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THE IONIZATION CROSS SECTION OF ATOMIC NITROGEN

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Photoionization Research on Atomic
III. The Ionization Cross Section of Atomic Nitrogen

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Recently, calculations of the photoionization cross section of atomic oxygen and atomic nitrogen have been published in numerous publications. Oxygen and nitrogen are unstable in atomic form. Absorption research on these systems has, for that reason, been primarily conducted on the "active" form, i.e. a particle mixture, that imparts an electrical charge. Primarily, these mixtures consist of the particular atoms and not dissociate molecules, that are partially excited. A measurement of the inionization cross sections must however be purposefully conducted with pure components. For this reason, particle beams, that contain the particular atoms in a defined atomic state, are required. Such experiments were first conducted with hydrogen and oxygen atom beams.[1,2.] This study will report on the photoionization of the nitrogen atom in the basic state.

SETTING UP THE APPARATUS

The structural order to measure the photoionization on atomic beams has already been described elsewhere.[1.] The measuring equipment consisted of a monochromator in Seya-formation (series) and a time-of-flight mass spectrometer. Atomic and photon beams cross vertically in the ionization chamber of the mass spectrometer. The formed ions are shot into the ion tube vertically to both. In contrast to early measurements of hydrogen and oxygen atomic beams, the nitrogen atoms were generated in

a condensed discharge. Only weak nitrogen atom concentrations result from an unconcentrated discharge.

The discharge tube had a length of about 130 cm and was structed in a U-form. At a pressure of 0.1 to 0.2 Torr, a discharge condensed through 0.2 μF burned in nitrogen between two aluminum electrodes; 10% argon were added to the nitrogen. Argon was used to measure the temperature at the portal (aperture) of the atomic beam generator, where the gases shot out.[2.] The noble gas did not measureably affect the discharge. The discharge sparked twice/second at a tension of 3.5 kV. Nitrogen atom production with regards to stability and intensity was optimal at this frequency. Because of the long life span of the ntrogen atom, the low discharge frequency had little effect on the established measurement speed. The N^+ ion current indicator was stable. The attained atom concentration was between 25 and 30%. Atom concentrations of up to 50% could also be attained. To assure stability, the measurements were conducted with an atom concentration of 25%.

MEASUREMENT RESULTS AND DISCUSSION

The measurement of the N ionization cross section was accomplished in two stages: 1. Measurement of N ionization as a function of the beam in wavelength in random units, and 2. Determination of the cross section of the N atom for a fixed wavelength λ_0 in absolute units. Therefore, Part 1 of the measurement consisted of the N+ production according to equation 1:

$$N(^4S) + h\nu \rightarrow N^+ + e^- \qquad (1)$$

(1)

as a function to determine N^+ production as function of the wavelength and tied to the photoelectronic yield of a gold cathode.[1.] Therewith, all processes that lead to N^+ formation through other procedures are to be rejected. On the one hand, photoionization causes metastable excited

N atoms to move towards N^+ formation before the ionization boundary, and on the other, this ion is formed through dissociative ionization of N_2. Besides the $-^4S$ basic state, the two excited states ^2D and ^2S belong to the s^2p^3 electron configuration of the N atom. Both states are metastable. Since a transition to the ionic basic state is optically permissible, both of the ionization boundaries lie above 852 A (1020 and 1130 A respectively). The contribution of the metastable atoms to N^+ ionization can therefore be measured directly before the ionization boundary (limit) of the ^4S atom, by measuring N^+ formation. Figure 1 shows the N^+ ion current for the wavelengths 830 to 923 A. At 852 A, N^+ formation increases rapidly. The proportion of metastable N atoms in th measured N^+ ion current is maximally 0.3%. The formation of nitrogen ions through dissociative ionization according to equation (2), starts at a threshhold energy of 24.4 eV (508 A):

$$N_2 + h\nu \rightarrow N^+ + N + e^- . \qquad (2)$$

(2)

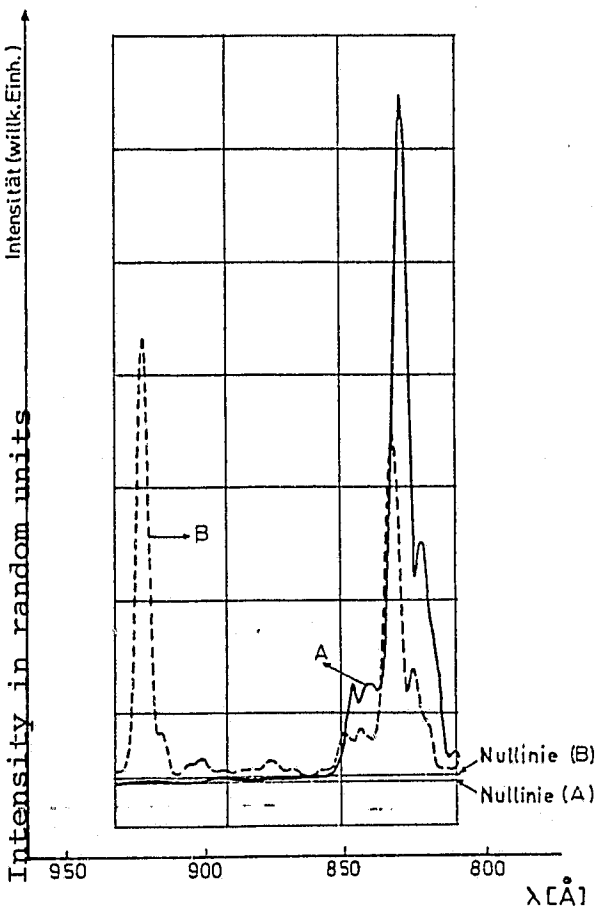

Figure 1. N^+ ion current (A) and Photoelectron current (B) as a function of wavelength

Zero-lines (A) and (B)

An earlier calculation reported the value 511 A. The contribution of ion formation according to (2) was measureable, and was considered in the calculation of the effective cross section.

For the second portion of the measurement, the mass spectrometer was for the time bring replaced by an ionization chamber and the N_2^+ formation for a fixed wavelength λ_0=554 A was determined. The effective cross section $\sigma(N_2)$ for the process

$$N_2 + h\nu \rightarrow N_2^+ + e^- \qquad (3) \qquad (3)$$

can be recovered from the measured values for the N_2 pressure, ion current, and photocell current. Measurements were conducted for 10 different N_2 pressures. According to (2), the wavelength 554 A did not suffice for dissociative ionization, and lies in a range of the N_2 ionization curve, where little or no structure is to be expected.[3,4]. Calculation of the N_2 ionization cross section (N) proceeds according to equation (4)

$$\sigma(N) = \sigma(N_2)\frac{J(N^+)}{J(N_2^+)} \cdot \frac{A(N_2^+)}{A(N^+)} \cdot \frac{1-\alpha}{\alpha} \qquad (4) \qquad (4)$$

To facilitate this for a particular atom concentration , the ion current relationship $J(N^-)/J(N_2^+)$ and the relationship of the secondary electron yield $A(N_2^+)/A(N^-)$ must be determined with the mass spectrometer. After consideration of the probe gas temperature in the atomic beam through means of an argon measurement, the atom concentration in the N_2^+ current with and without charge was determined. The relationship of the secondary electronic yields results from the median impulse height of the Poisson distribution resultant to both ion types at the exit portal of the multiplier. To finish determining the atom concentration it's still necessary to determine the proportion of metastable molecules in the beam. Fig. 2 shows the N_2^+ current in the range between 756 and 851 A Small N_2^+ currents were measured before the ionization limit at 796 A; their proportion, compared with the ionization below the limit wavelength, was

maximally 1.5% of the ion current.

The effective cross section σ (N) for the photoionization of the nitrogen atom in the basic state for the entire wavelength range is obtainable through the adjusting of relative values to the value absolute measured for 554 A. Figure 3 shows the measured points and a connecting median curve M. Additionally, curves A, B, and C are shown, that show the effective cross section calculated by HENRY[5] in the dipole length and dipole velocity approximations (A and B respectively), as well as the DALGARNO and PARKINSON [6]. calculation of the effective cross section in the dipole velocity approximation (C).

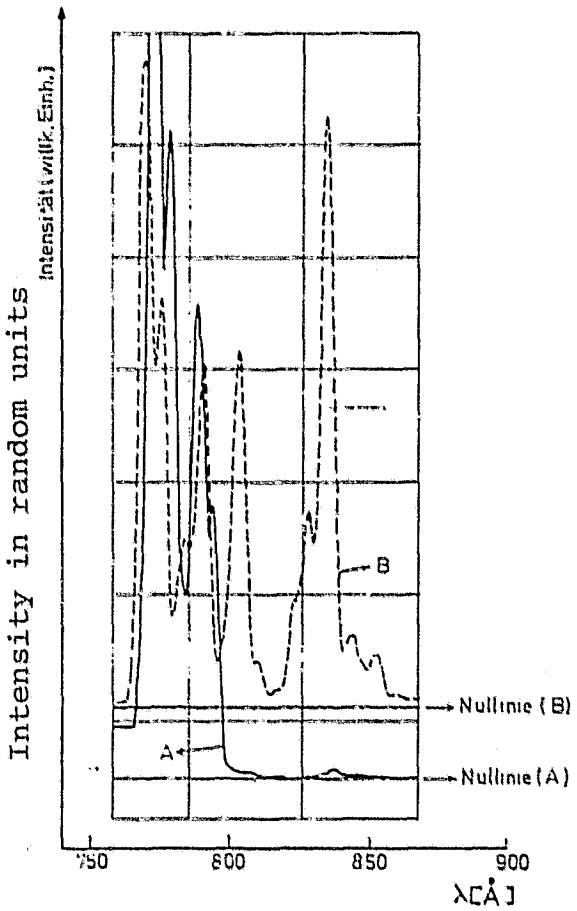

Fig. 2. N_2^+ Ion Current (A) and Photoelectron Current (B) as a Function of Wavelength.

Zero line (B)

Zero line (A)

HENRY's findings according to the dipole velocity approximation are mirrored best in the measurements up to a wavelength of 500 A. Under 500 A, the calculated values of this approximation deviate significantly from the measured findings. As is apparent in Fig. 3, the measured curve shows a much stronger declivity than the calculated ones, whose slope in the short wave portion of the indicated wavelength range is about equal. A characteristic deviation of the measured curve shows up between 600 and 700 A. In absorption and ionization measurements, it was demonstrated that a Rydberg series exists in this spectral range, that converges to the ^5S state of the ion, and whose termini decay through autoionization.[7,8.] The ^5S state is the lowest state of the ion in which an optically permissible transition of the N atom out of the basic state is to be expected. The convergence limit discovered in measurements in active nitrogen[7.] correlates well to ERIKSSON's established value for the excitation energy of this state.[9.] The Rydberg series is distinguished through the transitions $^4S^0 - 2s2p^3(^5S^0)np\,^4P$.[10.] The selection rules allow a reciprocal action of these states with the continual states of the series $2p^2(^3P)ns$ and $2p^2(^3P)nd$. The broadening and assymetry of the absorption lines occasioned by autoionization is easy to see. The value $Q \approx 1$ for the line form parameter was deduced from this.[8.] The divergence from the theoretical ionization curve caused by the Rydberg series results from that fact that these transitions were not even taken into consideration during the calculations. This is to be undertaken in these calculations.[11.]

The measured points are widely scattered in the neighborhood of the ionization limit. The measurement clearly shows that the stronger divergencies lie outside the error limit and can not be explained by statistical scattering. Transitions into the ^1D and ^1S ionic states, that likewise result from the $2s^22p^2$ configuration and whose entrance potentials lie at 755 and

667 A, are spin prohibitted and should not occur within the absorption spectrum.

Since the ionization curve was only measured for discrete wavelengths and not with a continual spectrum, statements about potential new termini in the ionization continuum of the nitrogen atom are extremely problematica However, it seems possible to repeat the measurements reported here against the background of a continuum.

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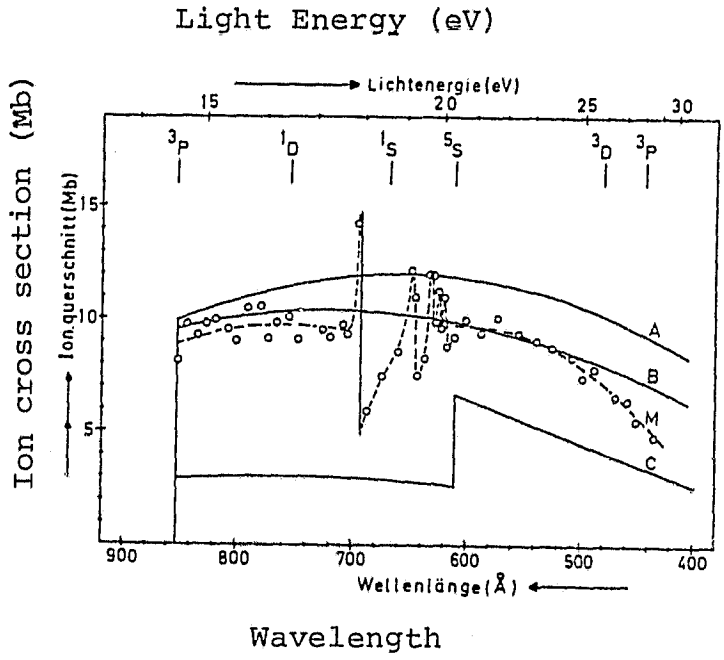

Figure 3. Effective Cross Section for the Photoionization of th N-atom.

M: Measured Curve

A&B: HENRY[11].
Dipole Length
Dipole Velocity

C: DALGARNO/PARKINSON[6].
Dipole Velocity

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