# LETTERS TO THE EDITOR

#### **ASTROPHYSICS**

### Origin of $NH(A^3\Pi) \rightarrow NH(X^3\Sigma^{-})$ Emission in Comets

The presence of NH radicals in the coma of comets has been generally attributed to photodissociation of ammonia. However, vacuum ultra-violet photolysis<sup>1</sup> (1236 Å) of ammonia results in emission at 3240 Å:

$$NH(c^{1}\Pi) \rightarrow NH(a^{1}\Delta) + hv_{3240} \tag{1}$$

while the cometary emission at 3360 Å corresponds to:

$$NH(A^3\Pi) \rightarrow NH(X^3\Sigma^-) + hv_{3360} \tag{2}$$

The energy-level diagram for NH showing the position of the states and the transitions under discussion is shown in Fig. 1. In the vacuum ultra-violet flash photolysis of ammonia<sup>2,3</sup>, the NH absorption band at 3360 Å  $(A\Pi^3 \leftarrow X^3\Sigma^-)$  was observed.

These results may be explained<sup>3</sup> by initial formation of NH in the singlet system:

$$NH_3 + h\nu \rightarrow NH(a^1\Delta, c^1\Lambda) + H_2$$
 (3)

with collision-induced transformation to ground state NH.

$$NH(a^1\Delta) + NH_3 \rightarrow NH(X^3\Sigma^-) + NH_3$$
 (4)

Ground state NH could also be formed directly in decomposition of NH3:

$$NH_3 + h\nu \rightarrow NH(X^3\Sigma^-) + 2H$$
 (5)

Formation of  $\mathrm{NH}(X^{2}\Sigma^{-})$  and  $\mathrm{H_{2}}$  is spin forbidden since the excited state of NH<sub>3</sub> formed on absorption of light in the region 1220-1440 Å (state III) is a singlet4. Whatever the mechanism for production of ground state NH, it is evident that in photodecomposition of ammonia, NH is formed to some extent in the singlet system. Since the  $a^1\Delta \to X^3\Sigma^-$  is highly forbidden,  $NH(a^1\Delta)$  will have a long lifetime in absence of collision with other molecules. Evidence for the fact that radicals do not suffer collisions from the time of their formation near the nucleus until resonance fluorescence occurs further out in the coma comes from the observation that the C2 radical shows a vibrational and rotational distribution, which corresponds to a temperature of about 2500° K, while CN simulates

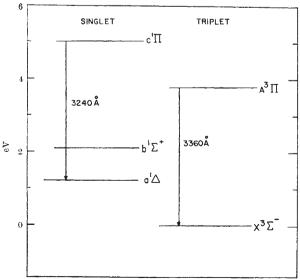


Fig. 1. Energy-level diagram of NH

a very low-temperature distribution. A completely symmetrical molecule like C, has no permanent dipole and is therefore unable to emit vibrational and rotational energy. Energy may therefore be transferred only by collisions. The fact that C2 retains excess vibrational and rotational energy suggests that it has suffered few, if any, collisions from the time of its formation to the time of its excitation by a fluorescence process. Thus in the coma of a comet, considerable concentration of  $NH(a^1\Delta)$ should accumulate if ammonia is the source of NH radicals. Emission from NH( $c^1\Pi$ ) at 3240 Å by a fluorescence process should be observed in cometary spectra along with the 3360 Å emission from the triplet system of NH. Since only the 3360 Å emission is observed, an alternative source of NH radicals which produces only the triplet system on photodecomposition is required.

Recent results obtained in our laboratory on emission spectra from hydrazine vapour during photolysis at the krypton resonance lines (1236 Å and 1165 Å) are pertinent to this problem. While the work was in progress, Becker and Welge reported<sup>5</sup> results on the emission spectra during photolysis of hydrazine which are in complete agreement with our observations. When hydrazine, carefully purified of ammonia, is photolysed at  $50\mu$  mercury pressure, emission at 3360 Å is observed. This is undoubtedly the 0,0 band of the  $A^3\Pi \to X^3\Sigma^-$  NH transition. Emission is not observed at 3240 Å (0,0 band of the  $c^1\Pi \to a^1\Delta$ transition). Detection of emission at 3240 Å in presence of emission at 3360 Å is within the resolution of our grating, and emission at 3240 Å amounting to a few per cent of that at 3360 Å could have been detected. Thus photodecomposition of hydrazine appears to produce NH radicals in the triplet system only. On this basis we would suggest that the immediate precursor of NH radicals in comets is hydrazine or a hydrazine-type molecule and that the role of ammonia in the comet model needs reconsideration.

This research was supported by the National Aeronautics and Space Administration under contract NASw-

> L. J. STIEF V. J. Decarlo

Research Division. Melpar, Inc., 3000 Arlington Boulevard, Falls Church, Virginia.

- <sup>1</sup> Becker, K. H., and Welge, K. H., Z. Naturforsch., 18a, 601 (1963).
- Bayes, K. D., Becker, K. H., and Welge, K. H., Z. Naturforsch., 17a, 676 (1962).
- <sup>3</sup> Stuhl, F., and Welge, K. H., Z. Naturforsch., 18a, 900 (1963).
- <sup>4</sup> Thomson, R. J., and Duncan, A. B. F., *J. Chem. Phys.*, **14**, 273 (1946). <sup>5</sup> Becker, K. H., and Welge, K. H., *Z. Naturforsch.*, **19a**, 1006 (1964).

#### **RADIOPHYSICS**

## Dependence of the Critical Frequency of the Ionospheric E-layer on Solar Zenith Angle and the Annual Variation in E-layer Ionization

It is generally known that  $f_0E$ , the critical frequency of the ionospheric E layer, varies in a fairly regular manner with a law of the form:

$$f = f_0 \cos n \chi \tag{1}$$

where X is the solar zenith angle. This form can be applied to both diurnal and annual variations, and generally both  $f_o$  and n are different for these two variations. To distin