

VUV Radiation by Dissociative Excitation of NH₃

N. BÖSE and W. SROKA

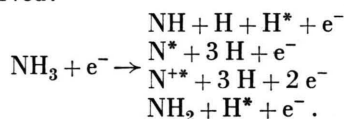
Institut für Angewandte Physik der Universität Hamburg, Germany

(Z. Naturforsch. 26 a, 1491—1495 [1971]; received 22 June 1971)

The NH₃ molecule is dissociated in a single step process into excited atoms and ions, which emit a radiation in the VUV. We have observed the Ly series and several lines of N I and N II. Only for Ly α we have found a structure in the shape of the excitation function.

There are only two papers on dissociative excitation processes in NH₃^{1,2}. In the first paper the production of Ly α radiation was investigated. But no information about the dissociation into other states than H(2p) was obtained. The second paper deals with dissociative excitation processes induced by photons.

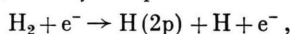
This work reports on the dissociation of NH₃ into higher states of the H-atom and into excited N-atoms and ions. The following processes have been observed:



Apparatus

An electron beam of variable energy (10–480 eV) and variable current (10^{−6} to 6·10^{−4} A) passes the collision chamber through pressure stages. A magnetic field of 400 Gauss confines the beam. The pressure within the cell (10^{−4} to 10^{−2} Torr) is measured with a capacitance manometer (MKS Baratron). During the operation the gun is heated to a temperature of 220 °C. The light emitted at the collisional process is observed at right angles to the beam with a vacuum monochromator (McPherson, Model 235) and with a Bendix multiplier (M 306) as detector. A slit width of 100 μ was used. So the wavelength resolution amounted to 3 Å. The energy scale of the electron beam is calibrated by measuring the appearance potential of the He line at 584 Å, or the molecular line N₂ [$p^1\Sigma_u^+(0) \rightarrow X^1\Sigma_g^+(0)$]. This line appears with high intensity in the N₂ emission spectrum. Until now it was only known from absorption measurements³.

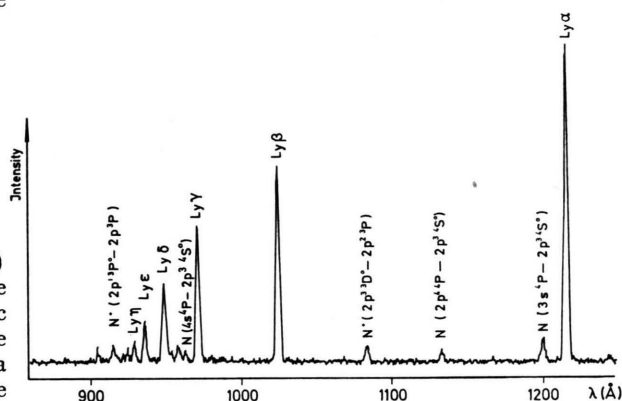
The calibrated value of the excitation function of Ly α was obtained by comparison with the process



the cross section of which was determined in⁴, but the value given there was later corrected by the factor 0.56 by the same author.

Furthermore, the variation of the grating reflectance (1200 lines per mm, Pt-coated, blazed for 800 Å) and the quantum yield of the multiplier cathode (tungsten) with wavelength has to be taken into account. Therefore the sensitivity of the apparatus at 500 Å is about a factor 20 larger than at 1250 Å.

A more detailed description of the apparatus can be found in⁵.

Fig. 1. Dissociation spectrum of NH₃.

Spectrum

Figure 1 shows the spectrum obtained by electron bombardment of NH₃ at a pressure of 2.2×10^{-3} Torr and a beam current of 320 μ A. The electron energy amounted to 200 eV. The spectrum shows five lines of the Ly series of H and lines of the nitrogen atom and ion. The H-lines are excited with a high intensity, whereas the cross sections for the formation of N and N⁺ are considerably smaller.

¹ J. W. MCGOWAN, J. F. WILLIAMS, and D. A. VROOM, Chem. Phys. Letters 3, 614 [1969].

² K. D. BEYER and K. H. WELGE, Z. Naturforsch. 22 a, 1161 [1967].

³ G. M. LAWRENCE, D. L. MICKEY, and K. DRESSLER, J. Chem. Phys. 48, 1989 [1968].

⁴ D. A. VROOM and F. J. DE HEER, J. Chem. Phys. 50, 580 [1969].

⁵ W. SROKA, Z. Naturforsch. 23 a, 2004 [1968].



The low intensity line at 959 Å originates from the background. Turning off the gas flow, this line does not change its intensity, whereas all other lines disappear*. Considering the intensity calibration, one gets the intensity ratio for the Ly series at 140 eV as given in Table 1.

Table 1. Intensity ratios of the Ly series.

Ly	α	β	γ	δ	ϵ	η
Intensity	23.8	3.6	1.9	1.0	0.5	≈ 0.2

In gases such as CH₄, C₂H₄, n-butane etc. we have found nearly the same intensity ratios. This will be discussed in a later paper.

Excitation Processes

a) Excitation of the Ly Series

Figure 2 shows the excitation functions of the Ly series near the onset potentials. The measured onset potentials are listed in Table 2.

For Ly α , the onset potential amounts to 16.1 eV. Furthermore there is a remarkable break at 21.8 eV. At the first critical potential the energy is only sufficient for the reaction given in Eq. (1)

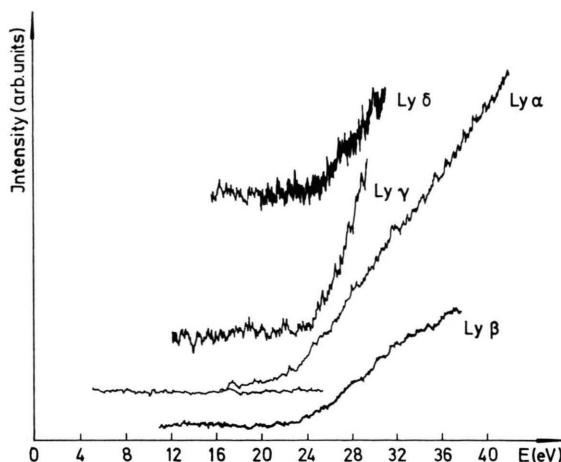
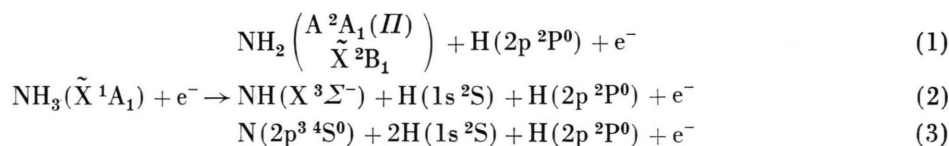
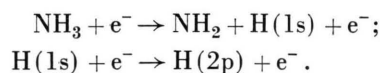
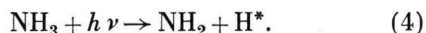


Fig. 2. Excitation functions of some members of the Ly series immediately above threshold. The curves are measured with different intensity scales.

The NH₂ molecule may be in the ground state or in the excited one. Unfortunately it was not possible to measure the current dependence of this line below 21.8 eV because of the low intensity. Therefore it could be possible that H(2p) may be excited in a two step process, for instance

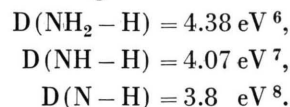


But in ² reaction (1) was found in a similar photo dissociation process (4) which fortifies that reaction (1) takes place.



Also in ² a second onset of the intensity was observed at a primary photon energy of about 600 Å. This corresponds to the break of the excitation function at 21.8 eV of our measurement. At the second critical potential reaction (2) is energetically possible. The dissociation products carry off an energy excess of about 3 eV. But the NH molecule may also be in an excited state. These interpretations are

based on the following dissociation energies:



At 21.8 eV total dissociation according to reaction (3) is impossible by energetical reasons. There is no further measurable break in the excitation function of Ly α . From this we can conclude, that the cross section for total dissociation (3) must be small.

In the case of Ly β , Ly γ , Ly δ and Ly ϵ the measured appearance potential is large enough for the

⁶ G. HERZBERG, Molecular Spectra and Molecular Structure III, D. van Nostrand, New York 1966.

⁷ R. J. REED and W. SNEDDEN, J. Chem. Soc. 1959, 4132.

⁸ G. HERZBERG, Molecular Spectra and Molecular Structure I, D. van Nostrand, London 1967.

Table 2. Summary of the results.

λ (Å)	Transition	Measured Appearance Pot.	Calc. (eV)	For the Process	σ (140 eV) $\times 10^{18}$ (cm ²)
1215.7	Ly α	16.1 ± 0.4 21.8 ± 0.4	14.6 18.7 22.5	NH ₂ + H* NH + H + H* N + 2H + H*	7.3
1200.2	3s 4P \rightarrow 2p ³ 4S ⁰ N I	24.6 ± 0.7	22.5	N* + 3H	0.51
1134.4	2p ⁴ 4P \rightarrow 2p ³ 4S ⁰ N I	23.3 ± 0.7	23.1	N* + 3H	0.12
1085.7	2p ³ 3D ⁰ \rightarrow 2p ² 3P N II	46.4 ± 1.5	37.9	N* + 3H	0.12
1025.7	Ly β		16.5 20.6 24.4	NH ₂ + H* NH + H + H* N + 2H + H*	1.1
972.5	Ly γ	24.2 ± 0.4	17.1 21.2 25.0	NH ₂ + H* NH + H + H* N + 2H + H*	0.58
965.0	4s 4P \rightarrow 2p ³ 4S ⁰ N I	—	17.4	N* + 3H	—
949.7	Ly δ	24.8 ± 0.7	21.5 25.3	NH ₂ + H* NH + H + H* N + 2H + H*	0.31
937.8	Ly ϵ	24.9 ± 0.5	17.7 21.8 25.6	NH ₂ + H* NH + H + H* N + 2H + H*	0.15
930.7	Ly η	—	—	—	≈ 0.073
916.0	2p ³ 3P ⁰ \rightarrow 2p ² 3P N II	—	—	N* + 3H	—
906.4	4d 4P \rightarrow 2p ³ 4S ⁰ N I	—	—	N* + 3H	—

processes (1) and (2). Immediately above threshold reaction (3) can be excluded. With the exception of Ly γ the excitation functions don't show any measurable break. There could be a break at about 27.5 eV in the case of Ly γ . It is possible that there exists a process with an extremely low onset potential for the other members of the Ly series, which is similar to the excitation of Ly α . But the cross section of this process should be lower than 10^{-20} cm² immediately above threshold. It follows that process (2) is probably the dominating reaction for the formation of excited H-atoms.

Figure 3 shows the excitation functions of the Ly series up to 480 eV. These curves are corrected with reference to pressure, beam current and long-time change of sensitivity of the apparatus. The cross sections are listed in Table 2. These values are related to the cross section measurement from ⁴. Using a cross section of 9×10^{-18} cm² at 140 eV for the excitation of He 584 Å⁹, the values have to be multiplied by a factor 0.72. All excitation functions may include cascading from higher levels.

Figure 4 and Fig. 5 show the intensity of some lines in dependence on the beam current and pressure. The electron energy amounted to about 140 eV.

The linearity is a proof that the observed lines are excited in a single step process.

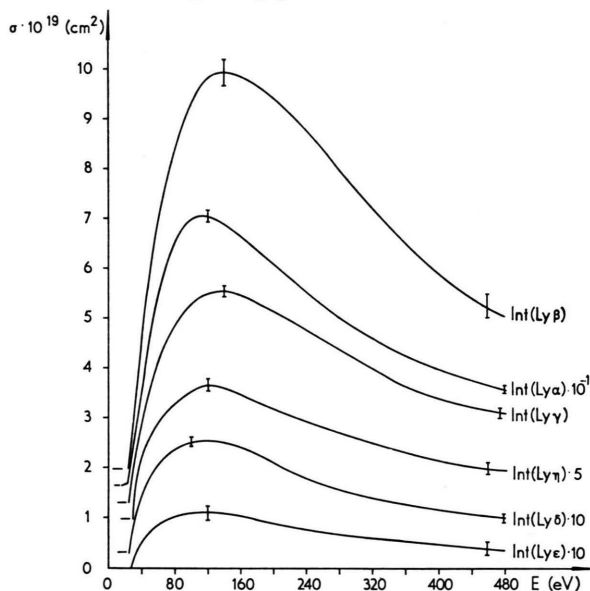


Fig. 2. Excitation functions of some members of the Ly series Fig. 3. Excitation functions of H-atoms in NH₃. Here the cross sections are calibrated with He 584 Å. The intensities of some lines have to be multiplied with factors given in the picture. Pay attention to the shifted zero levels of the intensity scale!

* In a later measurement we succeeded in reducing the background pressure. The line at 959 Å disappeared whereas the other spectrum did not change at all.

⁹ J.D. JOBE and R.M. ST. JOHN, Phys. Rev. **164**, 117 [1967].
— A. H. GABRIEL and D. W. O. HEDDLE, Proc. Roy. Soc. London A **258**, 124 [1960].

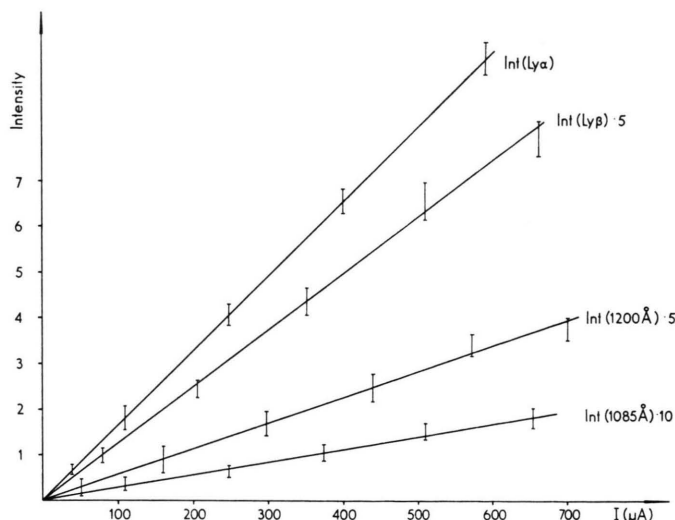


Fig. 4. Intensity versus beam current.

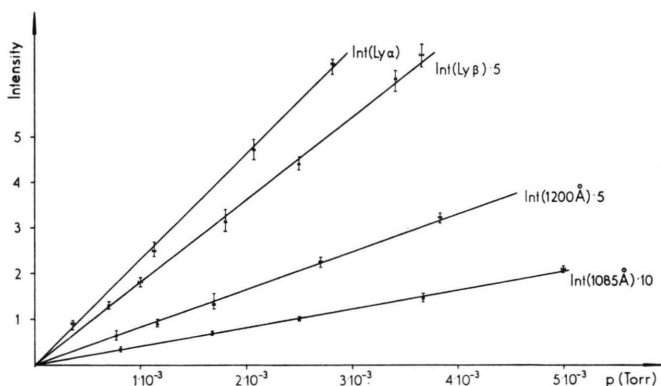


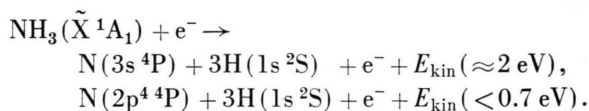
Fig. 5. Intensity versus pressure within the collision cell.

b) Excitation of Nitrogen Atoms and Ions

The intensity of the nitrogen atomic and ionic lines is considerably lower than that of the Ly series. Compared with dissociative excitation processes of N_2 ¹⁰ and N_2O ¹¹ the cross sections for NH_3 are about a factor 5 to 10 smaller for these lines. Furthermore in NH_3 there are only two N II lines and three N I lines. Both N II lines are excited by ejection of a 2s electron, therefore no cascading processes are involved. Under the same conditions we find for example in N_2O five N II lines with quite different intensity ratios. The excitation functions don't show any structure immediately above threshold, see Figure 7. This is understandable since the lines can only be excited by total dissociation.

In the case of the N I line at 1200 Å the energy excess is about 2 eV, but it is smaller than 0.7 eV at 1134 Å. This energy is carried off by the dissociative products in form of kinetic energy.

These processes may be written:



The $2p^3^3D^0$ state of N II (1085 Å) must be populated via a highly repulsive state of the molecule, since the excess energy amounts to about 8 eV. This energy is not sufficient for simultaneous excitation of the recoiling H-atoms. We can write this process as follows:

¹⁰ W. SROKA, Z. Naturforsch. **24 a**, 398 [1969].

¹¹ N. BÖSE and W. SROKA, presented to the VII. ICPEAC, Amsterdam 1971.

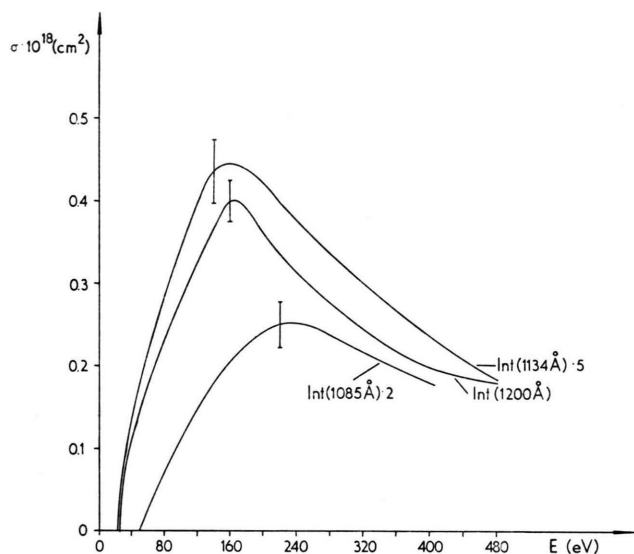
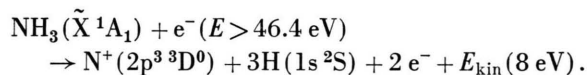


Fig. 6. Excitation functions of the N lines. The intensity scales for two lines have to be multiplied by a factor.



For the energy range up to 480 eV the excitation functions are given in Figure 6. The mean error of the measurement is relatively large because of the low intensity. As in the case of the Ly series there is also a linear dependence of the intensity on beam current and pressure within the collision chamber, see Figures 4 and 5.

General Remarks

Our measurements are in good agreement with the results of ¹ and ², which mainly discussed the formation of Ly α . Beyond that we succeeded in measuring the production of excited NI and NII and higher members of the Ly series. In literature often the excitation of H₂ by electron bombardment of NH₃ was discussed. We could not find any ra-

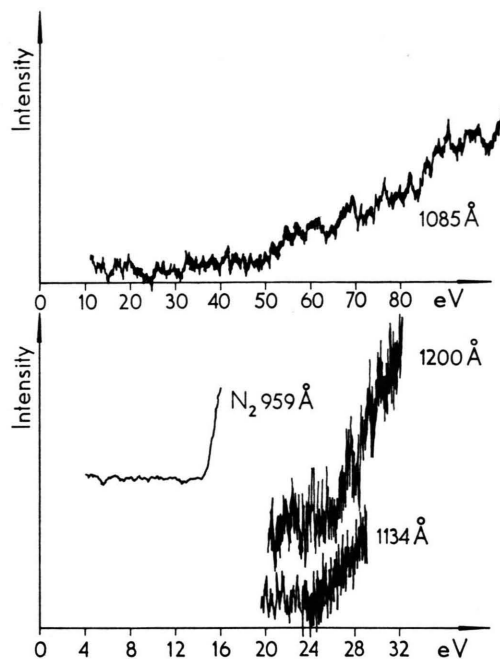


Fig. 7. Threshold behavior of the N lines.

diation component of H₂ in the wavelength region below 1300 Å. If there exists such a process, the cross section must be lower than 10⁻²⁰ cm².

We have repeated all the NH₃ measurements with ND₃. The only isotopic effect we could find was a lower intensity of the lines in ND₃. But this effect was difficult to measure since it is smaller than 5%.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft. The authors are indebted to H. HERTZ, E. KISKER, and H. G. W. MÜLLER for experimental help and valuable discussions **.

** Note added in proof: Dr. DE HEER sent us kindly his unpublished work on NH₃. He has carried out Bethe plots, which give together with our measurements above threshold more detailed information about the quantum mechanical states of the potential surfaces.