

# The photodissociation lifetimes of the NH radical in comets\*

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**Summary.** The photodissociation lifetimes of the NH radical through absorption of solar radiation into the  $A^3\Pi_1$  state are calculated as a function of the heliocentric velocity of the comet, and the velocity distributions of the product atoms are determined. For 1 AU sun-comet distance, the lifetimes vary from  $1.3 \cdot 10^4$  s to  $2.3 \cdot 10^4$  s and photodissociation of NH produces hydrogen and nitrogen atoms with velocities  $15 \text{ km s}^{-1}$  and  $1 \text{ km s}^{-1}$ , respectively, relative to the parent NH molecule. The photodissociation of the NH radical is a source of a high velocity component of H-atoms ( $15 \leq v_H \leq 25 \text{ km s}^{-1}$ ) derived from hydrogen Lyman-alpha emission studies in several comets. The convolution diaphragm model scale length of the NH parent for comet Bennett (1970 II), when compared with the  $\text{NH}_3$  scale length estimated at  $r_h = 1 \text{ AU}$ , shows that  $\text{NH}_3$  is probably the parent of the NH radical. Photodissociation of  $\text{NH}_3$  leads H atoms with an average velocity distribution of about  $8 \text{ km s}^{-1}$ , relative to  $\text{NH}_3$ , and is a weak source of low velocity H-atoms as found in several comets.

**Key words:** lifetimes of NH in comets – atomic and molecular processes

## 1. Introduction

The NH (imidogen) radical is of astrophysical importance and has been detected in the spectra of cool stars (Lambert and Beer, 1972; Lambert et al., 1984), including the Sun (Roach, 1939; Grevesse and Sauval, 1973), and comets (Swings et al., 1941; Swings and Haser, 1956; Arpigny, 1965; A'Hearn, 1982; Cucchiari and Malaise, 1982). Douglas and Elliott (1965) have pointed out that NH may be observable in interstellar space. Kerns and Duncan (1972) have developed this suggestion in a semi-quantitative way and have predicted that NH should be searched for in low temperature sources, in particular regions near the galactic center where isocyanic acid (HNCO) has been detected (Snyder and Buhl, 1972). Crutcher and Watson (1976) have attempted to detect NH in the direction of Omicron Persei and have placed an upper limit of  $0.3 \text{ mÅ}$  for the  $R_1(0)$  line at  $\lambda 3358$  of the  $0, 0$  band of the  $\text{NH}(A^3\Pi_1 - X^3\Sigma^-)$  transition. Their

attempt has been unsuccessful in confirming NH in the direction of  $\sigma$  Per.

NH is iso-electronic to  $\text{OH}^+$  and has been found as one of the most conspicuous emitters in the ultraviolet, along with OH and CN, in the emission spectra of cometary comae (Code and Savage, 1972). The NH molecule is usually detectable by its electronic lines at around  $\lambda 3360$  in large and bright comets (Swings and Haser, 1956) when the heliocentric distance of the comet is about 1.7 AU; its average extent into the coma is about  $3.16 \cdot 10^5 \text{ km}$  from the nucleus (Giguere and Huebner, 1978). For comet Bennett (1970 II), Malaise (1976) has presented sunward and tailward profiles of the  $\text{NH}(A^3\Pi_1 - X^3\Sigma^-)$  transition and using these profiles (April 6, 1970 observation) Combi (1978) has derived first convolution model scale lengths of  $1.8 \cdot 10^5 \text{ km}$  and  $2.4 \cdot 10^3 \text{ km}$  for NH and its parent(s), respectively, at a heliocentric distance of about 0.664 AU. Cucchiari and Malaise (1982) have recently developed dynamic models for comet Bennett (1970 II) and fitting the observed NH profiles to model profiles yields lifetimes of  $1.5 \cdot 10^5 \text{ s}$  and  $8 \cdot 10^3 \text{ s}$  for NH and its parent(s), respectively, for April 9 and 10, 1970 observations when the comet was about 0.714 AU from the sun. Recently, Litvak and Kuiper (1982) have performed intensity calculations of the  $3360 \text{ Å}$  and the submillimeter-wave rotational transitions of the ground  $X^3\Sigma^-$  state of the NH molecule in cometary comae. Their calculations show typically  $\pm 10\%$  changes in the integrated intensity of the Q branch with heliocentric velocity and inverted populations in the lowest submillimeter-wave transitions, which may result in weak maser emission near 1 THz from cometary and interstellar NH.

High resolution lifetime studies of the NH molecule (Smith et al., 1976) show pre-dissociations of NH in  $A^3\Pi_1$  and  $C^1\Pi$  states. In this paper, we present photodissociation rates of NH by absorption of solar radiation into the  $v' = 2$  level of the  $A^3\Pi_1$  state as a function of radial velocity for a comet at a heliocentric distance of 1 AU. The photodissociation of NH results in velocity distributions of about  $1 \text{ km s}^{-1}$  and  $15 \text{ km s}^{-1}$  for nitrogen and hydrogen atoms, respectively, with respect to NH. By comparing the convolution model lifetime of the NH parent for comet Bennett (1970 II) with the photochemical lifetime of  $\text{NH}_3$  against solar photon flux at 1 AU we infer that  $\text{NH}_3$  is probably the parent of NH radical observed in comets.

## 2. Photodissociation of NH

In the laboratory, the  $\text{NH}(A^3\Pi_1 - X^3\Sigma^-)$  system has been the subject of vibrational and rotational analyses since 1935 (Funke,

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**Table 1.** Franck-Condon factors,  $r$ -centroids (in Å), Band origins (in  $\text{cm}^{-1}$ ), electronic transition moments (in a.u.), electronic transition probabilities (in  $\text{s}^{-1}$ ) and absorption oscillator strengths for the bands of the  $\text{NH}(\text{A}^3\Pi_1 - \text{X}^3\Sigma^-)$  transition

$v'$ \ $v''$	0	1	2
0	(a) 0.99967(+0)	0.29075(-3)	0.35617(-4)
	(b) 1.056	1.66	2.23
	(c) 29776.76	26651.16	23681.16
	(d) 0.2629	0.0397	-0.1708
	(e) 2.237(+6)	1.255(+4)	1.351(+5)
	(f) 7.564(-3)	5.297(-5)	7.222(-4)
1	(a) 0.29919(-3)	0.99760(+0)	0.19517(-2)
	(b) 0.72	1.096	1.66
	(c) 32810.66	29685.17	26715.17
	(d) 0.3870	0.2481	0.0397
	(e) 7.484(+4)	1.969(+6)	2.178(+4)
	(f) 2.084(-4)	6.702(-3)	9.149(-5)
2	(a) 0.26695(-4)	0.20347(-2)	0.99063(+0)
	(b) 0.67	0.73	1.139
	(c) 35647.46	32521.98	29551.98
	(d) 0.4055	0.3833	0.2322
	(e) 2.080(+5)	4.862(+5)	1.690(+6)
	(f) 4.907(-4)	1.378(-3)	5.802(-3)

#### Notes

(a) Franck-Condon factors ( $q_{v'v''}$ ). Figure in parenthesis is power of 10

(b)  $r$ -centroids ( $r_{v'v''}$ ) – For  $\Delta v = 0$  sequence,  $r_{v'v''}$  are by using realistic Klein-Dunham potentials (Jarman, 1971) and, for  $\Delta v \neq 0$  sequence,  $r_{v'v''}$  are by using Morse potentials (Nicholls and Jarman, 1956) for the  $\text{A}^3\Pi_1$  and  $\text{X}^3\Sigma^-$  states of NH (see text)

(c) Band origins ( $\nu_{v'v''}$ )

(d) POL-CI electronic transition moments under  $r$ -centroid approximation computed by Eq (2), see the text

(e) Electronic transition probabilities ( $A_{v'v''}$ );  $A_{00}$  is the average of Smith and Liszt (1971), Fink and Welge (1964) and Bennett and Dalby (1960).  $A_{11}$ ,  $A_{21}$ ,  $A_{22}$  are calculated from Eq (3).  $A_{01}$ ,  $A_{12}$  and  $A_{10}$  are from measurements made by Lents (1973), see text. Other  $A_{v'v''}$  are calculated with  $A_{v'}$  constant approximation for  $v' = 0, 1$  and 2 of the  $\text{A}^3\Pi_1$  state (see text)

(f) Absorption oscillator strengths ( $f_{v'v''}$ )

1935; 1936; Dixon, 1959; Murai and Shimauchi, 1966; Malicet et al., 1970). These analyses have resulted in accurate vibrational and rotational constants for  $v' \leq 2$  and  $v'' \leq 2$  for  $\text{A}^3\Pi_1$  and  $\text{X}^3\Sigma^-$  states of the NH molecule and these together with other molecular constants are listed in a recent compilation by Huber and Herzberg (1979). The observed  $\Delta G_{1/2}$  and  $\Delta G_{3/2}$  separations (Malicet et al., 1970) in the  $\text{X}^3\Sigma^-$  as well as  $\text{A}^3\Pi_1$  states can be accurately reproduced using these listed molecular constants for the NH molecule. Having these molecular constants we have calculated realistic Franck-Condon factors (Jarman, 1971) for the  $(2 \times 2)$  array of bands of the  $\text{NH}(\text{A}^3\Pi_1 - \text{X}^3\Sigma^-)$  system which are tabulated in Table 1, together with other parameters described therein. In Table 2, we list  $B_v$ ,  $E_v$  and turning points computed from realistic Klein-Dunham potentials for  $\text{NH} \text{A}^3\Pi_1$  and  $\text{NH} \text{X}^3\Sigma^-$  states (Jarman, 1971). Evidently,  $B_v$  and  $E_v$  values (Table 2) are accurately reproduced from the Klein-Dunham

potential for the two participating states and the orthogonality test (Noise factor) of the wavefunctions is excellent (Jarman, 1971). Our realistic Franck-Condon factors for the  $\Delta v = 0$  sequence are in good agreement with those listed by Smith and Liszt (1971) and Lents (1973) but differ for the  $\Delta v \neq 0$  sequence. The difference is due to different molecular constants used by Lents (1973) and Smith and Liszt (1971) with those listed in Huber and Herzberg (1979). The  $r$ -centroids obtained, using realistic Klein-Dunham potentials for  $\text{A}^3\Pi_1$  and  $\text{X}^3\Sigma^-$  states of NH, agree well for the  $\Delta v = 0$  sequence with those listed by Smith and Liszt (1971). Smith and Liszt (1971) do not list  $r$ -centroids for  $\Delta v \neq 0$  sequence bands and values obtained from a realistic Klein-Dunham potential are erratic. The reason for the erratic behaviour of  $r_{v'v''}$  for  $\Delta v \neq 0$  sequence is not clear to us. For  $\Delta v \neq 0$  bands we have calculated  $r$ -centroids by the graphical method described by Nicholls and Jarman (1956) where they use Morse potentials for the two participating electronic states concerned in an electronic transition. These values are listed in Table 1.

High resolution lifetime measurements, using high-frequency deflection technique (Smith et al., 1976), for individual rotational levels of  $v' = 0$  and  $v' = 1$  for the  $\text{NH} \text{A}^3\Pi_1$  state show that the  $\text{A}^3\Pi_1$  state undergoes pre-dissociations similar to the well known pre-dissociations of the  $\text{A}^2\Sigma^+$  state in OH. Smith et al. (1976) interpret their results as (1) pre-dissociation caused by  $\text{NH}(\text{A}^3\Pi_1, \text{X}^3\Sigma^-)$  interaction via spin-rotation coupling with the ground state (Erman, 1977; Kovacs, 1969), and (2) pre-dissociation due to an  $(\text{A}^3\Pi_1, {}^5\Sigma^-)$  interaction via spin-orbit coupling (Erman, 1977). They further demonstrate that pre-dissociation due to the  $\text{NH}(\text{A}^3\Pi_1, \text{X}^3\Sigma^-)$  interaction is very small and is unmeasurable, whereas, the  $\text{NH}(\text{A}^3\Pi_1, {}^5\Sigma^-)$  interaction is closely analogous to the type of pre-dissociation in OH where a crossing of the discrete by the continuum potential occurs at the outer turning point. For NH the crossing of the perturbing  ${}^5\Sigma^-$  state occurs at  $r_c \simeq 1.36 \text{ \AA}$  with the  $\text{A}^3\Pi_1$  state (see Fig. 7 of Smith et al., 1976). This inter-nuclear crossing distance corresponds to the outer turning point ( $r_{\text{max}} = 1.3598 \text{ \AA}$ ) of the  $v' = 2$  level of the  $\text{NH} \text{A}^3\Pi_1$  state and hence  $v' = 2$  level would follow pre-dissociation, analogous to the OH  $\text{A}^2\Sigma^+$  state, via spin-orbit coupling. We assume that pre-dissociation efficiency for the  $v' = 2$  level is unity.

To our knowledge no calculations of relative populations of NH in the rotation-vibration levels of the ground  $\text{X}^3\Sigma^-$  state are available for 1 AU sun-comet distance. We assume that most of the NH molecules are in the lowest  $N'' = 0$ ,  $J'' = 1$  level of the  $\text{X}^3\Sigma^-$  state. This assumption is in agreement with the strong emissions observed at  $\lambda 3357.9$ ,  $\lambda 3350.8$  and  $\lambda 3354.1$  identified as  $R_1(0)$ ,  ${}^R P_{31}(0)$  and  ${}^R Q_{21}(0)$  lines, respectively, of the 0, 0 band of  $\text{NH}(\text{A}^3\Pi_1 - \text{X}^3\Sigma^-)$ , in several comets (Swings and Haser, 1956). From  $N'' = 0$ ,  $J'' = 1$  of the  $v'' = 0$  level ( $\text{X}^3\Sigma^-$  state of NH) six absorption electronic lines:  $R_1(0)$ ,  ${}^R Q_{21}(0)$ ,  ${}^R P_{31}(0)$ ,  ${}^S R_{21}(0)$ ,  ${}^S Q_{31}(0)$  and  ${}^T R_{31}(0)$  are accessible to a vibrational level in the  $\text{A}^3\Pi_1$  state of NH. With the assumption that  $\Lambda$ -doubling separations for  $v' = 1$  and 2 are the same (at least for small rotation) we have computed the positions of these six absorption lines for the (2, 0) band of the  $\text{NH}(\text{A}^3\Pi_1 - \text{X}^3\Sigma^-)$  transition. The wavelengths in air ( $n_{\text{air}} = 1.000294$ ) of these six electronic rotational lines are listed in Table 3 together with their Hönl-London factors which were calculated using the formulae listed by Schadee (1964) and were normalized according to the prescription of Whiting and Nicholls (1974) and Whiting et al. (1980).

**Table 2.** Turning points ( $R_{\min}$  and  $R_{\max}$ ), eigen-values ( $E_v$ ) and rotational constants ( $B_v$ ) of the  $A^3\Pi_i$  and  $X^3\Sigma^-$  states of NH. Noise factors are about  $0.13 \cdot 10^{-14}$  and  $0.94 \cdot 10^{-13}$  for the  $NH A^3\Pi_i$  and  $NH X^3\Sigma^-$  states, respectively (see the text).  $D_e(A^3\Pi_i) = 21274.60 \text{ cm}^{-1}$  and  $D_e(X^3\Sigma^-) = 27510.20 \text{ cm}^{-1}$  were used in the calculation (Gaydon, A.G.: 1968, *Dissociation Energies*, p. 277; Smith et al., 1976.  $B_v$  and  $E_v$  are in  $\text{cm}^{-1}$ .  $R_{\min}$  and  $R_{\max}$  are in Å. Dev.  $\equiv$  Deviation)

$v$	$B_v$ (calc.)	$B_v$ (obs.)	Dev.	$E_v$ (cal.)	$E_v$ (obs.)	Dev.	$R_{\min}$	$R_{\max}$
<i>NH A<sup>3</sup>Π<sub>i</sub> state</i>								
0	16.3024	16.3018	+0.0006	1590.5615	1590.9500	-0.3885	0.9437	1.1572
1	15.5507	15.5564	-0.0057	4624.5695	4624.9500	-0.3805	0.8882	1.2681
2	14.7751	14.8110	-0.0359	7461.8238	7461.7500	+0.0738	0.8552	1.3598
<i>NH X<sup>3</sup>Σ<sup>-</sup> state</i>								
0	16.3738	16.3748	-0.0010	1623.0585	1621.5500	+1.5085	0.9429	1.1542
1	15.7253	15.7258	-0.0005	4747.7925	4747.1200	+0.6725	0.8868	1.2604
2	15.0694	15.0768	-0.0074	7714.0914	7715.9900	-1.8986	0.8534	1.3462

Experimental spontaneous emission rates ranging from  $2.15 \cdot 10^6 \text{ s}^{-1}$  to  $2.46 \cdot 10^6 \text{ s}^{-1}$  are available (Fink and Welge, 1964; Bennett and Dalby, 1960; Smith and Liszt, 1971; Harrington et al., 1966) for the 0, 0 band of the  $NH(A^3\Pi_i - X^3\Sigma^-)$  transition. We obtain an absorption oscillator strength of  $f_{00} = 7.56 \cdot 10^{-3}$  corresponding to an average spontaneous rate  $A_{00} = 2.237 \cdot 10^6 \text{ s}^{-1}$  of Smith and Liszt (1971), Fink and Welge (1964) and Bennett and Dalby (1960). This  $f_{00}$  is in close agreement with the recommended value  $f_{00} = 7.45 \cdot 10^{-3}$  derived from lifetime studies (Smith and Liszt, 1971). Harrington et al. (1966) from shock tube studies have found a trend of increasing spontaneous emission rates ( $A_{22} > A_{11} > A_{00}$ ) for the  $\Delta v = 0$  sequence of the  $NH(A^3\Pi_i - X^3\Sigma^-)$  transition. Lents (1973) has pointed out this trend of  $A_{v'v''}$  for the  $\Delta v = 0$  sequence as due to the possible overlapping of the measured  $Q$  branches by the  $R$ ,  $P$  and  $Q$  branches of the other vibrational bands. Further, he suggests that  $A_{11}$  and  $A_{22}$  listed by Harrington et al. (1966) are too high. Thus, we have ignored the  $A_{v'v''}$  values of Harrington et al. (1966) in this study.

For (0, 1), (1, 2) and (1, 0) bands, laboratory measurements (Lents, 1973) show spontaneous emission rates

$A_{01} = 0.00561 A_{00}$ ;  $A_{12} = 0.01106 A_{11}$  and  $A_{10} = 0.0380 A_{11}$ , respectively. With  $A_{00} = 2.237 \cdot 10^6 \text{ s}^{-1}$  we obtain  $A_{01} = 1.255 \cdot 10^4 \text{ s}^{-1}$  which corresponds to an  $f_{01}$  value equal to  $5.297 \cdot 10^{-5}$ . No estimates of spontaneous emission rates or absorption oscillator strengths of other bands of  $NH(A - X)$  are

**Table 3.** Wavelengths in air (nm) and Hönl-London factors ( $S_J$ ) of electronic lines arising from  $N'' = 0$ ,  $J'' = 1$ ,  $v'' = 0$  level of the  $X^3\Sigma^-$  state for the (2, 0) band of  $NH(A^3\Pi_i - X^3\Sigma^-)$

Line	Wavelength in air (nm)	$S_J/2J + 1$
$R_1(0)$	280.491	0.6667
$^R Q_{21}(0)$	280.203	0.3333
$^S R_{21}(0)$	279.741	0.3333
$^R P_{31}(0)$	280.048	0.2222
$^S Q_{31}(0)$	279.621	0.3333
$^T R_{31}(0)$	278.918	0.1111

Index of refraction of air = 1.000294 (Pearse and Gaydon, 1976)

available in the literature. Estimates of  $A_{v'v''}$  for other bands can be obtained using the  $r$ -centroid approximation (Larsson, 1983; Hay and Dunning, 1976):

$$A_{v'v''} = |R_e|^2 (\Delta E)^3 q_{v'v''} (1.063 \cdot 10^6 \text{ s}^{-1}) \quad (1)$$

where  $R_e$  is the electronic transition moment expressed in atomic units ( $ea_0$ ),  $\Delta E$  is the energy involved, in eV, for ( $v', v''$ ) and  $q_{v'v''}$  is the Franck-Condon factor; the probability is averaged over initial states and summed over final states for degenerate cases. Usually  $R_e$  is a varying function of inter-nuclear distance ( $R$ ) and, for the  $NH(A^3\Pi_i - X^3\Sigma^-)$  system, the electronic transition moments for N - H distances ranging from 1.50 to 3.00 Bohr are calculated by Hay and Dunning (1976), using polarisation-configuration interaction (POL-CI) wavefunctions. The POL-CI calculations have been shown to yield spectroscopic constants for the valence states of the NH radical in agreement with experiments (see Table V of Hay and Dunning, 1976). The POL-CI electronic transition moments for the  $X^3\Sigma^- \rightarrow A^3\Pi_i$  transition of NH radical can be linearly interpolated for  $1.50 \leq R \leq 3.00$  Bohr by the expression:

$$R_e = 0.653 - 0.196R \quad (2)$$

where  $R$  is in Bohr, and  $R_e$  in atomic units ( $ea_0$ ). Under the  $r$ -centroid approximation ( $R_e \approx R_e(r_{v'v''})$ ) the  $R_e$  of bands are calculated from Eq. (2) and these values are listed in Table 1. For a  $\Delta v = \text{constant}$  sequence, we have from Larsson (1983):

$$\frac{A_{v'v''}}{A_{v'+1, v''+1}} = \left( \frac{v_{v'v''}}{v_{v'+1, v''+1}} \right)^3 \left( \frac{q_{v'v''}}{q_{v'+1, v''+1}} \right) \left( \frac{(R_e)_{v', v''}}{(R_e)_{v'+1, v''+1}} \right)^2 \quad (3)$$

and thus, ( $A_{00}/A_{11} = 1.136$  or  $A_{11} = 1.969 \cdot 10^6 \text{ s}^{-1}$  and ( $A_{11}/A_{22} = 1.165$ ; ( $A_{21}/A_{10} = 6.498$ . Having  $A_{00}$ ,  $A_{11}$ ,  $A_{21}$  and  $A_{22}$  and keeping in mind that  $A_{v'}$  is constant for  $v' = 0, 1$  and 2 (Smith and Liszt, 1971; Dumont and Remy, 1982) we can determine  $A_{v'v''}$  for other bands of ( $2 \times 2$ ) array of  $NH(A^3\Pi_i - X^3\Sigma^-)$  transition. These values are listed in Table 1 together with their respective  $f_{v'v''}$  values determined from the expression:

$$f_{v'v''} = 1.499 \frac{(2 - \delta_{0, A'+A''}) A_{v'v''}}{(2 - \delta_{0, A''}) v_{v'v''}^2} \quad (4)$$

recommended by Larsson (1983). The spontaneous emission rate  $A_{20} = 2.08 \cdot 10^5 \text{ s}^{-1}$  corresponds to an absorption oscillator strength  $f_{20} = 4.907 \cdot 10^{-4}$ .

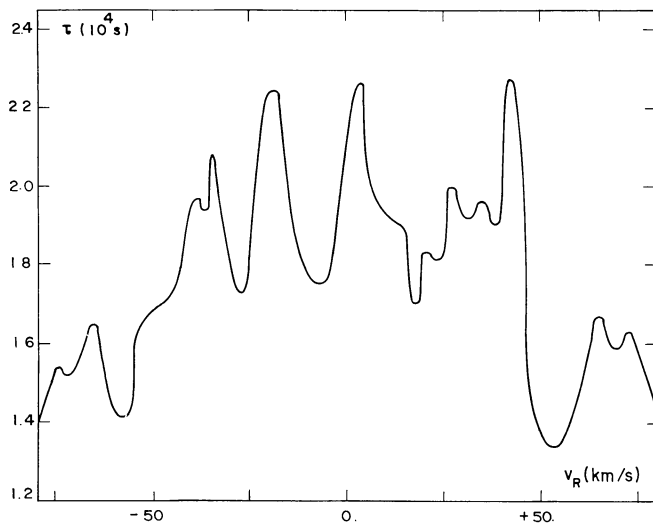
**Table 4.** Photodissociation rates by predissociation of NH through  $A^3\Pi_i$  state at 1 AU as a function of heliocentric radial velocity ( $v$ ) in unit of  $10^{-5} s^{-1}$

$v$ (km s <sup>-1</sup> )	Rate <sup>a</sup> ( $10^{-5} s^{-1}$ )
± 80	6.99 (7.16)
± 70	6.31 (6.47)
± 60	6.86 (7.01)
± 50	7.06 (6.00)
± 40	4.90 (5.19)
± 30	5.17 (5.73)
± 20	5.47 (4.53)
± 10	5.24 (5.59)
0	4.74

$v_+$  is taken positive when the comet is approaching the Sun and,  $v_-$  is negative when the comet is moving away from the Sun. Figure in parenthesis is the rate for  $v_-$

<sup>a</sup> Solar spectrum used in this study is that of Kohl et al. (1978).

Note: Velocity ranges between ± 40 to ± 80 km s<sup>-1</sup> are relevant only for heliocentric distances less than 1 AU, but then the solar flux increases proportional to  $r_h^{-2}$  which has not been taken into account in the rates listed above

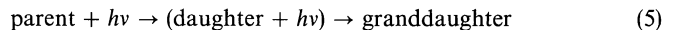


**Fig. 1.** Variation of photodissociation lifetime of NH radical with radial velocity of a comet at sun-comet distance of 1 AU. The ranges between ± 40 to ± 80 km s<sup>-1</sup> are relevant only for heliocentric distances less than 1 AU, but then the solar flux increases proportional to  $r_h^{-2}$  which has not been taken into account in the variation of photodissociation lifetime of NH radical

With  $f_{20}$  (Table 1), Hönl-London factors and wavelengths of the six absorption lines (Table 3) we have calculated the photodissociation rates of the NH molecule for cometary velocities ranging from +80 to -80 km s<sup>-1</sup> when the comet-sun distance is 1 AU. These data are tabulated in Table 4. Figure 1 shows the variation of photochemical lifetime of NH with heliocentric radial velocity from +80 km s<sup>-1</sup> to -80 km s<sup>-1</sup> for a comet 1 AU from the sun.

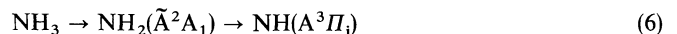
Combi (1978), using Malaise's (1976) absolute sunward and tailward brightness profiles of NH from photometric scans of the coma of comet Bennett (1970 II), has derived NH and its parent(s) diaphragm convolution model scale lengths 1.8 10<sup>5</sup> km and 2.4 10<sup>3</sup> km, respectively, for a heliocentric distance ( $r_h$ ) = 0.664 AU (April 6, 1970 observation). Recently, Cucchiaro and Malaise (1982) have derived NH and its parent(s) dynamic model scale lengths 9.75 10<sup>4</sup> km and 5.2 10<sup>3</sup> km, respectively, with most probable velocity of Maxwellian distribution ~ 0.65 km s<sup>-1</sup> using April 9 and 10, 1970 comet Bennett (1970 II) observations ( $r_h = 0.714$  AU). Festou et al. (1982) by analysing IUE spectrographs of eight comets have come to the conclusion that: (a) all previous determinations of the NH scale lengths are questionable; (b) sunward NH profiles should be preferred to antisolar profiles; and (c) the NH scale length in comets cannot be greater than 1.4 10<sup>5</sup> km at  $r_h = 1$  AU. Comparisons of sunward NH diaphragm convolution (see Fig. 4 of Combi, 1978) and dynamical model brightness profiles (see Fig. 8 of Cucchiaro and Malaise, 1982) with those of NH observed profiles in comet Bennett (1970 II) show a preference for the diaphragm convolution model over the dynamical model. If the NH parent scale length varies as  $r_h^2$  (as for CN and C<sub>3</sub>, Newburn and Spinard, 1984) the diaphragm convolution model NH parent scale length of April 6, 1970 comet Bennett (1970 II) observation ( $r_h = 0.664$  AU) would be about 5.4 10<sup>3</sup> km for  $r_h = 1$  AU.

For NH, C<sub>2</sub> and C<sub>3</sub> radicals observed in comets, Jackson (1982) has proposed the following scheme:



The analysis of some recent cometary data has supported the above suggestion (Yamamoto, 1980). NH<sub>3</sub>, N<sub>2</sub>H<sub>4</sub> and HNCO molecules have been suggested in the literature as potential parents of NH (Cucchiaro and Malaise, 1982; Jackson, 1976). Recent probable detection of NH<sub>3</sub>(3,3) in comet 1983d (Iras-Araki-Alcock) by radio observations (Altenhoff et al., 1983) shows a preference of NH<sub>3</sub> over N<sub>2</sub>H<sub>4</sub> and HNCO molecules. A production rate of 6 10<sup>26</sup> molecules s<sup>-1</sup> for NH<sub>3</sub> has been derived for comet 1983d and suggests that NH<sub>3</sub> forms roughly 6% of the gases sublimating from the nucleus. The total NH<sub>3</sub> molecular column density averaged over the beam has been found to be equal to 27.6 ± 1.0 10<sup>12</sup> cm<sup>-2</sup> for comet 1983d (Altenhoff et al. 1983).

For an excitation wavelength,  $\lambda \leq 193$  nm, the dissociation of NH<sub>3</sub> may occur:



with thermodynamic thresholds 5.7 eV for parent (NH<sub>3</sub>) to daughter (NH<sub>2</sub>) and 6.3 eV for daughter (NH<sub>2</sub>) to granddaughter (NH) (Distefano et al., 1977; Donnelly et al., 1979). A very small amount of excess energy is available to the fragments, and yet NH(A<sup>3</sup>Π<sub>i</sub>) is formed with rotational energy (Haak and Stuhl, 1984; Hofzumahaus et al., 1985, unpublished). The mode of re-

action (6) is possible but the quantum yield of  $\text{NH}_2(\tilde{A}^2A_1)$  is very low, of the order of a few percent (DiStefano et al., 1977; Donnelly et al., 1979). The hydrogen atoms released in the reaction (6) would have an average velocity of about  $8 \text{ km s}^{-1}$  with respect to  $\text{NH}_3$ . Because the  $\text{NH}_3$  abundance in comets is only 6% or less, reaction (6) would be a weak source of low velocity H-atoms (about  $8 \text{ km s}^{-1}$ ) found in several comets (Keller, 1976; Drake et al., 1976; Keller and Thomas, 1975; Opal and Carruthers, 1977; Festou et al. 1979; Keller and Meier, 1980; Weaver et al. 1981a, 1981b; Festou et al., 1983).

The heliocentric and geocentric distances for comet 1983d were about 1 AU and 0.03 AU, respectively, for May 11, 1983 observation (Altenhoff et al., 1983; Walker et al., 1984). For  $r_h = 1 \text{ AU}$ , Huebner and Carpenter (1979) have derived a total photochemical lifetime of  $5.65 \cdot 10^3 \text{ s}$  for  $\text{NH}_3$  against solar photon flux. Thus, the production rate of  $6 \cdot 10^{26} \text{ NH}_3 \text{ molecules s}^{-1}$  corresponds to  $\sim 10^{30} \text{ NH}_3$  molecules for comet 1983d. With our NH photochemical lifetime which varies with the radial velocity of the comet and, considering that  $\text{NH}_3$  is the main source of the NH radical [ $(\text{NH}_3/\tau_{\text{NH}_3}) \approx (\text{NH}/\tau_{\text{NH}})$ ], we derive  $\sim 10^{30} \text{ NH}$  molecules for a comet at  $r_h = 1 \text{ AU}$ . Further, if we assume  $1 \text{ km s}^{-1}$  outstreaming velocity for  $\text{NH}_3$  (as is usually the case in a Haser model) the above photochemical lifetime, i.e.  $5.65 \cdot 10^3 \text{ s}$ , corresponds to a  $\text{NH}_3$  scale length of  $5.65 \cdot 10^3 \text{ km}$  in a comet at 1 AU from the sun. This  $\text{NH}_3$  scale length correlates very well with the above diaphragm convolution model NH parent scale length reduced to 1 AU for comet Bennett (1970 II).

### 3. Velocity distribution

Photodissociation of NH by absorption of solar photons of energy 4.42 eV would result in N and H atoms in their respective ground states:  $\text{N}(^4S_{3/2}^0)$  and  $\text{H}(^2S_{1/2})$ . The dissociation energy of NH molecule in its ground state is about 3.47 eV and excess energy of the order of 1 eV would result in a velocity distribution of about  $15 \text{ km s}^{-1}$  and  $1 \text{ km s}^{-1}$  for hydrogen and nitrogen atoms, respectively, with respect to the parent NH molecule. The derived high velocity of H-atoms is consistent with the cometary hydrogen atoms of velocity in the  $15\text{--}25 \text{ km s}^{-1}$  range (Festou et al., 1983).

### 4. Conclusions

The oscillator strength of the (2, 0) band ( $f_{20}$ ) of the  $\text{NH}(A^3\Pi_1 - X^3\Sigma^-)$  transition is not known. The photodissociation rates of NH (Table 4) through the  $A^3\Pi_1$  state are based on the value (see above)  $f_{20} = 4.907 \cdot 10^{-4}$ . If one finds  $f_{20} = y$  (say), the rates corresponding to  $f_{20} = y$  would be (rates of table 4/ $4.907 \cdot 10^{-4}$ ) $y$ . Photodissociations of  $\text{NH}_3$  and NH molecules produce low (about  $8 \text{ km s}^{-1}$ ) and high velocity (about  $15 \text{ km s}^{-1}$ ) components of H-atoms and are weak additional sources for H-atoms as found in several comets. The diaphragm convolution model scale length of NH parent for comet Bennett (1970 II) scaled to  $r_h = 1 \text{ AU}$  when compared with the  $\text{NH}_3$  scale length ( $r_h = 1 \text{ AU}$  and assuming  $1 \text{ km s}^{-1}$  as outstreaming velocity from nucleus of the comet) shows that  $\text{NH}_3$  is probably the parent of the NH radical.

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### References

- A'Hearn, M.F. in 'Comets' ed. by L.L. Wilkening, The University of Arizona Press, Tucson, AZ. (1982) and other references cited therein
- Arpigny, C.: 1965, *Ann. Rev. Astron. Astrophys.* **3**, 351
- Altenhoff, W.J., Batrla, W., Huchtmeier, W.K., Schmidt, J., Stumpff, P., Walmsley, M.: 1983, *Astron. Astrophys.* **125**, L19
- Bennett, R.G., Dalby, F.W.: 1960, *J. Chem. Phys.* **32**, 1716
- Combi, M.R.: 1978, *Astron. J.* **83**, 1459
- Code, A.D., Savage, B.D.: 1972, *Science*, **177**, 213
- Cucchiari, A., Malaise, D.: 1982, *Astron. Astrophys.* **114**, 102
- Crutcher, R.M., Watson, W.D.: 1976, *Astrophys. J.* **209**, 778
- Donnelly, V.M., Baronavski, A.P., McDonald, J.R.: 1979, *Chem. Phys.* **43**, 27
- Douglas, A.E., Elliott, G.A.: 1965, *Can. J. Phys.* **43**, 496
- DiStefano, G., Lenzi, M., Margani, A., Nguyen Xuan, C.: 1977, *J. Chem. Phys.* **67**, 3832
- Dixon, R.N.: 1959, *Can. J. Phys.* **37**, 1171
- Drake, J.F., Jenkins, E.B., Bertaux, J.L., Festou, M.C., Keller, H.U.: 1976, *Astrophys. J.* **209**, 302
- Dumont, M.N., Remy, F.: 1982, *Spectrosc. Letters* **15**(9), 699
- Erman, P.: 1977, *Phys. Scripta* **16**, 60
- Fink, E., Welge, K.H.: 1964, *Z. Naturf.* **A19**, 1193
- Funke, G.: 1935, *Z. Phys.* **96**, 787
- Funke, G.: 1936, *Z. Phys.* **101**, 104
- Festou, M.C., Feldman, P.D., Weaver, H.A.: 1982, *Astrophys. J.* **256**, 331
- Festou, M.C., Keller, H.U., Bertaux, J.L., Barker, E.S.: 1983, *Astrophys. J.* **265**, 925 (and other references cited therein)
- Festou, M.C., Jenkins, E.B., Keller, H.U., Barker, E.S., Bertaux, J.L., Drake, J.F., Upson, W.L.: 1979, *Astrophys. J.* **232**, 318
- Grevesse, N., Sauval, A.J.: 1973, *Astron. Astrophys. J.* **27**, 29
- Giguere, P.T., Huebner, W.F.: 1978, *Astrophys. J.* **223**, 638
- Haak, H.K., Stuhl, F.: 1984, *J. Phys. Chem.* **88**, 2201
- Harrington, J.A., Modica, A.P., Libby, D.R.: 1966, *JQSRT* **6**, 799
- Hay, P.J., Dunning, Jr., T.H.: 1976, *J. Chem. Phys.* **64**, 5077
- Huber, K.P., Herzberg, G.: 1979, *Constants of Diatomic Molecules* Van Nostrand Reinhold Co., NY, p. 456
- Huebner, W.F., Carpenter, C.W.: 1979, Los Alamos Scientific Lab., LA-8085-MS, Los Alamos, New Mexico 87545
- Jackson, W.M.: 1982, in *Comets*, ed. L.L. Wilkening, Univ. of Arizona Press, AZ
- Jarmain, W.R.: 1971, *JQSRT* **11**, 421
- Jackson, W.M.: 1976, *J. Photochem.* **5**, 107
- Kerns, B., Duncan, A.B.F.: 1972, *Astrophys. J.* **172**, 331
- Keller, H.U.: 1976, *Space Sci. Rev.* **18**, 641
- Keller, H.U., Thomas, G.E.: 1975, *Astron. Astrophys.* **39**, 7
- Keller, H.U., Meier, R.R.: 1980, *Astron. Astrophys.* **81**, 210
- Kohl, J.L., Parkinson, W.H., Kurucz, R.L.: 1978, *Center and Limb Solar Spectrum in High Resolution 225.2 nm to 319.6 nm*, Harvard Smithsonian Center for Astrophysics, Cambridge, MA
- Kovacs, I.: 1969, *Rotational Structure in the Spectra of Diatomic Molecules*
- Larsson, M.: 1983, *Astron. Astrophys.* **128**, 291
- Litvak, M.M., Kuiper, E.N.R.: 1982, *Astrophys. J.* **253**, 622
- Lambert, D.L., Jeffrey, A.B., Hinkle, K.H., Johnson, H.R.: 1984, *Astrophys. J.* **284**, 223
- Lambert, D.L., Beer, R.: 1972, *Astrophys. J.* **177**, 541
- Lents, J.M.: 1973, *JQSRT* **13**, 297

- Malicet, J., Brion, J., Guenebaut, H.: 1970, *J. Chim. Phys. Phys. Chim. Biologique*, Paris **67**, 25
- Murai, T., Simauchi, M.: 1966, *Sci. Light* **15**, 48
- Malaise, D.J.: 1976, in *The Study of Comets* eds B. Donn, M. Mumma, W. Jackson, M.F. A'Hearn, R. Harrington, NASA-SP-393, p. 740
- Newburn, Jr., R.L., Spinard, M.: 1984, *Astron. J.* **89**, 289
- Nicholls, R.W., Jarmain, W.R.: 1956, *Proc. Phys. Soc.* **A69**, 253
- Opal, C.B., Carruthers, G.R.: 1977, *Icarus* **31**, 503
- Pearse, R.W.B., Gaydon, A.G.: 1976, *The Identification of Molecular Spectra*, 4th edn., Chapman and Hall, London, p. 391
- Roach, R.E.: 1939, *Astrophys. J.* **89**, 99
- Smith, W.H., Liszt, H.S.: 1971, *JQSRT* **11**, 45
- Swings, P., Elvey, C.T., Babcock, H.W.: 1941, *Astrophys. J.* **94**, 320
- Swings, P., Haser, L.: 1956, *Atlas of Representative Cometary Spectra*, Louvain Ceuterick Press
- Snyder, L.E., Buhl, D.: 1972, *Astrophys. J.* **177**, 619
- Schadee, A.: 1964, *Bull. Astron. Inst. Neth.* **17**, 311
- Smith, W.H., Brzozowski, J., Erman, P.: 1976, *J. Chem. Phys.* **64**, 4628
- Weaver, H.A., Feldman, P.D., Festou, M.C., A'Hearn, M.F.: 1981a, *Astrophys. J.* **251**, 809
- Weaver, H.A., Feldman, P.D., Festou, M.C., A'Hearn, M.F., Keller, H.U.: 1981b, *Icarus* **47**, 449
- Whiting, E.E., Nicholls, R.W.: 1974, *Astrophys. J. Suppl.* **27**, 1
- Whiting, E.E., Schadee, A., Tatum, J.B., Hougen, J.T., Nicholls, R.W.: 1980, *J. Mol. Spectrosc.* **80**, 249
- Walker, R.G., Aumann, H.H., Davies, J., Green, S., De Jong, T., Houck, J.R., Soifer, B.T.: 1984, *Astrophys. J.* **278**, L11
- Yamamoto, T.: 1980, Inst. Space Aeronautical Sci., University of Tokyo, RN 133: 1-24