

NH₂ FLUORESCENCE EFFICIENCIES AND THE NH₃ ABUNDANCE IN COMET HALLEY

STEPHEN TEGLER AND SUSAN WYCKOFF

Department of Physics, Arizona State University

Received 1988 October 31; accepted 1989 January 16

ABSTRACT

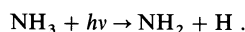
If NH₃ is the dominant source of the NH₂ observed in comet spectra, then the ammonia abundance can in principle be accurately determined. Fluorescence efficiencies for the (0, v_2 , 0) → (0, 0, 0) progression of NH₂ bands in the \tilde{A}^2A_1 - \tilde{X}^2B_1 system are calculated for NH₂ bands likely to be observed in the 4500–8200 Å region of comets. Our results differ from previous determinations of the NH₂ band fluorescence efficiencies by factors in the range 1.4–5.9, leading to significant changes in previously reported NH₂ production rates in comets. A recalculation of the ammonia-to-water abundance ratio in comet Halley gives NH₃/H₂O ~ 0.5% ± 0.2%, in better agreement with the *Giotto* ion mass spectrometer results of Allen and coworkers.

Subject headings: abundances — comets — molecular processes — transition probabilities

I. INTRODUCTION

Because comets represent physically and chemically unprocessed primordial solar nebula material, cometary abundances provide significant constraints on models of the early solar system (Lewis and Prinn 1980; Prinn and Fegley 1981, 1988). In particular, the NH₃ abundance in comets is an especially sensitive indicator of primordial conditions and the extent of chemical processing in the early solar nebula (Prinn and Fegley 1988; Lunine 1989; Fegley and Prinn 1989).

Ammonia has not yet been directly observed in comets. The *Giotto* mass spectrometer results for comet Halley led to a model-dependent and somewhat controversial determination of the NH₃ abundance (Allen *et al.* 1987; Marconi and Mendis 1988; Ip 1989). Consequently, at present the most direct way of determining the NH₃ abundance in comet Halley, and the only means of studying the ammonia abundances in a sample of comets, is to study the emission spectrum of NH₂, the primary photodissociation product of NH₃. Previous ground-based determinations of the NH₃ abundances in comets have been based on the spectroscopy of NH₂ in the visible region of several comets (A'Hearn, Hanisch, and Thurber 1980; A'Hearn 1982; Johnson, Fink, and Larson 1984; Wyckoff *et al.* 1988). The photolytic reaction for photodissociation of ammonia,



has a 95% branching ratio (Allen *et al.* 1987). Therefore, provided that NH₃ is the dominant source of NH₂, the abundance of NH₂ is essentially a direct measurement of the abundance of NH₃ in comets.

The first observation of NH₂ bands in comets was by Swings, McKellar, and Minkowski (1943). Higher resolution spectra confirmed the NH₂ identification (Greenstein and Arpigny 1962) shortly after a comprehensive laboratory rotational analysis of the NH₂ spectrum was completed by Dressler and Ramsay (1959). This analysis was later extended to longer wavelengths by Johns, Ramsay, and Ross (1976). The cometary NH₂ features arise from an $\tilde{A}^2A_1 \rightarrow \tilde{X}^2B_1$ transition which has a long progression of bands extending from 4500 to 9500 Å with alternating Σ and Π subbands. Sixteen bands in the bending mode (0, v_2 , 0) → (0, 0, 0) progression have been identified in laboratory spectra with upper vibronic levels $v_2' = 3$ –18. (Dressler and Ramsay 1959; Johns, Ramsay, and

Ross 1976). In comets NH₂ bands arising from the levels $v_2' = 5$ –14 have been observed in coma spectra. Transitions involving the stretch mode, v_1 , have been observed in laboratory fluorescence spectra (i.e., Halpern *et al.* 1975), but not in comets. Here we designate an NH₂ band by its bending vibronic quantum numbers, $v_2'-v_2''$, as an abbreviation of the generalized notation (v_1', v_2', v_3') → (v_1'', v_2'', v_3'') for a transition between the vibronic levels in the upper and lower electronic states.

For fluorescent scattering by solar radiation, the abundance of NH₂ in a comet can be related to the observed emission band flux by a fluorescence efficiency or *g*-factor. For an optically thin gas, the integrated flux of an NH₂ band is related to its column density by

$$N = \frac{4\pi F}{g\Omega}, \quad (1)$$

where *N* is the column density in molecules cm⁻², *F* is the integrated band flux in photons cm⁻² s⁻¹ Å⁻¹, Ω is the solid angle (in steradians) subtended by the observing aperture at the comet, and *g* is the band *g*-factor or fluorescence efficiency in photons s⁻¹ molecule⁻¹ of a particular molecular transition.

A previous calculation of NH₂ *g*-factors (A'Hearn 1982) used the NH₂ experimental lifetimes of Halpern *et al.* (1975). Here we present calculations of band NH₂ *g*-factors based on more recent laboratory data (Mayama, Hiraoka, and Obi 1984) and on the theoretical band transition probabilities of Jungen, Hallen, and Merer (1980). We extend the calculation of the NH₂ fluorescence efficiencies to include the bands (15–0) Σ, (14–0) Π, (13–0) Σ, (6–0) Π, (5–0) Σ, (4–0) Π, and (3–0) Σ. The fluorescence efficiencies given here are intended to be particularly useful for interpreting the extensive ground-based and spacecraft spectra of comet Halley (e.g., Krasnopolsky *et al.* 1986; Magee-Sauer 1989; Wyckoff *et al.* 1988). We also present a rediscussion of the ammonia abundance derived from NH₂ bands observed in comet Halley.

II. NH₂ FLUORESCENCE EFFICIENCIES

The excitation mechanism for the observed NH₂ emission bands in comets is probably dominated by resonance fluorescence. The fluorescence excitation rate for a molecule in

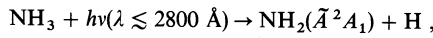
ground state to an upper vibronic level, v'_2 , is given by

$$J_f = \pi F_{\odot} \left[\frac{\pi e^2}{mc^2} \right] \lambda^2 f_{0v'_2}, \quad (2)$$

where πF_{\odot} is the solar irradiance, λ is the wavelength of the band origin, and $f_{0v'_2}$ is the band oscillator strength. For a comet 1 AU from the Sun, $J_f \sim 4 \times 10^{-3} \text{ s}^{-1}$ for a typical NH_2 band, which corresponds to a fluorescence time scale $\tau_f \sim 3$ minutes.

Collisional excitation of the $\text{NH}_2 \tilde{A}^2A_1$ state cannot be significant, since an excitation energy $\sim 2 \text{ eV}$ is required which corresponds to molecular velocities in the coma $v_{\text{rms}} \sim 3.4 \text{ km s}^{-1}$. Such velocities are a factor ~ 10 times larger than the *in situ* measurements indicated in the collision region of the coma of comet Halley (Lämmerzahl *et al.* 1987).

Prompt emission from the photodissociation process,



could also produce the observed bands in comet spectra, provided that NH_3 is a dominant source of the NH_2 . Prompt emission in a comet 1 AU from the Sun occurs for NH_2 at a rate $J_{\text{PE}} = J_{\text{PD}}(\text{NH}_3)y$, where the total photodissociation rate is $J_{\text{PD}}(\text{NH}_3) \sim 2 \times 10^{-4} \text{ s}^{-1}$ (Huebner 1988) and the fractional yield into the $\text{NH}_2 \tilde{A}^2A_1$ state is $y \sim 0.1$ (Suto and Lee 1983), giving $J_{\text{PE}} \sim 2 \times 10^{-5} \text{ s}^{-1}$, which corresponds to a time scale $\tau_{\text{PE}} \sim 14 \text{ hr}$. The ratio of the competing excitation rates, $J_f/J_{\text{PE}} \sim 200$ for NH_2 , then clearly indicates that fluorescence dominates prompt emission as an excitation mechanism in a comet. Since both rates have the same solar distance dependence, we conclude that resonance fluorescence is most probably the dominant excitation mechanism of NH_2 at any heliocentric distance, and we shall assume here that excitation of NH_2 in a comet is entirely due to resonance fluorescence.

We also note that the lifetime of an NH_2 molecule in the upper \tilde{A} electronic state, $\sim 10 \mu\text{s}$, is negligibly small compared with the time scale for absorption of a solar photon, 175 s. Thus at any time virtually all NH_2 molecules in a comet are in their lowest electronic states. Moreover, in the absence of collisions pure vibrational spontaneous de-excitation occurs on a time scale of $\lesssim 1 \text{ s}$, so that the NH_2 radicals in a comet are also vibrationally relaxed. An upper limit on the neutral gas temperature measured in the coma of comet Halley, a moderately productive comet, at a distance from the nucleus $\sim 10^3 \text{ km}$ was $T \lesssim 300 \text{ K}$ (Lämmerzahl *et al.* 1987), corresponding to a collisional excitation energy $E \sim 0.02 \text{ eV}$. Since $\sim 0.1 \text{ eV}$ is required to collisionally excite NH_2 to the first vibrational state in the ground electronic state, collisions would have a marginally significant effect on redistributing the populations of the low-lying vibrational levels within the ground electronic state. Here we neglect this small effect. Fluorescence equilibrium at a distance from the Sun of 1 AU is established on a time scale of minutes. Thus, in fluorescence equilibrium, to a very good approximation, the NH_2 molecules in the coma of a comet are in their lowest electronic and vibrational states.

In this calculation we consider the NH_2 molecule to be initially in the lowest vibrational level, $v'_2 = 0$, of the ground electronic state, \tilde{X}^2B_1 . The molecule absorbs a photon of wavelength $\lambda_{v'_20}$, which results in excitation to the upper electronic state, \tilde{A}^2A_1 , and an associated upper vibrational level, v'_2 . After a characteristic time $\tau_{v'_20}$ the molecule decays to \tilde{X}^2B_1 and $v'_2 = 0$, emitting a photon with wavelength $\lambda_{v'_20}$. Halpern *et al.* (1975) observed the laboratory fluorescence

spectrum of NH_2 resulting from excitation of the $2_{1,2}-2_{0,2}$ transition in the Π and Φ subbands of the $v'_2 = 10$ vibronic level of the \tilde{A}^2A_1 state. Downward transitions into the (1, 0, 0), (0, 2, 0), (0, 1, 0), and (0, 0, 0) levels of the \tilde{X}^2B_1 state produced observable emission features in the spectral regions 7000, 6850, 6200–6300, and 5800–6000 \AA , respectively. In fluorescence equilibrium the intensity of the (0, 10, 0) \rightarrow (0, 0, 0) Π transition in laboratory spectra was observed to be 10 times greater than the intensities of transitions into the (0, 2, 0), (0, 1, 0), or (1, 0, 0) levels of the \tilde{X}^2B_1 state (Halpern *et al.* 1975). Transitions from the upper vibronic level $v'_2 = 10$ to the ground-state levels $v'_2 > 2$ would be expected to have even smaller intensities because of the λ^{-3} dependence of the downward transitions. As a check on the branching of downward transitions to the stretching mode levels, v'_1 , in the \tilde{X}^2B_1 state, we have examined spectra of comets Halley and Crommelin for the (0, 10, 0) \rightarrow (1, 0, 0) band at 7000 \AA . We find that the intensity of this NH_2 band must be $\lesssim 5\%$ of the intensity of the (0, 10, 0) \rightarrow (0, 0, 0) transition at 5700 \AA . Therefore we consider here only bending mode transitions from the vibronic levels in the upper \tilde{A}^2A_1 electronic state which branch into the ground electronic state \tilde{X}^2B_1 v'_2 levels. We include branching from the upper electronic state v'_2 levels into all v'_2 levels in the lower electronic state which lie at energies below the v'_2 level, and we estimate the error induced in the g -factors by ignoring downward transitions into the v'_1 and v'_3 levels to be less than a few percent at most.

The g -factor which relates the excitation rate of an NH_2 radical with the probability for downward transitions into the $v'_2 = 0$ levels of the lower electronic state is given by (cf. Chamberlain and Hunten 1987)

$$g_{v'_20} = \left[\frac{\pi e^2}{mc^2} \right] \frac{\pi F_{\odot}(\lambda_{v'_20})}{r^2} \lambda_{v'_20}^2 f_{v'_20} \tilde{\omega}_{v'_20}, \quad (3)$$

where r is the heliocentric distance of the comet in AU, $\pi F_{\odot}(\lambda_{v'_20})$ is the solar irradiance at 1 AU at the wavelength of the exciting transition, $\lambda_{v'_20}$, in photons $\text{cm}^{-2} \text{ s}^{-1} \text{ \AA}^{-1}$, $f_{v'_20}$ is the absorption oscillator strength of the band, $\pi e^2/mc^2 = 8.85 \times 10^{-21} \text{ cm}^2 \text{ \AA}^{-1}$, and $\tilde{\omega}_{v'_20}$ is the albedo for a single scattering or the branching ratio for de-excitation into the lower state of the observed transition, given by

$$\tilde{\omega}_{v'_20} = A_{v'_20} \left(\sum_{v'_2} A_{v'_2v'_2} \right)^{-1}. \quad (4)$$

The solar irradiance used in calculating the g -factors was averaged over wavelength bandwidths 10–20 \AA and was taken from Tables Xa and Xb of Neckel and Labs (1984), which tabulate the solar spectrum, with terrestrial absorption features removed, in units of vacuum wavelength.

The oscillator strengths and the branching ratios were obtained from data given by Jungen, Hallen, and Merer (1980), who computed the bending mode vibronic energy levels and relative band intensities for the $\tilde{A}^2A_1-\tilde{X}^2B_1$ transition of NH_2 . Their calculation included orbital angular momentum coupling between the two electronic states. Comparison of the calculated and experimental NH_2 spectra shows that the vibronic coupling is well reproduced (Jungen, Hallen, and Merer 1980). Moreover, the experimental and theoretical lifetimes agree to within 25% (Jungen, Hallen, and Merer 1980; Yamaya, Hiraoka, and Obi 1984). Because of this good agreement, together with the fact that the calculations of the relative transition moments include the entire matrix of possible

branching transitions in NH₂, we used the calculations of Jungen *et al.* to compute the branching ratios and the oscillator strengths for NH₂. The relative total transition rate for a vibronic level in the upper electronic state as given by Jungen *et al.* is

$$\sum_{v''_2} a_{v'_2 v''_2} = \frac{4h^3}{3m_e^2 e^2} \sum_{v''_2} v_{v'_2 v''_2}^3 \left\langle v'_2 \left| \sin \left(\frac{\rho}{2} \right) \right| v''_2 \right\rangle^2, \quad (5)$$

where h is Planck's constant, m_e is the mass of the electron, e is the electrostatic charge of an electron, $v_{v'_2 v''_2}$ is the wavenumber for the observed transition as given in Table 3 of Jungen *et al.*, and $\langle v'_2 | \sin(\rho/2) | v''_2 \rangle$ is the relative vibronic transition moment. The absolute total transition rate out of the upper level v'_2 in the upper electronic state is then given by

$$\sum_{v''_2} A_{v'_2 v''_2} = \left| \frac{\mu_e^{(0)} m_e e}{\hbar^2} \right|^2 \sum_{v''_2} a_{v'_2 v''_2}, \quad (6)$$

where the square of the electronic transition moment, $|\mu_e^{(0)} m_e e / \hbar^2|^2$, in atomic units is taken from an *ab initio* calculation (Peyerimhoff and Buenker 1981) to be 0.1, which gives calculated lifetimes,

$$\tau_{v'_2} = \left(\sum_{v''_2} A_{v'_2 v''_2} \right)^{-1},$$

in very good agreement with the experimental lifetimes as discussed by Jungen, Hallen, and Merer (1980). Thus, to determine the total relative transition rates for each upper vibronic level from equation (5), we read the summed transition moments times the frequency factor, $\sum_{v''_2} v_{v'_2 v''_2}^3 \langle v'_2 | \sin(\rho/2) | v''_2 \rangle^2$, directly from Table 9 of Jungen *et al.*, and calculated $\sum_{v''_2} a_{v'_2 v''_2}$ from equation (5). The total absolute transition rate could then be calculated from equation

(6), where $\sum_{v''_2} A_{v'_2 v''_2} = 0.1 \sum_{v''_2} a_{v'_2 v''_2}$. The relation between the bent, v_b , and linear, v_l , molecular vibrational bending quantum numbers is

$$v_l = 2v_b + |l|, \quad (7)$$

where l is the vibrational angular momentum quantum number. The correspondence between the bent and linear nomenclature can also be determined from Table 10 of Jungen *et al.* The summations, $\sum_{v''_2}$, include all permitted transitions from the upper electronic state to vibrational levels of the \tilde{X}^2B_1 state which occur at $E_{v''_2} < E_{v'_2}$.

To evaluate the rates $A_{v'_2 v''_2}$ for individual transitions $v'_2 \rightarrow v''_2$, we used the relative vibronic transition moments, $\langle v'_2 | \sin(\rho/2) | v''_2 \rangle$, for the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ transition of NH₂ given in Table 7 of Jungen, Hallen, and Merer (1980). The absolute transition rates were then calculated from

$$A_{v'_2 v''_2} = (0.1) \frac{4h^3}{3m_e^2 e^2} v_{v'_2 v''_2}^3 \left\langle v'_2 \left| \sin \left(\frac{\rho}{2} \right) \right| v''_2 \right\rangle^2, \quad (8)$$

where the band origin wavenumbers were taken from Table 3 of Jungen *et al.* The branching ratios were then calculated from equation (4) and are listed in Table 1.

Since the sum of the rotational transitions over each band was not included in the relative transition moments given by Jungen, Hallen, and Merer (1980), the table entries for the II subbands were averaged. The selection rule for the observed NH₂ bands is $\Delta K = \pm 1$. For the Σ subbands $v''_2(\text{bent}) = 0$, while $K' = 0$ and $K'' = +1$. For the II subbands $v''_2(\text{bent}) = 1$ and $K' = 1$, while there are two allowed transitions to the lower level, namely, $K'' = 0$ and 2. Thus there were two transition moments listed for each II subband, which in each case were averaged to weight the rotational transitions properly, as suggested by Jungen *et al.*

TABLE 1

NH₂ FLUORESCENCE EFFICIENCIES AT $r = 1$ AU

NH ₂ ($v'_2 - v''_2$)	$\pi F_{\odot}(\lambda_{v'_2 0})^b$ $\times 10^{13}$	$\lambda_{v'_2 0}$ (Å)	$f_{v'_2 0}$ $\times 10^{-4}$	$\bar{\omega}_{v'_2 0}$	$g_{v'_2 0}^b$ $\times 10^{-3}$	$g_{v'_2 0}^c$ $\times 10^{-3}$	Swings Effect ^d
(3-0) Σ	4.55	8159	0.38	0.208	0.21	...	b
(4-0) Π	4.63	7935	0.36	0.256	0.24	...	a
(5-0) Σ	4.85	7356	1.36	0.422	1.33	...	a
(6-0) Π	4.95	6988	1.60	0.537	1.84	...	a
(7-0) Γ	4.96	7106	1.53	0.428	1.45	...	a
(7-0) Σ	5.20	6624	3.09	0.652	4.07	5.83	a
(8-0) Π	5.30	6312	3.67	0.721	4.95	17.0	a ^e
(9-0) Σ	5.44	5982	4.64	0.750	6.00	9.42	b
(9-0) Δ	5.33	6060	3.89	0.747	5.03	...	a
(10-0) Π	5.23	5704	4.83	0.728	5.30	8.58	a ^f
(11-0) Σ	5.14	5418	4.83	0.647	4.17	7.61	a
(12-0) Π	4.33	5182	4.30	0.548	2.43	14.4	a ^e
(13-0) Σ	4.70	4935	3.60	0.418	1.52	...	b
(14-0) Π	4.78	4726	2.61	0.313	0.77	...	a ^e
(15-0) Σ	4.80	4514	1.97	0.205	0.35	...	a

^a Units: photons $\text{cm}^{-2} \text{s}^{-1} \text{Å}^{-1}$ at 1 AU.

^b Units: photons s^{-1} molecules $^{-1}$ at 1 AU. This calculation.

^c Units: photons s^{-1} molecules $^{-1}$ at 1 AU (A'Hearn 1982).

^d The rating "a" indicates a $-30 \text{ km s}^{-1} < \dot{r} < +30 \text{ km s}^{-1}$ Swings effect on band g -factor $< 25\%$. The rating "b" indicates that for $-30 \text{ km s}^{-1} < \dot{r} < +30 \text{ km s}^{-1}$ there can be a radial velocity which gives rise to at least one wavelength coincidence with a Fraunhofer line, causing a reduction of the band g -factor by $>25\%$.

^e See text.

^f Perturbation gives rise to significant discrepancy between experimental and calculated lifetimes in the $v'_2 = 10$ state. However, see Mayama, Hiraoka, and Obi 1984.

To determine the oscillator strengths from the absolute transition rates calculated from equation (8) for the NH_2 bands, we used the relation (e.g., Lutz 1987)

$$f_{v'v''} = \frac{1.499(G'/G'')A_{v'v''}}{v_{v'v''}^2}, \quad (9)$$

where G'/G'' is the ratio of the upper and lower state electronic statistical weights, which for the NH_2 $\tilde{A}^2A_1-\tilde{X}^2B_1$ transition is unity. The vacuum wavenumbers of the band origins, $v_{v'v''}$, in cm^{-1} were taken from Table 3 of Jungen, Hallen, and Merer (1980), and the absolute transition rates, $A_{v'v''}$, were determined from equation (8) as discussed above. The f -values for each band are listed in Table 1.

Each NH_2 band observed in comet spectra consists of lines arising from ro-vibronic levels $N' \lesssim 4$. Hence each band consists of less than six emission lines with sufficient strength to contribute significantly to the band. We have examined a high-resolution (0.005 Å) solar spectrum (Kurucz 1985) to assess the influence of the Swings effect (Swings 1941) on the band g -factors calculated here. Because of the orbital motion of the comet and the gas outflow from the nucleus, the NH_2 molecules have a net radial component of motion with respect to the Sun that imposes a Doppler shift on the excitation wavelength of the solar flux. For net motion of the NH_2 molecules away from the Sun, each NH_2 molecule is in effect excited by solar flux to the ultraviolet of the rest excitation wavelength. The typical heliocentric radial velocity component of a comet is in the range $\sim \pm 30 \text{ km s}^{-1}$ corresponding to Doppler shifts of $\pm 0.45 \text{ \AA}$ for the 15-0 NH_2 band at 4514 Å, and $\pm 0.82 \text{ \AA}$ for the 3-0 NH_2 band at 8159 Å. The solar spectrum was examined for coincidences of Fraunhofer absorption lines with the strongest rotational lines in all the NH_2 bands included in this g -factor calculation (see Table 1) within the velocity range. The last column in Table 1 gives a Swings effect rating for each NH_2 band. An "a" rating signifies a negligible ($< 25\%$) Swings effect on the g -factor for all heliocentric velocities of the NH_2 gas within the range $-30 \text{ km s}^{-1} < \dot{r} < +30 \text{ km s}^{-1}$. The "b" ranking for the NH_2 g -factors in Table 1 means that a potential wavelength coincidence between an NH_2 line and a solar Fraunhofer line could occur for the velocity range $-30 \text{ km s}^{-1} < \dot{r} < +30 \text{ km s}^{-1}$, which would affect the band g -factor by $\lesssim 25\%$. In addition, those bands in Table 1 which are flagged, (8-0) II, (12-0) II, (14-0) II, may not be optimum for observation in comets for reasons other than a significant Swings effect. The (8-0) II and (12-0) II bands have potential Swings effects of $\sim 20\%$. However, these NH_2 bands are further complicated by the fact that cometary [O I] lines and C_2 bands overlie the NH_2 bands. The (12-0) II band is flagged in Table 1 because of the close wavelength coincidence of the strong Mg I b resonance absorption lines (5167.32, 5172.68, 5183.60 Å) in the solar spectrum, although the Swings effect does not appear to affect the g -factor by $> 25\%$ for the velocity range considered. As can be seen from Table 1, the potential effect of the Fraunhofer spectrum on the fluorescence efficiencies of NH_2 is negligible for most bands.

In Table 1 we give the values used in equation (3) to calculate g -factors for each band arising from the upper states, $3 < v'_2 < 15$, and we list the final g -factor for each NH_2 band at a heliocentric distance of 1 AU. Because of the solar flux dependence on heliocentric distance, the g -factors are expected to scale as r^{-2} . The g -factors calculated by A'Hearn (1982) are given for comparison.

TABLE 2

COMPARISON OF CALCULATED AND EXPERIMENTAL LIFETIMES, $\tau_{v'_2}$

NH_2 ($v'_2-v'_2$)	CALCULATED $\tau_{v'_2}^a$ (μs)	EXPERIMENTAL		
		$\tau_{v'_2}^b$ (μs)	$\tau_{v'_2}^c$ (μs)	$\tau_{v'_2}^d$ (μs)
(5-0) Σ	25.1	...	45.6 ± 5.7	...
(6-0) Π	24.5	...	31.6 ± 3.6	...
(7-0) Γ	22.7	...	27.9 ± 4.1	...
(7-0) Σ	13.9	23_{-9}^{+41}
(8-0) Π	11.8	13 ± 2.5	...	$10.3_{-1.9}^{+2.9}$
(9-0) Σ	8.7	10.0 ± 1.7
(9-0) Δ	10.6	$13.5_{-3.5}^{+7}$
(10-0) Π	7.4	18 ± 4	...	$6.2_{-0.2}^{+0.4}$
.....	$7.2_{-0.3}^{+0.2}$
(11-0) Σ	5.9	8.1 ± 2
(12-0) Π	5.1	6.6 ± 1.1	...	5.0 ± 0.2

^a Jungen, Hallen, and Merer 1980.

^b Halpern *et al.* 1975.

^c Donnelly, Baronavski, and McDonald 1979.

^d Mayama, Hiraoka, and Obi 1984.

III. DISCUSSION

From Table 1 it can be seen that the branching ratios for downward transitions lie in the range $0.21 < \tilde{\omega} < 0.75$, which is significantly different from unity, the value assumed previously in calculating NH_2 g -factors (A'Hearn, Hanisch, and Thurber 1980). The branching ratios account for the main differences between our results and those of A'Hearn (1982). Since the NH_2 column densities scale linearly with g , NH_2 abundances determined with A'Hearn's g -factors will increase by factors ranging from 1.4 to 5.9, for the (7-0) and (12-0) bands, respectively.

Uncertainties in the g -factors computed here are determined essentially by the uncertainties in the transition rates, $A_{v'v''}$. The calculated lifetimes, $\tau_{v'_2}$ of Jungen, Hallen, and Merer (1980) compare quite well with lifetimes determined experimentally by Halpern *et al.* (1975), Donnelly, Baronavski, and McDonald (1979), and Mayama, Hiraoka, and Obi (1984), which are summarized in Table 2. From Table 2 it can be seen that the calculated lifetimes are within the errors of the experimental lifetimes, $\sim 20\%$ for most bands. The two exceptions are the (5-0) Σ lifetime measured by Donnelly, Baronavski, and McDonald (1979) and the (10-0) II lifetime measured by Halpern *et al.* (1975). Although the (10-0) state is perturbed (Halpern *et al.* 1975), Mayama, Hiraoka, and Obi (1984) measured a lifetime of the 1_{10} rotational level in the $v'_2 = 0$ \tilde{A}^2A_1 state which agreed within experimental errors with the theoretical prediction (Jungen, Hallen, and Merer 1980). Mayama *et al.* therefore concluded that the experimental and theoretical band intensities of all NH_2 bands agree to an accuracy of $\sim 25\%$.

From equation (1) we can see that the ratio of the g -factors of two NH_2 bands in a comet spectrum should be equivalent to the ratio of the observed integrated band strengths within the observational and experimental errors. Emission from NH_2 is relatively weak in comets, and for many of the NH_2 bands overlapping atomic or molecular features from the comet or the Earth's atmosphere contaminate the NH_2 emission. Therefore, not many comet spectra exist with accurately measurable NH_2 bands. A'Hearn, Hanisch, and Thurber (1980) observed NH_2 in comet West with low resolution (FWHM = 5-20 Å) and tabulated the band fluxes. Also, Wehinger, Belton, and

TABLE 3
COMPARISON OF OBSERVED AND CALCULATED BAND INTENSITY RATIOS

NH ₂ BAND FLUX RATIO	CALCULATED g_1/g_2	OBSERVED (F_1/F_2)	
		Comet West ^a	Comet Crommelin ^b
[(5-0) Σ]/[(7-0) Σ]	0.30	0.45 \pm 0.20	0.31 \pm 0.03
[(10-0) Π]/[(7-0) Σ]	1.51	1.10 \pm 0.55	1.01 \pm 0.08
[(5-0) Σ]/[(10-0) Π]	0.20	0.33 \pm 0.10	0.31 \pm 0.07

^a A'Hearn, Hanisch, and Thurber 1980.

^b International Halley Watch Crommelin Archive 1985.

Spinrad observed comet Crommelin, which had very strong NH₂ bands, and its spectrum was available from the NASA Comet Crommelin Archive of the International Halley Watch. We have measured the relative fluxes of NH₂ bands in the comet Crommelin spectrum. At low resolution the (5-0) Σ , (7-0) Σ , and (10-0) Π bands of NH₂ are relatively free from contamination by other cometary or terrestrial features. In Table 3 we compare the computed g -factor ratios with the observed comet flux ratios for these three NH₂ bands in comets West and Crommelin. From Table 3 we see that the calculated g -factor ratios are within $\sim 1 \sigma$ of the average observed flux ratios in the two comets. From the transition rate uncertainties and the observed flux ratios given in Table 3, we estimate that the g -factors are accurate to 25%, in the absence of strong Swings effects as discussed in § II.

Using the g -factors given in Table 1, we have recalculated the NH₂ production rate reported previously for an observation of comet Halley on 1986 March 13 (Wyckoff *et al.* 1988), and find for the same scale lengths using the vectorial model, $Q(\text{NH}_2) = 2.1 \times 10^{27}$ molecules s⁻¹. The water production rate on the date in question, determined by A'Hearn (1988) from an *IUE* spectrum of the OH band in comet Halley using the vectorial model, is $Q(\text{H}_2\text{O}) = 4.7 \times 10^{29}$ molecules s⁻¹.

Assuming that NH₃ is the dominant source of NH₂ in comet Halley, we find $Q(\text{NH}_3)/Q(\text{H}_2\text{O}) = 0.005 \pm 0.002$. The abundance of ammonia is therefore ~ 1.7 times greater than our previous result, and agrees within estimated model errors with the spacecraft ion mass spectrometer results (Allen *et al.* 1987) of $Q(\text{NH}_3)/Q(\text{H}_2\text{O}) \sim 1\% - 2\%$. The greatest sources of uncertainty in this ammonia-to-water abundance ratio are (1) determining whether NH₃ is the dominant source of NH₂ and (2) the models used for calculating the production rates of H₂O and NH₂. If NH₃ is not the dominant source of NH₂, then the ammonia-to-water abundance ratio should be regarded as an upper limit. A model incorporating a time-varying source (A'Hearn 1989) predicts the observed NH₂ spatial profiles in comet Halley with significantly improved accuracy (A'Hearn 1988) compared with the steady state Haser and vectorial models.

Useful discussions with Tim Steimle concerning the properties of NH₂, and with Michael A'Hearn regarding the H₂O and NH₂ production rates in comet Halley, are gratefully acknowledged. We also appreciate several useful comments by Michael A'Hearn on the manuscript. This research is supported by NASA grant NAGW-547.

REFERENCES

- A'Hearn, M. F. 1982, in *Comets*, ed. L. L. Wilkening (Tucson: University of Arizona Press), p. 433.
 ———. 1988, private communication.
 ———. 1989, *Adv. Space Res.*, in press.
 A'Hearn, M. F., Hanisch, R. J., and Thurber, C. H. 1980, *A.J.*, **85**, 74.
 Allen, M., *et al.* 1987, *Astr. Ap.*, **187**, 502.
 Arpigny, C. 1965, *Ann. Rev. Astr. Ap.*, **3**, 351.
 Chamberlain, J. W., and Hunten, D. 1987, in *Theory of Planetary Atmospheres* (2d ed.; Orlando: Academic), p. 290.
 Donnelly, V. M., Baranavski, A. P., and McDonald, J. R. 1979, *Chem. Phys.*, **43**, 283.
 Dressler, K., and Ramsay, D. A. 1959, *Phil. Trans. Roy. Soc. London, A*, **251**, 69.
 Fegley, B. F., and Prinn, R. G. 1989, in *The Formation and Evolution of Planetary Systems*, ed. H. A. Weaver, F. Paresce, and L. Danly (Cambridge: Cambridge University Press), in press.
 Greenstein, J. L., and Arpigny, C. 1962, *Ap. J.*, **135**, 892.
 Halpern, J. B., Hancock, G., Lenzi, M., and Welge, K. H. 1975, *J. Chem. Phys.*, **63**, 4808.
 Huebner, W. 1988, private communication.
 Ip, W.-H. 1989, *Adv. Space Res.*, in press.
 Johns, J. W. C., Ramsay, D. A., and Ross, S. C. 1976, *Canadian J. Phys.*, **54**, 1804.
 Johnson, J. R., Fink, U., and Larson, S. M. 1984, *Icarus*, **60**, 351.
 Jungen, C. H., Hallen, K.-E. J., and Merer, A. J. 1980, *Molec. Phys.*, **40**, 25.
 Krasnopolsky, V. A., *et al.* 1986, *Nature*, **321**, 269.
 Kurucz, R. 1985, private communication.
 Lämmerzahl, P., *et al.* 1987, *Astr. Ap.*, **187**, 169.
 Lewis, J., and Prinn, R. 1980, *Ap. J.*, **238**, 357.
 Lunine, J. I. 1989, in *The Formation and Evolution of Planetary Systems*, ed. H. A. Weaver, F. Paresce, and L. Danly (Cambridge: Cambridge University Press), in press.
 Lutz, B. L. 1987, *Ap. J. (Letters)*, **315**, L147.
 Magee-Sauer, K., Scherb, F., Roesler, F. L., and Harlander, J. 1989, *Icarus*, in press.
 Marconi, M. L., and Mendis, D. A. 1988, *Ap. J.*, **330**, 513.
 Mayama, S., Hiraoka, S., and Obi, K. 1984, *J. Chem. Phys.*, **80**, 7.
 Neckel, H., and Labs, D. 1984, *Solar Phys.*, **90**, 205.
 Peyerimhoff, S. D., and Buenker, R. J. 1981, *Canadian J. Chem.*, **59**, 1318.
 Prinn, R. G., and Fegley, B. F. 1981, *Ap. J.*, **249**, 308.
 ———. 1988, in *Origin and Evolution of Planetary and Satellite Atmospheres*, ed. S. Atreya, J. Pollack, and M. Matthews (Tucson: University of Arizona Press), in press.
 Suto, M., and Lee, L. C. 1983, *J. Chem. Phys.*, **78**, 4515.
 Swings, P. 1941, *Lick Obs. Bull.*, **19** (No. 408), 131.
 Swings, P., McKellar, A., and Minkowski, R. 1943, *Ap. J.*, **98**, 142.
 Wyckoff, S., Tegler, S., Wehinger, P., Spinrad, H., and Belton, M. 1988, *Ap. J.*, **325**, 927.

STEPHEN TEGLER and SUSAN WYCKOFF: Department of Physics, Arizona State University, Tempe, AZ 85287-1504