

EXCITED IONIC AND NEUTRAL FRAGMENTS PRODUCED

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BY DISSOCIATION OF THE N_2^{+*} H BAND

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ABSTRACT

NI and NII fluorescent radiation has been observed when N_2 was irradiated by undispersed synchrotron radiation with an upper energy limit of approximately 200 eV. The excited fragments originate from dissociation of a band of excited ionic states of N_2 lying between 34.7 and 44 eV.

INTRODUCTION

Photoelectrons produced by ionization of inner shell valence electrons can interact with the remaining orbital electrons to create excited states of the resulting ion. Such two electron transitions, or satellite states, have been observed in the photoelectron spectrum (PES) of N_2 by many groups who used photon energies ranging from 41 to 1487 eV.¹⁻⁸ The binding energies of the satellite states lie between 23 and 45 eV. These states appear to play a significant and interesting role in the photoionization of N_2 . For example, Krummacher *et al*⁸ have shown that the total cross section for producing these states amounts to roughly 30% of the total photoionization cross section between 43 and 65 eV. It also appears that these

states are responsible for most of the dissociative ionization that occurs in N_2 above the threshold at 24.3 eV.⁹⁻¹¹ Although considerable theoretical attention has been directed to understanding the electron configuration of these states¹²⁻²¹ there is little information on the products of dissociation. The H band is particularly interesting because, if it predissociates, it is the only band capable of producing atomic fluorescence. A composite of the PES data, taken from Krummacher *et al.*⁸ and Nyholm *et al.*⁷ is shown in Fig. 1 along with the various spectroscopic dissociation limits. Krummacher *et al.*⁸ note that the absence of any observable Auger decay in their PES data of the H band indicates that this band does predissociate. As can be seen from Fig. 1 the lowest dissociation limit that can produce fluorescence is $N^+(^3P) + N\ 3s(^4P)$ at 34.7 eV. The majority of the remaining limits lie between 34.7 eV and 38.9 eV, the $(N^+ + N^+)$ limit. All lie within the bounds of the H band. Langhoff *et al.*¹⁹ note that their calculations predict that the H band is comprised of a large number of $^2\Sigma_g^+$, $^2\Sigma_u^+$, and $^2\Pi_u$ ionic states converging on the N_2^{2+} limit (~ 43 eV). Sambe and Ramaker²¹ attribute the sharp structure observed in the H band as belonging to the lower members of the Rydberg series converging to N_2^{2+} .

It is the purpose of this paper to present evidence that the H band does predissociate into excited neutral and ionic atoms. The method chosen for this study was to observe and identify atomic fluorescence produced by dissociative photoionization of N_2 .

EXPERIMENTAL

Fluorescent radiation was produced by irradiating N_2 with undispersed synchrotron radiation. The band-pass of the radiation, after reflection from the focussing mirrors, ranged from the visible to about 60 Å. The radiation passed

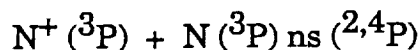
through a glass capillary (part of a differential pumping system) so that it would intercept a N_2 gas jet located about 2mm in front of the entrance slit of a 0.5 m Seya monochromator. The interaction chamber and monochromator were both pumped with turbomolecular pumps. The pressure in the interaction chamber was maintained at about 10^{-4} Torr. The monochromator had a 3 Å band-pass and was scanned from 645 to 1250 Å. The spectrum was detected with a multi-channel plate electron multiplier. The fluorescent radiation observed originated mainly from excited NI and NII states with a small amount from excited molecular states.

RESULTS AND DISCUSSION

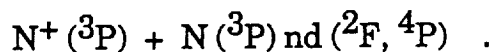
All NI and NII emission lines observed between 645 and 1250 Å are listed in Tables I and II, respectively. The threshold energies for the dissociation limits are given along with the relative intensity of each line observed. These intensities were obtained by dividing the measured signal with the ring current in the storage ring and dividing by a typical detection efficiency for the microchannel plate detector.²² Minor corrections were made for possible absorption of the fluorescent radiation by the N_2 background.

We have assumed that the fluorescence originates from the excited products of dissociative photoionization and this must be true for N^{+*} fluorescence. However, excited neutrals can be produced by simple photodissociation. The minimum threshold for producing $N(^4S) + N^*$ (1200 Å fluorescence) is 20.1 eV. Fluorescent radiation has been observed in this region (20 to 27 eV) by Beyer and Welge.²³ However, they measured the efficiency for fluorescence to be less than 1%. This is a narrow wavelength band where the photoionization yield is slightly less than 100%²⁴ and where the Codling Rydberg bands²⁵ are observed. These

states, in which autoionization and predissociation presumably compete, can be produced only through resonance absorption of the incident radiation. Thus, only an extremely narrow band of the undispersed synchrotron radiation could excite these states. On the other hand, N_2^{+*} can be excited continuously from its threshold to the energy limit of the incident radiation ($\sim 60 \text{ \AA}$). Fluorescence from higher excited states such as $(N^{+*} + N^*)$ or $(N^{+*} + N^+)$ may be possible but three electron transitions are about a factor of 10 to 100 times less probable than two electron transitions. We conclude, therefore, that the fluorescence observed in the present work originates from N_2^{+*} states and that the products of dissociation are mainly those given in Tables I and II. It is true that cascading will take place from most of the excited neutrals given in Table I. Thus, Table I reflects what is observed and not the relative probability for producing a specific product. However, it is clear that the main products of dissociation are,



and



To identify N_2^{+*} we note that from Table I we have a minimum threshold of 34.7 eV for producing the observed fluorescence. An upper limit can be determined by measuring the kinetic energies of the N^+ fragments. Measurements made with the 40.8 eV HeII line²⁶ yield N^+ energies ranging from zero to about 5 eV. Similar results were obtained by use of undispersed synchrotron radiation with the same band-pass as used in the present work.¹¹ In this case the high energy tail extended to about 6 eV. This results in a total fragment energy ranging from 0 to $< 12 \text{ eV}$. Thus, the major amount of fluorescence observed must origi-

nate from N_2^{+*} states in the energy range from 34.5 eV to < 51 eV (taking 2 N^+ as an upper limit). The only states observed within this energy range are those that make up the H band including the small peaks between 40 and 44 eV. No discernable structure above 44 eV has been observed in VUV or X-ray PES studies. The kinetic energy measurements of N^+ made by Wu *et al.*²⁷ are particularly significant. They studied the kinetic energy distribution of the fragments by measuring the N^+ signal in coincidence with any 1200 Å fluorescence emitted by N^+ . Their results show structure in the kinetic energy spectrum with ion energies ranging from 0.18 to 2.58 eV. Thus, the excited states of N_2^{+*} responsible for the 1200 Å fluorescence must lie between 35 and 40.8 eV. In fact the structure observed by Wu *et al.* appears to correlate with the structure observed by Krummacher *et al.*

We feel that the evidence supports the conclusion that the observed N_2^{+*} states lying between 34.7 and 44 eV dissociate and are responsible for producing the fluorescent radiation tabulated in Tables I and II.

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TABLE I. Observed fluorescence from excited neutral atoms produced from dissociative photoionization of N_2 . The core state of the atom is 3P unless otherwise indicated.

Fluorescence (Å)	Products	Dissociation limits (eV)	Relative Intensity (%)
1200	$N^+(^3P) + N\ 3s\ (^4P)$	34.7	34.2
1493	$3s\ (^2P)$	35.0	11.4
1135	$2s2p^4(^4P)$	35.3	5.2
1243	$3s'(^2D)$	36.7	4.1
965	$4s\ (^4P)$	37.2	3.5
1177	$4s\ (^2P)$	37.3	0.9
1168	$3d\ (^2F)$	37.3	1.7
954	$3d\ (^4P)$	37.4	3.1
910	$5s\ (^4P)$	38.0	1.3
905-907	$4d\ (^4P)$	38.0	1.7
1100.4	$5s\ (^2P)$	38.0	0.6
1097.2	$4d\ (^2F)$	38.0	1.0
887-888	$6s\ (2, ^4P)$	38.3	0.5
1067.6	$5d\ (^2F)$	38.4	0.8
1054.3	$7s\ (2, ^4P)$	38.5	0.3
875-877	$7s\ (^4P), 6d\ (^2F, ^4P)$	38.5	0.5
869.4	$8s\ (^4P), 7d\ (^2F, ^4P)$	38.6	0.3
1043-1044	$8s\ (^2P), 7d\ (^2F, 2, ^4P)$	38.6	0.3
862.1	$9d\ (^4P)$	38.7	0.2
865.95	$9s\ (^2P)$	38.7	
865.65	$2s2p^3\ (^5S^o)\ 3p\ (^4P)$	42.2	

TABLE II Observed fluorescence from excited atomic ions produced by dissociative photoionization of N_2

Fluorescence (Å)	Products	Dissociation limits (eV)	Relative Intensity (%)
1085.7	$N(^4S) + N^+ 2s2p^3 (^3D^o)$	35.8	18.3
916.7	$2s2p^3 (^3P^o)$	37.9	4.2
776	$2s2p^3 (^1D^o)$	42.2	0.8
747	$2s^22p (^2P^o) 3s (1, ^3P^o)$	42.8	1.4
670-672	$2s^22p (^2P^o) 3s (1, ^3P^o)$	42.8	1.9
645	$2s2p^3 (^3S^o)$	43.6	0.4
660	$2s2p^3 (^1P^o)$	45.0	0.3

FIGURES

- Fig. 1. Photoelectron spectrum of N_2 compiled from the data of Krummacher et al. (ref. 8) and Nyholm et al. (ref. 7) showing the E, G, and H bands of N_2^{+*} as a function of their binding energies. The dissociation limits relating to the observed NI and NII fluorescence is shown on the same energy scale.

OBSERVED FLUORESCENCE (Å)

