{}^+) + e \tag{11}$$

as well as of superexcited ammonia molecules. The quantum yield of process (11) is 0.40 ± 0.01 for NH_3 and 0.42 ± 0.01 for ND_3 (Table 1). The slight isotope effect in favor of the deuterated analogue observed in the photoionization quantum yield is commonly reported for most organic molecules and has been discussed extensively by previous investigators[19]. Dissociation of the parent ammonia ion is of negligible importance at these energies[20]. It is, however, of importance to consider briefly the possibility that the parent ion may yield unscavengeable hydrogen. In the pressure range at which the experiments listed in Tables 5 and 6 are carried out, the $NH_4{}^+$ ($ND_4{}^+$) ion formed in the fast reaction[20]:

$$NH_3{}^+(ND_3{}^+) + NH_3(ND_3) \rightarrow NH_4{}^+(ND_4{}^+) + NH_2(ND_2)$$
$$k = (1.5 \pm 0.2) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \tag{12}$$

will cluster with additional ammonia molecules. At a pressure of 10 Torr, the average cluster will contain five ammonia molecules[21]. The overall enthalpy of the process[21]:

$$NH_4{}^+ + 5NH_3 \rightarrow NH_4{}^+ (NH_3)_5 \tag{13}$$

is approximately 3.6 eV. Taking $\Delta H_f(NH_4{}^+) = 6.43$ eV[22] only two energetically plausible electron neutralization mechanisms have to be considered:

$$NH_4{}^+(NH_3)_5 + e \rightarrow H_2 + NH_2 + 5NH_3 \quad \Delta H \sim -1 \text{ eV} \tag{14}$$
$$\rightarrow H + 6NH_3 \quad\quad\quad \Delta H \sim -1 \text{ eV} \tag{15}$$

There is convincing evidence from gas phase radiolysis studies of ammonia that neutralization leads exclusively to the formation of H atoms[23], so we exclude neutralization mechanism (14) as a source of molecular hydrogen.

Assuming then that any molecular hydrogen results from the decomposition of neutral superexcited ammonia, we express the measured yields of $H_2(D_2)$ in the 106.7–104.8 nm photolysis as the number of molecules of D_2 produced per superexcited molecule $M(H_2)/N_{ex}$

$$M(D_2)/N_{ex} = \Phi(H_2) \times \frac{1}{1-\Phi_+} \qquad (IV)$$

Although fewer experiments were carried out at these short wavelengths, the data given in Table 5 show once more that the yield of D_2 is essentially invariant with pressure and the concentration of C_2H_4. Once more the NH_3–C_2D_4 data show less reliability and the values of $M(H_2)/N_{ex}$ exhibit a monotonic decrease with increasing concentration of C_2H_4. On this basis, a value of 0.52 ± 0.02 can be ascribed to the probability that a hydrogen molecule is eliminated from a superexcited ammonia molecule at 106.7–104.8 nm. This high value can in part be ascribed to process (3). According to the emission study of Okabe and Lenzi[7], the yield of $NH(c^1\pi)$ shows a nearly tenfold increase from 115 nm down to 105 nm. Even so, the estimated quantum yield at the latter wavelength is in the vicinity of 0.1, and therefore other processes contributing to the high yield of molecular hydrogen have to be considered. It should be pointed out that besides processes (5) and (6) which, as mentioned before, are probably the main contributors to the formation of molecular hydrogen at 147 and 123.6 nm, the overall dissociative process:

$$NH_3 + h\nu \rightarrow N + H_2 + H \qquad \Delta H = 7.63 \text{ eV} \qquad (16)$$

is energetically feasible both at 123.6 nm and 104.8–106.7 nm. The fact that N atoms have not been reported in previous investigations of the far ultra-violet photolysis of ammonia, in view of its high reactivity, does not necessarily militate against the occurrence of process (16). It is conceivable that a process such as (16) takes place via a highly internally excited NH_2 species formed after initial cleavage of an N–H bond in ammonia.

The present results support the view that the molecular hydrogen observed in the gas phase radiolysis of ammonia results mainly from the decomposition of neutral excited ammonia molecules. Neither the number of neutral excited molecules per ion pair, nor their energy distribution is known in the gas phase radiolysis. The recently reported[23] value of 0.7 molecules of molecular hydrogen per 100 eV absorbed by ammonia cannot presently be related to the photochemical data.

CONCLUSIONS

It is seen in this study that the quantum yield of the processes leading to the molecular hydrogen increases sharply with an increase of the photon energy. Because of the absence of the formation of molecular hydrogen at 184.9 nm and the very pronounced enhancement from 147 to 123.6 nm, it can be surmised that the onset of the molecular hydrogen is in the vicinity of 8 eV. The fact that an

isotope effect of any significant magnitude was only seen at 147.0 nm (8.4 eV) may be related to the fact that at 147 nm ε_{NH_3} is nearly twice as high as ε_{ND_3}. In view of the very pronounced structure[24] in the absorption spectrum in this wavelength region, such a correlation may be fortuitous. It is clear, however, that much stronger progressions of absorption bands start at wavelengths below approximately 145 nm and that it is in this region that molecular hydrogen elimination occurs with a high probability. It is at this point not possible to correlate the present quantum yield results with specific electronic states. In the far ultra-violet region many states are accessible and as in the case of other polyatomic molecules little is known about cross-overs from one state to another.

ACKNOWLEDGEMENTS

REFERENCES

1a J. R. McNesby, *J. Atmos. Sci.*, 26 (1969) 594.
 b D. F. Strobel, *J. Atmos. Sci.*, 26 (1969) 906.
2 J. P. Ferris and D. E. Nicadem, *Nature*, 238 (1972) 5362 and references cited therein.
3 For a review prior to 1965 see J. R. McNesby and H. Okabe, *Adv. Photochem.*, 3 (1964) 157.
4 O. Schnepp and K. Dressler, *J. Chem. Phys.*, 32 (1960) 1682.
5 K. D. Bayes, K. H. Becker and K. H. Welge, *Z. Naturforsch.*, 17a (1962) 676.
6 J. R. McNesby, I. Tanaka and H. Okabe, *J. Chem. Phys.*, 36 (1962) 605.
7 H. Okabe and M. Lenzi, *J. Chem. Phys.*, 47 (1967) 5241.
8 W. E. Groth, U. Schurath and R. N. Schindler, *J. Phys. Chem.*, 72 (1968) 3914.
9a K. H. Becker and K. H. Welge, *Z. Naturforsch.*, 18a (1963) 600.
 b F. Stuhl and K. Welge, *Z. Naturforsch.*, 18a (1963) 900.
 c K. D. Beyer and K. H. Welge, *Z. Naturforsch.*, 12a (1967) 1161.
 d W. Groth, H. Okabe and H. J. Rommel, *Z. Naturforsch.*, 19a (1964) 507.
10a S. Gordon, *J. Phys. Chem.*, 75 (1971) 2087.
 b M. Clerc, M. Schmidt, J. Hagege-Temman and J. Belloui, *J. Phys. Chem.*, 75 (1971) 2908.
11 R. Gorden, Jr., R. E. Rebbert and P. Ausloos, *Nat. Bur. Stand. Tech. Note No. 496* (1969) 55 pp.
12 R. E. Rebbert and P. Ausloos, *Nat. Bur. Stand. J. Res.*, 75A (1971) 481.
13 K. Watanabe, F. M. Matsunaga and H. Sakai, *Appl. Optics*, 6 (1967) 391.
14 C. E. Klots, *J. Chem. Phys.*, 56 (1972) 124.
15 R. Gorden, Jr. and P. Ausloos, unpublished results.
16 L. C. Glasgow and P. Potzinger, *J. Phys. Chem.*, 76 (1972) 138.
17 J. Y. Yang and F. M. Servedio, *Can. J. Chem.*, 46 (1968) 338.
18 R. Gorden, Jr. and P. Ausloos, to be published.
19 P. Ausloos and S. G. Lias, *Radiat. Res. Rev.*, 1 (1968) 75.
20 L. W. Sieck, L. Hellner and R. Gorden, jr., *Chem. Phys. Lett.*, 10 (1971) 502.
21 A. M. Hogg and P. Kebarle, *J. Chem. Phys.*, 43 (1965) 449.
22 A. P. Altshuller, *J. Am. Chem. Soc.*, 77 (1955) 3480.
23 J. A. Eyere and D. Smithies, *Trans. Faraday Soc.*, 66 (1970) 2199.
24 G. Hersberg, *Molecular Spectra and Molecular Structure*, Vol. III, Van Nostrand, Princeton, N.J., 1967, p. 515.