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CHEMILUMINESCENCE OF N_2, NH, and O_2 IN ARGON MATRICES

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ABSTRACT

The chemiluminescence spectra from O_2, NO, N_2 and NH have been obtained during warm-up of VUV photolyzed mixtures of argon containing small amounts of H_2O and/or NH_3. The spectra can be explained by recombination reactions between the trapped (ground state) atoms $N(^4S)$ and $O(^3P)$, and in the case of the observed NO_β system, also by the excited $N(^2D)$ atoms. The presence of $N(^2D)$ atoms during sample warm-up is further evidenced by the observed $N(^2D) \rightarrow N(^4S)$ transition. Recently chemiluminescence spectra have also been obtained from photolyzed $Ar/CH_4/H_2O$ mixtures. Among the many spectral features observed are the Cameron bands of CO.

INTRODUCTION

We are investigating the vacuum ultraviolet (VUV) photochemistry of mixtures of simple molecules such as NH_3, CO, H_2O and CH_4 condensed onto a substrate at 10 K in order to gain insight into the role played by dust grain mantles in interstellar chemistry (ref. 1, 2). Upon warm up from 10 to approximately 30 K a blue green luminescence is observed from a number of irradiated mixtures. In order to gain a better understanding of this behaviour we have studied the chemiluminescence of photolyzed argon matrices containing NH_3 and/or H_2O. Chemiluminescence is observed from the following diatomic molecules: N_2, NH, NO, and O_2. While emission from all of these species isolated in low temperature matrices has been stimulated using a wide variety of "in-situ" excitation techniques only one of these, O_2, has previously been observed in chemiluminescence after photolysis (ref. 3, 4). Here, we present some of the results which we have obtained sofar from the NH_3 and H_2O experiments.

EXPERIMENTAL

All matrices were deposited onto a cooled sapphire window (10 K) and irradiated with a hydrogen flow discharge lamp having a spectral output peaked between 150 and 170 nm (flux ∿ 2 x 10^{15} photons/sec). Spectra were measured using a Jarrell-Ash (model 82-410) f/3.6 monochromator with 500 μm slits (1.5 nm resolution) required for sufficient light collection in combination with an S-5 cathode PM tube. The temperature interval over which a spectrum could be obtained was determined by both the scan rate (200 nm/min) and warm-up rate (9 K/min from 10-22 K, 2 K/min from 30-60 K).

RESULTS AND DISCUSSION

When a mixture of NH_3:Ar (1:100) is allowed to warm-up after two hours of deposition with simultaneous photolysis, luminescence is observed which lasts until the substrate reaches 60 K. The spectrum of this emission measured between 25 and 31 K is shown in Figure 1. Comparison of peak positions and general appearance of these features with those obtained by others using various excitation techniques indicate that the principle features can be assigned to N_2 ($A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$, Vegard-Kaplan) emission (ref. 5, 6, 7). The very intense line observed at 337.9 nm and the much weaker emission at 377.5 nm assigned to the (0-0) and (0-1) transition of NH($A^3\Pi_i \rightarrow X^3\Sigma^-$) (ref. 8, 9). The weak (0-1) line could only be obtained with ultra pure samples because of line blending with the 377.6 nm line arising from Oxygen impurities.

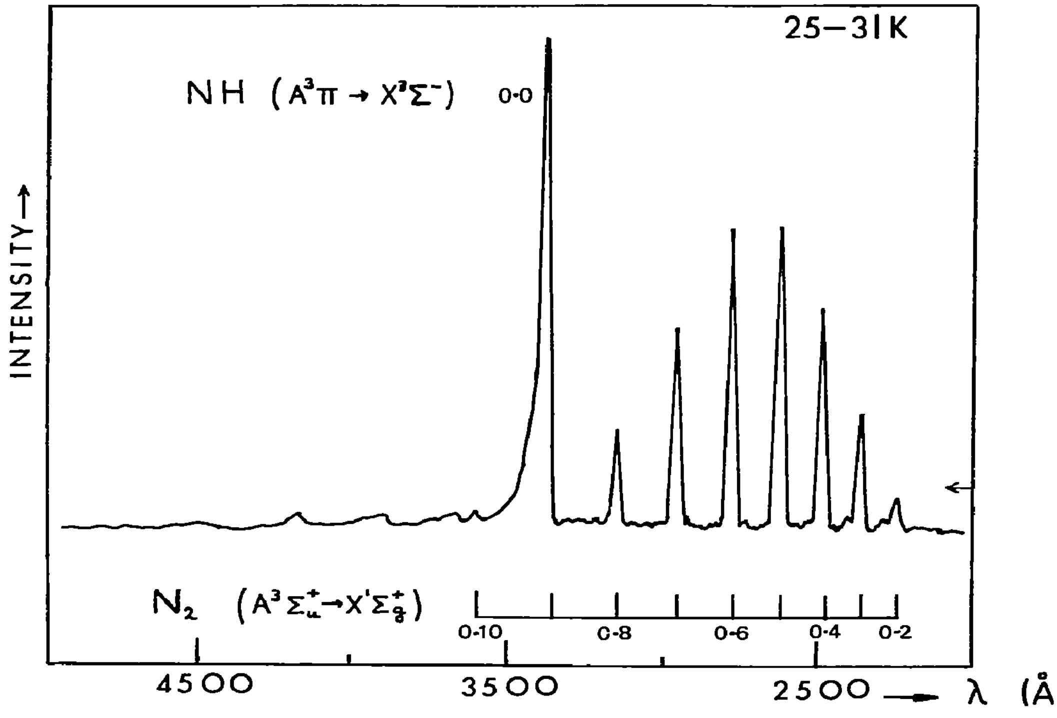

Fig. 1. Chemiluminescence spectrum obtained from a NH_3:Ar mixture (1:100).

With H_2O replacing NH_3 a different diatomic-like emission spectrum is obtained. The relative intensities and peak wavelenghts of this system compare favorably with those attributed to $^{16}O_2$ chemiluminescence by Smardzewski(ref. 3). Using state selective laser induced fluorescence techniques Goodman and Brus (ref. 10) showed this emission is to be due to the $O_2(C^3\Delta_1 \rightarrow X^3\Sigma_g^-)$ transition as suggested by Richards and Johnson (ref. 11). Chemiluminescence from the other isotopes of oxygen (present according to their natural abundance) is also observed.

When the temperature of a photolyzed argon matrix containing both H_2O and NH_3 is allowed to rise, in addition to N_2, NH and O_2 chemiluminescence, the strong emission system shown in Figure 2 is also observed. Initially, upon warm-up O_2 emission dominates this region of the spectrum, however once the substrate is above 30 K the O_2 lines are considerably reduced with the new spectrum now being the most intense. Comparison of the wavelengths of these lines with those attributed to NO($a^4\Pi \rightarrow X^2\Pi$, M-bands) emission excited with a variety of in-situ excitation techniques by Broida and Peyron (ref. 5 and 6), Frosch and Robinson (ref. 12) and Fournier et al. (ref. 13 and 14) provides the basis for attributing the new emission to the NO "M" bands.

Not shown in Figure 2 but also present in some of our spectra are the NO_β bands ($B^2\Pi \rightarrow X^2\Pi$) and the diffuse so-called B-bands.The presence and intensity of these bands depend upon initial experimental conditions.

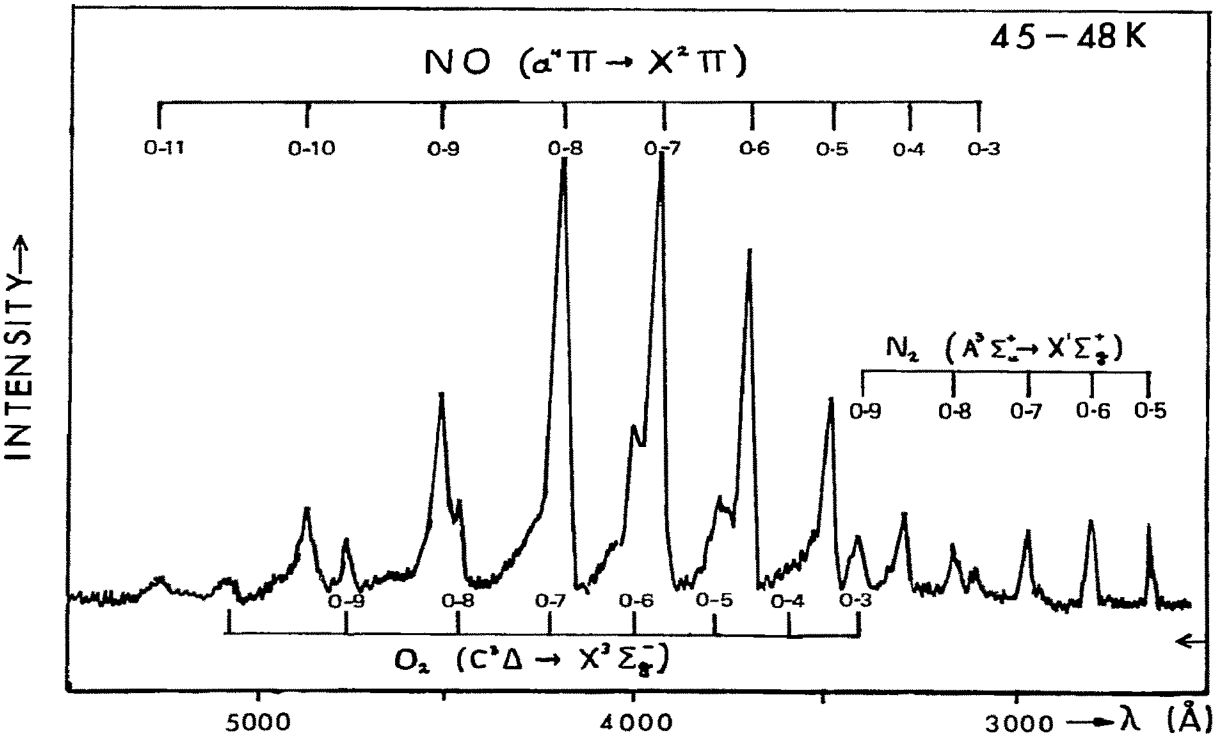

Fig. 2.Chemiluminescence spectrum obtained from NH_3:H_2O:Ar mixture (1:1000).

Emission from the excited diatomic molecules with the exception of NH and NO_β can be explained by straightforward recombination of the trapped ground state atoms $N(^4S)$ and $O(^3P)$. In the case of the NO_β system excited $N(^2D)$ atoms are involved: their presence follows from the observation of the $N(^2D) \rightarrow N(^4S)$ transition during sample warm-up. In this connection, it is interesting to note that the energy difference between two $N(^4S)$ atoms and the $A^3\Sigma_u^+$ state is more then enough to excite a nearby $N(^4S)$ atom to the $N(^2D)$ state. In all cases reported here, the exothermicity of the reactions is sufficient to populate the observed upper state. Population of $NH(A^3\Pi_i)$ may proceed by other channels.

Since very strong chemiluminescence has been observed from samples which were maintained for periods longer than 24 hours after photolysis it must be concluded that N and O atoms can be stored for long periods of time.

When irradiated $Ar/CH_4/H_2O$ mixtures are allowed to warm-up, in addition to the familiar O_2 system, the CO Cameron bands $(a^3\Pi \rightarrow X^1\Sigma^+)$ is observed. Many other features match surprisingly well the $(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$ (ref. 15 and 16) band system of C_2^-. This assignment awaits further verification by means of isotopic substitution.

The process of producing ground state atoms in matrices by VUV photolysis provide a unique opportunity to study low temperature reactions and to produce a variety of unusual diatomic molecules in specific states. Work is now in progress which is aimed at gaining a better understanding of the fundamental processes involved in these experiments, such as atom formation and storage, state selection criteria and energy transfer phenomena.

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