Published in: Advances in Mass spectrometry (1988), vol. 11A, pp. 780-781.
Status: Postprint (Author's Version)

The Dissociative Electroionization of NH_3 and ND_3. A Detailed Study of its Five Dissociation Channels

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INTRODUCTION.

The systematic study of all the ionic dissociation channels induced by electron impact in moderately complex molecules received a strong impulse when an appropriate experimental device was setup in our laboratory for the determination of the translational energy of the ions. This short paper will review the recent results for the decay of NH_3^+ and NH_3^{++} electronic states.

EXPERIMENTAL.

The experimental design has fully been described (Locht, 1974). It has recently been fully computerized (Servais, 1986).

RESULTS AND DISCUSSION.

The experimental results with their most probable interpretations are displayed in Fig. 1 for the decay of NH_3^+ and in Fig. 2 for the decomposition of NH_3^{++}. Final interpretations presented here have been summarized from papers presently accepted for publication (Locht, 1988). As far as NH_3^+ is concerned, Fig. 1 shows how complex the situation is. The appearance of fragment ions result from the decay of directly or indirectly populated ionic states (indirect population is the result of autoionization of highly excited Rydberg states). The directly or indirectly populated $\tilde{A}^2E$ state decays either to related dissociation limits or, through internal conversion to the $\tilde{X}^2A''$ state, giving rise to $NH_2^+(\tilde{X}^3B_1)$ (Krier, 1985) and by extension to $H^+ + NH_2(\tilde{X}^2B_1)$.

The $\tilde{B}^2A_1$ state appears always directly populated and decays to related dissociation limits. However an internal conversion process to the $\tilde{A}^2E$ state is needed to explain the appearance of three channels including $NH^+(B^2\Delta)$ only able to be correlated to A E. A special mention has to be made for the decay at 23.1 eV of a neutral state to $NH(^3\Sigma^-,v^*) + H_2(R^{**})$ decaying through dissociative autoionization to $N(^4S_u) + H + H_2^+$. This state can only be a $^3A_2$, and this configuration is only possible for an nf Rydberg state. The decay of NH_3^{++} correlations are made between the products and electronic state without details.

AKNOWLEDGMENTS.

We thank the Action de Recherche Concertée for support.

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Fig. 1. *Dissociative ionization diagram of NH_3^+. Observed threshold energies in eV : calculated threshold in ( ), dashed arrows (→) are unobserved processes.*

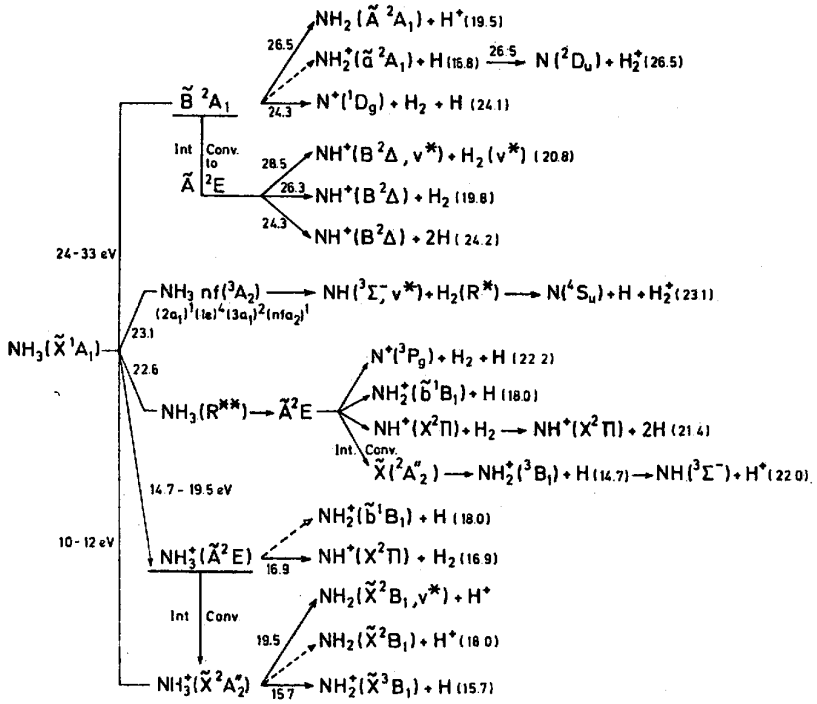

Fig. 2. *Dissociative ionization diagram of NH_3^{++}. Brackets show ion pairs. Threshold energies expressed in eV.*