Energy Imparted by Active Nitrogen

SPECTROSCOPIC evidence[1] shows that the maximum energy of excitation which a molecule of active nitrogen can impart to another molecule (or atom) is 9·45 eV. Lord Rayleigh, however, from a study of the incandescence of metals immersed in active nitrogen, finds[2] that each molecule of active nitrogen delivers to the metal energy of, at the least, 10 eV. These apparently conflicting results can be reconciled and satisfactorily explained on the hypothesis recently proposed by me, namely, that active nitrogen is simply the ionized molecule of nitrogen $N_2^+(X')$ produced by the discharge .

The molecules (or atoms) introduced into the vessel containing active nitrogen are excited by a three-body collision process as follows :

$$N_2^+ + e + M \rightarrow N_2 \text{ (excited)} + M \text{ (excited)}.$$

Now, the lowest electronic level of excitation to which N_2 can drop, on neutralization, is the A-level, with energy 6·1 eV. The levels lying immediately below it are high vibrational levels of the ground state (X) with distances of nuclear turning-points very different from the nuclear separation of $N_2^+(X')$. Transitions to any of these levels will violate the Franck-Condon principle. The maximum energy left over for exciting the third body is thus $15{\cdot}58 - 6{\cdot}1 = 9{\cdot}48$ eV. This explains why repeated attempts by spectroscopists have failed to produce excitation levels above 9·45 eV.

The possible levels below the A-level to which the neutralized N_2 molecule can drop are the ground-level (X) and a few of the vibration-levels immediately above it. But this would mean that nearly the whole of the energy of ionization is either radiated away or is taken up by M. The reaction in this case would be :

$$N_2^+ + e + M \rightarrow N_2 \text{ (normal state)} + M \text{ (excited state)}.$$

I do not know if the probability of such reactions has been studied. In my opinion the probability would be very small.

To explain the higher value of energy as obtained by Rayleigh we recall that for neutralization of N_2^+ on the surface of a solid, the latter acts as the third body. The electrons first arrive on the surface of the solid and remain there as surface charge. The N_2^+ ions then arrive and combine with the electrons, giving up the energy of recombination to the solid surface. Since the solid, with its complicated structure, has many modes of vibration, it can take up the whole of the released energy, 15·58 eV. This, in other words, means that though spectroscopically active nitrogen can impart energy only up to a maximum of 9·45 eV. to an atom or a molecule, it can impart much greater energy (15·58 eV.) to the surface of a solid. This explains the apparently conflicting results mentioned above.

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[1] Okubo, J., and Hamada, H., *Phil. Mag.*, (7), **5**, 272 (1928).
[2] Rayleigh, Lord, *Proc. Roy. Soc.*, A, **176**, 17 (1940).
[3] Mitra, S. K., *Science and Culture* (Calcutta), **9**, 49 (1942–43) ; **10**, 133 (1944–45) ; *Nature*, **154**, 212 and 576 (1944).