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A SOURCE OF HEATING IN THE THERMOSPHERE AND AURORAS?

by

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# RESONANT DISSOCIATION IN N<sub>2</sub> BY ELECTRON IMPACT: A SOURCE OF HEATING IN THE THERMOSPHERE AND AURORAS?

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An electron impact resonant dissociation process, leading to superthermal atom production in molecular nitrogen is described. The maximum cross section for this process is found to be  $2.5 \times 10^{-18}$  cm<sup>2</sup> at 10 eV. Measurements of scattered electrons indicate a value of -65 to -90 meV for the electron affinity of N. The possible role of resonant dissociation as a source of heating in the thermosphere and in auroras is discussed.

In an earlier report<sup>1</sup> and a brief publication,<sup>2</sup> we noted a new process leading to the dissociation of N<sub>2</sub> by electron impact at energies just above the dissociation threshold. The key feature of our observation was that a band of scattered electrons with abrupt onset at the dissociation limit, previously observed in threshold electron spectra, completely disappeared for scattered electron energies greater than our instrumental resolution of about 120 meV. These observations have recently been confirmed by Mazeau et al.<sup>3</sup> with better resolution.

Our data<sup>4</sup> are illustrated in Fig. 1 where we plot the scattered electron current in N<sub>2</sub> as a function of incident energy for six residual electron energies E<sub>r</sub>. The peaks correspond to the relative total cross sections for excitation of the labelled states at an energy E<sub>r</sub> above each respective threshold. The structure of interest is the broad continuum feature which is most prominent in curve D for scattered energy of 0.07 eV, and is entirely absent in curves A and F which correspond to scattered energies of 0.01 and 0.17 eV, respectively.

The energy distribution of scattered electrons is obtained by plotting the scattered electron current as a function of residual energy at a fixed impact energy. The scattered electron energy distribution we obtain at impact energies of 10.28 and 10.72 eV are shown in Fig. 2, where the distribution widths of 65 meV are considerably narrower than the overall energy resolution of our apparatus (about 115 meV).

Neither of these features, abrupt onset and narrow scattered electron distributions, are characteristic of excitation to a bound or repulsive state of N<sub>2</sub>. This formed the basis of our interpretation<sup>2</sup> that a resonance process forming a temporary negative ion N<sub>2</sub><sup>-</sup> was involved in a dissociation process analogous to the more familiar process of dissociative electron attachment.

The dissociative attachment process leading to the formation of negative ion and neutral fragments by electron impact on small molecules is well known.<sup>5</sup> Such processes in diatomic molecules, for example, are initiated by the attachment of an incident electron to form a temporary negative molecular ion, or resonance. If attachment occurs above the ionic dissociation limit, the molecule may dissociate yielding a neutral atom and a stable negative ion.

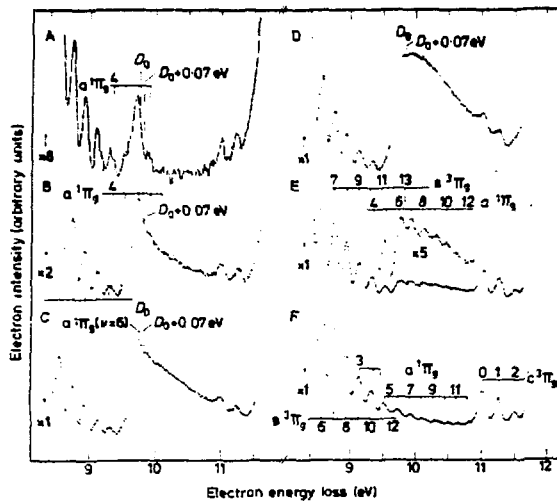


FIG. 1.--Energy-loss spectra in  $N_2$  taken with selected constant final electron energies,  $E_r$ , between 0.01 eV and 0.17 eV as a function of incident electron energy. Note the large continuum feature in curve D is not present for  $E_r=0.01$  and 0.17 eV. Values for  $E_r$  for the different curves are as follows: A, 0.01 eV; B, 0.04 eV; C, 0.06 eV; D, 0.09 eV; E, 0.15 eV; F, 0.17 eV.

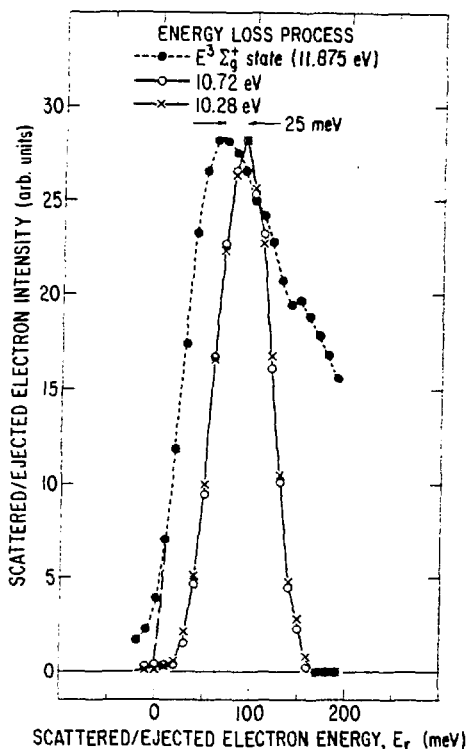
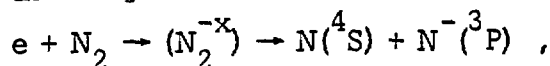


FIG. 2.--Ejected electron energy distributions taken at 10.72 and 10.28 eV incident energy with the continuum observed in Fig. 1. The two distributions have been normalized to equal magnitude. The total excitation function for excitation of the  $E^3\Sigma_g^+$  state obtained from the same experimental data is included as an aid in locating the zero energy of the scattered/ejected electrons.

Strictly speaking, a proper dissociative attachment process cannot take place in molecules whose component atoms possess only unstable negative ions, since the electron must ultimately detach in the separated atom limit. Nevertheless, the analogous process may be envisioned in which the unstable atomic negative ion survives to large internuclear separation and ejects an electron having a kinetic energy equal to the magnitude of the atomic electron affinity. The process provides a mechanism for dissociation through the intermediate formation of a temporary negative ion, and hence could be classified as "resonant dissociation by electron impact."

In nitrogen the mechanism of resonant dissociation is



followed by  $N(^3P) \rightarrow N(^4S) + e$ .

The above process is explained in more detail with reference to Fig. 3 where we have made a sketch of the relevant  $N_2$  and  $N_2^-$  potential energy curves, with the upper  $N_2^-$  potential curve being responsible for the resonant dissociation mechanism. In order to explain our observation, we must make only two very reasonable assumptions: (1) Such an  $N_2^-$  state exists, and it crosses its dissociation limit within the Franck-Condon region of  $N_2$ . This is necessary to explain the vertical onset for slow electron production. (2) This  $N_2^-$  state has a lifetime at least equal to one vibration period,  $\approx 10^{-14}$  sec. This is certainly true for  $X^2\Pi N_2^-$  state. Our measurements of the scattered electron energy distributions suggest a value for the electron affinity of  $-65$  to  $-90$  meV for N, in good agreement with the value of  $70 \pm 20$  meV obtained by Mazeau et al.<sup>2</sup> using superior resolution.

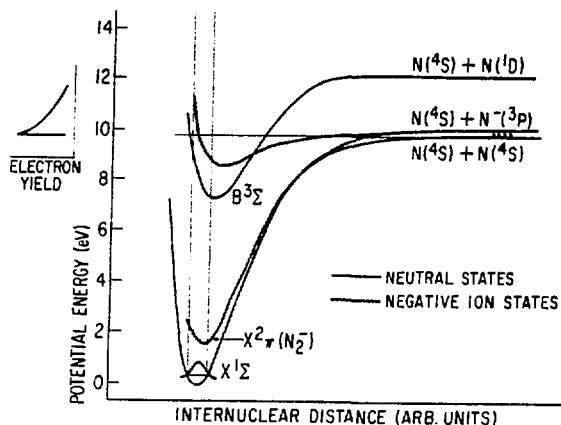


FIG. 3.--Schematic potential energy diagram of  $N_2$  and  $N_2^-$  with a sketch of the expected yield of slow electrons produced by decay of the upper  $N_2^-$  state.

The cross section for production of superthermal N atoms by resonant dissociation is shown as a function of electron impact energy by the shaded area of Fig. 4. We obtain the magnitude of the cross section for production of nitrogen atoms by resonant dissociation with reference to the  $B^3\Pi_g(v=5)$  peak, which we normalize to the absolute integral cross sections for this state (Cartwright et al., 1977).<sup>6</sup> Unfortunately, Cartwright et al. did not obtain absolute values of this state for energies below 10.0 eV, whereas our measurements only extend to 170 meV above threshold. We resolve this difficulty by referring to the differential measurements of the  $B^3\Pi_g$  state by Mazeau et al.,<sup>7</sup> where we note a vertical onset (which our measurements confirm), followed by a shallow dip and then a larger peak at about 10.0 eV. The differential data indicate that the cross section at 12 eV is approximately equal to the threshold peak, a feature which is fairly constant with respect to angle. The maximum dissociative cross section as plotted in Fig. 3 is thus  $2.5 \times 10^{-18}$  cm<sup>2</sup>. We estimate the total error in our value of the cross section to be about  $\pm 50\%$ .

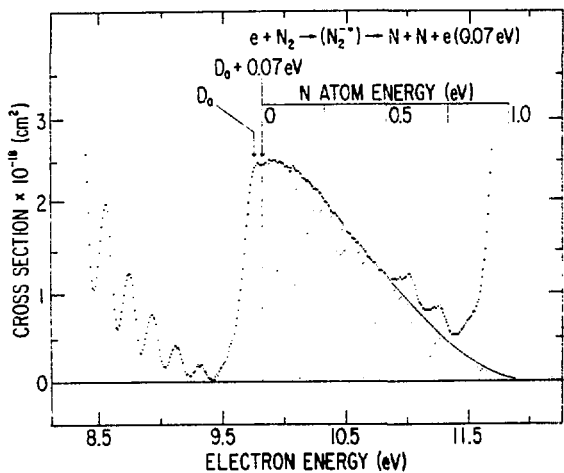


FIG. 4.--Total cross section for production of N atoms (shaded area) from the reaction  $e + N_2 \rightarrow (N_2^*) \rightarrow N + N + e(0.07 \text{ eV})$  as a function of incident electron energy. The estimated error in the cross section is  $\pm 50\%$ . The additional scale along the abscissa indicates the kinetic energies of the superthermal N atoms provided by this process.

The resonant dissociation mechanism discussed here provides a source of superthermal N atoms from N<sub>2</sub> at the lowest possible impact energy. Thus, it is likely to play a role of some importance in nitrogen plasmas (e.g., N<sub>2</sub> lasers and MHD plasmas) and in upper atmospheric phenomena.

In considering physical and chemical processes in the atmosphere, it is usual to regard the atmosphere as being divided into layers (more properly called regions). However, one must remember that these regions do not co-exist independently, in that in a vertical plane mass, momentum and energy transfer must be considered under the equilibrium conditions that exist. Thus, to a large extent, conditions in the lower atmosphere are dependent upon conditions existent at the highest reaches of the atmosphere, i.e., the thermosphere, which is defined as the region from an altitude of about 100 km to the far reaches of space. The thermosphere derives its name because of the large increase in kinetic temperature with altitude, about 200°K at 100 km, increasing to 1000°K at 300 km. A long-standing problem concerning mathematical modeling of the thermosphere has concerned the energy balance necessary to maintain the large temperature gradient. In order to calculate the energy input, two requirements are necessary: (1) a detailed knowledge of the flux of solar radiation onto the atmosphere as a function of photon energy, and (2) the fraction of this total energy converted into kinetic energy by known physical and chemical processes.

The constitution of the atmosphere at high altitudes is very simple, being approximately 20% molecular nitrogen and 80% atomic oxygen at 300 km.<sup>8</sup> All other species constitute only about 1% by composition. Whereas at lower altitudes (80–100 km) most of the energy input comes from O<sub>2</sub> absorption in the Schumann-Runge continuum,<sup>9</sup> at higher altitudes there is practically no O<sub>2</sub> for this mechanism to occur. The primary mechanism for energy deposition in the thermosphere is the photoionization of the constituents,<sup>9</sup> which then undergo various physical processes, such as dissociative recombination, converting photon energy to kinetic energy. A second conversion mechanism is dissociative ionization by the free electrons.

The energy-loss mechanisms of the thermosphere can be accurately calculated and are predominantly:<sup>9</sup> (a) conduction to lower layers, and (b) infrared emissions from the O ground state at a wavelength of 63 μm. These mechanisms are of comparable magnitude. However, mass spectrometric rocket measurements (see Ref. 10 and references therein) give rise to a problem, since the concentration of atomic nitrogen in the thermosphere is too high to be explained by known electron-impact dissociation cross sections.<sup>11,12</sup> In fact, it has been determined<sup>10</sup> that electron dissociation cross sections would have to be increased by a factor of 3 at 15 eV and scaled accordingly to account for the measured concentration of N.

Early attempts to balance the energy flow in the thermosphere were made by Bates<sup>9,13</sup> who, partially because of the relatively poor knowledge of the solar flux at wavelengths shorter than uv, found the heat input to the thermosphere to be too low by a factor of 20 to 60 to maintain the known temperature gradient when balanced against the well-characterized energy losses. To explain this imbalance Bates<sup>9</sup> proposed modifying factor (2) on the preceding page by postulating a mechanism of energy conversion by "hidden" dissociative recombination—hidden in the sense that the reaction rate would be too fast for radar detection of the true electron concentration.

More recent measurements of solar flux at a wavelength shorter than the uv, and x-ray region, have yielded a fairly well-characterized solar photon flux

distribution, thus improving factor (1) on the preceding page. However, recent model calculations<sup>14</sup> still yield a factor of 2 difference between the known energy input and that required to produce the large temperature gradient. Alternative sources of input such as joule heating of the atmosphere have been considered to balance the energy equation.<sup>15</sup>

However, an additional source of heating would be an increase in the conversion rate, i.e., factor (2) on the preceding page. A possible mechanism for this process could be that of resonant dissociation by electron impact discussed above. This process will produce superthermal atoms, which would probably be equilibrated with the surrounding species. Mazeau et al.<sup>3</sup> have found the same mechanism to occur in NO, although the concentration of NO in the thermosphere is too low for this mechanism to provide much energy conversion.

The electron concentration at 300 km is about  $10^{-3}$  of the total composition<sup>8</sup> during the daytime, and furthermore the energy distribution is known from the measurements of Doering et al.<sup>16</sup> to peak at about 10 eV (at  $\approx 100$  km), exactly the right energy for resonant dissociation of  $N_2$ . The electron flux falls off very rapidly with increasing energy, decreasing by 3 orders of magnitude from 10 eV to 60 eV.

It is instructive to examine the product of known cross sections for N atom production and the measured electron flux. Such a plot is shown in Fig. 5, which may be conveniently divided into 3 regions: (a) The sharp spike at 10 eV results from the resonant dissociation process producing superthermal atoms. Although the cross section for this process is low, the electron flux is at a maximum at the energy. (b) This large area results from straightforward electron-impact dissociation of  $N_2$  calculated from the measurements of Winters.<sup>11,12</sup> Although the area of b is very large, probably a large fraction results in thermal atoms which will not cause significant energy conversion. (c) This region results from dissociative ionization of  $N_2$  which is based on the measurements of Rapp et al.<sup>17</sup> for production of ions (and atoms) of energies  $\geq 0.25$  eV. The area of region c is seen to be comparable to that of region a. Although it is not possible to say that reaction a will result in a significant energy conversion, (and Fig. 4 would seem to indicate that reaction a provides little additional N to explain the anomalous N atom concentrations), we must point out that the cross-section data used to calculate region a were obtained for nitrogen in its ground vibrational level.

The significance of this is that the resonant dissociation process is the direct analog of dissociative electron attachment. Dissociative attachment cross sections are known to be often extremely dependent on the vibrational state of the

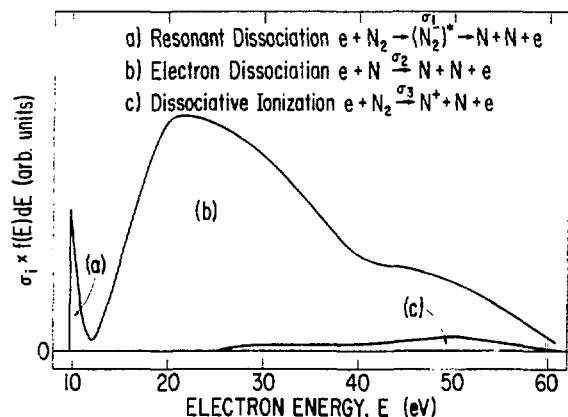


FIG. 5. --Plot of the product of cross section  $\times$  electron flux (arb units) as a function electron energy typical of conditions in the thermosphere. Three regions, a, b, c, corresponding to resonant dissociation, direct dissociation, and dissociative ionization by electron impact are indicated.

target gas, <sup>18-23</sup> and in some cases they can increase by several orders of magnitude for vibrationally and rotationally excited target states. Note that dissociative ionization cross sections also increase<sup>24,25</sup> but at a much slower rate.

We stress that at the present time the discussion above is highly speculative, but in view of the important nature of the problem, we feel that further study is justified. We note that in auroras there is also evidence of an unknown process pumping energy into the system, and that superthermal N atoms of unknown origin have been observed.<sup>26</sup>

#### REFERENCES

1. D. Spence and P. D. Burrow, Radiological and Environmental Research Division Annual Report, October 1976-September 1977, ANL-77-65, Part I, pp. 87-89.
2. D. Spence, R. H. Huebner, and P. D. Burrow, *Am. Phys. Soc.* 23, 143 (1978).
3. J. Mazeau, F. Greteau, R. I. Hall, and A. Huetz, *J. Phys. BL Atom. Molec. Phys.* 11, L557-60 (1978).
4. D. Spence and P. D. Burrow, *J. Phys. B: Atom. Molec. Phys.* 12, L179 (1979).
5. G. J. Schulz, *Rev. Mod. Phys.* 45, 423 (1973).
6. D. C. Cartwright, S. Trajmar, A. Chutjian, and W. Williams, *Phys. Rev. A* 16, 1041 (1977).
7. J. Mazeau, F. Greteau, R. I. Hall, G. Joyez, and J. Reinhardt, *J. Phys. B: Atom. Molec. Phys.* 6, 682 (1973).
8. DNA Reaction Rate Handbook, 2nd Edition, published by DASIAC DoD Nuclear Inf. and Analysis Center, General Electric, TEMPO, Santa Barbara, CA.
9. D. R. Bates, *Proc. Phys. Soc.* 64B, 805 (1951).
10. E. S. Oram, D. F. Strobell, and K. Maversberger, *J. Geophys. Res.* 83, 4877 (1978) and references therein.
11. H. F. Winters, D. E. Home, and E. E. Donaldson, *J. Chem. Phys.* 41, 2766 (1964).
12. H. F. Winters, *J. Chem. Phys.* 44, 1472 (1966).
13. D. R. Bates, *Proc. Roy. Soc.* 253A, 451 (1959).
14. R. G. Robb and R. E. Dickenson, *J. Geophys. Res.* 78, 249 (1973).
15. B. B. Hinton, *J. Geophys. Res.* 83, 707 (1978).
16. J. P. Doering, W. K. Peterson, C. O. Bostrom, and T. A. Potemra, *Geophys. Res. Lett.* 3, 129 (1976).
17. D. Rapp, P. Englander-Golden, and D. A. Briglia, *J. Chem. Phys.* 42, 4081 (1965).
18. W. R. Henderson, W. L. Fite, and R. T. Brockmann, *Phys. Rev.* 183, 157 (1969).
19. D. Spence and G. J. Schulz, *Phys. Rev.* 188, 280 (1969).
20. T. F. O'Malley, *Phys. Rev.* 150, 14 (1969).
21. D. Spence and G. J. Schulz, *J. Chem. Phys.* 58, 1800 (1973).
22. P. J. Chantry, *J. Chem. Phys.* 51, 3369 (1969).
23. M. Allan and S. F. Wong, submitted for publication.
24. D. Spence and K. T. Dolder, *New Experimental Techniques in Propulsion and Energetics Research*, Ed., D. Andrews and J. Suruque (Technivision Series, Slough, England, 1970), p. 423.
25. R. T. Brackmann, W. L. Fite, and W. M. Jackson, *Proc. 18th Ann. Conf. of Mass. Spectrosc. and Allied Topics*, San Francisco, 1970, p. B107.
26. T. Shyn, private communication.