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ANALYSIS OF NH SPECTRUM

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INTRODUCTION

The $A^3\Pi - X^3\Sigma^-$ transition of NH is a common feature of cometary spectra. Since the NH molecule is likely to be formed by photodissociation of molecules such as ammonia or hydrazine, identifying the final states of the photolysis would shed light on the identity of the parent. Stief and DeCarlo^{1/} noted that the photolysis of ammonia at 123.6 nm results in emission at 324.0 nm in the $c^1\Pi - a^1\Delta$ system. They suggested that in the absence of collisions in the coma, the $NH(a^1\Delta)$ should accumulate if ammonia is the source of NH radicals. The absence of the singlet system in this view would suggest another parent molecule than ammonia as the source of the NH radical. However, the pumping rate of the UV transitions in a comet is also very small. This note will show that the transition rate for the $a^1\Delta - X^3\Sigma^-$ transition is sufficiently fast to deplete any $a^1\Delta$ concentration formed in the original photolysis process.

This analysis focused on experimental spectra obtained by Lane and Stockton^{2/} observing the comet Kohoutek. The fluorescence pumping of the NH molecule is calculated for November 29, 1973 and January 25, 1974 using the model of radiative equilibrium which assumes no collisions^{3/}. Lane and Stockton observed the usual strong 336 nm triplet system but also noted a peak near 325.8 nm which can be assigned to the $c^1\Pi - a^1\Delta$ band system. The radiative equilibrium model will be used to examine this possible assignment.

Radiative Transition Probability ($a^1\Delta - X^3\Sigma^-$)

Since this transition is a singlet-triplet intercombination, the largest contribution to the transition probability is likely to be a spin-orbit induced electric-dipole transition, $a^1\Delta_2 - X^3\Sigma_1^-$, where the subscript represents the Ω value. These states can be expanded,

(1) $\phi(^3\Sigma_1^-) = \psi(^3\Sigma_1^-) + a_1\psi(^3\Pi_1) + a_2\psi(^1\Pi_1)$ and (2) $\phi(^1\Delta_2) = \psi(^1\Delta_2) + b_1\psi(^3\Pi_2)$, since the spin-orbit interaction mixes states of the same value of Ω . The dominant

molecular orbital configurations for ${}^3\Sigma_1^-$, ${}^3\Pi_2$, ${}^1\Delta_2$, and ${}^1\Pi_1$ states are, respectively,

$$\psi({}^3\Sigma_1^-): 1\sigma^2 2\sigma^2 3\sigma^2 \pi^+ \alpha \pi^- \alpha$$

$$\psi({}^3\Pi_2): 1\sigma^2 2\sigma^2 3\sigma \alpha \pi^+ \pi^- \alpha$$

$$\psi({}^1\Delta_2): 1\sigma^2 2\sigma^2 3\sigma^2 \pi^+ \pi^-$$

$$\psi({}^1\Pi_1): \frac{1}{\sqrt{2}} [1\sigma^2 2\sigma^2 3\sigma \alpha \pi^+ \pi^- \beta - 1\sigma^2 2\sigma^2 3\sigma \beta \pi^+ \pi^- \alpha].$$

The significant electric dipole interactions are between the $\psi({}^3\Sigma_1^-)$ and $\psi({}^3\Pi_2)$ states and the $\psi({}^1\Pi_1)$ and $\psi({}^1\Delta_2)$ states. The one-electron transition moment integral for both interactions is formally the same, $\langle 3\sigma | \vec{r} | 1\pi \rangle$. For valence states the orbitals do not vary greatly among the states and they will be assumed to be invariant for these valence states. The transition moment integral will be determined empirically from the known transition probability for the $A^3\Pi - X^3\Sigma^-$ transition^{3/} since the square of the integral is proportional to the probability divided by the cube of the transition energy.

The mixing coefficients in eq. 1 and 2 are also determined empirically. Diagonal spin-orbit matrix elements have been calculated for NH both empirically and by ab initio methods^{5/}. It will be assumed here that off-diagonal matrix elements can be calculated with the same hamiltonian. Accepting the value of 73 cm^{-1} for spin-orbit constant used by Lefebvre-Brion and Moser, the constants a_1 , a_2 , and b_1 are estimated to be $-1.2 \cdot 10^{-3}$, $0.8 \cdot 10^{-3}$, and $3.0 \cdot 10^{-3}$, respectively.

Since the spin-orbit induced mixing coefficients are of the order of 10^{-3} , the transition probability for the intra-multiplet transition will be about 10^{-6} of the usual electric-dipole allowed transition. In the present case even with the much smaller energy difference between the ${}^1\Delta$ and ${}^3\Sigma^-$ states, the transition probability is found to be 5 S^{-1} . In order to gauge the significance of this value an estimate of the pumping rate is obtained for the comet Kohoutek in the next section.

Calculation of the Fluorescence Pumping

Dixon^{6/} has determined accurate line positions and assignments for the A-X transition. The radiative equilibrium equations were solved considering only the $N'' = 0$ and 1 rotational states. Solar fluxes were estimated from the unpublished preliminary edition of the Kitt Peak Solar Atlas normalized to the mean intensities tabulated by Allen^{7/}. There are three important lines that excite the $N'' = 0$ level, the $R_1(0)$, $R_{Q_{21}}(0)$, and $R_{P_{31}}(0)$. There are strong Fraunhofer lines at the wavelengths which pump the first two on November 29, 1973. As a result the predicted fluorescent spectra on November 29, 1973 is a composite of lines pumped from both the $N'' = 0$ and 1 states, while on January 25, 1974, the spectrum is dominated by lines pumped from $N'' = 0$. The radiative equilibrium maintains significant population in only the $N'' = 0$ and 1 rotational states of the $X^3\Sigma^-$ ground electronic state with the relative populations for $N'' = 0$ equal to 0.7 on November 29 and 0.9 on January 25.

There is semi-quantitative agreement on the relative intensities of the fluorescent spectra for both observing days. Quantitative disagreements between the calculated and observed spectra can be attributed to uncertainties in the evaluation of the solar flux and the inability to resolve a number of blends. Fluorescent pumping from cold $X^3\Sigma^-$ ground state is certainly the preponderant source for the observed fluorescence. For November 29 the total fluorescent rate is only about $1.2 \cdot 10^{-3} \text{ S}^{-1}$ while on January 25 it is about $3.6 \cdot 10^{-3} \text{ S}^{-1}$. The $V'' = 0$ to $V'' = 1$ vibrational transition is estimated to be pumped at a rate of $2 \cdot 10^{-4} \text{ S}^{-1}$ by the solar flux near 3μ . The electronic pumping in the A-X system is quite weak and the possibility of vibrational pumping should be considered if a quantitative spectrum was required.

The pumping rate in the $c^1\pi-a^1\Delta$ system will be of the same order of magnitude as found for the A-X system. The electronic transition probabilities are comparable

for the A-X and c-a systems^{4/} while the solar flux is diminishing as the singlet transition is at shorter wavelength. Lane has noted a peak at about 325.8 nm which can be assigned to the $P_2(0)$ transition in the c-a system using the line list reported by Pearse^{8/}. The radiative equilibrium model would predict that rotationally cold $a^1\Delta$ would exhibit a very simple fluorescence spectra with predominant peaks 325.8 nm and 326.2 nm. The $P_3(1)$ peak at 326.2 nm should have an intensity about 1/3 of the peak at 325.8 nm. Since the 325.8 nm peak is weak, the $P_3(1)$ peak, if present, would be barely above the noise and the present data cannot be used to confirm the assignment of the c-a system.

Discussion

Photochemical dissociation of NH_3 is known to produce NH in the singlet state with high quantum yield. The radiative transition probability for the $a^1\Delta - X^3\Sigma^-$ system is estimated to be $5 S^{-1}$. The transition probability for the $b^1\Sigma^+ - X^3\Sigma^-$ system would be comparable. There is no evidence in the NH spectra of the wide distribution in V and J expected in the initial photochemical dissociation event. The NH is apparently quite cold as expected from the radiation equilibrium model. All the NH would then radiate to the $X^3\Sigma^-$ ground electronic state unless another mechanism were found to excite the molecule. The spin-orbit induced electric-dipole transition probability is 10^3 larger than the fluorescence pumping. Such a great discrepancy far exceeds the likely errors in estimating inter-multiplet transition probabilities. The photochemical origin of the NH radical is not to be uncovered by examining the fluorescence spectra.

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