

THE DISSOCIATIVE ELECTROIONIZATION OF NH₃. THE NH⁺ DISSOCIATION CHANNEL.

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Dissociative ionization work on NH₃ is relatively scarce. The most well investigated fragment ion is NH₂⁺. Numerous photoionization and electroionization experiments, including PIPECO measurements, were devoted to that ion. The most recent electroionization work, studying NH⁺ and N⁺, has been published by Morrison and Traeger¹. These authors measured onsets for both ions and interpretations are rather limited.

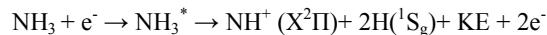
This work will deal with the NH⁺ dissociation channel of NH₃ investigated by electroionization with ion-energy analysis. The experimental set-up has extensively been described elsewhere². Ions produced in an ion source are energy-analyzed by a retarding field before mass analysis. First differentiated ionization efficiency curves at different retarding potential settings and ion KE-distributions at different electron energies are recorded.

The NH⁺ ion KE-distribution peaks at 0.47eV and extends up to 1.13 eV for 50 eV electron energy. The maximum continuously shifts down to zero by lowering the electron energy down to the onset. By recording the first differentiated ionization efficiency curves of NH⁺ (see fig.1) at different retarding potential settings, a KE-vs-AE plot is obtained and shown in fig.2.

The two first onsets at (16.9 ± 0.1) eV and (18.1 ± 0.1) eV (see region (1) in fig.2) correspond to the lowest dissociation limit calculated for the process



At (22.6 ± 0.4)eV the NH⁺ ions carry 0.12 eV kinetic energy. By the linear extrapolation of the KE-vs-AE diagram (see straight line (2) in fig.2), an energy of 21.5 eV is calculated. The excess energy with respect to this limit is entirely converted into translational energy of the fragments. The energy difference of (21.5 - 16.9) = (4.6 ± 0.4)eV has to be compared to the dissociation energy D₀^o(H₂)=4.48 eV. The onset at (22.6 ± 0.4) eV is interpreted by



where NH₃^{*} is very likely a member of a Rydberg series converging to the NH₃⁺ ($\tilde{B}^2 A_1$) state. The same interpretation would be valid for the onset at (24.4 ± 0.2) eV. A linear extrapolation leads to a dissociation limit at 23.6 eV. Only the vibrational excitation of NH⁺ could account for the energy difference of (23.6-21.6) = 2 eV³.

Results on the other dissociation channels of NH₃⁺, giving rise to N⁺, H⁺ and H₂⁺ will be available and will be discussed at the meeting.

REFERENCES.

1. J.D. Morrison, J.C.Traeger, Intern.J. Mass Spectrom. Ion Phys. 11 (1973) 277.
2. R.Locht, J.Momigny, Intern.J. Mass Spectrom. Ion Phys. 15 (1974) 361 .
3. R.Colin, A.E. Douglas, Can. J. Phys. 46 (1968) 61 .

FIG.1: 1st Differentiated IEC of NH^+/NH_3 .

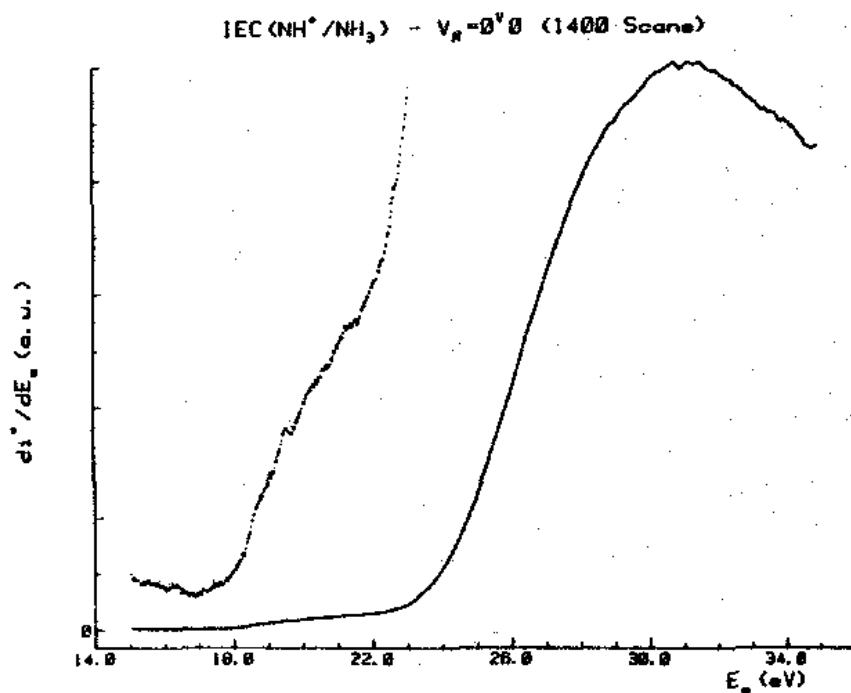


FIG.2: KE-vs-AE diagram for NH^+/NH_3 .

