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ON THE DISSOCIATION OF NITROGEN BY ELECTRON IMPACT AND BY E.U.V. PHOTO-ABSORPTION

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Abstract—The dissociation of N_2 by electron impact and by e.u.v. photo-absorption is studied, and it is shown that the forbidden predissociation of the numerous $^1\Pi_u$ and $^1\Sigma_u{}^+$ valence and Rydberg states of N_2 in the 11–24 eV energy range is the dominant mechanism for N atom production. By measuring the absolute emission cross sections for the e.u.v. singlet bands of N_2 and by using the generalized oscillator strength data of Lassettre (1974), it has been possible to construct a detailed model of the total N_2 dissociation cross section which is in good agreement with the measurements of Winters (1966) and Niehaus (1967) and provides some insights into the maximum possible $N(^2D)$ yield from dissociative excitation. The total cross section for exciting N_2 e.u.v. radiation in the 800Å–1100Å wavelength range has been measured and found to have a value of 3.4×10^{-17} cm^2 at 100 eV under optically thin conditions. Although this result implies that large fluxes of e.u.v. photons should be excited in auroral substorms and in the airglow, they are not observed, and we show that this development is a consequence of radiation entrapment and predissociation. The total cross section for dissociating N_2 by electron impact is given for optically thin and thick media. And some questions concerning the energy budget of a magnetospheric storm which are raised by these results, are discussed.

INTRODUCTION

Inelastic electron scattering studies (Lassettre and Krasnow, 1964; Silverman and Lassettre, 1965; Geiger and Schroeder, 1969; Lassettre, 1969; Williams and Doering, 1969a,b; Brinkmann and Trajmar, 1970; Lassettre, 1974) as well as extreme ultraviolet [e.u.v.] absorption measurements (Hauffman *et al.*, 1963; Tilford and Wilkinson, 1964; Cook *et al.*, 1965; Tilford *et al.*, 1965; Lawrence *et al.*, 1968; Carroll and Collins, 1969; Dressler, 1969; Huffman, 1969; Carroll and Yoshino, 1972) show that molecular nitrogen possess a large number of valence and Rydberg states in the energy range 11.5–40 eV. Many of these singlet states relax radiatively in direct dipole-allowed e.u.v. transitions to the ground state (Wilkinson and Houk, 1956; Wallace, 1962; Tilford and Wilkinson, 1964 a,b) and through weaker intercombination transitions to the $a^1\Pi_g$ state in the 2000–3000 Å wavelength range (Lofthus, 1957; McFarlane, 1965; 1966). Because the total cross section for electron impact excitation of this manifold of states is comparable in magnitude to the N_2 ionization cross section (Porter *et al.*, 1976) and because the radiative lifetimes of these states are generally in the range of 1 ns to 0.1 μs (Hesser and Dressler, 1966), modelers have predicted that large fluxes of e.u.v. radiation would be excited in the dayglow by energetic photoelectrons and in auroral substorms by precipitating electrons impacting on ambient N_2 molecules (Green and Barth, 1967; Stolarski and Green, 1967). The photochemical implications of an e.u.v. flux of this magnitude have been discussed by Zipf (1973a) who suggested that this radiation would produce significant modifications in the ion chemistry of an aurora because of selective photoionization of O_2 and O and that it would also contribute to the excitation of the OI green line (λ5577 Å) by photodissociation of O_2 (Zipf, 1973b; Lawrence and McEwan, 1973 . Initially these predictions appeared to be borne out by the photometric observations of Parcese *et al.* (1972) who found that the intensity of the extreme ultraviolet flux in the 900–1100 Å wavelength range in an IBC I aurora was approximately 20 times the brightness of the OI green line. The laboratory measurements of Sroka (1968a,b), which indicated very large emission cross sections for electron-impact excitation of N_2, seemed to provide additional support for this view. Likewise a careful examination of the overall energy budget of an auroral substorm suggested that approximately 16% of the energy deposited in an aurora is probably dissipated in the excitation of the e.u.v. component of the spectrum (Rees, 1975) in agreement with the photometer observations of Parcese *et al.* (1972).

Several groups have now carried out detailed *in situ* measurements of the auroral and dayglow e.u.v. spectrum using scanning monochromators

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(Christensen, 1976; Parks *et al.*, 1977) in order to identify the specific emission features that contributed to the large signals observed by Parcese *et al.* (1972). Although these measurements still have low resolution ($\Delta\lambda \sim 13$–20 Å) when compared with the laboratory data shown in Figs 2 and 3, nevertheless they still show clearly that molecular nitrogen does not contribute significantly to the observed e.u.v. flux, that the total e.u.v. flux is small compared to the OI green line (in disagreement with the broadband photometer measurements), and that only a small portion of the energy deposited in the aurora ($<2\%$) can be identified with the formation of e.u.v. photons (Parks *et al.*, 1977). The field observations are thus in complete disagreement with the results anticipated on the basis of our knowledge of the inelastic electron scattering spectrum of N_2 and from auroral energy conservation considerations (Rees, 1975).

It is the purpose of this paper to show from the results of laboratory experiments that most N_2 molecules excited to the manifold of singlet states observed by Lassettre and others are depopulated by predissociation and not by the emission of extreme u.v. photons as previously assumed, that this process is the principal mechanism by which N_2 is dissociated by solar e.u.v. absorption and by electron impact, that the total cross section for electron-impact dissociation of N_2 measured by Winters (1966) owes its quantum mechanical origin to the excitation of these singlet valence and Rydberg states, and that because of entrapment effects Winters' laboratory cross section measurement underestimates the total dissociation rate. Thus, these electron scattering experiments provide a physical explanation for the near absence of N_2 band radiation in airglow and auroral e.u.v. spectra, and they rule out the excitation of extreme u.v. radiation as a major factor in the overall energy economy of an auroral substorm.

EXPERIMENTAL RESULTS

E.U.V. spectroscopy

The early spectroscopic studies of the e.u.v emission spectrum of N_2 (Wilkinson and Houk, 1956; Wallace, 1962; Tilford and Wilkinson, 1964a,b) revealed a complex system of bands in the 800–1200 Å wavelength range. These high resolution measurements were primarily concerned with determining the quantum mechanical identity, the vibrational and rotational constants, and the term energy of the many singlet states contributing to the spectrum. For the most part these spectra were obtained with optically thick gaseous discharge sources and used photographic techniques that possessed limited dynamic range. At the time of this work accurate absolute calibration standards for this region were yet to be developed, so that quantitative measurements of the absolute excitation rates and emission cross sections were not possible. Nevertheless, the high-resolution emission and absorption data showed very clearly that the N_2 singlet bands were strongly perturbed by both homogeneous and heterogeneous interactions, that many bands were cut off at high J values, and that individual rotational lines were often broadened (Tilford and Wilkinson, 1964a,b; Lawrence *et al.*, 1968; Carroll and Collins, 1969; Dressler, 1969; Lefebrve-Brion, 1969). Furthermore a comparison of the emission and absorption data showed that a number of optically allowed transitions were conspicuously absent in the photographic emission data suggesting that predissociation competes effectively with radiation in depopulating these states. Since these observations generally involved the use of optically thick sources where entrapment effects could enhance the apparent efficiency of an otherwise weak predissociation process, the predissociation branching ratio (i.e., the fraction of excitations of the vibrational level v' of the electronic term k that predissociate),

$$B_{v',k} = \frac{I_{v',k}}{A_{v',k} + I_{v',k} + AI_{v',k} + S_{v',k}} \quad (1)$$

where $I_{v',k}$ is the spontaneous predissociation rate, $A_{v',k}$ is the total rate for spontaneous radiative transitions, $AI_{v',k}$ is the rate for spontaneous autoionization and $S_{v',k}$ the rate at which the level is collisionally quenched (Porter *et al.*, 1976), could not be quantitatively evaluated.

Nevertheless Hudson and Carter (1969) were the first to recognize that this forbidden predissociation process might be very efficient in general and that it might be an important process in the upper atmosphere where solar e.u.v. photons absorbed by N_2 in the 800–1200 Å region would be an effective source of N atoms in the daytime ionosphere. The absolute measurements described in this paper support this view.

Generalized oscillator strengths and the total excitation cross section

The total cross section for directly populating a specific N_2 singlet state at high incident electron energies ($E \geq 200$ eV) can be calculated from integrated generalized oscillator strength data using the procedure described by Vriens (1967) and by Vriens *et al.* (1968), and relative electron scattering

TABLE 1. ELECTRON-IMPACT CROSS SECTIONS AND OPTICAL OSCILLATOR STRENGTHS FOR THE N_2 SINGLET STATES IN THE 12.5 eV—14.86 eV ENERGY RANGE

Energy loss	State	v'	$\lambda(v', 0)$	f_0*	Cross† section (cm^2)
12.500	$b^1\Pi_u$	0	991.8Å	2.39(−3)	1.74(−19)‡
12.575	$b^1\Pi_u$	1	985.8	1.39(−2)	1.01(−18)
12.663	$b^1\Pi_u$	2	979.0	3.11(−2)	2.26(−18)
12.750	$b^1\Pi_u$	3	972.3	5.79(−2)	4.22(−18)
12.835	$b^1\Pi_u$	4	965.9	9.22(−2)	6.71(−18)
12.910	$c^1\Pi_u$	0	960.3	6.56(−2)	4.85(−18)
12.935	$c'^1\Sigma_u^+$	0	958.4	2.17(−1)	1.58(−17)
12.980	$b^1\Pi_u$	5	955.1	4.76(−3)	3.47(−19)
13.062	$b^1\Pi_u$	6	949.1	4.37(−3)	3.18(−19)
13.100	$o^1\Pi_u$	0	946.3	4.90(−4)	3.57(−20)
13.156	$b^1\Pi_u$	7	942.3	2.48(−2)	1.80(−18)
13.185	$c'^1\Sigma_u^+$	1	940.2	1.99(−3)	1.45(−19)
13.210	$c^1\Pi_u$	1	938.5	6.82(−2)	4.97(−18)
13.260	$b^1\Pi_u$	8	934.9	5.06(−4)	3.69(−20)
13.305	$b'^1\Sigma_u^+$	5	931.2	1.23(−3)	8.93(−20)
13.345	$b^1\Pi_u$ $o^1\Pi_u$	9 1	928.9	2.76(−2)	2.01(−18)
13.390	$b'^1\Sigma_u^+$	6	925.8	2.60(−3)	1.90(−19)
13.435	$b^1\Pi_u$	10	922.7	1.46(−2)	1.07(−18)
13.475	$c^1\Pi_u$	2	920.0	1.72(−2)	1.25(−18)
13.530	$b^1\Pi_u$	11	916.3	4.39(−3)	3.59(−19)
13.585	$o^1\Pi_u$	2	912.6	2.78(−2)	2.02(−18)
13.615	$b^1\Pi_u$	12	910.5	1.26(−3)	8.18(−20)
13.660	$b'^1\Sigma_u^+$	9	907.5	1.02(−2)	6.60(−19)
13.700	$b^1\Pi_u$	13	904.9		
13.720	$c'^1\Sigma_u^+$	3	903.6	2.07(−2)	1.34(−18)
13.760	$b'^1\Sigma_u^+$	10	900.9	1.73(−3)	1.12(−19)
13.785	$b^1\Pi_u$	14	899.3	1.31(−3)	8.46(−20)
13.820	$o^1\Pi_u$	3	897.0	3.29(−2)	2.13(−18)
13.830	$b'^1\Sigma_u^+$	11	896.4	3.67(−3)	2.37(−19)
13.870	$b^1\Pi_u$	15	893.8	8.87(−4)	5.75(−20)
13.910	$b'^1\Sigma_u^+$	12	891.2	3.16(−2)	2.04(−18)
13.950	$b^1\Pi_u$	16	888.7	7.52(−4)	4.87(−20)
13.980	$c'^1\Sigma_u^+$	4	886.8	5.92(−2)	3.84(−18)
13.990	$c^1\Pi_u$	4	886.1	5.30(−3)	3.43(−19)
13.998	$b'^1\Sigma_u^+$	13	885.6	4.55(−3)	2.95(−19)
14.050	$o^1\Pi_u$	4	882.3	5.06(−3)	3.28(−19)
14.070	$b'^1\Sigma_u^+$	14	881.1	4.24(−2)	2.75(−18)
14.150	$b'^1\Sigma_u^+$	15	876.1	4.93(−2)	3.59(−18)
14.230	$b'^1\Sigma_u^+$ $c^1\Pi_u$ $c'^1\Sigma_u^+$	16 5 5	871.2	6.76(−2)	4.38(−18)
14.275	$o^1\Pi_u$	5	868.4	3.21(−3)	2.08(−19)
14.300	$b'^1\Sigma_u^+$	17	866.9	3.68(−2)	2.38(−18)
14.330	$e^1\Pi_u$	0	865.1	2.14(−2)	1.39(−18)
14.350	$e'^1\Sigma_u^+$	0	863.9	8.96(−3)	5.80(−19)
14.400	$b'^1\Sigma_u^+$	18	860.9	3.29(−3)	2.13(−19)
14.465	$b'^1\Sigma_u^+$	19	857.0	2.08(−2)	1.35(−18)
14.478	$c'^1\Sigma_u^+$	6	856.3	1.76(−2)	1.13(−18)
14.525	$b'^1\Sigma_u^+$	20	853.5	1.77(−2)	1.15(−18)
14.585	$e^1\Pi_u$	1	850.0	8.54 −3)	5.53(−19)
14.680	$b'^1\Sigma_u^+$	22	844.5	5.22(−3)	3.38(−19)
14.720	$c^1\Pi_u$ $c'^1\Sigma_u^+$	7 7	842.2	4.39(−3)	2.84(−19)
14.737	$b'^1\Sigma_u^+$	23	841.2	8.80(−3)	5.70(−19)
14.795	$b'^1\Sigma_u^+$	24	837.9	3.56(−3)	2.31(−19)
14.839	$n = 5^1\Pi_u$	0	835.4	9.52(−3)	6.17(−19)
14.860	$e^1\Pi_u$	2	834.3	9.01(−4)	5.66(−20)

* Optical oscillator strength.
† Cross section value at 200 eV.
‡ Read 1.74×10^{-19} cm^2.

spectra such as given by Geiger and Schroeder (1969) after it is corrected for the geometrical properties of the analyzer used in the scattering experiment. The total cross sections for specific N_2 singlet states evaluated in this manner are given in Table 1 for an incident electron energy of 200 eV; the optical oscillator strength for each level is also tabulated. These results are based on the highly accurate generalized oscillator strengths (probable absolute error $< 3\%$) obtained by Lassettre (1974) and his collaborators. The energy dependence of the total cross section can also be inferred from the generalized oscillator strength measurements for $E > 200$ eV while the detailed studies of the radiation emitted by these excited states described in this paper permits one to determine the shape of the excitation function from threshold to 200 eV or more. Thus, with a knowledge of the electron energy flux distribution the absolute population rates for electron impact excitation of the multitude of N_2 Rydberg and valence states in the 11.4–40 eV energy range can be calculated accurately and the ultimate fate of these excited states studied.

Emission cross section measurements

In recent years major advances have occurred in e.u.v. technology. The improvements in gratings, coatings and detectors have spurred renewed interest in the e.u.v. wavelength region and have led to the development of adequate intensity calibration standards (Mumma and Zipf, 1971a,b; Mumma, 1972; Stone and Zipf, 1972) and to the construction of efficient optically thin electron-impact radiation sources (McLaughlin, 1977). As the result of these advances it is now possible to make accurate absolute emission cross section measurements in the heretofore very difficult middle e.u.v. region (500–1000 Å).

An apparatus developed for such studies is shown schematically in Fig. 1. Briefly, an electron gun, a diffuse gas source, and a Faraday cup (aligned co-linearly) are located in a large ultra-high vacuum chamber. The region of the diffuse gas source excited by the electron beam is viewed simultaneously by a one meter normal incidence McPherson monochromator and by a $\frac{3}{4}$-m Czerny–Turner monochromator. The normal incidence instrument provides data in the 500–2000 Å region while the $\frac{3}{4}$ m monochromator covers the wavelength range 1800–1 μm. The gas-handling system is also constructed from u.h.v. components and only reagent-grate gases have been used in these studies. Standard pressure measuring techniques are employed to determine the density of the target gas in the diffuse gas source, while the absolute sensitivity of the monochromator was determined by use of atomic and molecular branching ratio techniques. This calibration procedure was

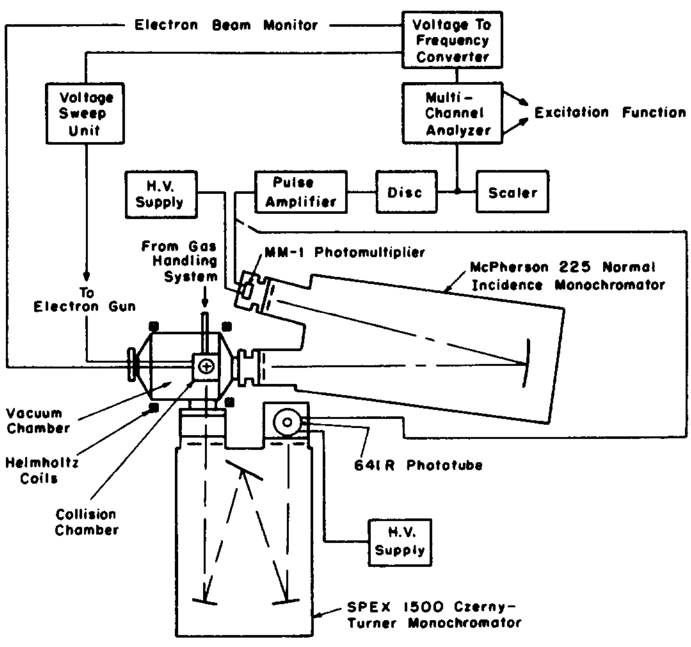
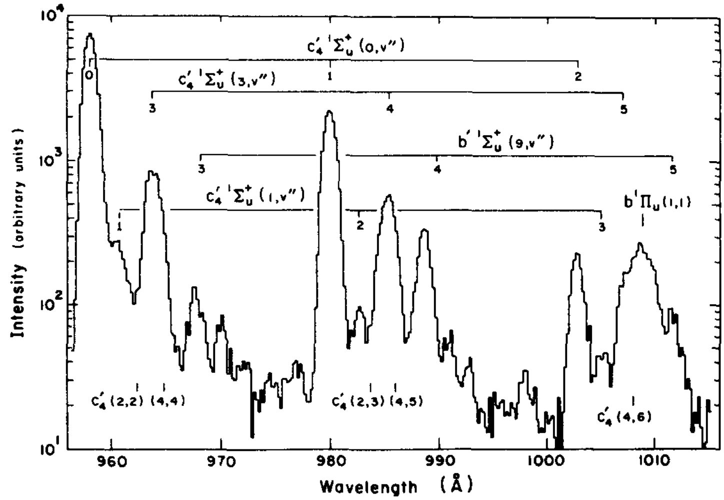


FIG. 1. DIAGRAM OF THE EXPERIMENTAL APPARATUS.

checked independently for the visible i.r. monochromator by using a conventional NBS tungsten ribbon lamp as a secondary standard.

In the visible wavelength region emission cross sections can be determined with an absolute accuracy of 15% or better when $\sigma > 10^{-19}\,\mathrm{cm}^2$. These absolute accuracies can also be achieved over limited wavelength intervals in the vacuum u.v. region, but in general probable absolute errors in emission cross section work between 15–25% are more typical. Beam current and pressure linearity tests were also carried out in our studies for every significant feature in the e.u.v. spectrum of air in the 800–1350 Å range. These checks proved to be particularly useful since entrapment effects for some transitions can be large. The experiment was carried out in two modes. Firstly, with the electron beam energy fixed in magnitude the e.u.v. spectrum was obtained by slowly scanning the normal incidence monochromator. Figures 2 and 3 show some typical spectra produced by the impact of 100 eV electrons on N_2 that were obtained in this manner with an instrumental resolution of 0.83 Å FWHM. Secondly, a particular emission feature could be isolated by the monochromator for detailed study. The electron gun was then programmed to sweep



FIGS. 2 AND 3. EXTREME ULTRAVIOLET SPECTRUM OF N_2 EXCITED BY 100 eV ELECTRONS. The data were obtained at an instrumental of 0.83 Å FWHM.

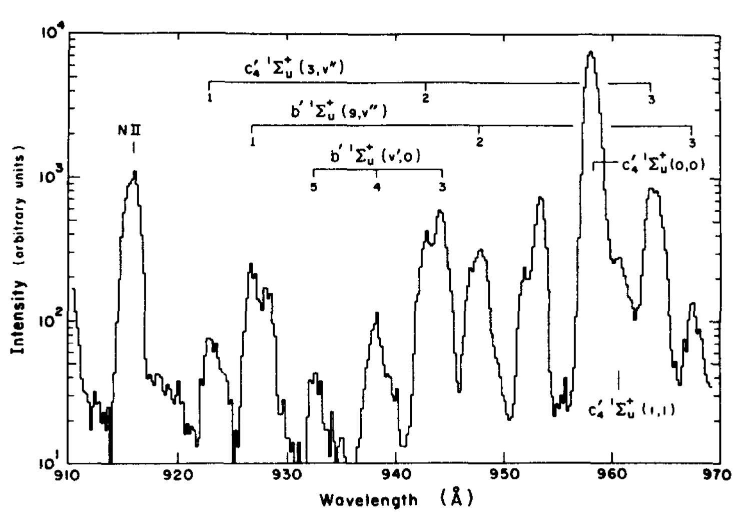


FIG. 3. SAME CAPTION AS FIG. 2.

the electron beam energy so that the emission cross section could be measured from threshold to approximately 300 eV. In this mode the beam energy was changed repetitively in discrete energy steps while the detected photoelectrons were coherently summed in order to improve the signal-to-noise ratio of the data. Figure 4 shows a representative excitation function for the intense $c_4'^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transition at λ958 Å.

By measuring the absolute cross section and excitation function for each band observed in the optically thin e.u.v. spectrum of N_2, the effective emission cross section for a specific transition could be compared with the total cross section for exciting the state given in Table 1 and the predissociation branching ratio estimated. The results of this type of cross comparison are presented in Table 2. Alternatively the total emission cross section for exciting e.u.v. band radiation in the 800–1100 Å could be evaluated empirically by simply integrating the measured spectrum after allowing for the response of the monochromator and subtracting the contributions due to NI and NII multiplet features. In Fig. 5 the total emission cross section (800–1100 Å; curve C) is compared with the cross section for exciting the (0, 0) first negative band of N_2^+ (curve A; Borst and Zipf, 1970). The molecular contribution to the total cross section is indicated by the dashed curve (B).

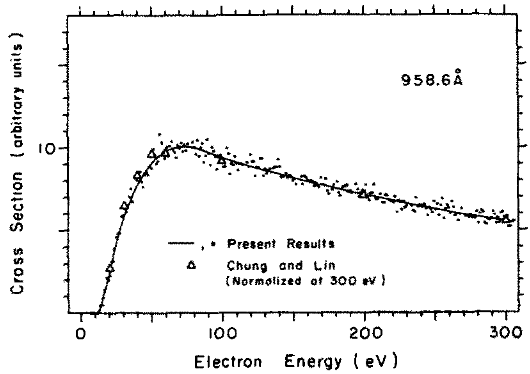


FIG. 4. EXCITATION FUNCTION FOR THE (0, 0) BAND OF THE $c_4'^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ SYSTEM.

The cross section has a value of 1.1×10^{-7} cm² at 200 eV.

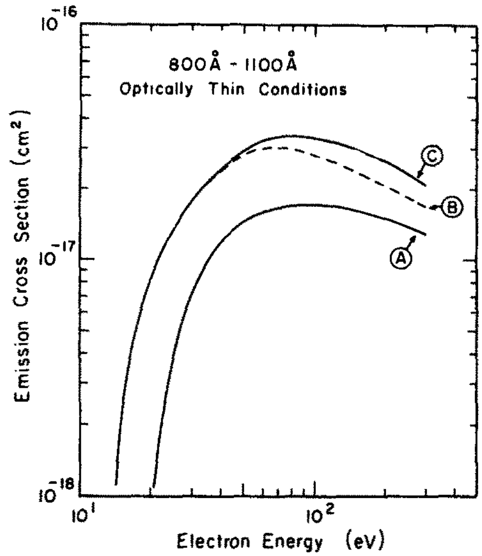


FIG. 5. THE TOTAL CROSS SECTION FOR EXCITING NITROGEN ATOMIC, IONIC AND MOLECULAR EMISSION FEATURES IN THE 800—1100 Å WAVELENGTH RANGE (CURVE C).

The molecular contribution to this cross section is shown by curve B, while curve A is the cross section for electron impact excitation of the N_2^+ (0, 0) first negative band (λ3914 Å).

TABLE 2. PREDISSOCIATION BRANCHING RATIOS*

State	Total cross section†	Emission cross section†	Predissociation branching ratio
$b^1\Pi_u$(0—13)‡	2.07(−17)§	6.5(−19)	0.97
$b'^1\Sigma_u^+$(0—20)	1.71(−17)	3.0(−18)	0.83
$c_4'^1\Sigma_u^+$(0—4)	2.01(−17)	1.7(−17)	0.15
$c_4'^1\Sigma_u^+$(5—7)	3.71(−18)	<2(−19)	>0.95
$e'^1\Sigma_u^+$	5.80(−19)	<2(−20)	>0.99
$c^1\Pi_u$(0—7)	1.20(−17)	<2(−20)	>0.99
$o^1\Pi_u$(0—4)	4.82(−18)	<2(−20)	>0.99
$e^1\Pi_u$(0—2)	2.00(−18)	<2(−20)	>0.99
$n = 5^1\Pi_u$	5.66(−20)	<2(−20)	>0.6
Total	8.10(−17)	2.2(−17)	0.73

* Under optically thin conditions.
† At 200 eV.
‡ Means that the vibrational levels $v' = 0$ through 13 were used in the tabulation.
§ Read 2.07×10^{-17} cm².

DISCUSSION

Observational problems

The experimental problems that must still be solved before adequate extreme u.v. spectra of the airglow and aurora can be obtained, are numerous and difficult. Further development of current rocket-borne e.u.v. instrumentation will be needed before these problems can be overcome. The laboratory data shown in Figs 2 and 3 illustrate the magnitude of some of these difficulties. Firstly, the extreme ultraviolet spectrum of N_2 excited by the impact of 100 eV electrons is very complex. The laboratory spectrum obtained at a resolution of 0.83 Å FWHM consists of a large number of narrow, closely-spaced molecular bands, NI multiplets, and minor NII emission features. For the most part the molecular bands are effectively line-like with half-widths of 1 Å or less. The relative intensity of the principal molecular features span nearly four orders of magnitude and are spaced 2 to 3 Å apart. Present day field instruments with bandpasses of 10–20 Å cannot resolve these details nor reflect, except grossly, the complex intensity re-distribution processes that ultimately shape the e.u.v. spectrum recorded by these broadband spectrometers. Secondly, the interpretation of the *in situ* spectra is complicated by radiation entrapment effects. At auroral and airglow altitudes the upper atmosphere is optically thick for most N_2 singlet bands that terminate on the lowest vibrational level of the ground state. For a number of the singlet states the $(v', 1)$ and $(v', 2)$ transitions are trapped as well. Resonance reabsorption of these bands ultimately promotes preferential re-emission of other molecular bands that originate from the same upper state but do not terminate on either $v'' = 0$, 1 or 2 of the ground state of N_2. Radiation entrapment thus leads to modifications in the apparent intensity distribution of a molecular progression in a manner which depends sensitively on the degree of optical opacity. This effect has been observed in the Martian airglow where the intensity distribution of the CO fourth positive system $[A^1\Pi \rightarrow X^1\Sigma^+]$ is significantly perturbed by entrapment (Thomas, 1971) and where the analysis is further complicated by the non-thermal kinetic energy distribution of the excited CO molecules and by the anomalous rotational state populations produced by dissociative excitation (Mumma *et al.*, 1975).

Unsuspected resonance trapping is also a hazard in laboratory experiments where it can lead to serious errors in cross section measurements. The spectra shown in Figs 2 and 3 illustrate this point. The bright emission feature at $\lambda 958$ Å is the (0, 0) band of the $c_4'^1\Sigma_g^+ \rightarrow {}^1\Sigma_g^+$ Rydberg system. In these data the intensity of the $\lambda 958$ Å transition is reduced by a factor of two while the companion (0, 1) band, which is emitted at $\lambda 980$ Å, is enhanced by 15% when compared with the intensity distribution in an optically thin source.

Competition between cascade transitions and predissociation

Radiation entrapment also enhances the numerous N_2 intercombination bands that originate chiefly from the various vibrational levels of the $c_4'^1\Sigma_u^+$ state and that terminate on the metastable $a^1\Pi_g$ state (Lofthus, 1957). For the most part the cross sections for electron-impact excitation of these bands are very small ($\sigma < 3 \times 10^{-20}$ cm^2; Aarts, 1970) so that these transitions would normally be difficult to observe in the laboratory and in airglow and auroral spectra [Dick, 1970] were it not for amplification effects produced by entrapment. The potential enhancement of the intercombination bands in the upper atmosphere could be very large in principle for they bear the same relationship to the primary e.u.v. transition as the analogous i.r. multiplets of atomic oxygen do to the intense resonance lines emitted at $\lambda 1026$ and $\lambda 989$ Å. In the atomic case the bulk of the initial excitation energy is predicted to be dissipated by cyclic pumping of the i.r. intercombination lines (Julienne and Davis, 1976), and at first sight the molecular transition ought to behave similarly.

However, there is an additional complication in nitrogen because predissociation competes effectively with radiation in depopulating the singlet states that contribute to the N_2 e.u.v. and intercombination spectrum. The electron scattering results presented in this paper show that N_2 singlet states with $^1\Pi_u$ terms predissociate with virtually 100% efficiency. Only the $v' = 1$, 5 and 6 vibrational levels of the $b^1\Pi_u$ valence state manage to radiate, but then only feebly. Thus the predissociation of the $^1\Pi_u$ states contributes significantly to the total cross section for the dissociation of nitrogen by electron impact. This contribution is indicated by curve A in Fig. 6. The excitation function for the family of $^1\Pi_u \rightarrow {}^1\Sigma_g^+$ transitions is well-developed at low electron impact energies and attains a peak value of 7.2×10^{-17} cm^2 at 34 eV. The shape of the $b^1\Pi_u$ cross section calculated theoretically by Chung and Lin (1972) closely parallels the measured excitation function for the $^1\Pi_u$ family below 100 eV, but the laboratory data fall off more slowly at impact energies greater than 100 eV. The shape

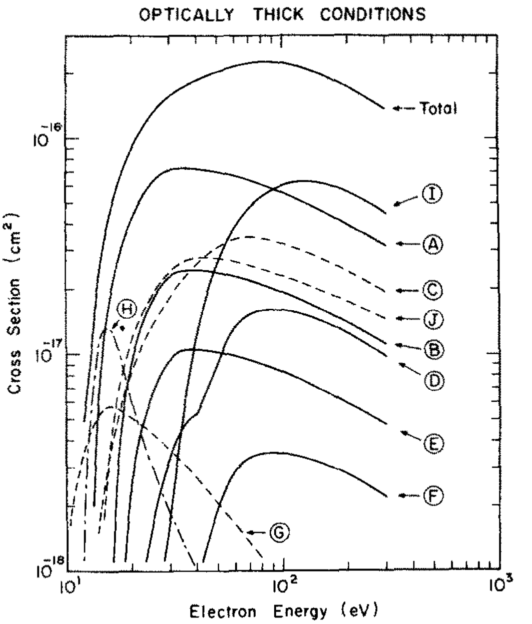


FIG. 6. THE TOTAL CROSS SECTION FOR ELECTRON-IMPACT DISSOCIATION OF N_2 UNDER OPTICALLY THICK CONDITIONS. The specific dissociation channels contributing to the total cross section include the excitation of:

(*A*) The family of $^1\Pi_u$ states,
(*B*) The states belonging to the 15.8 eV peak in the inelastic scattering data of Lassettre (1974),
(*C*) The $c_4'^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ system,
(*D*) The states leading to the production of excited N atoms that radiate at v.u.v. wavelengths,
(*E*) The States associated with the 17.3 eV peak of Lassettre,
(*F*) The states contributing to the formation of N Rydberg atoms,
(*G*) The $a^1\Pi_g$ state,
(*H*) The N_2 triplet manifold,
(*I*) The states contributing to dissociative ionization, and
(*J*) The $b'^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ system.

of the measured cross section is significantly different from that used in earlier phenomenological models (e.g. Stolarski and Green, 1967; Green and Stolarski, 1970; Peterson *et al.*, 1972; Porter *et al.*, 1976) with the result that the $^1\Pi_u$ manifold is more efficiently excited by photoelectrons and low-energy auroral electrons than previously suspected.

The effects of predissociation on nitrogen states with $^1\Sigma_u^+$ symmetry is variable. The $c_4'^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ Rydberg system is only slightly predissociated under optically thin conditions with a branching ratio, equation (1), of less than 15% for the $v' = 0$ and 3 levels. By contrast the $b'^1\Sigma_u^+$ valence state exhibits virtually complete predissociation of some vibrational levels (e.g., $v' \geq 11$), significant predissociation of others ($v' = 5, 10$), and essentially none at all the $v' = 9$ vibrational level. In previous emission studies Birge–Hopefield bands [$b'^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$] originating from the $v' = 0 \rightarrow 9$ vibrational levels have been observed by spectroscopists (Dressler, 1969) but none from higher levels. In our optically thin electron-impact source we are able to detect very weak emission from the vibrational levels $v' = 10$, 11, 12, 13, 14, 15, 16, 17 and 19. The predissociation branching ratio for these levels is very large (~99%) so that in the optically thick sources commonly used by photographic spectroscopists no net emission from these high-lying levels was ever very likely. The excitation function for the $b'^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transition peaks near 44 eV and has a shape quite different from that calculated theoretically by Chung and Lin (1972). The total cross section for exciting the $b'^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ system is shown by curve *J* in Fig. 6, while curve *C* is the total cross section for exciting the family of emission bands belonging to the $c_4'^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ system.

Apparent emission cross section under optically thin conditions

The total cross section for the excitation of molecular radiation by electron impact on N_2 attains a maximum value of about 3.0×10^{-17} cm^2 at an incident electron energy of 80 eV. These data are shown in Fig. 5 where they are compared with the cross section for exciting the (0, 0) first negative band of N_2^+. Based on these laboratory results the integrated N_2 e.u.v. flux in an auroral substorm would be approximately twice as bright as the N_2^+ λ3914 Å band under optically thin conditions. However, *in situ* measurements show that this expectation is not borne out. The observed e.u.v. radiation attributable to molecular transitions is less than 10% of the λ3914 Å brightness (Christensen, 1976; Park *et al.*, 1977). Even the intense λ958 Å feature which has a small predissociation branching ratio and a cross section comparable to the λ3914 Å band (1.47×10^{-17} cm^2 and 1.74×10^{-17} cm^2 at 100 eV respectively; Borst and Zipf, 1970) is present weakly or not at all in the auroral spectrum of Park *et al.* (1977). These data also show that the energy initially released in the form of λ958 Å photons is not recycled in a manner that leads to preferential emission of other bands (0, v'') of the $c_4'^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ system. Furthermore the energy of excitation is not dissipated by the emission of the $c_4'\Sigma_u^+(v') \rightarrow a^1\Pi_g$ intercombination bands for these features are exceedingly weak even in very intense auroral displays (Dick, 1970). Thus the observational results suggest that even though large quantities of extreme u.v. photons are produced by the electron impact excitation of the $N_2(^1\Sigma_u^+)$ manifold, these e.u.v. photons are effectively recycled by radiation entrapment so that even weakly predissociated states are ultimately depopulated by this process. The net result is that the excitation of the $N_2(^1\Sigma_u^+)$ manifold of states in the upper atmosphere leads to the creation of N atoms and not to the copious emission of extreme u.v. radiation or to strikingly enhanced intercombination emission.

Unfortunately, the intensity of the few molecular emission features that do survive the entrapment–predissociation process in the upper atmosphere cannot be predicted simply on the basis of our present knowledge of the optically thin e.u.v. spectrum of N_2. The effective predissociation rate varies not only among the different vibrational levels of a particular state but this rate is also a sensitive function of the rotational quantum number of each vibrational level. The magnitudes of the pertinent predissociation branching ratios have yet to be measured as a function of the quantum numbers v' and J. The analysis of the observational spectra is also impeded by a lack of knowledge of the transition probabilities for individual bands with a common upper state. Since the singlet terms of N_2 are highly perturbed, model transition probabilities based on Franck–Condon or r-centroid considerations are likely to be significantly in error. This complication would seem to be particularly important for the $b'^1\Sigma_g^+$ term whose vibrational excitation distribution departs strikingly from that obtained from Franck–Condon modeling (Geiger and Schroeder, 1969).

Electron-impact dissociation of N_2*—total cross section*

The dissociation of nitrogen by electron impact has been studied by Winters and his collaborators (Winters *et al.*, 1964; Winters, 1966) in a complex surface absorption experiment. The magnitude of the total cross section for simple dissociation,

$$e + N_2 \rightarrow N(^4S) + N(^4S) + e, \quad (2)$$

for dissociative excitation,

$$e + N_2 \rightarrow N^* + N + e, \quad (3)$$

and for dissociative ionization

$$e + N_2 \rightarrow N^+ + N^* + 2e. \quad (4)$$

where N^* is an excited nitrogen atom, was inferred from pumping speed measurements by assuming that the probability, α, that a nitrogen atom would be absorbed by the collection surface was independent of the kinetic energy of the atom, was the same for $N(^4S)$, $N(^2D)$, and $N(^2P)$ atoms as well as for N^+ ions and for nitrogen atoms in Rydberg and high-lying metastable states, and was unity. Although at first sight it would seem unlikely that $\alpha = 1$ unilaterally, Winters carried out a series of tests that supported this assumption, and the analysis presented below is consistent with that view point.

The total dissociation cross section obtained by Winters applies under optically thin conditions. In his apparatus the radiation produced by the excitation of the $c_4'^1\Sigma_u^+$ and $b'^1\Sigma_u^+$ states was absorbed by the walls and did not contribute to the production of nitrogen atoms. In the upper atmosphere these photons are trapped and recycled until predissociation finally converts them into N atoms. Thus the effective total dissociation cross section for upper atmosphere applications is the sum of Winters' value and the total molecular emission cross section shown in Fig. 5.

The electron scattering experiment described in this paper shows quantitively that the predissociation of the N_2 singlet states listed in Table 1 accounts for nearly 60% of the nitrogen atoms observed by Winters at electron energies below 50 eV. These states are identified with the 12.93 and 13.99 eV peaks in the inelastic scattering data of Lassettre and his collaborators (Lassettre, 1974). Photoabsorption studies reveal an abundance of additional $^1\Sigma_u^+$ and $^1\Pi_u$ states with term energies greater than 14.85 eV that also contribute to the production of N atoms. Silverman and Lassettre (1965) have measured the generalized oscillator strengths for the discrete states in the energy ranges 15.0–16.8 eV, 16.8–19.0 eV and 19–25.0 eV, and the differential oscillator strengths at electron energies above 24 eV. None of the discrete N_2 states above 14.85 eV are observed to radiate. Thus the discrete states that lie in the energy range between 14.85 and 15.68 eV, where ionization begins, simply dissociate and their contribution to the total dissociation cross section can be evaluated from the data of Lassettre (1974) and Gieger and Schroeder (1969), and from the excitation functions obtained in this work. Those discrete N_2 states in the energy range 15.68–24.3 eV, where dissociative ionization commences, either autoionize forming N_2^+ ions or dissociate. The probability of dissociation can be estimated for these states from photoabsorption and photoionization cross section measurements (Cook *et al.*, 1965; Huffman *et al.*, 1963; Stolarski and Johnson, 1972), and the effective dissociation cross section can be calculated by the procedure outlined above.

Our knowledge of the N_2 states that are located beyond 24.3 eV is very poor. It is evident from time-of-flight [TOF] data (Smyth *et al.*, 1973; Wells *et al.*, 1976) and from dissociative ionization and excitation experiments (Aarts and de Heer, 1971; Mumma and Zipf, 1971) that a large number of states are involved, but virtually nothing is known about the details. The total cross section has been measured for both dissociative ionization and dissociative excitation. Unfortunately, there is some ambiguity in using these results because some dissociation events almost surely produce both N^+ ions as well as an excited N atom companion. Thus the cross sections for these channels, which are shown in Figs 6 and 7, represent the maximum possible net contribution to the total dissociative cross section. A similar comment also applies to the contribution identified with the formation of Rydberg atoms (Wells *et al.*, 1976).

Finally it is worth noting that while most aeronomical calculations are based on the cross section data presented in Fig. 4 of Winters', 1966 paper, Niehaus (1967) has measured the excitation

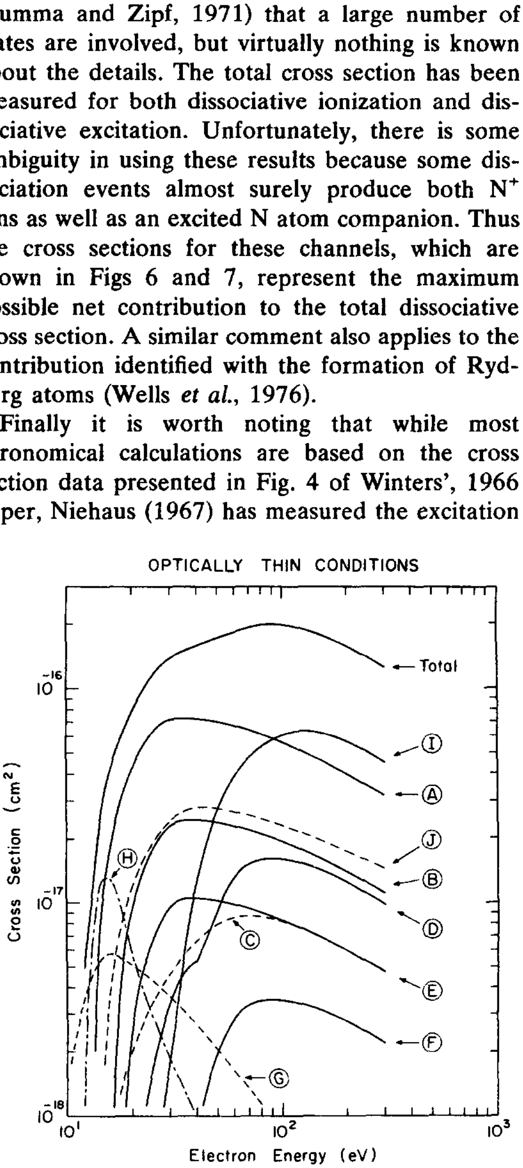


FIG. 7. THE TOTAL CROSS SECTION FOR ELECTRON-IMPACT DISSOCIATION OF N_2 UNDER OPTICALLY THIN CONDITIONS. The identity of the specific curves is given in the caption for Fig. 6.

function for the production of N atoms from the dissociation of N_2 by electron impact from an apparent threshold of 9.6–90 eV. In this experiment, which has been largely overlooked, N atoms from all dissociative processes are detected but N^+ ions from dissociative ionization are specifically excluded in contrast to the technique employed by Winters. This difference in method provides a convenient means for testing the internal consistency of the two dissociation measurements and the dissociative ionization work of Rapp *et al.* (1965). The comparison, which shows that there is good agreement between these independent measurements, is particularly useful because it examines both the shape and absolute magnitudes of this set of cross sections. The cross section measurements of Winters and Niehaus can be used in conjunction with the optical measurements reported in this paper, with the metastable excitation results of Borst (1972), and with the electron scattering data of Finn and Doering (1976) to estimate the contribution to the total dissociation cross section from the predissociation of the $a\,^1\Pi_g$ state and nearby low-lying triplet states. These results are also shown in Figs 6 and 7.

Our findings can now be summarized. Figure 6 shows the various inelastic processes involved in the excitation of the manifold of singlet states of N_2 without regard to the ultimate fate of these states. Under optically thick conditions the total cross section for electron-impact induced dissociation of nitrogen can be obtained by summing the individual contributions shown in Fig. 6. Figure 7 shows the inelastic channels that yield N atoms and N^+ ions under optically thin conditions. The total cross section obtained by summing these contributions can be compared directly with the surface absorption results of Winters (1966) or alternatively by subtracting the N^+ component from Fig. 7 the effective cross section for producing NI fragments can be calculated and compared with the measurements of Niehaus (1967). The results of such a comparison are shown in Fig. 8. Considering the complexities the agreement between model and measurement is quite good. The total cross section for the dissociation of N_2 by electron impact based on the results of this paper is given in Table 3 from threshold to 100 eV for optically thin and thick conditions.

Implications for the auroral energy balance and the odd-nitrogen problem

Based on a complex, time-dependent model of an aurora (Jones and Rees, 1973; Rees and Jones,

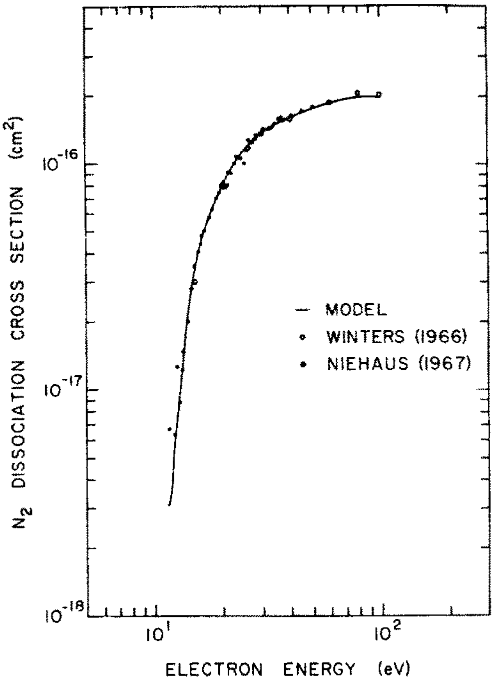


FIG. 8. A COMPARISON OF THE DISSOCIATION DATA OF WINTERS (1966) AND NIEHAUS (1967) WITH A MODEL OF THE TOTAL N_2 DISSOCIATION CROSS SECTION UNDER OPTICALLY THIN CONDITIONS DERIVED FROM THE RESULTS SHOWN IN FIG. 7.

TABLE 3. TOTAL CROSS SECTION FOR THE DISSOCIATION OF N_2 BY ELECTRON IMPACT

Energy	Optically thin cross section	Optically thick cross section
10.0	1.27(−18)	1.27(−18)
10.5	1.87(−18)	1.87(−18)
11.0	2.49(−18)	2.49(−18)
12.0	4.92(−18)	4.92(−18)
13.0	1.10(−17)	1.12(−17)
14.0	2.35(−17)	2.43(−17)
15.0	3.36(−17)	3.58(−17)
16.0	4.41(−17)	4.75(−17)
18.0	6.23(−17)	6.82(−17)
20.0	7.74(−17)	8.56(−17)
22.0	9.46(−17)	1.05(−16)
26.0	1.21(−16)	1.36(−16)
30.0	1.39(−16)	1.58(−16)
35.0	1.50(−16)	1.72(−16)
40.0	1.59(−16)	1.83(−16)
50.0	1.75(−16)	2.03(−16)
60.0	1.86(−16)	2.16(−16)
70.0	1.94(−16)	2.24(−16)
80.0	1.97(−16)	2.27(−16)
90.0	1.98(−16)	2.27(−16)
100.0	1.96(−16)	2.24(−16)

1973); Rees (1975) showed that approximately 16% of the total energy deposited in a magnetospheric substorm cannot be unaccounted for, and he argued that the bulk of this energy must reside in extreme ultraviolet radiation originating from highly excited atomic, molecular, and ionic states. This conclusion appeared plausible at the time in view of the very large e.u.v. cross-section values reported by Sroka (1968) and the photometric measurement of Parcese *et al.*, (1972). However, the cross section measurements presented in this paper and recent *in situ* e.u.v. studies in auroras show that the early work of Sroka and Parcese is incorrect. Thus the unaccounted for 16% of the auroral energy budget must be identified with either some other inelastic process or the assumptions on which the time-dependent auroral model are based, need to be reconsidered.

In the substorm model developed by Rees approximately 35% of the energy is consumed by ionizing N_2,

$$e + N_2 \rightarrow N_2^+ + 2e \tag{5}$$

$$e + N_2 \rightarrow N + N^+ + 2e. \tag{6}$$

If the missing inelastic scattering process has a cross section similar in shape to the total ionization cross section, then it would have to have a peak value of 1.1×10^{-16} cm² near 100 eV in order to account for the missing 16%. This process cannot involve exciting discrete N_2 states for these have already been accounted for in the present study. Only continuous dissociative processes remain. In his study Rees used the cross section data of Winters to calculate the net dissociation rate. If the additional 16% of the energy budget is assigned to this inelastic channel, then Winters' cross section values would have to be increased significantly. Since the average energy consumed per dissociation is about 25 eV (Porter *et al.*, 1976), the dissociation cross section at 100 eV would have to be increased by $(33/25) \times 1.1 \times 10^{-16}$ cm² relative to the total ionization cross section. The peak value would then be 3.6×10^{-16} cm². These results would imply that the collection efficiency in Winters' surface absorption experiment $\alpha \sim 0.6$, and that the shape of the omitted contribution is essentially the same as the results presented in Table 3. Thus, if the auroral energy budget is accurately described by the model developed by Rees, it is difficult to avoid the conclusion that nitrogen atoms are being produced by the electron-impact dissociation of N_2 at nearly twice the rate previously assumed in both auroral substorms and the dayglow. But this development seems unlikely for the results of this paper show that there is a high degree of quantitative self consistency between a large body of absolute cross section measurements that all but rules out the possibility that an inelastic electron-scattering process with a peak cross section magnitude between 1 and $1.5 \times 10^{-16}\,cm^2$ has been overlooked. This development suggests that the difficulty lies in our understanding of the energy budget of a magnetospheric substorm.

The measurements described in this paper do not provide detailed information on the specific yield of $N(^2P)$, $N(^2D)$, and $N(^4S)$ atoms when N_2 is dissociated by electron impact. However, a useful upper limit on $N(^2D)$ production can be derived from these data based on energy conservation considerations and the relative contribution of each loss channel to the total cross section. This analysis is possible because the N atoms are created for the most part from the excitation of discrete states that subsequently predissociate. The initial energy is therefore precisely defined. Thus, for example, the bulk of the $^1\Pi_u$ and $^1\Sigma_u^+$ states identified in Table 1 can energetically produce one $N(^2D)$ atom at most. The discrete states associated with the 15.8 and 17.3 eV peaks in Lassettre's (1974) data could conceivably excite two $N(^2D)$ atoms though this is unlikely. Similarly dissociative ionization could yield one $N(^2D)$ per electron-ion pair although the work of Ehrhardt and Kresling (1967) suggest that although a metastable species is produced in virtual every dissociative ionization event the final products may be distributed equally between excited atoms and ions. Finally, the predissociation of the low-lying $a^1\Pi_g$ state and the triplet manifold probably produce only $N(^4S)$ atoms. Thus the maximum $N(^2D)$ yield is obtained under optically thick conditions (Fig. 6) assuming that an $N(^2D)$ atom is formed whenever energetically possible. Figure 9 shows the maximum $N(^2D)$ yield as a function of electron-impact energy calculated in this manner.

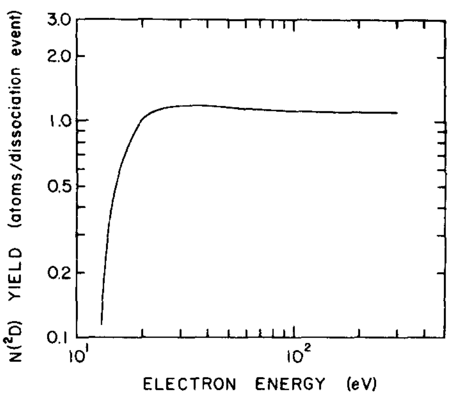


FIG. 9. $N(^2D)$ YIELD FROM THE DISSOCIATIVE EXCITATION OF N_2 BY ELECTRON IMPACT BASED ON THE DATA OF FIG. 6 AND THE ASSUMPTION THAT $N(^2D)$ ATOMS ARE CREATED BY THE DISSOCIATION PROCESS WHENEVER ENERGETICALLY POSSIBLE.

The curve is an upper bound on the actual production rate.

SUMMARY

We now summarize the principal results of this study: (1) The dissociation of the numerous $^1\Pi_u$ and $^1\Sigma_u^+$ states evident in inelastic electron scattering data and in photo-absorption and photoionization studies is the dominant mechanism in the dissociation of N_2 by electron impact and by the absorption of extreme u.v. photons. (2) The large fluxes of e.u.v. photons anticipated by modelers under dayglow and auroral conditions are not observed because predissociation (aided by radiation entrapment effects)—not radiation is the ultimate sink for the energy transferred to N_2 by inelastic electron collisions. N atoms, not e.u.v. photons, are the final by-products. (3) The predictions of an e.u.v.-modified auroral ion chemistry and of enhanced $O(^1S)$ excitation from the photodissociation of O_2 have been shown to be incorrect. (4) The numerous excitation channels contributing to the total cross section for the dissociation of N_2 by electron impact have been identified and their cross sections and excitation functions determined. The total cross section determined in this manner is in good agreement with measurements of Winters (1966) and Niehaus (1967). (5) Indirect evidence suggests that current models of a magnetospheric substorm overestimate the total energy budget by approximately 16%.

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