



# Energy transfer from metastable electronically excited N2, Ar, Kr, and Xe to CH3OH, H2O2, CH3NH2, and N2H4

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### Energy transfer from metastable electronically excited N<sub>2</sub>, Ar, Kr, and Xe to CH<sub>3</sub>OH, H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>NH<sub>2</sub>, and N<sub>2</sub>H<sub>4</sub>

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The products of the reactions of metastable  $N_2(A^{3}\Sigma_{\mu}^{+})$  with the isoelectronic molecules CH<sub>3</sub>OH, H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>NH<sub>2</sub>, and N<sub>2</sub>H<sub>4</sub> have been studied using the discharge-flow technique, coupled with atomic resonance fluorescence and laser induced fluorescence detection. In the reaction with  $H_2O_2$ , the weak central bond is broken efficiently, but in the other reactions, scission of the central bond is unimportant compared to that of the stronger terminal X-H bonds. The behavior for all four reagent molecules parallels their UV photochemistry, but contrasts with IR multiphoton dissociation of  $CH_3OH$  and  $CH_3NH_2$ . The reactions of  $N_2(A)$ appear to parallel those of the excited metastable noble gases  $Ar({}^{3}P_{0,2})$ ,  $Kr({}^{3}P_{2})$ , and  $Xe({}^{3}P_{2})$ , but scaled to the lower energy of  $N_{2}(A)$ .

#### I. INTRODUCTION

Electronic-to-electronic energy transfer is an important channel in the collisional quenching of a wide range of electronically excited atomic and molecular species.<sup>1-3</sup> This process can result in sensitized fluorescence or in dissociation or ionization of the collision partner; the nature of the products can give information concerning the mechanism of the energy transfer process, which may include a long range process induced by multipole coupling, curve crossing at short range, or the intermediacy of a charge transfer or a longlived complex. Because relatively little is known concerning the excited electronic states involved, comparison with the photochemistry of the acceptor molecule can provide additional relevant information.

This paper describes energy transfer from the lowest electronically excited state of N<sub>2</sub>, the metastable  $A^{3}\Sigma_{\mu}^{+}$ state, which has an energy of 6.2 eV. Rate constants for deactivation of this state by several molecules have been measured<sup>4-7</sup> and range over four orders of magnitude. Deactivation by chemical reaction with atomic<sup>8</sup> and molecular<sup>9</sup> oxygen to yield, respectively, NO and N2O has been found to constitute a minor channel. In contrast, efficient sensitized fluorescence from added NO,<sup>10</sup> CO,<sup>11</sup> and IF<sup>12</sup> shows the importance of electronic-to-electronic energy transfer. Because of the large excitation energy of  $N_2(A)$ , collisional dissociation of most molecules is energetically allowed and has recently been shown to be an important process in the reactions with NH<sub>3</sub>, CH<sub>3</sub>OH, and O<sub>2</sub>.<sup>9,13</sup>

The present study concerns dissociation channels in the reactions of N<sub>2</sub>(A) with CH<sub>3</sub>OH, H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>NH<sub>2</sub>, and N<sub>2</sub>H<sub>4</sub>. The reaction with CH<sub>3</sub>OH has a rate constant of  $4 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup> for N<sub>2</sub>(A,v = 0),<sup>7</sup> but the other reactions occur at close to the collision rate.<sup>14</sup> These reagent molecules, besides each having 14 valence electrons, are characterized by a central bond (C-O, C-N, N-N, O-O) which is weaker than the terminal C-H, N-H, or O-H bonds. Despite this, UV photodissociation of these molecules appears to favor cleavage of the stronger terminal bonds, except for  $H_2O_2$  for which O-O cleavage is observed.

We find that the reactions with  $N_2(A)$  closely parallel

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Stainless-Steel **Reaction Vessel** 

Pressure Monometer



FIG. 1. Experimental reaction vessel used for laser-induced fluorescence

the photochemistry in terms of the probability of cleavage of the central bond. The products are detected by H-atom reso-

nance fluorescence and laser-induced fluorescence (LIF) in

discharge-flow systems. This paper also reports on several of

the reactions of Ar( ${}^{3}P_{0,2}$ ), Kr( ${}^{3}P_{2}$ ), and Xe( ${}^{3}P_{2}$ ) with these

molecules, and on the reactions of  $N_2(A)$  and Ar<sup>\*</sup> with

NH<sub>3</sub>, which were used as reference reactions in this study.

The discharge-flow apparatus used for the H-atom resonance fluorescence measurements has been described in de-

tail previously.<sup>15,16</sup> The stainless-steel reaction vessel used

for the OH and NH<sub>2</sub> LIF measurements is shown in Fig. 1.

Pumo

II. EXPERIMENTAL

Lase In

measurements.

The metastable excited species are produced in a weak dc discharge through flowing Ar or through the appropriate mixture of N<sub>2</sub>(0.1%-1%), Kr, or Xe in Ar. The linear gas velocity in the Pyrex inlet tube is about 2000-5000 cm s<sup>-1</sup> and the total gas pressure is typically 1–5 Torr, with a metastable concentration of typically  $1 \times 10^{10}$  to  $1 \times 10^{11}$  cm<sup>-3</sup>. In the experiments described here, the reagent was added through the downstream reagent inlet. The mixing zone was about 2 ms upstream of the LIF observation region, and sufficient reagent was added to drive the reaction to completion before the observation region. A quartz window allowed observation of the reaction zone, emission being monitored by a filtered 1P28 photomultiplier.

LIF detection employed an excimer-pumped dye laser (Lambda-Physik 101E, 2002E) in the fundamental or frequency-doubled mode. Fluorescence was detected at right angles to the laser beam and the gas flow, and collected by two lenses before detection by a filtered, cooled, red-sensitive photomultiplier (RCA C31034), attached to a gated, pulsecounting system (Ortec 9315/9320). The gate opened approximately 0.5  $\mu$ s following the laser pulse, to eliminate detection of scattered light and electrical (rf) interference. The measurements employed Sulfarhodamine B dye, operating between 597 and 610 nm for NH<sub>2</sub> detection via the  $\tilde{A}^{2}A_{1} - \tilde{X}^{2}B_{1}$  (090–000) band,<sup>17</sup> and frequency doubled for OH and OD detection via the  $A^{2}\Sigma^{+}-X^{2}\Pi$  (0,0) and (1,1) bands.<sup>18</sup> According to specifications, the excimer laser pulse width is approximately 10 ns; pulse repetition rates of between 3 and 10 Hz were typically used. The dye laser pulse energy was measured with a pyroelectric sensor (Gentec ED-200); typical pulse energies were 0.1-10 mJ in the fundamental region and 0.01-1 mJ frequency doubled.

The determination of absolute branching fractions for dissociation channels involved comparison of fluorescence signals from the reaction of interest and from a reference reaction.<sup>13,15,16</sup> For H-atom resonance fluorescence, H<sub>2</sub> or NH<sub>3</sub> was used as the reference reagent and, where necessary, correction for absorption of the resonance radiation by the reagent was made.<sup>19</sup> For LIF, the 2 ms delay between the reaction and observation zones allowed nearly complete rotational and vibrational relaxation<sup>20</sup> of NH<sub>2</sub> and rotational relaxation of OH, as verified by scans of the rotational structure of the relevant bands by laser excitation spectroscopy. The OH(X, v = 1) level was detected weakly in several reactions, but was readily removed by the reagent molecules  $H_2O_2$  and  $CH_3OH$  as well as by  $H_2O$ , which was used as a reference reagent. For H<sub>2</sub>O, the mechanism is clearly vibrational relaxation, so that measurement of the (0,0) band at moderate to high H<sub>2</sub>O concentrations allowed all OH to be detected. This is not necessarily true for CH<sub>3</sub>OH or H<sub>2</sub>O<sub>2</sub>, from which H-atom abstraction by OH, v = 1 is energetically possible. However, careful comparison of the band intensities showed that the yields of OH, v = 1 were much smaller than those of OH, v = 0 in the reactions of  $H_2O_2$  and CH<sub>3</sub>OH presented here, and these contributions are neglected in the present work.

Electronic quenching of the fluorescing states of  $OH(A^{2}\Sigma^{+})^{21}$  and  $NH_{2}(A^{2}A_{1})^{22,23}$  became significant at high reagent concentrations. Quenching rate constants were

measured by monitoring the temporal decay of the fluorescence, using the Ortec counting system in the "Boxcar" mode.

The reagents NH<sub>3</sub> (anhydrous, 99.99%) and CH<sub>3</sub>NH<sub>2</sub> (98%, Matheson) were used without purification. CH<sub>3</sub>OH (Baker), N<sub>2</sub>H<sub>4</sub> (anhydrous, Aldrich), and H<sub>2</sub>O were purified by freeze-pump-thaw cycles, and held in reservoirs at suitable temperatures, from which flows of the vapor were drawn. H<sub>2</sub>O<sub>2</sub> (90%, FMC Corporation) was titrated against standardized KMnO<sub>4</sub> to verify its purity, then stored in a low temperature trap. The vapor was carried into the reaction vessel by a small flow of Ar; the flow of H<sub>2</sub>O<sub>2</sub> was adjusted by varying the Ar flow or bath temperature, but no absolute concentrations of H<sub>2</sub>O<sub>2</sub> in the reaction vessel were measured.

#### **III. RESULTS**

### A. NH<sub>2</sub> laser-induced fluorescence: Quenching of $NH_2(\tilde{A}^2A_1)$

A portion of the NH<sub>2</sub> laser excitation spectrum from the reaction of Ar\* with NH<sub>3</sub> is shown in Fig. 2; this illustrates the good signal-to-noise ratio obtained and the good resolution (linewidth  $\sim 0.2 \text{ cm}^{-1}$ ). The kinetic measurements used the 090-000 band, with the laser set to either one of the 603.40, 603.53 nm lines, or to a stronger group of three closelying lines  $3_{03}$ - $3_{13}$ ,  $4_{04}$ - $4_{14}$ , and  $5_{05}$ - $5_{15}$  at 597.9 nm.<sup>17</sup> LIF intensities were measured as a function of reagent concentration in the reactions of  $Ar^*$  with  $NH_3$  and  $N_2H_4$  (Fig. 3), and exhibit a steady decrease with increasing concentration over much of the range. One cause of this behavior is quenching of the fluorescing  $NH_2(\tilde{A}^2A_1)$  state by the reagent, which can decrease the signal in two ways: first, by decreasing the fluorescence quantum efficiency; and second, by decreasing the fraction of fluorescence intensity detected during the finite gate period, which typically extended from  $t_1 = 0.5 \,\mu s$  to  $t_2 = 10.5 \,\mu s$  following the laser pulse. Thus, if the fluorescence exhibits exponential decay, the measured intensity,  $I_{\ell}$ , is given by

$$I_f = I_0(k_r/k_{\rm eff}) \left[ \exp(-k_{\rm eff} t_1) - \exp(-k_{\rm eff} t_2) \right], \qquad (i)$$

where  $I_0$  is the time-integrated fluorescence intensity in the absence of any quenching,  $k_r$  is the radiative decay rate, and  $k_{\text{eff}}$  is the effective first-order decay rate:

$$k_{\rm eff} = k_r + k_{\rm Ar} [\rm Ar] + k_{\rm N_2} [\rm N_2] + k_{\rm Q} [\rm Q],$$
 (ii)

where Q is NH<sub>3</sub> or N<sub>2</sub>H<sub>4</sub>. NH<sub>2</sub> fluorescence exhibited exponential decays over the time period 0.5–10.5  $\mu$ s following the laser pulse, as shown in Fig. 4. Effective quenching rate constants for Ar, NH<sub>3</sub>, and N<sub>2</sub>H<sub>4</sub> were determined from experiments, in which the decay rates were measured as a function of the concentration of the relevant reagent. The data are summarized in Fig. 5: in panel (a), the concentration of NH<sub>3</sub> or N<sub>2</sub>H<sub>4</sub> was varied at constant Ar pressure of 2.3 Torr; in panel (b), the total pressure was varied at constant NH<sub>3</sub> mole fraction,  $x_{\rm NH_3} = 0.0050$ . The plots were analyzed to yield:  $k_r = (1.1 \pm 0.5) \times 10^5 \, {\rm s}^{-1}$ ;  $k_{\rm Ar} = (4.5 \pm 0.5) \times 10^{-12} \, {\rm cm}^3 \, {\rm s}^{-1}$ ;  $k_{\rm NH_3} = (2.3 \pm 0.2) \times 10^{-10} \, {\rm cm}^3 \, {\rm s}^{-1}$ ; and  $k_{\rm N_2H_4} = (3.0 \pm 0.3) \times 10^{-10} \, {\rm cm}^3 \, {\rm s}^{-1}$ . Because of the low [N<sub>2</sub>] used in the N<sub>2</sub>(A) + RNH<sub>2</sub> experiments, the effect of

$$NH_2 (\tilde{A}^2A_1 - \tilde{X}^2B_1) (0,9,0) - (0,0,0)$$



FIG. 2. Laser excitation spectrum of NH<sub>2</sub>( $A^2A_1-X^2B_1$ ). A portion of the (090-000) band.

 $N_2$  in Eq. (ii) was expected to be small and the value  $k_{N_2} = k_{NH_3}/2.5$  (Ref. 23) was assumed. In the experiments with CH<sub>3</sub>NH<sub>2</sub>, the very small NH<sub>2</sub> yields were corrected for quenching, assuming CH<sub>3</sub>NH<sub>2</sub> to quench NH<sub>2</sub>( $\tilde{A}$ ) with similar efficiency to NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub>.

Data corrected for quenching by  $RNH_2$  by use of Eq. (i) are included in Fig. 3. For  $NH_3$ , it is seen that the resulting data are essentially independent of concentration. However, the  $N_2H_4$  data show a residual decrease with increasing con-



FIG. 3. Dependence of LIF intensity on reagent concentration.  $\bigcirc \blacksquare$ : Ar\* + NH<sub>3</sub>;  $\square \blacksquare$ : Ar\* + N<sub>2</sub>H<sub>4</sub>. Unfilled points: raw data; filled points: corrected for quenching of NH<sub>2</sub>(A) by the reagent.

centration, probably due to secondary reactions of  $NH_2$  in this system (see Sec. IV). In the study of the  $NH_2$  yields in the reactions of Ar\*, Xe\*, and  $N_2(A)$  with  $N_2H_4$ , data were extracted at  $[N_2H_4] \le 2 \times 10^{14}$  cm<sup>-3</sup>.

#### B. The reactions of $N_2(A)$ and $Ar^*$ with $NH_3$

The reaction of  $N_2(A)$  with NH<sub>3</sub> occurs at close to the collision rate,<sup>6</sup> and the only exothermic dissociation channels are

$$N_2(A) + NH_3 \rightarrow N_2 + NH_2 + H \tag{1}$$

$$\rightarrow N_2 + NH + H_2. \tag{2}$$

Large H-atom and  $NH_2$  signals were detected from this reaction. To establish this as a reference reaction, the H-atom



FIG. 4. Decay of NH<sub>2</sub> LIF following the laser pulse (t = 0); NH<sub>2</sub> formed in the reaction Ar<sup>•</sup> + NH<sub>3</sub> at 2.3 Torr total pressure. NH<sub>3</sub> concentrations:  $O 6.0 \times 10^{13} \text{ cm}^{-3}$ ;  $\Delta 7.2 \times 10^{14} \text{ cm}^{-3}$ ;  $\Box 1.66 \times 10^{15} \text{ cm}^{-3}$ .



FIG. 5. Dependence of NH<sub>2</sub> LIF decay rate on concentration. (a)  $\Box$  N<sub>2</sub>H<sub>4</sub>;  $\bigcirc$  NH<sub>3</sub>. Total pressure: 2.3 Torr of Ar. (b) [NH<sub>3</sub>]/[Ar] = 0.0050.

resonance fluorescence signal,  $S_{\rm H}$ , was compared with that from the well-studied reaction of Ar\* with H<sub>2</sub>:<sup>16</sup>

$$Ar^* + H_2 \rightarrow Ar + H + H, \qquad (3)$$

which has a branching fraction f = 1.0. The relative concentrations of Ar<sup>\*</sup> (no N<sub>2</sub> added before the discharge) and N<sub>2</sub>(A) at the reagent inlet point were determined separately by comparing the integrated N<sub>2</sub>(C-B) and NO(A-X) emission intensities I from the reactions:

$$Ar^* + N_2 \rightarrow Ar + N_2(C^3 \Pi_u), f = 0.95 \pm 0.05, (4)$$

$$N_2(A) + NO \rightarrow N_2(X) + NO(A^2\Sigma^+),$$

$$f = 1.0$$
 (Ref. 10). (5)

The branching fraction for reaction (1) is given by

$$f = \frac{S_{\rm H} [N_2(A) + \rm NH_3]}{0.50S_{\rm H} (\rm Ar^* + \rm H_2)} \cdot \frac{I(\rm Ar^* + \rm N_2)}{0.95I [N_2(A) + \rm NO]}.$$
 (iii)

From two experiments with  $[N_2(A)]/[Ar^*]$  in the range 3.9–5.5, the branching fraction was determined as  $0.9 \pm 0.2$ . The principal source of uncertainty was drift in the ratio  $[N_2(A)]/[Ar^*]$  between the resonance fluorescence and emission measurements. Thus dissociation to  $NH_2 + H$  was concluded to be the dominant channel for the reaction of  $N_2(A)$  with  $NH_3$  and a branching fraction of unity was used in the remainder of this study.

A previous study<sup>16</sup> of the reaction of  $Ar^*$  with  $NH_3$  revealed two separate channels: chemi-ionization,

$$Ar^* + NH_3 \rightarrow Ar + NH_3^+ + e^-, f = 0.42 \pm 0.04;$$
  
(6)

and dissociation to yield  $0.62 \pm 0.04$  H atoms per reactive event. In the present experiment using LIF, NH<sub>2</sub> was detected with a yield of  $0.95 \pm 0.10$  determined by comparison with Xe\* + NH<sub>3</sub><sup>16</sup>:

$$Xe^* + NH_3 \rightarrow Xe + NH_2 + H, f = 1.0.$$
 (7)

The relevant ratio  $[Ar^*]/[Xe^*]$  was measured by comparing the integrated emission intensities from reactions (4) and<sup>24</sup>

$$Xe^* + CFCl_3 \rightarrow XeCl^* + CFCl_2, \quad f = 0.15.$$
(8)

The data for the  $Ar^* + NH_3$  reaction are consistent with two principal primary channels, Eq. (6) and

$$Ar^* + NH_3 \rightarrow Ar + NH_2 + H, f = 0.53 \pm 0.11,$$
 (9)

the remaining  $NH_2$  arising from the extremely fast secondary reaction:

$$\mathrm{NH}_{3}^{+} + \mathrm{NH}_{3} \rightarrow \mathrm{NH}_{4}^{+} + \mathrm{NH}_{2}. \tag{10}$$

The branching fraction for dissociation to NH + H + H is deduced to be only  $0.04 \pm 0.06$ .

## C. The reactions of $N_2(A)$ with CH<sub>3</sub>OH, CH<sub>3</sub>NH<sub>2</sub>, $N_2H_4$ , and $H_2O_2$

In the resonance fluorescence experiments, the H signals were compared with those from reference reactions, such as  $N_2(A) + NH_3$ : the first three reactions produced large yields of H atoms. In the LIF experiments, the  $NH_2$ signals from the reactions with  $CH_3NH_2$  and  $N_2H_4$  were much smaller than those from  $N_2(A) + NH_3$ . The OH yield from the reaction with  $CH_3OH$  was also shown to be small, but the reaction with  $H_2O_2$  yielded a large OH signal, calibrated by comparison with the reference reaction  $Ar^* +$  $H_2O$ . Details of these measurements are given below.

H-atom resonance fluorescence signals from the reactions of  $N_2(A)$  with  $CH_3NH_2$  and  $CH_3OH$  are shown as a function of reagent concentration in Fig. 6. After correction for absorption of the resonance radiation by the reagent, the signals reach constant values at large concentrations, corre-



FIG. 6. Dependence of H-atom resonance fluorescence intensity on reagent concentration. Circles:  $N_2(A) + CH_3NH_2$ ; Squares:  $N_2(A) + CH_3OH$ . Unfilled points: raw data; filled points; corrected for absorption of the resonance radiation by the reagent.

sponding to complete conversion of the flux of  $N_2(A)$  molecules into reaction products. For  $CH_3NH_2$ , the ratio of the plateau signal to that for the reference reaction was  $S_H(CH_3NH_2)/S_H(NH_3) = 1.00 \pm 0.02$ , corresponding to one H atom produced per reactive event involving  $CH_3NH_2$ .

A similar study of the  $N_2(A) + CH_3OH$  reaction yielded  $S_H (CH_3OH)/S_H (NH_3) = 0.86 \pm 0.05$ . This large value prompted a determination of the H atom yields in the reactions of  $N_2(A)$  with CH<sub>3</sub>OD and CD<sub>3</sub>OH; the ratios  $S_H (methanol)/S_H (NH_3)$  were, respectively,  $0.21 \pm 0.05$ and  $1.0 \pm 0.1$ , indicating preferential cleavage of the O-H, rather than the C-H, bond of CH<sub>3</sub>OH.

A large H-atom signal was obtained also from the reaction of  $N_2(A)$  with  $N_2H_4$ , but it decreased by a factor of 4 over the reagent concentration range  $5 \times 10^{11}$  to  $1.5 \times 10^{13}$ cm<sup>-3</sup>. This decrease is much too large to be explained by possible Lyman- $\alpha$  absorption by  $N_2H_4$  and was ascribed to an unexpectedly rapid secondary reaction between H atoms and  $N_2H_4$ . Because of this, no quantitative H yield could be determined and the dissociation products were deduced from the NH<sub>2</sub> yield.

The yields of NH<sub>2</sub> in the reactions of N<sub>2</sub>(A) with N<sub>2</sub>H<sub>4</sub> and CH<sub>3</sub>NH<sub>2</sub> were measured relative to the reference reaction N<sub>2</sub>(A) + NH<sub>3</sub>, using the precautions and corrections described in Sec. III A. The yields were  $S_{\rm NH_2}(N_2H_4)/S_{\rm NH_2}(\rm NH_3) = 0.11 \pm 0.01$  and  $S_{\rm NH_2}(\rm CH_3NH_2)/S_{\rm NH_2}(\rm NH_3) = 0.04 \pm 0.01$ . These small yields are consistent with the large H-atom yields from these reactions.

For the very rapid  $N_2(A) + H_2O_2$  and reference Ar\* + H<sub>2</sub>O reactions, conditions were chosen, employing relatively slow flow and low reagent concentrations [(1-5)×10<sup>13</sup> cm<sup>-3</sup>], such that the primary reactions were driven to completion without significant quenching of the fluorescing OH( $A^{2}\Sigma^{+}$ ) state by the reagent molecule. The H<sub>2</sub>O<sub>2</sub> reaction produced a very large OH signal, and kinetic data were obtained via the  $Q_1(4)$  line. Most measurements employed a H<sub>2</sub>O<sub>2</sub> bath temperature of about 0 °C, with a carrier flow of Ar, which was approximately 3% of the total Ar flow rate. The total OH yield from this reaction, normalized relative to the Ar\* + H<sub>2</sub>O reaction, was 2.1 ± 0.3 radicals per reactive event, corresponding to dissociation of H<sub>2</sub>O<sub>2</sub> to OH + OH with essentially unit efficiency.

For the reaction of  $N_2(A)$  with  $CH_3OH$ , the OH LIF signal did not exceed the background level and, by comparison with the signals from the reactions  $Ar^* + CH_3OH$  (see below) and  $N_2(A) + H_2O$ , it was concluded that the branching fraction for OH production was  $0.01 \pm 0.01$ . The product yields are summarized in Table I.

### D. Reactions of the excited noble gases with $N_2H_4, \ CH_3NH_2, \ and \ CH_3OH$

It is of interest to seek analogies between the reactions of  $N_2(A)$  (excitation energy 6.2 eV) and those of  $Xe^*({}^{3}P_2)$  (8.3 eV),  $Kr^*({}^{3}P_2)$  (9.9 eV), and  $Ar^*({}^{3}P_{0,2})$  (11.6 eV). The reactions with  $H_2O_2$  could not be studied because of the appreciable  $H_2O$  contaminant in the samples, which reacts rapidly with the excited noble gas atoms, in contrast to its very slow reaction with  $N_2(A, v = 0)$ . The reactions stud-

TABLE I. Product yields in the reactions of  $Ar({}^{3}P_{0,2})$ ,  $Xe({}^{3}P_{2})$ , and  $N_{2}(A {}^{3}\Sigma_{u}^{+})$ .

Reagent	Product	$Ar({}^{3}P_{0,2})$	$Xe({}^{3}P_{2})$	$N_2(A^{3}\Sigma_u^+)$
H <sub>2</sub> O <sub>2</sub>	ОН	•••		$2.1 \pm 0.3$
CH <sub>3</sub> OH	н	1.45 ± 0.03*	1.49 ± 0.03*	0.86 ± 0.05
CH <sub>3</sub> OD	н	$1.01 \pm 0.03^{*}$	$0.81 \pm 0.02^{*}$	$0.21 \pm 0.05$
CD <sub>3</sub> OH	Н	•••	•••	$1.0 \pm 0.1$
CH <sub>3</sub> OH <sup>b</sup>	OH	0.13 ± 0.02	$0 \pm 0.02$	0.01 ± 0.01
CH <sub>3</sub> OD	OD	0.15 ± 0.02	0.01 ± 0.01	•••
$N_2H_4$	NH <sub>2</sub>	0.45 ± 0.02	$0.24 \pm 0.02$	0.11 ± 0.01
CH <sub>3</sub> NH <sub>2</sub>	Н	•••	•••	$1.00 \pm 0.02$
CH <sub>3</sub> NH <sub>2</sub>	$NH_2$	$0.06 \pm 0.03$	~0.04	$0.04\pm0.01$

\* Reference 16.

<sup>b</sup>OH yield from  $Kr({}^{3}P_{2}) + CH_{3}OH$  was  $0 \pm 0.02$ .

ied were Ar\*,  $Xe^* + CH_3NH_2$ ,  $N_2H_4$  and Ar\*, Kr\*,  $Xe^* + CH_3OH$ , using LIF detection: H yields from the reactions with CH<sub>3</sub>OH have already been reported.<sup>16</sup> In the reactions with  $N_2H_4$  and  $CH_3NH_2$ , the appropriate reaction of Ar\* or Xe\* with NH<sub>3</sub> served as the reference. Reactions with  $H_2O^{15}$  served as the reference in the CH<sub>3</sub>OH study. In the  $Kr^*$ ,  $Xe^* + CH_3OH$  study, the OH signal did not exceed the background (impurity) level which was in this case about 10% of the reference signal. As a check, and to avoid this background, the reactions of CH<sub>3</sub>OD with Ar\* and Xe\* were examined and yielded consistent results. The results, included in Table I, show extremely small yields of NH<sub>2</sub> in each reaction of  $CH_3NH_2$  studied. Kr<sup>\*</sup> and Xe<sup>\*</sup> +  $CH_3OH$ yielded essentially no OH, but the Ar\* reaction produces a significant amount of OH. N<sub>2</sub>H<sub>4</sub> shows an increasing NH<sub>2</sub> yield, as the metastable energy is increased.

#### **IV. DISCUSSION**

#### A. Reliability of data

The principal data presented here are absolute branching fractions for dissociation channels in selected reactions of  $N_2(A^{3}\Sigma_{u}^{+})$  and of excited noble gas atoms. The technique, involving comparison with reference reactions, has been discussed in detail previously.<sup>15,16</sup> In the present study, an additional calibration was required to allow comparison of  $N_2(A)$  reactions with those of Ar\* or Xe\*. The main uncertainty concerns the branching fractions for the reference reactions (4) and (8):

$$Ar^* + N_2 \rightarrow N_2(C^3 \Pi_u) + Ar,$$
 (4)

$$Xe^* + CFCl_3 \rightarrow XeCl^* + CFCl_2.$$
(8)

For channel (4), the most recent emission studies<sup>25,26</sup> yielded branching fractions of 0.6 and 1.0. The most probable competing channel, dissociation of N<sub>2</sub> to N + N, has been shown<sup>27</sup> to account for only a few percent of the reaction, and so the value  $f = 0.95 \pm 0.05$  was adopted for channel (4). A single value, f = 0.15, is available<sup>24</sup> for channel (8); the uncertainty in this value based on the measurement<sup>28</sup> and on the observation of competing channels is estimated as 30%.

As described in the Results section, the LIF measurements were corrected for quenching of the fluorescing state by the reagent molecule. This correction failed to yield signals independent of reagent concentration in the reactions with N<sub>2</sub>H<sub>4</sub>. Although this could be ascribed to possible complexities in the kinetics of electronically excited NH<sub>2</sub>( $\tilde{A}$ ), the fact that the simple correction was successful for NH<sub>3</sub> suggests that the N<sub>2</sub>H<sub>4</sub> reactions were subject also to secondary reactions. As discussed previously,<sup>15,16</sup> the only secondary reactions (of neutral species) of possible importance in our system are those between product species and the parent reagent. Under the conditions used, only N<sub>2</sub>H<sub>4</sub> is expected to undergo such reactions. The residual decrease in NH<sub>2</sub> signal with increasing N<sub>2</sub>H<sub>4</sub> concentration can be explained by the secondary reaction:

$$\mathbf{NH}_2 + \mathbf{N}_2\mathbf{H}_4 \rightarrow \mathbf{NH}_3 + \mathbf{N}_2\mathbf{H}_3 \tag{11}$$

with  $k = 5.0 \times 10^{-13}$  cm<sup>3</sup> s<sup>-1</sup>.<sup>29</sup> The very rapid decrease in the H-atom signal with N<sub>2</sub>H<sub>4</sub> concentration is likewise ascribed to the reaction:

$$H + N_2 H_4 \rightarrow N_2 H_3 + H_2.$$
 (12)

However, the reported rate constant at 300 K,  $3 \times 10^{-13}$  cm<sup>3</sup> s<sup>-1</sup>,<sup>29,30</sup> is too small to explain the observed effect. It is possible that, despite the vast excess of Ar bath gas,  $[Ar]/[N_2H_4] \ge 10^4$ , the H atoms are not completely cooled translationally before reaction with N<sub>2</sub>H<sub>4</sub>; an acceleration of this reaction under these conditions has been postulated previously.<sup>31</sup> The additional possibility that such a reaction of hot H atoms with N<sub>2</sub>H<sub>4</sub> is responsible for the observed NH<sub>2</sub> via an alternative channel to channel (12) is of interest, but would be expected to cause an *increase* in NH<sub>2</sub> signal with N<sub>2</sub>H<sub>4</sub> concentration, in contrast to the observed behavior.

In concluding this section, it is appropriate to comment on the NH<sub>2</sub>( $\tilde{A}^2A_1$ ) fluorescence quenching data. The values for NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub> are comparable to literature data,<sup>22,23</sup> but that for Ar is much smaller than that measured by Halpern *et al.*<sup>23</sup> In the present experiment, total fluorescence between 650 and 850 nm is collected, so that the removal by Ar must represent electronic quenching by Ar; in the former experiment,<sup>23</sup> narrow band filters were employed and rotational and possibly vibrational relaxation are responsible for the higher rate constant. The rate constants must, at present, be considered as phenomenological, until the details of the time evolution of electronically excited NH<sub>2</sub> are understood.

### B. The reactions of $N_2(A)$ and comparison with photochemistry

The unexpected result of this study is that, in the reactions of  $N_2(A)$  with  $CH_3OH$ ,  $N_2H_4$ , and  $CH_3NH_2$ , cleavage of the weak central bond is much less probable than that of the stronger terminal bonds. The threshold energies for relevant dissociation channels are shown in Table II. The energy of  $N_2(A, v = 0)$  is 6.2 eV, equivalent to a photolysis wavelength of 200 nm, and it is thus of interest to compare the observed products with those from UV photodissociation of these molecules. Although there are considerable uncertainties concerning the photochemistry, the importance, or lack of importance, of central bond cleavage appears closely to parallel the present results. Thus, for  $H_2O_2$ , the absence of product H or O atoms has been taken as evidence<sup>32</sup> that

TABLE II. Energetics of dissociation of CH<sub>3</sub>OH, H<sub>2</sub>O<sub>2</sub>, N<sub>2</sub>H<sub>4</sub>, and CH<sub>3</sub>NH<sub>2</sub>.

Process	Dissociation energy, eV
$CH_3OH \rightarrow CH_3 + OH$	4.0
$\rightarrow$ CH <sub>2</sub> OH + H	4.0
$\rightarrow CH_3O + H$	4.5
$\rightarrow CH_2O + 2H$	5.4
$\rightarrow CH_3 + O + H$	8.4
$\rightarrow CH_2 + H + OH$	8.7
$H_2O_2 \rightarrow OH + OH$	2.2
$\rightarrow$ H + HO <sub>2</sub>	3.8
$\rightarrow O_2 + 2H$	5.9
$N_2H_4 \rightarrow NH_2 + NH_2$	2.5
$\rightarrow$ H + N <sub>2</sub> H <sub>3</sub>	4.1
$\rightarrow N_2H_2 + 2H$	5.7
$\rightarrow NH_2 + NH + H$	6.4
$CH_3NH_2 \rightarrow CH_3 + NH_2$	3.5
$\rightarrow CH_2NH_2 + H$	4.1
$\rightarrow$ CH <sub>3</sub> NH + H	4.5

photodissociation to OH + OH is dominant at 253.7 and 147 nm. Based on the stable end-products, <sup>32,33</sup> the UV photodissociation channels for CH<sub>3</sub>OH appear to be limited to

CH<sub>3</sub>OH + 
$$h\nu(\lambda \sim 185 \text{ cm})$$
 → CH<sub>3</sub>O + H (13)  
→ CH<sub>2</sub>O + H<sub>2</sub> (14)

with branching fractions of, respectively, 0.8 and 0.2. The weakness of cleavage of the C–O and C–H bonds is supported by recent *ab initio* calculations.<sup>34</sup>

An ESR study<sup>35</sup> of the 184.9 nm photodissociation of  $CH_3NH_2$  at 77 K has identified the following major channel:

$$CH_3NH_2 + hv \rightarrow CH_3NH + H.$$
(15)

This is consistent with a gas-phase study at the same wavelength,<sup>36</sup> in which stable products from mixed H/D labeled species were measured: this study suggested a 10% yield of  $CH_3 + NH_2$ . The data for  $N_2H_4$  have proved particularly difficult to interpret, because of the rapidity of secondary reactions, as indicated above. However, a time-resolved<sup>31</sup> study has shown clearly that  $NH_2$  is not a primary product of the photodissociation at 193 nm, consistent with dominance of the channel

$$N_2H_4 + h\nu \to N_2H_3 + H,$$
 (16)

which has been observed in earlier studies.<sup>37</sup>

Contrasting behavior has been found in the infrared multiphoton dissociation of  $CH_3OH^{38}$  and  $CH_3NH_2$ ,<sup>39</sup> for which simple rupture of the central bond appears to be a major process. For  $CH_3OH$ , dissociation to  $CH_2OH + H$  has also been detected as a minor channel, but there is no evidence for dissociation to  $CH_3O + H$ . These findings thus provide an alternative reference viewpoint, reflecting a statistical or RRKM product distribution, with which to compare the present results.

The comparable weakness of cleavage of the weakest bond in the  $N_2(A)$  energy transfer to and UV photochemistry of CH<sub>3</sub>OH,  $N_2H_4$ , and CH<sub>3</sub>NH<sub>2</sub>, shows clearly that the energy transfer process does not involve a long-lived complex and suggests strongly that it involves a near-vertical transition in the molecule to an excited state which subsequently dissociates. For reactions of  $N_2(A^{3}\Sigma_{u}^{+})$ , an excited triplet is expected to be involved, offering a possible contrast with the photochemistry. In particular, different correlations with dissociated products can exist for the first excited singlet and triplet states. For instance, cleavage of a C-H bond in singlet-excited CH<sub>3</sub>OH must lead adiabatically to electronically excited CH<sub>2</sub>OH, whereas the triplet state correlates with ground-state products. Both states can correlate with ground state  $CH_3O + H$  and  $CH_3 + OH$  because of the orbital electronic degeneracy of CH<sub>3</sub>O and OH; the weakness of photodissociation to  $CH_3 + OH$  is ascribed to a small barrier in the reaction path.<sup>34</sup> lt might be expected, therefore, that the  $CH_2OH + H$  channel would be relatively favored in energy transfer from  $N_2(A)$ , as compared to the UV photolysis. The present results show that this channel is minor compared to that leading to  $CH_3O + H$ . However, the reactions of the higher-energy species Xe\* and Kr\* with CH<sub>3</sub>OD show much smaller D yields,<sup>16</sup> implying increased importance of the  $CH_2OD + H$  primary channel. Its weakness in the  $N_2(A)$  reaction can thus be ascribed to an energy barrier. The  $CH_3 + OH$  channel, however, remains essentially closed in the Xe\* and Kr\* reactions, suggesting that dynamical effects are responsible. Buenker et al.<sup>34</sup> have suggested that O-H scission is favored over C-OH scission in part because of the high velocity of the departing light H atom. A similar puzzle exists for CH<sub>3</sub>NH<sub>2</sub> and N<sub>2</sub>H<sub>4</sub>: the lowest triplet state, unlike the excited singlet, is expected to correlate with ground state  $R + NH_2$ , and yet this channel is still very weak in the energy transfer process.

The reaction with CH<sub>3</sub>OH has additional interest. Unlike the reactions with N<sub>2</sub>H<sub>4</sub> and CH<sub>3</sub>NH<sub>2</sub>, which we find to occur at close to the collision rate, the reaction of N<sub>2</sub>(A) with CH<sub>3</sub>OH has a rate constant<sup>7</sup> of  $4 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup>, nearly a factor of 100 slower. The fact that the products of this reaction parallel those of the faster reactions implies no significant change in mechanism for this slower reaction. The results remain consistent with our previous model,<sup>16,19</sup> whereby the energy transfer occurs at medium-to-long range, but they imply that the probability of energy transfer is considerably smaller for N<sub>2</sub>(A) + CH<sub>3</sub>OH than in the other reactions.

#### C. Energy transfer to NH<sub>3</sub>

The reaction of  $N_2(A)$  with NH<sub>3</sub> leads to dissociation to NH<sub>2</sub> + H, paralleling the reaction with Xe(<sup>3</sup>P<sub>2</sub>). There is no

evidence for dissociation to  $NH + H_2$  or of E-V energy transfer. The higher energy species  $Ar({}^{3}P_{0,2})$  has additional dissociation channels in its reaction with  $NH_3$ :

$$Ar^* + NH_3 \rightarrow Ar + NH_2 + H + 7.0 \text{ eV}$$
 (17)

$$\rightarrow \mathbf{Ar} + \mathbf{NH} + \mathbf{H}_2 + 7.5 \,\mathrm{eV} \tag{18}$$

$$\rightarrow$$
 Ar + NH + H + H + 3.0 eV. (19)

The present results show that channel (17) is strongly favored. This behavior contrasts strongly with analogous reactions with H<sub>2</sub>O and CH<sub>4</sub>, in which loss of two H atoms, involving energetics comparable to that of process (19), is a major process.<sup>16</sup> This finding is consistent with our previous discussion concerning the symmetry of the dissociative state of the acceptor molecule, two-atom loss being favored where  $C_{2v}$  symmetry is expected.<sup>19</sup> For NH<sub>3</sub>,  $C_{3v}$  symmetry is more likely with three equivalent repulsive bonds. Simultaneous cleavage of three bonds cannot occur and, in the subsequent conformational changes leading to rupture of one bond, sufficient energy is apparently transferred to the departing H or Ar atom to prevent further dissociation.

#### D. Energy transfer to CH<sub>3</sub>OH

The data in Table I can be combined with H-atom, Oatom, and ion yields measured previously<sup>16</sup> to give considerable insight into the dissociation pathways in the reactions of  $Ar^*$ ,  $Kr^*$ , and  $Xe^*$  with CH<sub>3</sub>OH.

Our previous study of these reactions revealed large yields of H atoms, implying that cleavage of the C–O bond, the weakest in the molecule, is a minor process. The present study of OH LIF confirmed this conclusion. With these additional data, branching fractions for the allowed channels were deduced and listed in Table III. The Ar\* reaction is of particular interest. If it is assumed that three-atom loss, to HCO + 3H, is not important, then this reaction shows at least three separate channels, each involving cleavage of two bonds:

$$Ar^* + CH_3OH \rightarrow Ar + CH_2O + H + H$$
 (20)

$$\rightarrow Ar + CH_3 + O + H \tag{21}$$

$$\rightarrow Ar + CH_2 + OH + H; \qquad (22)$$

while cleavage of just one bond is apparently insignificant. In this reaction it is hard to envisage *simultaneous* cleavage of the two bonds; thus, sequential cleavage is more likely, the first dissociation releasing insufficient kinetic energy to pre-

TABLE III. Product distributions in the reactions of	of Ar( <sup>3</sup> P <sub>0.2</sub> ), Kr(	$({}^{3}P_{2})$ , and Xe $({}^{3}P_{2})$ with CH <sub>3</sub> OH.
------------------------------------------------------	---------------------------------------------	-------------------------------------------------------------------

	7711-1	Branching fraction		
Products	energy, eV	Ar*	Kr*	Xe*
CH <sub>3</sub> + OH	4.0	~0	< 0.03	< 0.03
$CH_2OH + H$ $CH_2O + H$	4.0 4.5	$\sim_{0}^{0}$ }	0.28 ± 0.03	0.49 ± 0.03
$CH_2O + 2H$	5.4	$0.62\pm0.02$	0.71 ± 0.03	$0.50 \pm 0.03$
$CH_3 + O + H$	8.4	$0.04 \pm 0.02$	0 ± 0.02	b
$CH_2 + OH + H$	8.6	$0.13 \pm 0.02$	< 0.03	Ъ
CHO + 3H	9.3	0ª	0ª	b
$CH_3OH^+ + e^-$	10.8	$0.20\pm0.01$	b	b

\* Assumed value.

<sup>b</sup>Endothermic.

vent subsequent dissociation of the residual fragment. Qualitative evidence for production of  $CH_2$  in Eq. (22) was obtained in the reaction of  $Ar^*$  with  $CH_3OD$ , by addition of  $O_2$ downstream of the primary reaction zone. An *OH* signal was produced,<sup>14</sup> ascribed to the reactions:

$$CH_2 + O_2 \rightarrow CHO + OH \tag{23}$$

$$\rightarrow CO + H + OH. \tag{24}$$

The H and D atom yields in the  $CH_3OD$  reaction (1.01 and 0.46, respectively, per reactive event) are not consistent with  $CH_2O$  as the sole product of channel (20). The relatively small D yield implies appreciable formation of CHOD, which may rearrange to CHDO.

In the reactions of CH<sub>3</sub>OH with Kr<sup>\*</sup> and Xe<sup>\*</sup>, the oneatom loss channels become increasingly important as the metastable energy decreases; it is thus expected that the CH<sub>3</sub>O and CH<sub>2</sub>OH are born with appreciable vibrational excitation.

#### E. Energy transfer to CH<sub>3</sub>NH<sub>2</sub> and N<sub>2</sub>H<sub>4</sub>

The reactions with  $CH_3NH_2$  appear to show considerable similarity to those of  $CH_3OH$ . Thus the very small yields of  $NH_2$  in the reactions with Xe\* and Ar\* imply large yields of H atoms, and probably significant chemi-ionization by Ar\*. The reactions of  $N_2H_4$  yield significant amounts of  $NH_2$ . Because quantitative H atom yields could not be obtained, the relative importance of dissociation to  $NH_2 + NH_2$  and to  $NH_2 + NH + H$  (requiring 6.4 eV of energy) could not be ascertained.

The products of the reactions of  $Ar({}^{3}P_{0,2})$ ,  $Kr({}^{3}P_{2})$ ,  $Xe({}^{3}P_{2})$ , and  $N_{2}(A {}^{3}\Sigma_{u})$  have now been investigated for NH<sub>3</sub>, CH<sub>3</sub>OH, CH<sub>3</sub>NH<sub>2</sub>, N<sub>2</sub>H<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub>O, SO<sub>2</sub>, Cl<sub>2</sub>, NO, H<sub>2</sub>O, CF<sub>3</sub>Cl, CF<sub>2</sub>Cl<sub>2</sub>, CFCl<sub>3</sub>, CF<sub>2</sub>HCl, and HCl. In the majority of cases, the products of the  $N_2(A)$  reactions parallel those of the excited noble gas atoms, but scaled to the lower energy of  $N_2(A)$ . Thus, in addition to the reagents studied here, N2O, O2, H2O, HCl and the chlorofluoromethanes<sup>13-16,19</sup> show dissociation channels to be dominant, even though the rate constants of the reactions with  $N_2(A)$  are lower (much lower in some cases) than those with Xe\*. Cl<sub>2</sub> also suffers dissociation,<sup>14</sup> in contrast to noble gas chloride excimer formation. Dissociation of NO is endothermic for  $N_2(A, v < 2)$ , and excitation transfer to NO( $A^2\Sigma^+$ ) is the observed efficient channel. This need not be considered as a discrepancy with the data for the excited noble gases, as the efficient dissociation of NO observed in these reactions probably arises via predissociation of higher energy states of NO.  $SO_2$  is the sole anomaly among this group of reagents, in showing very little dissociation to SO + O in the reaction with  $N_2(A)^{27}$  although it is energetically allowed and observed in the photolysis of SO<sub>2</sub> with photons of energy greater than 5.7 eV. A rich fluorescence spectrum is observed, implying efficient population of nondissociated excited states of  $SO_2$ .

The general similarity of behavior between  $N_2(A)$  and the metastable noble gas atoms for this class of reagent should allow a better understanding of the mechanisms of the reactions of the latter species. These exhibit extensive dissociation channels, several including cleavage of two bonds [cf. reactions (20)-(22)]. Clearly, the lowest energy channels are not favored in these reactions but, because of the large amounts of energy transferred and the difficulty in comparing fragmentation into two particles and fragmentation into three particles by statistical models, it has not been possible to establish conclusively that the observed channels represent a nonstatistical set of products. The present results for the N<sub>2</sub>(A) reactions suggest that the high energy dissociation channels observed in many of the reactions of the excited noble gases do in fact represent strongly nonstatistical effects in the energy transfer, so that the product distribution is determined by dynamical effects.

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