

## Electron impact excitation of the electronic states of $N_2$ . II. Integral cross sections at incident energies from 10 to 50 eV<sup>†</sup>

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Normalized integral cross sections for the electron impact excitation of the lowest three singlet ( $a', a, w$ ) and lowest five triplet ( $A, B, W, B', C$ ) valence electronic states of  $N_2$ , and of the two ( $3s\sigma_g$ ) Rydberg states ( $E, a''$ ), have been determined at seven incident electron energies ranging from 10 to 50 eV. These cross sections were obtained by integrating the differential cross section reported in the preceding paper, over all scattering angles. The cross sections for excitation of the  $W$ ,  $B'$ , and  $a'$  states are considerably larger than previously estimated, that for excitation of the  $C$  state is in excellent agreement with previously reported values, while those for the  $A$ ,  $B$ , and  $a$  states are smaller than previous results. Theoretical cross sections obtained with Born-type theories give *integral* cross sections that are in surprisingly good agreement for many of the excited states, but in a few cases ( $A, W, B', a'$ ) the theoretical cross sections are in poor agreement.

### I. INTRODUCTION

Integral cross sections for the electron-impact excitation of various electronic states of molecular nitrogen play an essential role for understanding auroral and ionospheric phenomena, as well as a variety of gas discharge processes. The interest in these cross sections for the study of atmospheric processes is based on the fact that molecular nitrogen is the major atmospheric constituent to altitudes of about 200 km and the primary fraction of the radiated energy in many atmospheric phenomena appears in molecular nitrogen band systems.<sup>1</sup> For most atmospheric processes, absolute integral cross sections (and their energy dependence) are required because characteristic nitrogen emission features are produced by a spectrum of secondary electrons resulting from either photoionization or ionization by the incident auroral electrons. The role of molecular nitrogen integral cross sections in understanding the overall auroral processes has been recently well summarized by Jones,<sup>1(a)</sup> and in determining the detailed vibrational populations of molecular nitrogen under auroral conditions by Cartwright *et al.*<sup>2</sup>

The considerable work involving afterglow processes<sup>3</sup> in molecular nitrogen gas discharges and, more recently, in studies<sup>4</sup> of the various laser transitions in molecular nitrogen, has also generated a need for integral cross sections for electron impact excitation of  $N_2$ . The vibrational population in the  $N_2(B^3\Pi_g)$  state under a variety of discharge excitation and pressure conditions is still not understood, and the theoretical modeling of

such processes has been handicapped by the absence of a consistent set of excitation cross sections. Similarly, of the six different electronic systems in  $N_2$  that are known to lase, only one ( $C^3\Pi_u \rightarrow B^3\Pi_g$ , second positive) has an upper-state excitation cross section that is well enough known to permit accurate theoretical modeling to be undertaken. The lasing transitions among the lower-lying electronic states, primarily in the infrared,<sup>5</sup> involve electronic states whose excitation cross sections are either known poorly, or not at all. The modeling of these laser systems, many of which have peculiar characteristics depending on the excitation and pressure conditions,<sup>6</sup> has therefore been severely limited by lack of fundamental cross-section data.

The need for the electron impact excitation cross sections of molecular nitrogen has stimulated a number of good experimental efforts to determine them, as will be summarized below. These previous measurements, although providing useful information about the *effective* (or apparent) excitation cross section for a given electronic state, have generally been unable to separate the *cascade* and *direct* excitation contributions to the population process of the upper electronic state.

The method that has been most frequently employed is to pass electrons of known energy through the molecular gas and measure the absolute intensity of the radiation produced. If there are no cascade processes from higher electronic states, or if they can be quantitatively accounted for, such data can yield absolute-integral cross sections for electron impact excitation of the up-

per (emitting) electronic state. This method has been used to obtain apparent excitation cross sections for three excited electronic states ( $C^3\Pi_u$ ,  $B^3\Pi_g$ ,  $a^1\Pi_u$ ) of molecular nitrogen but, as will be discussed in considerable detail below, only that for excitation of the  $C$  state is approximately the same as the direct-excitation cross section. The other two electronic states for which this type of measurement has been made contain cascade contributions ranging from 30 to 250%, depending on the state and the incident electron energy. If the emissions from these specific excited states are the only quantities of interest, such apparent excitation cross sections are sufficient. However, if the details of the population processes involving the other excited states are of interest, the direct-excitation cross section must be known.

Another method that has been used successfully to obtain *apparent* integral electron impact excitation cross sections for certain  $N_2$  metastable electronic states ( $E^3\Sigma_g^+$ ,  $a^1\Pi_g$ ,  $A^3\Sigma_u^+$ ) is to cross a molecular beam with an electron beam of known energy and detect the metastable excited states with a surface detector. Although these methods have also provided useful information about the apparent excitation cross sections for some states that cannot be determined by the photon emission method, the obtained cross sections usually contain significant cascade contributions as in the photon emission case.

The only previous attempt to obtain absolute-integral *direct* electron impact excitation cross sections for molecular nitrogen was by Brinkmann and Trajmar,<sup>7</sup> who used electron-energy-loss data to estimate the differential cross sections (unpublished), from which they obtained the integral values. It was difficult for them to obtain accurate cross-section values because the data they used, although the best available at that time, was of relatively low resolution, contained a nonuniform background, and extended only to a scattering angle of  $90^\circ$ . In addition, they did not have at their disposal a spectrum decomposition technique to thoroughly analyze the electron energy-loss data. However, their integral cross sections represent the most complete and only consistent set of direct-excitation cross sections available. The results reported here are based on the differential cross sections (DCS's) reported in the preceding paper,<sup>8</sup> hereafter referred to as I, and represent a significant improvement over the previously available integral cross sections for excitation of the electronic states of  $N_2$ . As discussed in I, the electron energy-loss data covered the range of scattering angles from  $5^\circ$  to  $138^\circ$ , were of higher resolution, and generally contained only small background contributions. A numerical spectrum

analysis technique also allowed the DCS's for excitation of all the electronic states present in the spectra to be extracted in a consistent fashion.

Integral cross sections for excitation of the electronic states of  $N_2$  have also been obtained theoretically by application of first-order (Born-type) scattering theories. The first quantum-mechanical results reported on  $N_2$  were by Rozsnyai,<sup>9</sup> who used the Born-Ochkur approximation to calculate integral cross sections for excitation of the  $a^1\Pi_g$  and  $b^1\Pi_u$  states. Cartwright<sup>10</sup> applied the Ochkur-Rudge approximation to obtain integral cross sections for excitation of the lowest triplet states of  $N_2$ . These first two theoretical efforts used molecular orbitals based on Slater-type atomic orbitals which, due to the two-center nature of the molecular wave functions, required that a number of approximations be made in order to evaluate the associated matrix elements. Chung and Lin<sup>11</sup> subsequently recalculated the integral cross sections in the Born-Ochkur-Rudge approximation using Gaussian-type atomic orbitals to represent the molecular wave functions. The associated matrix elements can then be evaluated without approximation. Although the difference between the cross sections obtained with the two different wave functions are generally fairly small, the integral cross sections reported in this work will be compared to the theoretical results of Chung and Lin<sup>11</sup> since they considered the largest number of molecular excited states.

## II. DATA ANALYSIS

### A. Integral cross sections

The integral cross sections reported here were obtained from the DCS's reported in I in the following straightforward manner. The DCS's, extracted from the electron energy-loss data over the range  $5$ – $138^\circ$ , were smoothly extrapolated to  $0^\circ$  and  $180^\circ$  (see I) and the integral cross section obtained by straightforward numerical integration from

$$\sigma_x^{n'}(E) = 2\pi \int_0^\pi \frac{d\sigma^{n'}}{d\Omega}(\theta; E) \sin\theta d\theta, \quad (1)$$

where  $\sigma_x^{n'}(E)$  represents the integral cross section for excitation of electronic state  $n'$  from the ground electronic state ( $X$ ),  $d\sigma^{n'}/d\Omega(\theta; E)$  is the DCS for excitation of state  $n'$  at scattering angle  $\theta$  and incident electron energy  $E$ . It was found that, since none of the DCS's considered in this incident electron energy region were extremely forward peaked, a standard Simpson's rule integration scheme could be used without difficulty. Since the DCS's were determined for at most seven incident electron energies (10, 12.5, 15, 17, 20, 30, and 50

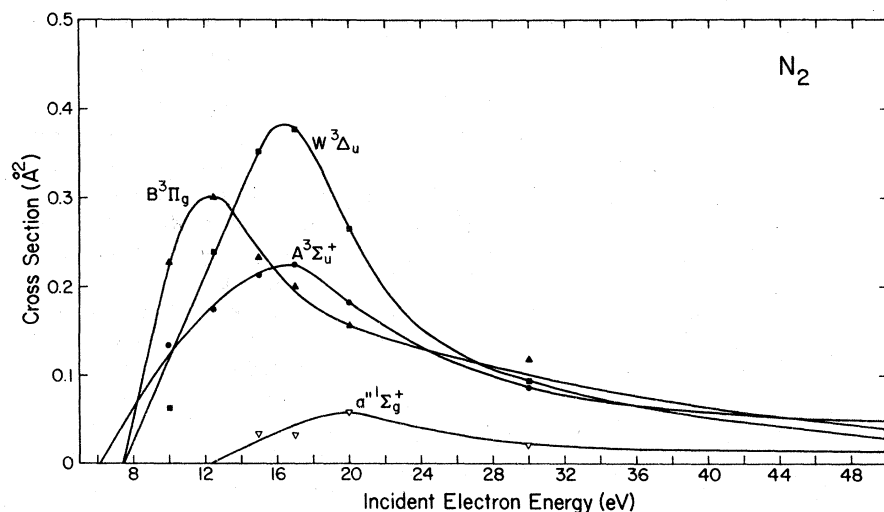


FIG. 1. Integral cross sections ( $\text{\AA}^2$ ) as a function of incident electron energy (eV) for excitation of the  $A$ ,  $B$ ,  $W$ , and  $a''$  electronic states of  $N_2$ . Error bars are not shown with these data points but are shown in subsequent figures and discussed in the text.

eV), these are the energies at which integral cross-section values were obtained. For some electronic states whose excitation thresholds are near 10 eV (or above), integral cross sections were obtained at fewer energy values. The integral cross sections presented in Sec. III were obtained by drawing smooth curves through these seven (or fewer) energy points.

#### B. Error analysis

The extrapolation of the DCS's to  $0^\circ$  and  $180^\circ$ , and the numerical integration of the DCS's, generally introduce negligible errors in the integral cross section compared to uncertainties associated with the shapes of the DCS's. However, due to the large variation in the shapes of the DCS's with the final electronic state and with incident electron energy (see I), it is not possible

to accurately quantify the errors in the integral cross-section values. Based on the statistical uncertainties in the DCS's and the estimated normalization errors (see I), the integral cross sections values reported here are believed to be accurate to 25%, except near the peaks of the large cross sections where the error is closer to 20%. For small cross sections ( $E^3\Sigma_g^+$ ,  $a''^1\Sigma_u^+$ ), the error may be 50% in some cases.

### III. RESULTS

#### A. Summary of present results

Figures 1–3 present the integral cross sections for the ten lowest electronic states of molecular nitrogen obtained in this study. The actual, unadjusted data points are shown by the various symbols from which error bars have been omitted

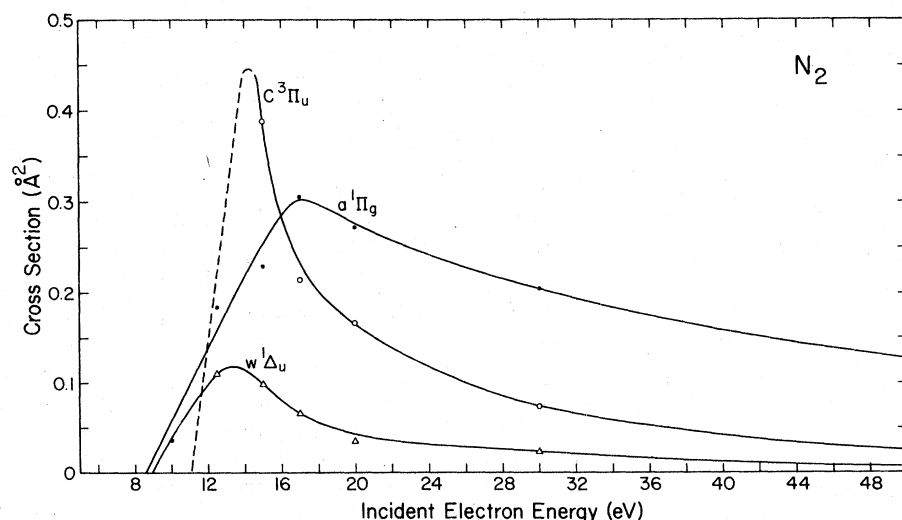


FIG. 2. Integral cross sections ( $\text{\AA}^2$ ) as a function of incident electron energy (eV) for excitation of the  $C$ ,  $a$ , and  $w$  electronic states of  $N_2$ . The dashed portion of the  $C$ -state integral cross section was not determined in this study but taken from the results of Imami and Borst (Ref. 12) (see text). Error bars associated with the data points are discussed in the text and shown in subsequent figures.

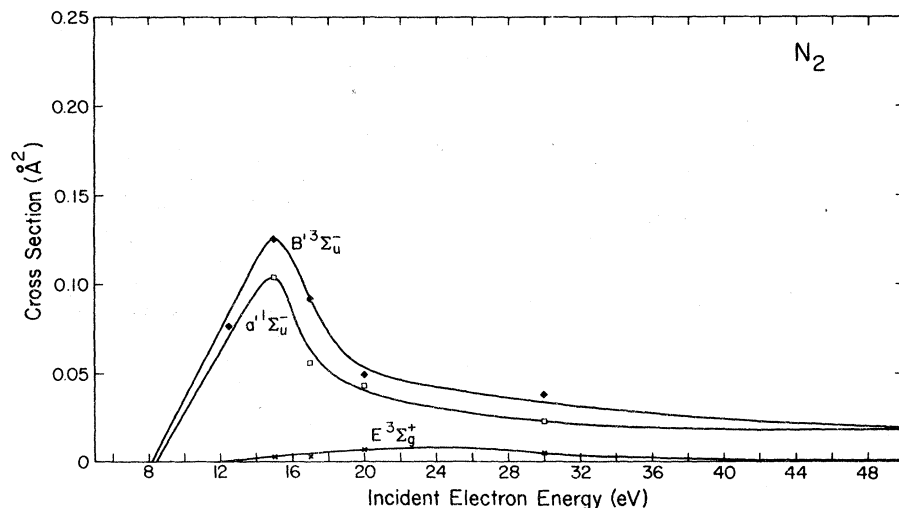


FIG. 3. Integral cross sections ( $\text{\AA}^2$ ) as a function of incident electron energy (eV) for excitation of the  $B'$ ,  $a'$ , and  $E$  electronic states of  $N_2$ . Error bars associated with the data points are discussed in the text and shown in subsequent figures.

for purposes of clarity. The solid curves drawn through the data points represent the best estimate of the integral cross section for each electronic state as determined by these data. These integral cross-section curves do not necessarily pass through the center of each data point, but rather represent smooth curves that pass through as many data points as possible and within the error bar associated with each data point. These smooth curves were then used to obtain the integral cross section for values of the incident electron energy other than the measured ones. Integral cross-section values obtained in this manner are tabulated for these ten electronic states in Table I, for selected values of the incident electron energy to 50 eV.

#### B. Comparison with other cross sections

##### 1. $C^3\Pi_u$

Figure 4 contains a comparison between the present results, the cross section estimated earlier<sup>7</sup> from electron energy-loss data, the results from Born-type calculations,<sup>10,11</sup> and the apparent excitation results of Imami and Borst.<sup>12</sup> The latter data are the only apparent excitation cross sections shown in Fig. 4, although there have been a large number of apparent excitation cross-section measurements on this electronic state made during the past fifteen years. Although most of the apparent excitation cross-section measurements of the  $C$  state generally agree well for energies below about 25 eV, serious discrepancies are found at higher incident electron energies. These discrepancies appear to be due to the difficulty in some of the previous experiments in accounting for secondary electrons produced under certain

experimental conditions. This is particularly true in the data of Shemansky and Broadfoot<sup>13</sup> and to a lesser degree in the earlier work of Jobe *et al.*<sup>14</sup> and of Burns *et al.*<sup>15</sup> A thorough analysis of these previous measurements has been made by Finn and Doering,<sup>16</sup> Imami and Borst,<sup>12</sup> Finn *et al.*,<sup>17</sup> and Aarts and deHeer.<sup>18</sup> The estimates of the  $C$  state excitation cross section obtained by analysis of electron swarm data<sup>19</sup> in  $N_2$  have not been included here because of the general difficulty in obtaining  $N_2$  cross sections from these kind of data due to the large number of electronic states within 11 eV of the ground state.

The integral cross section reported here for the  $C$  state (which was not determined for incident electron energies below 15 eV) is somewhat smaller than the apparent excitation cross sections of Imami and Borst over the energy range 15–30 eV. Although the difference is less than the combined error bars of the two measurements, it may be real and due to a small cascade contribution from the  $E^3\Sigma_g^+$  state to the  $C$ -state cross section determined by Imami and Borst.<sup>12</sup> The  $E$  state is known<sup>20</sup> to cascade into the  $C$  state, and such a contribution could easily account for the difference shown in Fig. 4. When account is made for a small cascade contribution to the apparent excitation cross section, the present results are in excellent agreement with those of Ref. 12, although the two results were obtained by entirely different methods.

The integral cross section for the  $C$  state obtained earlier by Brinkmann and Trajmar<sup>7</sup> from electron energy-loss data is also in very good agreement with the present results. This agreement is expected because the vibrational levels of the  $C$  state in the electron energy-loss spectra

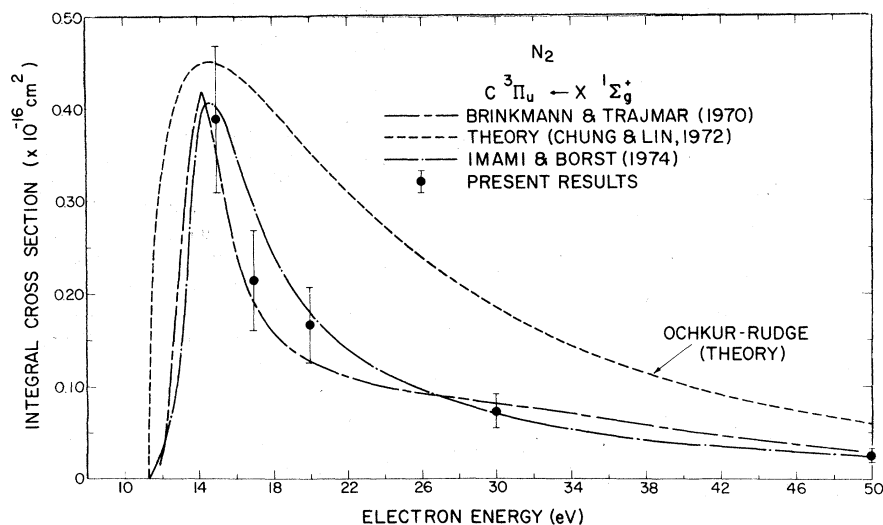


FIG. 4. Integral cross section ( $\text{cm}^2$ ) as a function of incident electron energy (eV) for excitation of the C state of  $N_2$  as obtained by various methods. The present results are shown by the solid circles with error bars but have not been connected by a line for purposes of clarity. See text for further discussion.

are essentially not overlapped by features from any other electronic state (see Fig. 5 of I). The higher resolution of the more recent energy-loss data, upon which the present results are based, therefore provides no substantial advantage over

the older data for determining the C-state cross section. The theoretical integral cross section for the C state shown in Fig. 4, obtained in the Ochkur-Rudge approximation,<sup>10,11</sup> agrees well in magnitude but is considerably broader when com-

TABLE I.  $N_2$  integral cross sections  $\sigma_n(E)$  in units of  $10^{-16} \text{ cm}^2$ .

$E_0$ (eV)	$A^3\Sigma_u^+$	$B^3\Pi_g$	$W^3\Delta_u$	$B'^3\Sigma_u^-$	$a'^1\Sigma_u^-$	$a^1\Pi_g$	$w^1\Delta_u$	$C^3\Pi_u$	$E^3\Sigma_g^+$	$a''^1\Sigma_g^+$
(threshold)	(6.1693)	(7.3529)	(7.3623)	(8.1647)	(8.3987)	(8.5489)	(8.8948)	(11.0316)	(11.8766)	(12.2530)
7	0.030	...	...	...	...	...	...	...	...	...
8	0.062	0.054	0.027	...	...	...	...	...	...	...
9	0.094	0.140	0.074	0.016	0.010	0.019	0.002	...	...	...
10	0.122	0.225	0.120	0.035	0.027	0.059	0.039	...	...	...
11	0.148	0.278	0.166	0.055	0.045	0.099	0.071	...	...	...
12	0.171	0.299	0.213	0.074	0.062	0.140	0.099	0.146	0.0005	...
13	0.189	0.297	0.260	0.094	0.080	0.180	0.117	0.298	0.001	0.008
14	0.204	0.271	0.306	0.113	0.096	0.220	0.115	0.443	0.0021	0.018
15	0.215	0.241	0.351	0.125	0.104	0.256	0.100	0.389	0.0030	0.028
16	0.223	0.216	0.380	0.114	0.085	0.286	0.081	0.284	0.0040	0.037
17	0.225	0.195	0.376	0.092	0.064	0.302	0.066	0.234	0.0050	0.045
18	0.214	0.179	0.350	0.073	0.052	0.297	0.056	0.202	0.0056	0.052
19	0.199	0.166	0.309	0.061	0.0455	0.287	0.049	0.181	0.0062	0.057
20	0.183	0.156	0.265	0.054	0.041	0.276	0.043	0.165	0.0070	0.058
22	0.155	0.142	0.197	0.047	0.0345	0.258	0.036	0.139	0.0078	0.051
24	0.132	0.130	0.153	0.043	0.0300	0.242	0.032	0.118	0.0080	0.041
26	0.113	0.120	0.126	0.0395	0.0275	0.228	0.029	0.100	0.0080	0.034
28	0.099	0.110	0.108	0.0363	0.0250	0.216	0.026	0.086	0.0065	0.028
30	0.087	0.101	0.094	0.0337	0.0230	0.204	0.023	0.074	0.0050	0.023
32	0.078	0.092	0.0835	0.0313	0.0215	0.194	0.021	0.066	0.0040	0.020
34	0.072	0.084	0.074	0.0292	0.0200	0.184	0.018	0.059	0.0032	0.019
36	0.066	0.076	0.066	0.0275	0.0195	0.175	0.016	0.052	0.0027	0.017
38	0.062	0.070	0.059	0.0260	0.0187	0.166	0.014	0.047	0.0020	0.0165
40	0.058	0.064	0.052	0.0245	0.0185	0.159	0.013	0.042	0.0018	0.016
42	0.056	0.058	0.047	0.0230	0.0184	0.152	0.011	0.038	0.0013	0.015
44	0.054	0.054	0.042	0.0220	0.0183	0.145	0.010	0.034	0.0010	0.015
46	0.052	0.049	0.038	0.0210	0.0182	0.139	0.009	0.031	0.0009	0.0145
48	0.501	0.045	0.034	0.0200	0.0181	0.134	0.008	0.028	0.0008	0.0144
50	0.050	0.040	0.030	0.0190	0.0180	0.127	0.007	0.026	0.0007	0.0143

pared to the experimental results. The validity of the Born-Ochkur-Rudge theory in predicting integral cross sections will be discussed in a later section.

The excellent agreement between the present  $C$  state integral cross section and the previous results is important because it suggests that the techniques used in this work to obtain integral cross sections are reliable.

## 2. $A^3\Sigma_u^+$

A comparison between the present integral cross section for excitation of the  $A$  state and that reported earlier by others is shown in Fig. 5. It should be noted that the present results show a maximum in the cross section at an energy 5–6 eV higher than previous results. The cross section from Borst<sup>21</sup> was determined by the molecular beam method. This method, although reasonably good for determining *direct* integral excitation cross sections for metastable excited states which receive little or no cascade contribution (e.g.,  $E$  state), is difficult to apply accurately to the determination of the *direct*  $A$ -state integral cross section because of the very large cascade contribution received by the  $A$  state. All the energy deposited in the  $N_2$  triplet states eventually cascades into the  $A$  state and most of it cascades in less than 20  $\mu\text{sec}$ . The total *cascade* contribution to the  $A$  state is at least a factor of 2 larger than the *direct* excitation contribution for the lower  $A$ -state vibrational levels.<sup>2,22</sup> The difference between the  $A$ -state

cross section reported by Borst<sup>21</sup> and the present results is believed to be due to the difficulty of quantitatively accounting for these complicated energy-dependent cascade processes.

The  $A$ -state integral cross section reported earlier by Brinkmann and Trajmar<sup>7</sup> is in only fair agreement with the present results, primarily because it shows a peak at 10-eV incident electron energy while the present results show a peak at 16.5 eV. This discrepancy is believed to be due to the fact that the earlier results<sup>7</sup> were obtained by simply reading peak heights from earlier electron energy-loss spectra of much lower resolution. Since the vibrational levels of the  $A$  state with the largest Franck-Condon factors for direct excitation are always overlapped by features due to the  $B^3\Pi_g$ ,  $W^3\Delta_u$  and higher states, it is necessary to employ the spectrum decomposition technique discussed in I to obtain accurate cross sections for these states.

The theoretical Ochkur-Rudge excitation cross section for the  $A$  state<sup>10,11</sup> is nearly an order of magnitude larger than the present experimental results. The reason that the Ochkur-Rudge approximation substantially overestimates the  $A$ -state cross section while predicting reasonable magnitudes for the  $C$  state (and  $B$  state; see below) is not understood. The most obvious explanation is that the single configuration wave functions used to represent the  $N_2$  target states<sup>10,11</sup> is a very poor representation of the "true" molecular state in the case of the  $A^3\Sigma_u^+$  state.

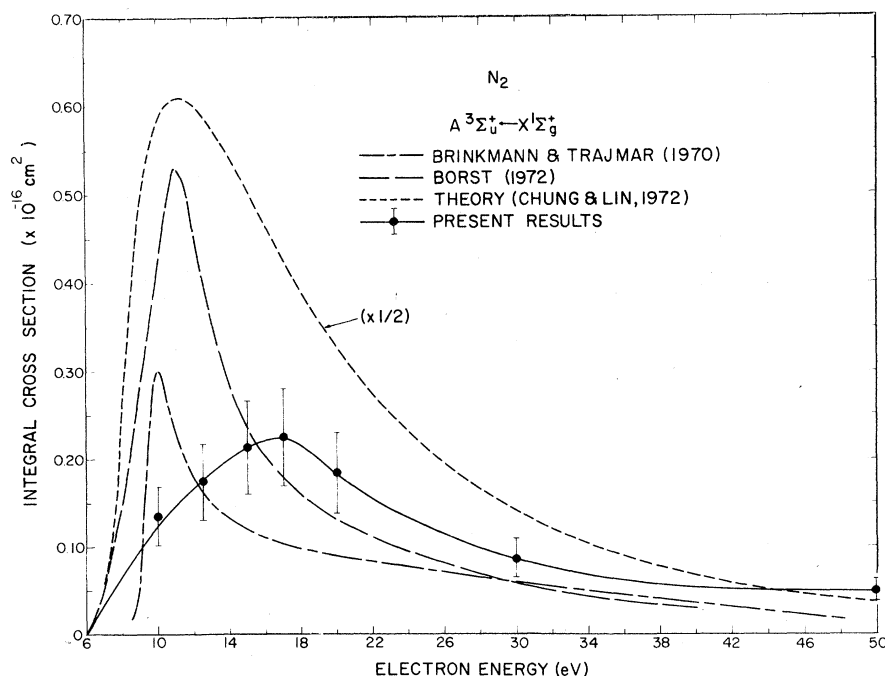


FIG. 5. Integral cross section ( $\text{cm}^2$ ) as a function of incident electron energy (eV) for excitation of the  $A$  state of  $N_2$  as determined by various methods. The present results are shown by the solid circles with error bars and with a continuous curve drawn through them. The theoretical cross section (dashed curve) has been reduced by a factor of 2 before plotting.

3.  $B^3\Pi_g$ 

Figure 6 contains a comparison of the present integral cross section for excitation of the  $B$  state, the apparent excitation cross section of Stanton and St. John,<sup>23</sup> the results of Brinkmann and Trajmar,<sup>7</sup> and the theoretical cross section obtained<sup>10, 11</sup> in the Ochkur-Rudge approximation. Brinkmann and Trajmar estimated a  $B$ -state cross section with a larger maximum value, and at somewhat lower energy, than the present results. These differences are due entirely to the fact that the  $N_2$  electron energy-loss spectra are strongly overlapped and the peak height method they employed did not account for the other overlapping states.

The apparent excitation cross section for the  $B$  state of Stanton and St. John<sup>23</sup> is the only one of its type shown in Fig. 6, although there have been a few others reported. The  $B$ -state apparent excitation cross section of McConkey and Simpson<sup>24</sup> is in good agreement with their results, as discussed by Stanton and St. John. These authors<sup>23</sup> also evaluate the other  $B$ -state apparent excitation cross sections reported prior to 1970. Shemansky and Broadfoot have also reported<sup>13</sup> an apparent excitation cross section for the  $B$  state, but their results are substantially larger than those of Stanton and St. John

and of McConkey and Simpson. The reason that the apparent excitation cross section for the  $B$  state is so much larger than the present direct-excitation cross section is simply due to the large cascade contributions to that state. A total of six triplet electronic states cascade into the  $B$  state and produce a vibrational population<sup>2</sup> substantially different than that produced by direct excitation.

The  $B$ -state integral cross section predicted<sup>10, 11</sup> in the Ochkur-Rudge approximation is in amazingly good agreement with the present results. This agreement is perhaps fortuitous or may be due to the fact that the target wave functions used for the  $B$  state were relatively better than those used for the  $A$  state.

4.  $a^1\Pi_g$ 

Previous measurements of the integral cross section for excitation of the  $a$  state are compared with the present results in Figs. 7(a) and 7(b). Two of the other cross sections shown are based on a peak-height analysis of electron energy-loss spectra. Both Brinkmann and Trajmar,<sup>7</sup> and Finn and Doering,<sup>25</sup> analyzed electron energy-loss data for scattering angles out to  $90^\circ$  and for selected incident electron energies by measuring peak heights associated with vibrational levels of the

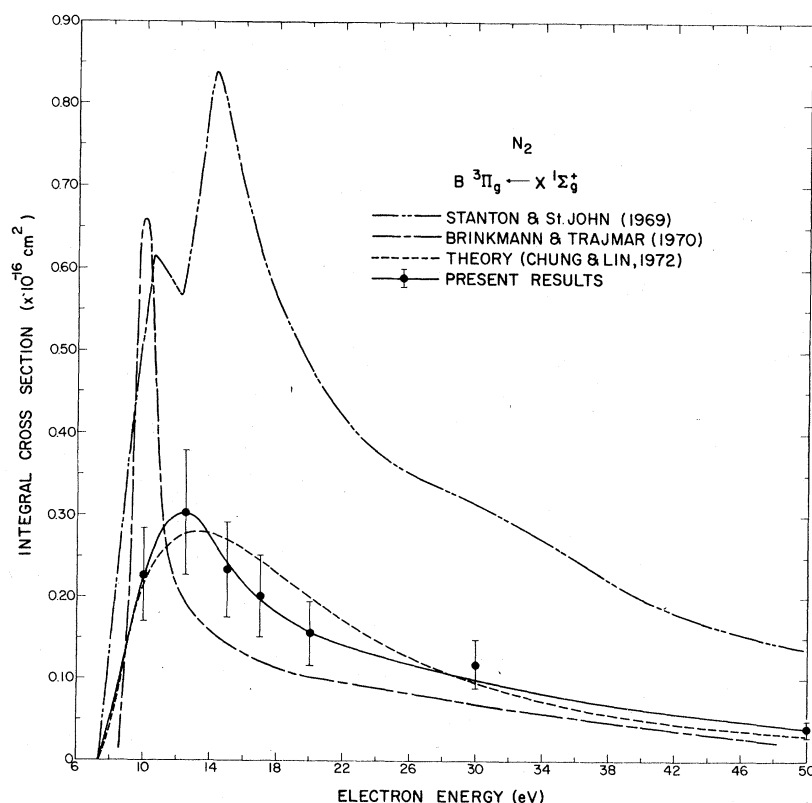


FIG. 6. Integral cross section ( $\text{cm}^2$ ) as a function of incident electron energy (eV) for excitation of the  $B$  state of  $N_2$  as determined by various methods. The present results are shown by the solid circles with error bars and with a continuous curve drawn through them.

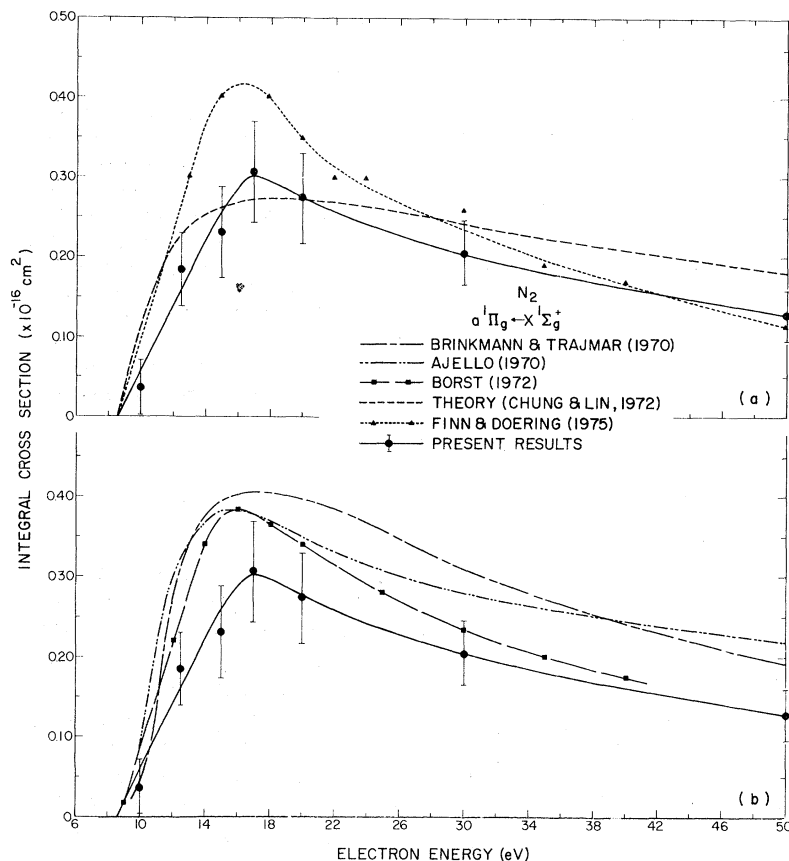


FIG. 7. Integral cross section ( $\text{cm}^2$ ) as a function of incident electron energy (eV) for excitation of the  $a$  state of  $\text{N}_2$  as determined by various methods. The present results are shown by the solid circles with error bars and with a continuous curve drawn through them. The present results are shown in both upper and lower panels for comparison with the other results.

$a$  state. The relative DCS's obtained by this method were extrapolated to cover the entire angular range, integrated over all scattering angles, and normalized to the apparent excitation cross section of the  $C$  state to obtain absolute cross sections. Since neither of these studies accounted for the overlapping of the vibrational levels of the  $a$  state by levels from the other electronic states, the cross sections they obtained should be (and are) larger than those obtained in the present study. Although their results are somewhat larger than those of the present study, the *shapes* of the cross sections are generally in good agreement.

Ajello has determined<sup>26</sup> the apparent excitation cross section of the  $a$  state by passing electrons of known energy through  $\text{N}_2$  gas and measuring the absolute intensity of selected band systems emitted by the  $a$  state. Since both the  $a' 1\Sigma_u^-$  and  $w 1\Delta_u$  states are known<sup>2(b),5,27</sup> to cascade populate the  $a$  state, the emission cross section determined by Ajello should be larger than that determined in this study. The comparison in Fig. 7(b) shows that this is indeed the case. Borst also determined<sup>21</sup> the integral cross section for excitation of the  $a$  state by the molecular beam method described above. Determination of the  $a$ -state cross section required

subtraction of the cross sections for excitation of the  $A$  and  $E$  states from the measured metastable excitation function. As shown in Fig. 7(b), this relatively imprecise process results in a cross section that is in surprisingly good agreement with the other apparent excitation cross sections. The cross section determined by Borst contains cascade contributions from higher electronic states and hence should be larger than the present results, as shown in Fig. 7(b). The comparisons shown in Fig. 7 indicate, and detailed calculations substantiate<sup>27,2(b)</sup> that about 30% of the  $a$ -state population develops from cascade from higher electronic states. A theoretical cross section for excitation of the  $a$  state, obtained<sup>9,11</sup> in the Born-Ochkur approximation, agrees well [Fig. 7(a)] with the present results.

##### 5. $W^3\Delta_u, w^1\Delta_u$

Integral cross sections for excitation of the  $W$  and  $w$  states are compared in Fig. 8 with the respective theoretical cross section obtained<sup>10,11</sup> in the Ochkur-Rudge approximation. There are no other cross sections, experimental or theoretical, to which the present results can be compared. Figure 8 shows that the theoretical cross sections



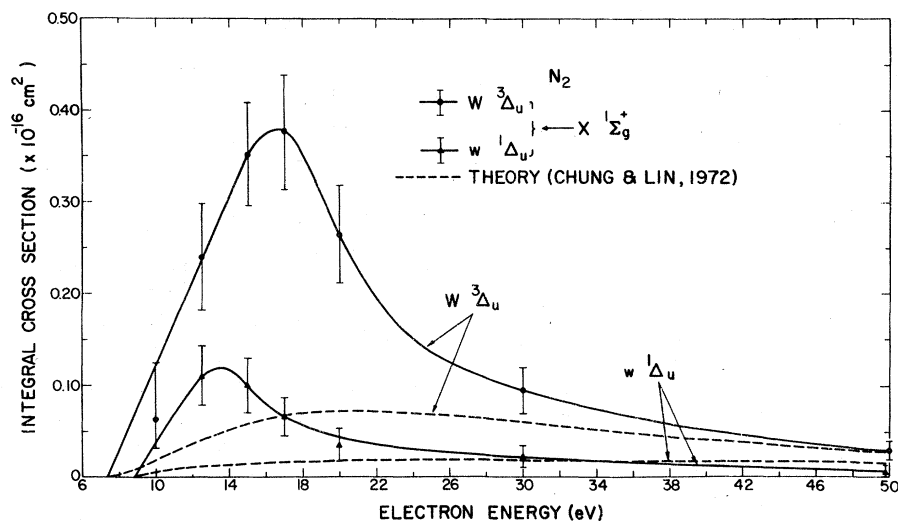


FIG. 8. Integral cross section ( $\text{cm}^2$ ) as a function of incident electron energy (eV) for excitation of the  $W$  and  $w$  electronic states of  $N_2$ . The present results are shown by the solid circles with error bars and with the solid line drawn through them. The theoretical cross sections are shown by the dashed lines.

agree poorly with the present results in both magnitude and shape. It should be noted here that the  $W$  state excitation cross section results in the largest rate for excitation in both auroral<sup>(b)</sup> and discharge<sup>28</sup> processes for any of the  $N_2$  states. This somewhat surprising fact, which has important ramifications in both auroral and discharge processes, cannot be recognized by visual inspection of electron energy-loss spectra in  $N_2$  (see I).

#### 6. $E^3\Sigma_g^+$

Figure 9 shows a comparison of the cross section for excitation of the  $E$  state obtained in this study with other experimental and theoretical re-

sults. The present results are substantially smaller than all the cross sections obtained earlier. The  $E$  state is known to support a resonant state,<sup>29</sup> and will therefore have a narrow, relatively strong peak in the integral cross section close to its threshold. The resonance excitation contribution is believed to be that observed by Borst *et al.*,<sup>30</sup> while the cross section determined in the present study is clearly the nonresonant component of the excitation. An effective cross section similar to that obtained by combining the resonant<sup>30</sup> and nonresonant (present results) cross section shown in Fig. 9 has been observed by Kurzweg *et al.*<sup>20</sup> in a study of delayed cascade contributions to the  $C$  state. The above

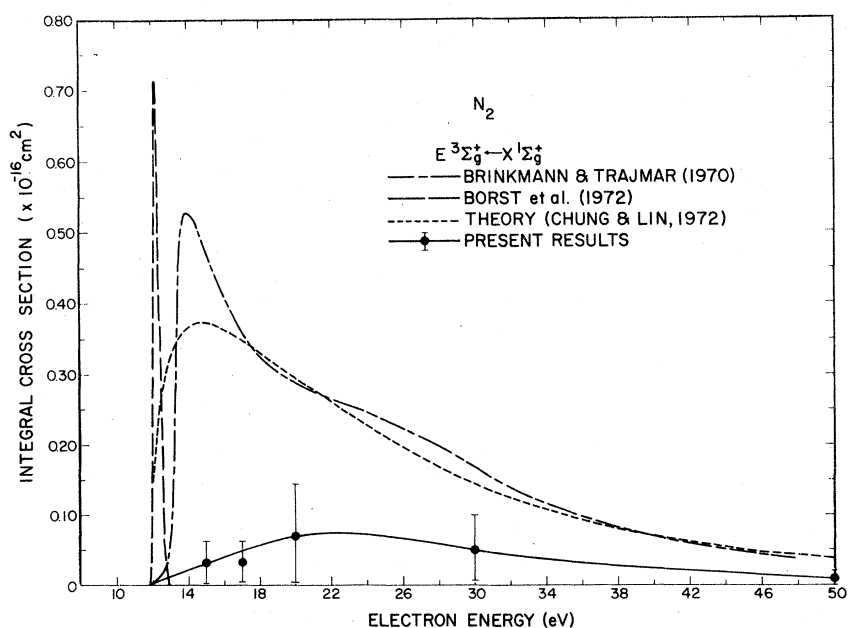
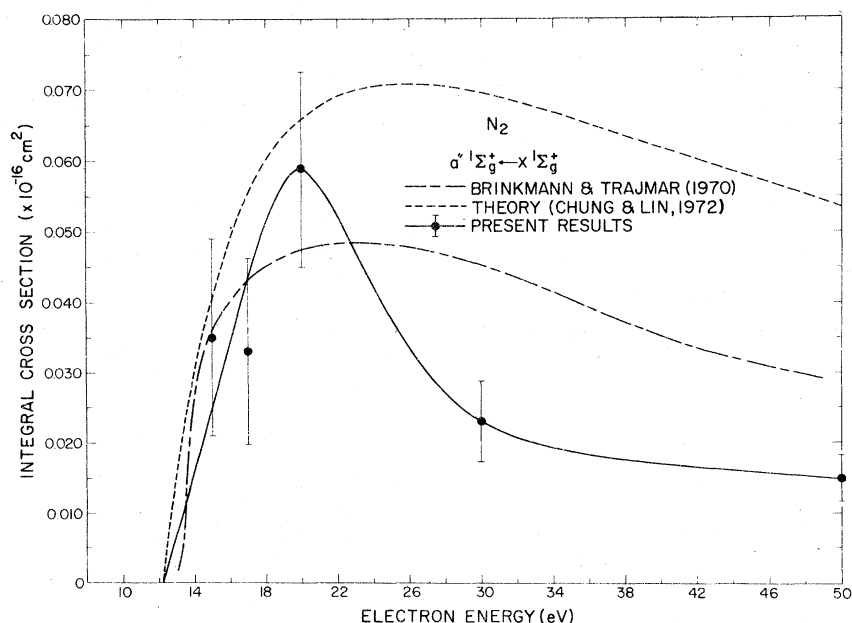


FIG. 9. Integral cross section ( $\text{cm}^2$ ) as a function of incident electron energy (eV) for excitation of the  $E$  state of  $N_2$  as determined by various methods. The present results are shown by solid circles with error bars with the solid line drawn through them. See text for a discussion of the other results.

mentioned combination of cross sections is in qualitative agreement with the findings of Kurzweg *et al.*<sup>20</sup> The earlier results of Brinkmann and Trajmar<sup>7</sup> are much larger than the present cross section, although both cross sections were obtained by analysis of electron energy-loss data. Since the earlier data were of significantly poorer resolution, it is likely that the peak due to the  $E$  state ( $v'=0$ ) was not clearly resolved from peaks due to higher vibrational levels of the  $C$  state. This would have resulted in an overestimation of the  $E$ -state cross section in that earlier study. The agreement between the theoretical cross section<sup>9,10</sup> (Ochkur-Rudge) and the results of Brinkmann and Trajmar<sup>7</sup> is believed to be fortuitous.

### 7. $a''^1\Sigma_g^+$

Figure 10 contains a comparison of the integral cross section obtained for the  $a''$  state in the present study with the earlier results of Brinkmann and Trajmar<sup>7</sup> and with the theoretical cross section obtained in the Born-Ochkur approximation.<sup>11</sup> The present results are in reasonably good agreement with the cross section obtained by Brinkmann and Trajmar from an analysis of earlier electron energy-loss spectra, although they reported a somewhat broader integral cross section. The theoretical cross section, obtained in the Born-Ochkur approximation, is also substantially broader than either of the experimental cross sections but of approximately the same magnitude as the present results. There seem to be no other results to which our present results can be compared.



## IV. CONCLUSIONS

Except for the  $C$  state, the integral excitation cross sections presented here are different from those previously reported. With the exception of that for the  $W$  state, and possibly the  $a''$  state, all integral cross sections obtained in this study are smaller than the previous estimates and many of them reach their maximum value at a higher electron energy than previously reported cross sections. These results represent the first consistent set of electron impact excitation cross sections for  $N_2$  that include all singlet and triplet states within 12.25 eV of the ground state. The large cross section for the  $W$  state, and the nonnegligible cross sections for the  $B'$ ,  $a'$ , and  $w$  states, have important ramifications in interpreting the detailed vibrational population processes.<sup>2</sup> It has been shown, for example, that all possible cascade processes must be included to properly account for the energy flow through the molecular nitrogen excited states in order to explain the observed infrared emissions and vibrational populations under auroral<sup>2</sup> and gas discharge<sup>27,31</sup> conditions.

The ability of the Born-type theories to predict reliable *integral* electron impact cross sections is substantially better than their ability to predict reliable DCS's (see paper I). First-order theories have a general failing in that they can't be applied to obtain excitation cross sections for *all* final molecular electronic states. For example, they predict<sup>10</sup> cross sections that are identically zero for  $\Sigma^+ \leftrightarrow \Sigma^-$  transitions while, as shown in Fig. 3, the experimentally determined cross sections are appreciable. In addition, the reason that these

FIG. 10. Integral cross section ( $\text{cm}^2$ ) as a function of incident electron energy (eV) for excitation of the  $a''$  state of  $N_2$  as determined by various methods. The present results are shown by the solid circles with error bars and with the solid line drawn through them. See text for a discussion of the other results.

theories do relatively poorly for certain initial-final state combinations ( $^3\Delta$ ,  $^3\Sigma - ^1\Sigma$ ), while very well for others ( $^1\Pi$ ,  $^3\Pi - ^1\Sigma$ ), is not understood. It may be associated with the fact that excited states of  $\Pi$  symmetry are much better represented by the simple one (or two) spatial configurations that have so far been employed. Results obtained by improving the target wave functions are presently under study to see if the explanation is indeed as simple as the one given above. To go beyond the Born-type theory in the low-medium energy region

is presently an arduous task for molecular targets and, until improved theories are developed, Born-type *integral* cross sections can probably be used as an estimate of the "true" cross section, subject to the above-mentioned caveats. However, as shown in I, Born-type theories fail badly in predicting correct DCS's. Consequently, theoretical results obtained in Born-type approximations will not provide accurate "finer detail" of the scattering process of importance in various phenomena such as the inelastic momentum transfer.<sup>28</sup>

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