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Electron impact total excitation cross section of the a $^1\Pi_g$ state of N_2

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Abstract. The normalised total cross section for the excitation of the a $^1\Pi_g$ metastable state in N_2 is measured using a time of flight technique for incident electron energies from threshold to 150 eV. Comparison is made with theory and experimental work both for cross section and lifetime measurements.

1. Introduction

In recent years more accurate theoretical methods of calculating scattering from diatomic molecules have been developed by many workers, e.g., the Born approximation (Chung and Lin 1972, 1974) supplemented by the impact parameter method (Hazi 1981, Hazi *et al* 1979), the distorted wave method (Rescigno *et al* 1976, Fliflet *et al* 1979, 1980) and the close-coupling method (Chung and Lin 1978, Weatherford 1980, Holley *et al* 1981).

The Lyman-Birge-Hopfeld (LBH) system of N_2 is the most prominent vacuum ultraviolet emission feature of the nitrogen molecule. Excitation of this band system by electron impact has received extensive theoretical and experimental attention because of the geophysical importance of the LBH system in electron-excited aurora. A comparison of the various experimental results below 100 eV shows that the general features of electron impact excitation near threshold are fairly well established. The cross section rises rapidly from threshold (8.55 eV) to a broad maximum at an energy of about 16 eV followed by a slow decrease to an almost constant value at higher energies. However, the available data do not agree very well and few experiments have measured the cross section over the wide range of energies from threshold to 150 eV. Only the data of Ajello (1970), Ajello and Shemansky (1985) and Finn and Doering (1976) fulfil this prerequisite and they differ widely both in shape and magnitude. It is therefore necessary to perform an experiment over this energy range exploring both the low-energy region where the peak occurs (<20 eV) and energy regions (>100 eV) where Born type theoretical calculations may be applied with some confidence.

Optical emission measurements on a metastable radiating species such as the a $^1\Pi_g$ state of N_2 are intrinsically difficult even without the additional problems of cascade and secondary electrons which if present in the interaction region distort the measured value of the optical cross section in higher energy regions. One method devised to circumvent the problems inherent in optical fluorescence experiments is the integration of the electron energy loss differential cross section over all scattering angles to produce an 'integral cross section' free of cascade effects. This technique has been used by Brinkmann and Trajmar (1970), Finn and Doering (1976) and Cartwright *et al* (1977) but, as recent experiments in the electron excitation of rare-gas atom metastable states have shown (Mason and Newell 1987), the method tends to overestimate the cross section. In a molecule the requirement of the summation over all vibrational states will tend to add to the error of this method.

An easier experiment is to examine the product molecule itself since, as the lifetime of the a $^1\Pi_g$ state is 115 ± 20 μs (Borst and Zipf 1971), the metastable molecule will drift some centimetres before decaying and may therefore be detected at the channeltron which is located 4 cm from the interaction region. Due to the higher energy of the a $^1\Pi_g$ state (8.55 eV) a conventional channeltron with a work function of about 8 eV will detect the metastable molecule by Penning ionisation at its surface with the added advantage of discriminating against the lower lying A $^3\Sigma_u^+$ (6.17 eV) metastable state which lies below the channeltron work function. The excitation cross section of the a $^1\Pi_g$ state may therefore be monitored by direct measurement of the metastable flux.

Borst (1972) studied the metastable production in N_2 and determined the a $^1\Pi_g$ state cross section by subtraction of the cross sections for excitation of the A $^3\Sigma_u^+$ and E $^3\Sigma_g^+$ (11.87 eV) states from the measured metastable excitation function. This relatively imprecise process resulted in a cross section that is in surprisingly good agreement with measurements by other methods and proved the usefulness of the metastable technique. Therefore if all effects of the A $^3\Sigma_u^+$ state are removed by using a detector of high work function and if the E $^3\Sigma_g^+$ cross section, which is only important for a small (1-2 eV) energy region at 4 eV above the a $^1\Pi_g$ threshold, is removed from the data, the metastable yield will be a direct measure of the a $^1\Pi_g$ state total cross section extending from threshold to energies in excess of 100 eV and hence embracing the ranges of the existing optical and integral cross section data.

In this paper the a $^1\Pi_g$ state is studied by monitoring metastable production between threshold and 150 eV; comparison with other experimental data is found to be excellent at both low and high incident electron energy. Theory is shown to be inadequate in calculating the observed cross sections over this range and further effort incorporating the effect of target polarisation and distortion is probably required.

2. Experimental method

The experimental arrangement used consists of an electron gun which produces a beam of 1 μA at an energy of 6 eV incident on an electrostatic hemispherical monochromator. The monochromated electron beam is then accelerated to the required impact energy and intersected at right angles with a molecular nitrogen gas beam produced by a hypodermic needle. Spectroscopic grade gas was used. Since there is a net momentum transfer to the metastable molecular beam it is necessary to place the detector at an angle which accommodates the effect of the momentum transfer to the metastable molecules to ensure that all those produced are detected. The channel electron multiplier is therefore placed at a scattering angle $\theta = 73°$ with respect to the incident electron beam direction. A full discussion of the apparatus has been given in Mason and Newell (1986).

A 10 V 250 μs pulse applied to a gun lens is sufficient to modulate the electron beam. The time of flight spectrum consists of photons which arrive as a prompt pulse, followed by scattered electrons which arrive at the detector within 30 ns of the trailing edge of the primary electron pulse and finally the metastable molecules and ions which have flight times of approximately 100 μs. The positive ions are removed by the application of a small positive voltage at the entrance to the detector. The data are stored as a time of flight spectrum in a multichannel analyser, and then integrated over a finite time range and normalised to unit electron current.

If the metastable species lifetime is greater than the transit time (t) to the detector then the velocity distribution of metastables is Maxwellian and the time of flight distribution $P(t)$ is given by (see Mason and Newell 1987)

$$P(t)\,dt = C(1/t^4)\,e^{-\beta/t^2}\,dt \qquad (1)$$

where

$$\beta = md^2/2kT.$$

m being the mass of the molecule, d the detector-interaction region separation, k is Boltzmann's constant, T is the temperature of the gas beam and C is a normalisation constant.

However, if a fraction of metastables decay in flight before reaching the detector, because the metastable lifetime is of the order of the transit time to the detector, then the time of flight distribution for a single metastable state decaying with lifetime τ is given by

$$P_\tau(t) = C'(1/t^4)\,e^{-\beta/t^2}\,e^{-t/\tau}. \qquad (2)$$

Excitation of N_2 metastable states A $^3\Sigma_u^+$, a $^1\Pi_g$, E $^3\Sigma_g^+$ by a pulsed electron beam will allow the time of flight distribution to be studied and the lifetimes determined. As the incident energy is changed and a metastable species of different lifetime (τ_2) with a cross section of similar magnitude is excited, then the time of flight distribution will change requiring a more general form of equation (2) to be used:

$$P(t) = (C''/t^4)\,e^{-\beta/t^2}|(K_1\,e^{-t/\tau_1} + K_2\,e^{-t/\tau_2})| \qquad (3)$$

where K_1 and K_2 are constants dependent on the surface detection efficiencies of the excited species.

In the present work the time of flight curve for the production of metastable nitrogen molecules was studied at selected energies between threshold and 150 eV; for all energies at and above 20 eV a lifetime deduced from the time of flight curve, figure 1,

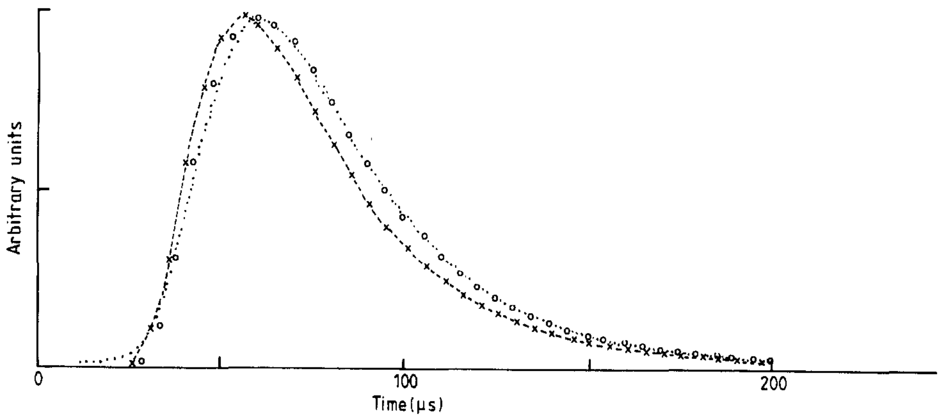


Figure 1. Time of flight spectra of the metastable state a $^1\Pi_g$ and E $^3\Sigma_g^+$ in N_2 measured at 12 (· · · ·) and 20 eV (- - -); computed decay curves for metastable species with lifetimes of 115 (×) and 150 μs (○). See text for discussion.

was estimated to be 115 ± 10 μs in excellent agreement with the lifetime of the a $^1\Pi_g$ state determined by Borst and Zipf (1971) (115 ± 20 μs). Therefore we may conclude that in this energy range the metastable cross section observed, if not solely due to the a $^1\Pi_g$ state, is dominated by this state.

At energies between 12 and 13 eV the time of flight curve yields a lifetime of 150 ± 10 μs. This indicates the presence of a second longer lived metastable state and may be ascribed to the appearance of the E $^3\Sigma_g^+$ state of lifetime 190 ± 20 μs (Borst and Zipf 1971).

The E state is known to support a resonance feature and has been clearly observed in the high resolution study of N_2 metastable production both in this laboratory and in others (Borst *et al* 1972, Lawton and Pichanick 1973, Brunt *et al* 1978, Newman *et al* 1983). This resonance feature is however extremely narrow and only expected to be observed between 12 and 13 eV, in good agreement with the region of the observed lifetime change. The non-resonant cross section of the E state above 13 eV is, at maximum, an order of magnitude lower in intensity than that of the a $^1\Pi_g$ state above this region. Consequently at all other energies the excitation of the E $^3\Sigma_g^+$ state will not perturb the total metastable cross section which will be solely that of the a $^1\Pi_g$ state.

We may therefore conclude that by using a channel electron multiplier to discriminate against the low-lying A $^3\Sigma_u^+$ metastable state, direct detection of the metastable production of N_2 molecules will yield an accurate estimate of the total excitation cross section of the a $^1\Pi_g$ state.

3. Results and discussion

Figure 2 shows the a $^1\Pi_g$ excitation cross section determined using the present recoil technique compared with earlier work. The present results agree well with those of earlier workers and illustrate the strength of the present metastable recoil method.

Although it is possible to determine the number density of the gas beam it has not been possible to make the present data absolute since the detection efficiency of the channel electron multiplier for metastable N_2 molecules in the a $^1\Pi_g$ state is unknown. Therefore all the previous experimental data are normalised to the peak in the present cross section for direct comparison. The magnitude of this peak has been well established by earlier workers as lying between 3 and 4×10^{-17} cm^2, with all the experiments performed in this threshold region providing evidence for a peak located between 15 and 18 eV; the present data are therefore normalised to a cross section value of $(3.5 \pm 0.5) \times 10^{-17}$ cm^2 at the peak (Ajello and Shemansky 1985, Cartwright *et al* 1977, Borst 1972).

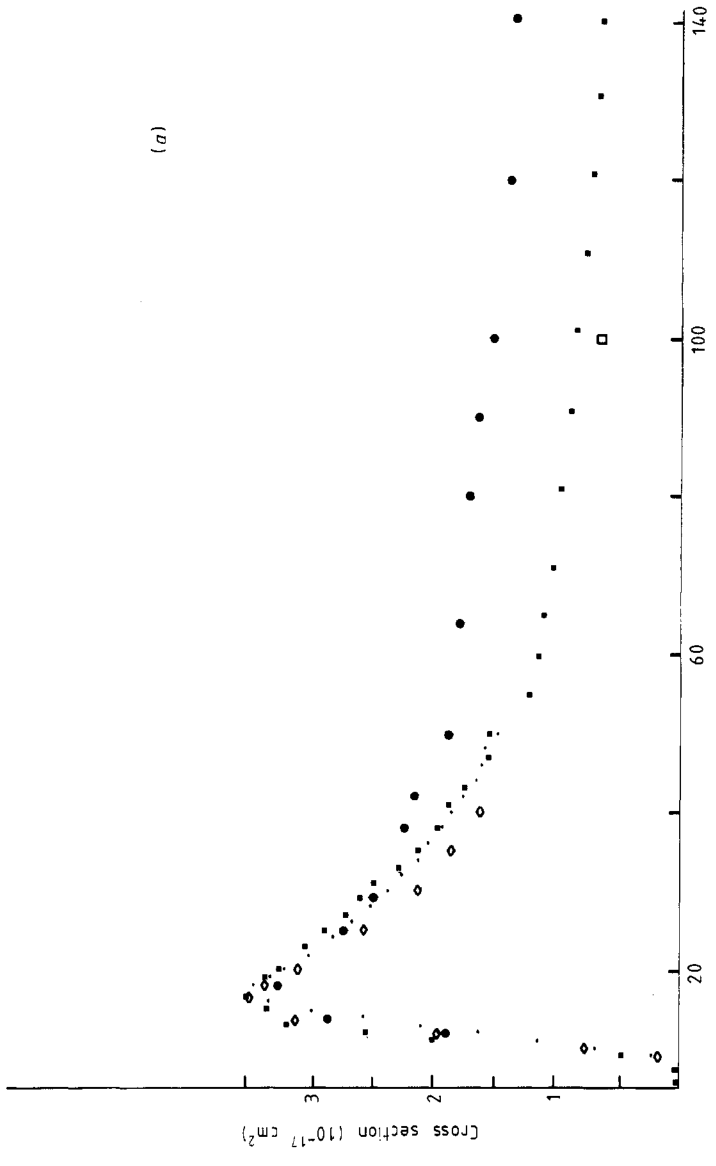
The present data when normalised at 17 eV to 3.5×10^{-17} cm^2 agree very well with the data of Aarts and de Heer (1971) at energies of 60 to 150 eV and also with the single point of Holland (1969) (100 eV). The results of Ajello (1970) clearly overestimate the cross section at energies above 30 eV and this is possibly an indication of cascade effects. In their later paper Ajello and Shemansky (1985) ascribed the error in the early work of Ajello (1970) to a problem of back scattering of secondary electrons in the interaction region. Their recent data are found to agree extremely well over the entire energy range from threshold to 150 eV with the present data (see figure 2). The integral cross section data of Finn and Doering (1976) lie lower than the present data and this may be due either to cascade in the present data *or* an indication of the contribution of higher lying vibrational states not summed in their work: they estimated these should add about 12% to the total cross section, a figure which, if added to their data, would bring their results into closer agreement with the present data at all energies above 20 eV. Oda and Osawa (1981) have derived a total cross section from generalised oscillator strength (GOS) measurements which lie higher than the average of the other experimental measurements, a difference which could result from the difficulty in transforming from a GOS, expressed in terms of momentum and a differential cross section, to the total cross section form. The present results for the first time bridge the threshold cross section data with those obtained by optical fluorescence at incident energies greater than 100 eV; agreement in both magnitude and shape is found to be good and therefore the experimental excitation cross section of the a ${}^1\Pi_g$ state of N_2 may be considered to be clearly established.

Figure 3 compares the present experimental results with the available theoretical cross sections. The calculations of Chung and Lin (1972) and Holley *et al* (1981) agree well with each other in shape but lie some 30% below the experimental data at the peak, while the Born approximation calculation of Rozsnyai (1967) underestimates the observed cross section by some 70%. In addition, neither the Born calculation of Rozsnyai nor the close-coupling calculation of Holley *et al* is able to predict the cross section peak position accurately while the Born-Ochkur-Rudge calculation of Chung and Lin surprisingly gives better agreement with experiment than the two-state close-coupling calculation of Holley *et al.* For convenience the present data are listed in table 1 with their corresponding uncertainties.

In recent years the influence of polarisation effects on electron-atom collisions has become apparent (Burke and Williams 1977) and if theoretical scattering calculations for N_2 are to improve, especially in the threshold region, then the target polarisation and non-local exchange potentials should perhaps be included since the incident electron will distort the N_2 charge cloud as it approaches the molecule. To date these

Table 1. Total cross sections for the a ${}^1\Pi_g$ state in N_2. N = normalisation point.

Energy (eV)	$\sigma(10^{-17}\ cm^2)$	Energy (eV)	$\sigma(10^{-17}\ cm^2)$
9	0.48 ± 0.02	35	2.10 ± 0.12
10	1.27 ± 0.07	38	1.97 ± 0.11
11	2.00 ± 0.11	41	1.88 ± 0.11
12	2.54 ± 0.14	43	1.75 ± 0.09
13	3.18 ± 0.18	47	1.56 ± 0.09
14	3.26 ± 0.18	50	1.56 ± 0.10
15	3.34 ± 0.19	55	1.24 ± 0.07
16	3.45 ± 0.20	60	1.14 ± 0.06
17N	3.50 ± 0.20	65	1.11 ± 0.06
18	3.44 ± 0.20	71	1.05 ± 0.06
19	3.34 ± 0.19	81	0.99 ± 0.06
20	3.25 ± 0.19	91	0.89 ± 0.05
23	3.02 ± 0.17	101	0.84 ± 0.05
25	2.86 ± 0.16	111	0.76 ± 0.04
27	2.70 ± 0.15	121	0.72 ± 0.04
29	2.58 ± 0.15	131	0.67 ± 0.04
31	2.48 ± 0.14	141	0.65 ± 0.04
33	2.29 ± 0.13		


(a)
Incident energy (eV)
Cross section (10^-17 cm^2)
20
60
100
140
1
2
3

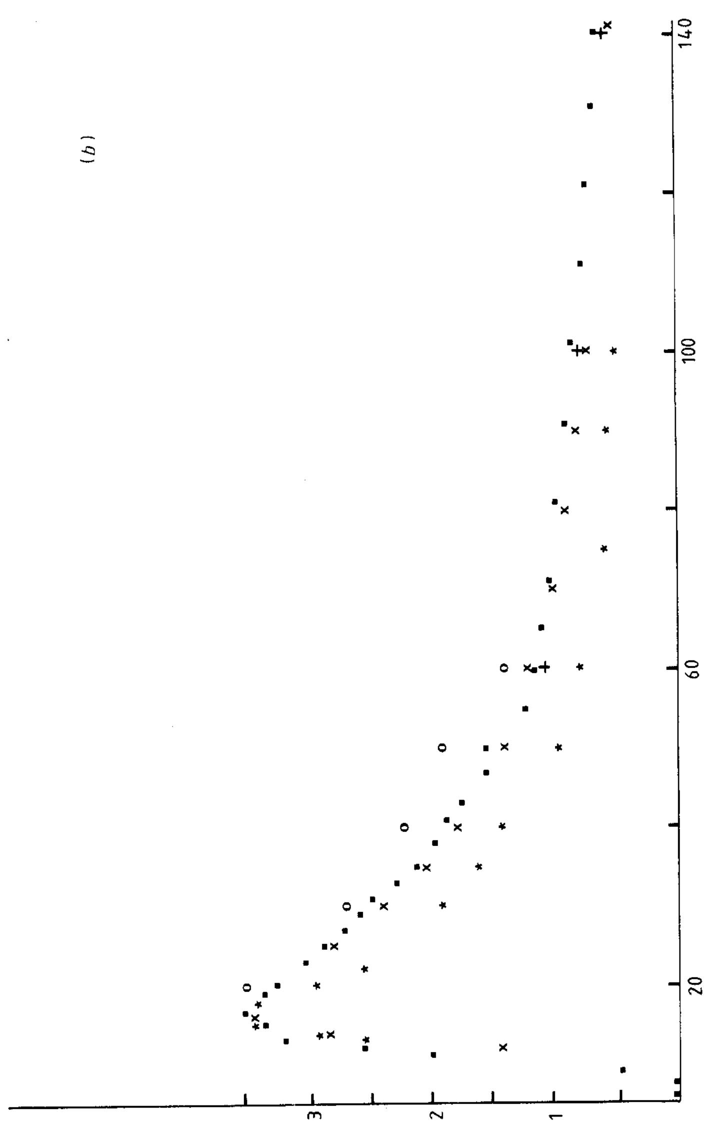


Figure 2. (*a*), (*b*) Experimental total cross sections for the excitation of the a $^1\Pi_g$ state in N_2. Present results, ■; Finn and Doering (1976), *; Borst (1972), ◇; Aarts and de Heer (1971), +; Cartwright *et al* (1977), · · ·; Holland (1969), □; Brinkman and Trajmar (1970), ○; Ajello (1970), ●; Ajello and Shemansky (1985), ×. (Note that all data except those of Aarts and de Heer and Holland have been normalised; see text.)

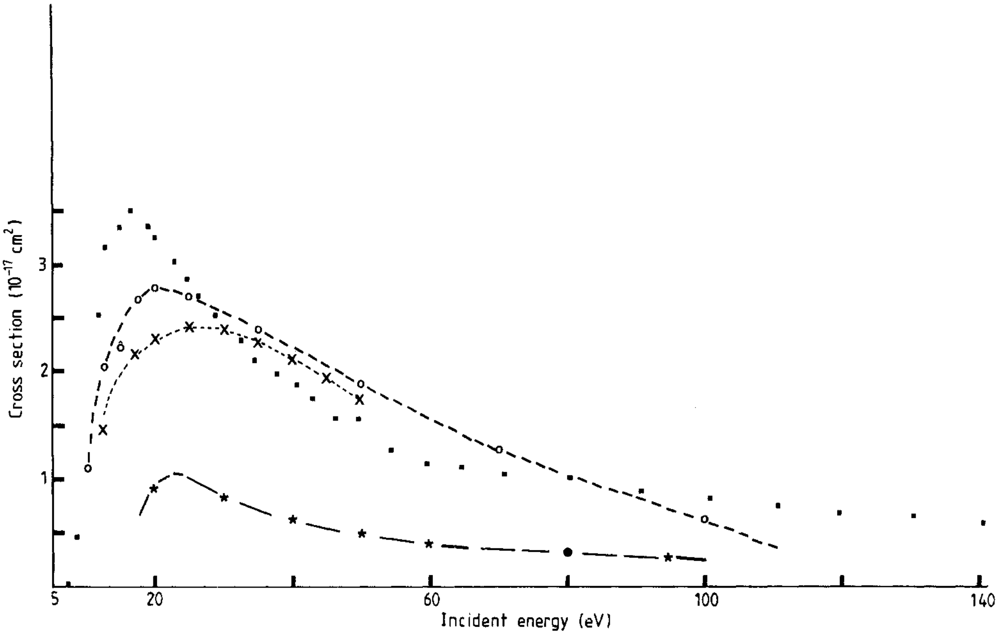


Figure 3. Theoretical total cross sections for the excitation of the a $^1\Pi_g$ state in N_2. Present results, ■; Chung and Lin (1972), —○—; Holley *et al* (1981), —×—; Rozsnyai (1967), —*—. See text for discussion.

effects have not been considered together and hence agreement between experiment and theory is often poor; for a concise review see Trajmar *et al* (1983) and Trajmar (1985). The wealth of experimental data for the a $^1\Pi_g$ state obtained from quite different experimental techniques would seem to make it an ideal candidate as a testing ground of theoretical methods.

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