Measurement of the 13 to 100 eV electron impact excitation cross section for the $X^1\Sigma^+_g \rightarrow a^1\Pi_g$ transition in N_2*

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The electron impact excitation cross section for the $X^1\Sigma^+_g \rightarrow a^1\Pi_g$ transition in N_2 has been measured from 13 to 100 eV by an inelastic electron scattering technique. The cross section varies from a maximum value of 3.6×10^{-17} cm^2 between 15 and 18 eV to 5.2×10^{-18} cm^2 at 100 eV. The incident electron impact energy was calibrated by an optical technique. The agreement between the measured intensities of the $v'=0$–6 vibrational bands of the transition and the intensities predicted by the Franck–Condon factors was found to be within experimental error. The cross section results of the present experiment are in excellent agreement with those of previous investigators obtained with a variety of techniques up to 30 eV. At the higher energies, the present values agree within experimental error with the results of Holland at 100 eV and those of Aarts between 60 and 100 eV.

I. INTRODUCTION

The Lyman–Birge–Hopfield (LBH) system of N_2 is the most prominent vacuum ultraviolet emission feature of the nitrogen molecule.[1] Excitation of this band system by electron impact on N_2 has received extensive previous theoretical and experimental attention because of the geophysical importance of LBH band emission in electron-excited aurorae as well as the fact that the forbidden transition $a^1\Pi_g \rightarrow X^1\Sigma^+_g$ has been found to proceed by a combination of magnetic dipole and electric quadrupole processes.[2] Theoretical calculations of the electron impact excitation cross section have been carried out recently by Chung and Lin.[3] These authors have summarized previous theoretical work. The excitation cross section has been measured in optical fluorescence experiments by Holland[4] between 100 and 2000 eV electron impact energy, from threshold to 208 eV by Ajello,[5] and from 60 to 2000 eV by Aarts.[6] Lassettre and his co-workers[7] have determined the generalized oscillator strength for the transition from 300–500 eV by measuring the small angle inelastic scattering of electrons directly. Measurements at very high kinetic energies have been reported by Wong, *et al.*[8] The relative excitation cross section for the transition $X^1\Sigma^+_g \rightarrow a^1\Pi_g$ has been measured in a metastable detection experiment by Borst.[9] Brinkman and Trajmar[10] have measured the differential scattering cross section (DCS) at 15, 20, 30, 60, and 80 eV and scattering angles from 0° to 80° in an inelastic scattering experiment and have integrated the DCS data over the range 0° to 180° with the aid of extrapolations and normalization to other cross section results to give the total cross section.

A comparison of the various experimental results below 100 eV shows that the general features of the electron impact excitation cross section near threshold are fairly well established. The cross section rises rapidly from threshold to a broad maximum at an energy of approximately 16 eV followed by a long, monotonic decrease at higher energies. However, the available data near 100 eV do not agree very well. Ajello's 100 eV cross section[5] is about three times as large as the results of Holland[4] or Aarts.[6] Part of this disagreement undoubtedly arises from the difficulty of making optical emission measurements on a metastable radiating species such as the $a^1\Pi_g$ state of N_2. Also, due to the maximum of the cross section at low energies, secondary electrons having low energies will, if present in the interaction region, significantly distort the measured value of the cross section in the higher energy range. The results of Brinkman and Trajmar,[10] which are the only previous inelastic scattering measurements in this energy range, are closer to the lower optical values at the higher energies; but are still somewhat higher than the results of Aarts[6] or Holland.[4] Brinkman and Trajmar's direct excitation results would be expected to be free from effects of secondary electrons and diffusion of metastable molecules out of the observation region which are significant difficulties in optical fluorescence experiments.

In this paper, we report the results of a new investigation of the $X^1\Sigma^+_g \rightarrow a^1\Pi_g$ electron excitation cross section from 13 eV to 100 eV. We have used the method of inelastic electron scattering to measure the differential scattering cross section from N_2 at a number of energies between 13 and 100 eV. Elastic scattering as well as excitation of the $C^3\Pi_u$ state was also measured. We have used the well-established electron impact optical excitation cross section for the $C^3\Pi_u \rightarrow B^3\Pi_g$ transition to put our relative measurements on an absolute scale. Measurement of the elastic scattering cross section of N_2 over the same energy range have been published previously.[11] The methods used for the present investigation were quite similar to those used for the elastic scattering work; however, the measurement of the vibrational band system produced by the $X^1\Sigma^+_g \rightarrow a^1\Pi_g$ transition is considerably more complicated than the measurement of the elastic scattering process. In addition to the excitation cross section, we report measurements of the degree of agreement between the observed vibrational band intensities and those predicted by the Franck–Condon principal at various impact energies and scattering angles.

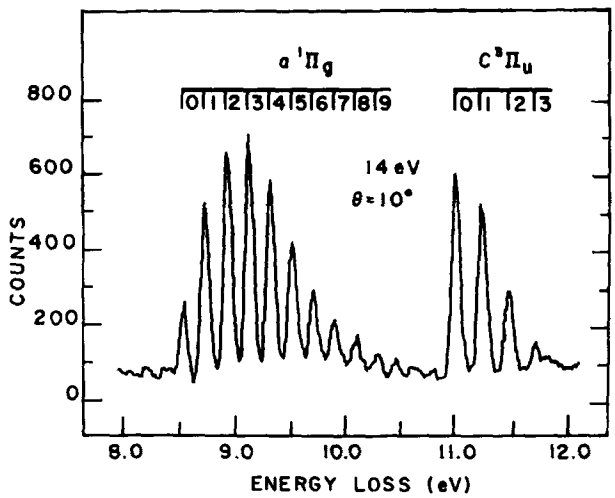

FIG. 1. Medium resolution energy loss spectrum of N_2 at 10° scattering angle and 14 eV impact energy. This spectrum is an example of the data used to calculate the differential cross sections.

II. EXPERIMENTAL

The experimental arrangement has been described previously.[11] Briefly, a high energy resolution electron spectrometer was used to measure the differential scattering cross section for the $X\,^1\Sigma_g^+ - a\,^1\Pi_g$ and $X\,^1\Sigma_g^+ - C\,^3\Pi_u$ transitions in N_2. The energy loss spectrum was repeatedly scanned by means of a multichannel analyzer coupled to the electron spectrometer until a satisfactory signal to noise ratio was achieved. The energy of the incident electron beam was measured optically with a photometer tuned to the N_2 second positive band system as described previously.[11]

A scan of the energy loss region of interest to the present work is shown in Fig. 1. This medium energy resolution spectrum illustrates the type of raw data from which the various band intensities were measured. As can be seen in Fig. 1, the vibrational bands of the $a\,^1\Pi_g$ state extend from 8.5 to 11 eV energy loss while those of the $C\,^3\Pi_u$ state extend from 11 to 12 eV energy loss. At impact energies less than 20 eV, it was necessary to use an energy resolution of 80 MeV FWHM to separate the first few members of the $a\,^1\Pi_g$ state from the N_2 $B\,^3\Pi_u$ state. At higher impact energies it was possible to use an energy resolution of 130 MeV and so reduce the time necessary for collection of the data. The intensities of the various vibrational bands were calculated from the peak heights in the energy loss spectrum.

During the actual experiments, the $X\,^1\Sigma_g^+ - a\,^1\Pi_g$ and $X\,^1\Sigma_g^+ - C\,^3\Pi_u$ transitions were either measured with respect to each other or with respect to the elastic scattering process. In cases such as shown in Fig. 1 where the transitions were of comparable intensities, it was convenient to measure their intensities with respect to each other. In some cases, however, where the two intensities were very different, measurements with respect to the elastic scattering peak were used.

The possibility of contributions to the observed scattered intensity by multiple scattering processes was investigated using the method of Lassettre and Francis.[12] Plots of signal/pressure vs pressure for the bands of the $a\,^1\Pi_g$ transition measured at 90° scattering angle were linear up to 22 mTorr, indicating the lack of multiple scattering in this channel. Similar results were obtained for the elastic and $C\,^3\Pi_u$ state channels as reported previously. During the actual experiments, the pressure was maintained at a few mTorr.

The $C\,^3\Pi_u$ state optical excitation cross section was used as a calibration standard for energies above 24 eV as described previously.[11] At energies below 24 eV, the $C\,^3\Pi_u$ state excitation cross section was not an effective secondary standard because of the experimental difficulties discussed before. We therefore used a relative calibration involving the energy dependence of the elastic scattering cross section at 30° instead of the $C\,^3\Pi_u$ state calibration. This technique has been described in detail previously.[11] Values of the total excitation cross section for the $X\,^1\Sigma_g^+ - a\,^1\Pi_g$ transition obtained by this method are so indicated when presented later in Table II.

Although it was possible to detect the vibrational bands of the $X\,^1\Sigma_g^+ - a\,^1\Pi_g$ transition from $v' = 0$ to above $v' = 10$, we generally used only the bands $v' = 1, 2, 3, 4, 5$ for our measurements. These five bands contain about 75% of the intensity of the electronic transition. Although the $v' = 3$ vibrational state excitation has the largest cross section, it can be seen from Fig. 1 that it contains only a small fraction of the total intensity of the electronic transition (18% according to the Franck–Condon factors of Benesch *et al.*[13]). Rather than measure only the $v' = 3$ band and then calculate the total band intensity from the $v' = 3$ band intensity and the Franck–Condon factors for the vibrational states of the electronic transition, we chose instead to measure the five bands mentioned above and calculate the $v' = 3$ intensity by multiplying the total intensity in the five vibrational bands by the ratio of the $v' = 3$ Franck–Condon factor to the sum of the $v' = 1$–5 Franck–Condon factors obtained from Benesch *et al.*[13] This calculation of the $v' = 3$ intensity was convenient since it also allowed us to test the validity of the assumption that the relative vibrational band intensities in this electronic transition are accurately predicted by the relative Franck–Condon factors by a simple comparison of the calculated and observed $v' = 3$ intensities. The results are presented in a later section.

III. RESULTS AND DISCUSSION

A. Differential scattering cross sections

Relative values of the DCS for the $X\,^1\Sigma_g^+ - a\,^1\Pi_g$ transition are given in Table I for a number of scattering angles between 5° and 92° and incident energies from 13 to 100 eV. The relative DCS at 13, 20, 40, and 100 eV are also shown in Fig. 2. Typical plots of the $X\,^1\Sigma_g^+ - C\,^3\Pi_u$ transition DCS have been published earlier.

Examination of the DCS for excitation of the $a\,^1\Pi_g$ state shows that the DCS falls off very slowly with increasing angle near threshold. However, as the energy

TABLE I. Relative $X^1\Sigma_g^+ \rightarrow a^1\Pi_g$ differential scattering cross section $(d\sigma/d\Omega)$.

Energy, eV \ Scattering angle degrees	5	7	9	11	14	19	23	28	38	47	56	65	74	83	92
13			1.3		1.3	1.2	1.3	1.2	0.99		0.62		0.46		0.29
15			1.8		1.8	1.8	1.8	1.8	1.3		0.66		0.51		0.42
18			2.8		2.8	2.4	2.0	1.8	1.2		0.57		0.50		0.40
20	3.5		2.9		2.9	2.2	1.8	1.5	1.0	0.66	0.50	0.35	0.37	0.42	0.40
22			3.1		2.9	2.2	1.8	1.5	0.90	0.63	0.42	0.35	0.31		0.29
24	4.4	4.6			2.9	2.4	2.2	1.5	0.88	0.64	0.33	0.26	0.31		0.29
30	3.7		2.9		2.4	1.8	1.5	1.0	0.63	0.31	0.22	0.24	0.26	0.37	0.29
35			3.7		2.6	1.8	1.6	1.3	0.51	0.31	0.18	0.17	0.31	0.22	0.15
40	3.9	2.9	3.1	2.2	1.8	1.7	1.3	0.85	0.48	0.26	0.13	0.13	0.14	0.14	0.14
50	3.9	3.1	2.9	2.6	1.8	1.1	0.85		0.20		0.10				0.090
60	2.9	2.6	2.4	1.8	1.5	1.0	0.75	0.44	0.17		0.075		0.068		0.059
75	3.3			2.4	2.0	1.3	0.68	0.42	0.16	0.081		0.068			0.033
90	2.9	2.6	2.0	1.7	1.5	0.88	0.51	0.28	0.13	0.072		0.042			0.024
100	3.1	2.4	2.0	1.7	1.4	0.83	0.44	0.26	0.079	0.048		0.044			0.020

is increased, the transition becomes forward-peaked in the angular region below about 60°. Above 60°, the transition flattens and becomes nearly isotropic, even at 100 eV. The behavior of the DCS as a function of energy shown in Fig. 2 is midway between what is expected for allowed and forbidden transitions. The forward peaked behavior at the higher energies is characteristic of an allowed transition; but it is interesting to note that the flat, isotropic tail above 60° appears to be present up to at least 100 eV. The DCS for this transition is, therefore, much less isotropic than that for the $X^1\Sigma_g^+ \rightarrow C^3\Pi_u$ transition shown previously,[11] but is not as forward-peaked as would be expected for an allowed transition.

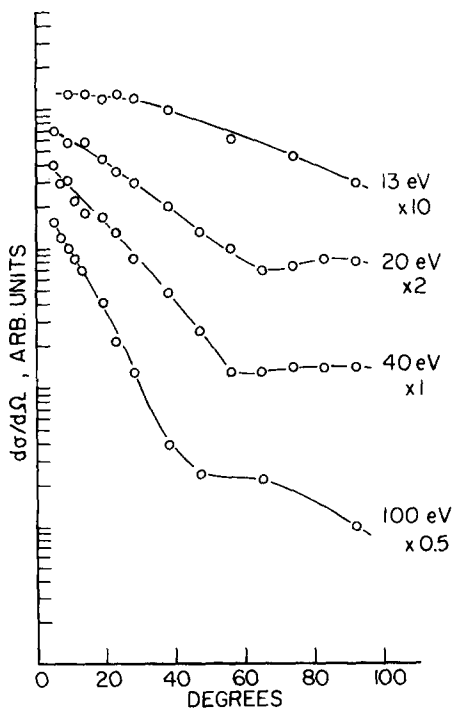

FIG. 2. Relative inelastic $X^1\Sigma_g^+ \rightarrow a^1\Pi_g$ DCS for excitation of N_2 by 13, 20, 40, and 100 eV electrons. The same units were used for each energy; but the DCS were multiplied by the indicated factors to clarify the presentation of the data. The $v' = 3$ "effective" DCS is shown here (see text).

Note that the small angle values given in Table I were actually measured and are not extrapolated results of higher angle data. Although the experimental difficulties in measuring this DCS were smaller than those reported previously for the elastic DCS,[11] interference from the primary beam at small scattering angles and low energies was still severe enough to restrict us to the angular range above 9° below 20 eV.

B. Calculation of the total excitation cross section

The considerations involved in the selection of the $C^3\Pi_u \rightarrow B^3\Pi_g$ optical excitation cross section as a secondary standard have been discussed previously.[11] The cross section values adopted for the present work were those of Aarts and deHeer.[14] The branching ratios of Shemansky and Broadfoot[15] were used to relate the $C^3\Pi_u \rightarrow B^3\Pi_g$ (0, 0) band optical excitation cross section to the intensity of the $C^3\Pi_u$ $v' = 0$ vibrational band observed in the electron impact spectrum.

The extrapolation of the $C^3\Pi_u$ cross section from 0° to 5° and from 90° to 180° has been previously described.[11] For the $a^1\Pi_g$ state cross section, a similar extrapolation was necessary from 5° to 0° and from 92° to 180° since the apparatus measured the differential cross section from 5° to 92° only. The extrapolation from 5° to 0° was performed in the same way as for the $C^3\Pi_u$ state.[11] Since measurements of the $a^1\Pi_g$ state differential scattering cross section show that the cross section flattens and becomes nearly isotropic above 60°, we assumed that the cross section was constant from 90° to 180° and calculated the total cross section accordingly. This method had the advantage of providing a simple, consistent means for calculation of the total cross section. In Table II, we show what percentage of the calculated total cross section lay between 90° and 180°. The percentage varies from 33% at 20 eV to 10% at 100 eV. In light of the uncertainties in the

TABLE II. Total $X\,^1\Sigma_g^+ \rightarrow a\,^1\Pi_g$ ($v' = 0$–6) cross section.

Energy (eV)	Cross section ($\times 10^{-18}$ cm^2)	Calculated 92°–180° contribution[b]
13	[a]27	28%
15	[a]36	32
18	[a]36	30
20	[a]31	33
22	[a]27	28
24	27	28
30	23	33
35	17	27
40	15	25
50	10	23
60	8.0	19
75	7.5	13
90	5.6	11
100	5.2	10

[a]The cross section at these energies was calculated using an internal calibration method (see Ref. 11) rather than the $C\,^3\Pi_u$ cross section.

[b]The 92°–180° contribution to the total cross section was calculated assuring a constant cross section equal to the value at 90° from 90° to 180°.

experiment and the total error limits that we assign to the final cross section values, we do not feel that any more involved procedure for the calculation of the backward hemisphere contribution is justified.

The total excitation cross section for the $a\,^1\Pi_g$ state as a function of energy is shown in Table II. As stated above, the total excitation cross section was calculated from the "effective" $v' = 3$ differential excitation cross section by the use of the Franck–Condon factors of Benesch *et al.*[13] It should be noted at this point that in comparing our results to the optical emission measurements, we have adopted the measure of the "total" cross section used by Ajello, Holland, and others[4,5] which is the cross section for excitation of vibrational levels 0–6. Optical emission from vibrational levels with v' greater than 6 is not observed because of predissociation.[4,5] We have therefore calculated the total cross section for comparison with the optical results as the cross section for excitation of the $v' = 0$–6 levels, although the vibrational bands with v' greater than 6 are clearly visible in our direct excitation spectra as shown in Fig. 1. The contribution of the levels with v' greater than 6 to the total electron impact excitation cross section can be estimated from the Franck–Condon factors by Benesch *et al.*[13] and is about 12% of the total cross section.

The use of the Franck–Condon factors for the transition $X\,^1\Sigma_g^+ - a\,^1\Pi_g$ to calculate the total excitation cross section for the electronic transition from measurements of only a few of the vibrational components of the transition obviously involves the assumption that the relative vibrational band intensities are accurately predicted by the relative Franck–Condon factors. Comparisons of the observed optical emission band intensities with the intensities predicted by the relative Franck–Condon factors have been made by Holland,[4] Ajello,[5] and Lassettre and his co-workers.[16] Holland[4] obtained reasonably good agreement for the intensities of the observed vibrational bands. Ajello[5] summed the intensities of bands originating at a particular vibrational level and compared the populations of the levels with those predicted by the Franck–Condon factors. Ajello's agreement with the calculated values is also good (it should be noted that the values of the Franck–Condon factors of Benesch *et al.*[13] used by Ajello are evidently those for the isotopically substituted N_2 molecule). Lassettre *et al.*[16] have measured the probabilities for direct excitation of the $a\,^1\Pi_g$ vibrational levels in electron scattering experiments and have found that for scattering angles up to 16°, the probabilities were proportional to the relative Franck–Condon factors for impact energies from 60 to 400 eV.

Table III shows our values for the ratio of the calculated to observed $v' = 3$ intensity as described above. Results are shown at scattering angles of 5° to 92° and impact energies of 20, 40, 60, and 100 eV. Since we have not made a detailed study of the behavior of the individual vibrational bands, our results are not conclusive as to the presence or lack of small deviations from the relative intensities predicted by the Franck–Condon factors; however, the agreement between the observed and calculated values in Table III is good enough that we can say that any deviations must be small compared to the accuracy of the present experiment.

We estimate the error in our total cross section measurements as follows: uncertainty in the $C\,^3\Pi_u$ cross section of Aarts and deHeer,[14] 15%; uncertainty in the measurement and extrapolation of the $a\,^1\Pi_g$ and $C\,^3\Pi_u$ differential cross sections, 35%; total expected uncertainty, ±50%.

In Fig. 3 we compare the present results with those of previous investigators including the optical results of Aarts,[6] Holland,[4] and Ajello,[5] the electron scattering results of Brinkman and Trajmar,[10] and the metastable measurements of Borst.[9] It is interesting to note the large number of different techniques of measurements

TABLE III. $X\,^1\Sigma_g^+ \rightarrow a\,^1\Pi_g(v' = 3)$.

Intensity ratio: $\frac{\text{Measured } (v'=3)}{\text{Calculated } (v'=3)}$ vs scattering angle at various energies

Scattering angle, degrees	Energy, eV 20	40	60	100
5	100×10^{-2}	99×10^{-2}	97×10^{-2}	98×10^{-2}
9	98	97	100	98
11		100	97	105
14	99	100	97	101
19	97	100	99	94
23	96	93	101	97
28	98	95	97	88
38	90	98	94	96
47				106
56	92	104	93	
65	92	88		111
74	89	91	96	
83		89		110
92	90	90		
Mean	0.95	0.96	0.97	1.00
Standard deviation	0.04	0.05	0.03	0.07

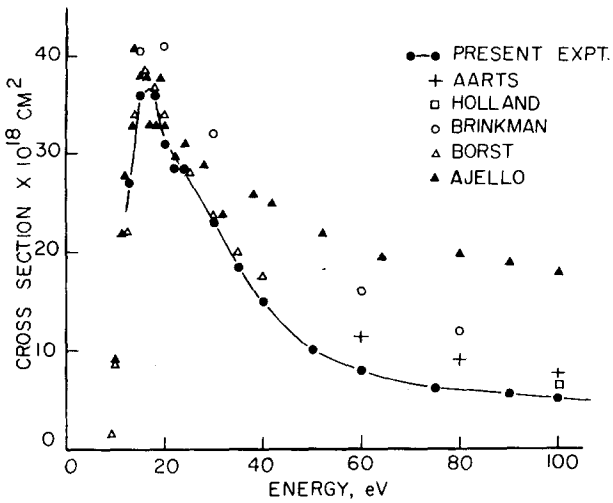

FIG. 3. Total $X\,^1\Sigma_g^+ \rightarrow a\,^1\Pi_g$ $v' = 0$–6 cross section vs energy. The results of the present experiment are compared to those of Aarts,[6] Holland,[4] Brinkman and Trajmar,[10] Borst,[9] and Ajello.[5]

and normalization of results to absolute scales which were used to obtain the data shown in Fig. 3. It is also interesting to note that the differences among the various results do not show any obvious relationship to the method of measurement used.

Our results are somewhat smaller than the others shown in Fig. 3 over the entire energy range although they agree extremely well with those of Borst[9] at energies up to 40 eV. All the values for the cross section at the peak near 16 eV appear to be in agreement to within ± 15%. The main differences in results appear at the higher energies. This is the energy region where difficulty would be expected from secondary electrons in the optical experiments; however, it should be noted that the results of Brinkman and Trajmar[10] which are not subject to this difficulty are somewhat higher in this energy range than the optical results of Aarts.[6]

Our 60–100 eV results are about 30% smaller than the results of Aarts[6] and our 100 eV value is 20% lower than Holland's.[4] In light of the expected errors in our experiment, we can say that we agree within experimental error with the results of Aarts and Holland at the higher energies and with the other investigators below 30 eV. Aside from the results of Ajello,[5] it appears that all the available experimental data now agrees to within ± 50%.

Our data agree reasonably well near threshold with Chung and Lin's calculation[3] for the case in which the Ochkur exchange modification is included, but are somewhat smaller at the higher energies.

IV. CONCLUSIONS

We have measured the electron impact excitation cross section for the $X\,^1\Sigma_g^+ \rightarrow a\,^1\Pi_g$ transition in N_2 from 13 to 100 eV. The relative cross section was calculated by integration of the relative differential scattering cross section at various energies. The relative values of the cross section were put on an absolute scale by comparison of the relative cross sections to those for excitation of the $X\,^1\Sigma_g^+ \rightarrow C\,^3\Pi_u$ transition and use of the electron impact optical emission cross section for the $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ transition as a secondary standard.

The results of the present experiment agree within experimental error with previous results up to an energy of 30 eV. At the higher energies, the results agree within experimental error to the previous optical excitation measurements of Aarts[6] and Holland,[4] are about a factor of 2 lower than the previous electron scattering results of Brinkman and Trajmar[10] at 60 and 80 eV, and a factor of 3 lower than the optical emission results of Ajello[5] from 60–100 eV.

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