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Excitation of the C $^3\Pi_u$ state of N_2 by electron impact in the near-threshold region

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Abstract. The total cross section for excitation of the $v' = 0, 1, 2$ vibrational levels and the total electronic cross section of the C $^3\Pi_u$ state of nitrogen have been determined for incident electron energies from threshold at 11.03 eV to 17.5 eV. The emission cross section of the (0, 0) line (337 nm) of the second positive band of nitrogen has been also obtained in this energy region. Strong non-Franck–Condon excitation of vibrational levels has been observed. The present data are compared with previous experimental and theoretical results.

1. Introduction

Electron impact excitation of the triplet, C $^3\Pi_u$, state of nitrogen is drawing much attention due to its importance in atmospherical photophysics (Solomon 1989) and modelling of gaseous discharges (Loureiro and Ferreira 1989). The C $^3\Pi_u$ state belongs to a group of nitrogen excited states having high excitation cross section. In its decay it significantly contributes, via two-step cascading C $^3\Pi_u \rightarrow$ B $^3\Pi_g \rightarrow$ A $^3\Sigma_u^+$, to the population of the A $^3\Sigma_u^+$ metastable state. This decay is also a strong source of light emission from the second positive system corresponding to the C $^3\Pi_u \rightarrow$ B $^3\Pi_g$ transition in the visible region. Therefore an accurate knowledge of the excitation cross sections of the C $^3\Pi_u$ state is of primary interest for the understanding of several important phenomena in nitrogen.

The electronic differential cross sections for the excitation of the C $^3\Pi_u$ state have been measured for selected incident energies from 15 to 50 eV by Cartwright *et al* (1977a) (renormalized by Trajmar *et al* 1983) and by Brunger and Teubner (1990). These two sets of the differential measurements do not agree very well and show significant differences. For example at 17.5 eV and a scattering angle of 50° they differ by about a factor of two. From the differential data the total cross sections have been determined by Cartwright *et al* (1977b) which have been renormalized by Trajmar *et al* (1983). However it has been shown recently that an increase of the total cross section of Trajmar *et al* (1983) by a factor of two would improve the agreement between calculated and measured excitation coefficients of the C $^3\Pi_u$ state (Phelps and Pitchford 1985). Therefore further studies of the differential and total cross sections of the C $^3\Pi_u$ state are needed to resolve these discrepancies.

The emission cross section corresponding to the most intense, $v' = 0 \rightarrow v'' = 0$, line (337 nm) of the second positive system has been measured by Jobe *et al* (1967), Aarts and de Heer (1969), Burns *et al* (1969), Shemansky and Broadfoot (1971b) and Shaw and Campos (1983) in the energy region from threshold at 11.03 eV to 100 eV. These

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measurements yielded values of maximum cross section from 10.4 to 11.9×10^{-22} m^2 at an energy of about 14 eV and showed that the cross section is decreasing for higher energies. The relative emission cross section of the (0, 0) line has been also obtained by Imami and Borst (1974) up to 1000 eV. The maximum emission cross sections of other (v', v'') lines have been measured by Jobe *et al* (1967), Burns *et al* (1969) and Shaw and Campos (1983).

In the present work the total cross sections for excitation of the $v' = 0, 1, 2$ vibrational levels of the $C\,^3\Pi_u$ state and the total cross section for electronic transition have been determined in the energy regions from threshold to about 17.5 eV by studying emission of the second positive system in the 290–410 nm spectral range. Excitation functions of several optical lines have been measured and normalized to obtain absolute values of the cross sections. The present measurements have been carried out with higher electron energy resolution and more accurate incident energy calibration than the previous studies of the emission cross sections. This has allowed the energy dependence of the cross sections to be established with higher accuracy and the excitation cross sections to be determined in the near-threshold region. These cross sections can be used as a calibration reference in the optical measurements for other molecules (see, for example, McConkey *et al* 1992). The results of the present work may also be used to test several theoretical methods developed recently to study electronic excitation of molecules including N_2 (Gillan *et al* 1990).

2. Experiment

The electron impact spectrometer used to study the optical excitation is shown schematically in figure 1. It consists of an electron monochromator to produce a collimated beam of electrons, a collision region filled with a target gas and a system to collect and spectrally analyse the emitted radiation. This experimental set-up has been used previously to study optical excitation of triatomic molecules (Zubek 1989). The incident beam with an energy spread of 80–100 meV and a typical intensity of a few nA is produced by a trochoidal selector and is accelerated to the collision region by electrodes F and G. After passing the interaction region the electrons are collected by a current monitor consisting of electrodes R_1 to R_3 and M. The electric field between R_2 and R_3 prevents the electrons backscattered from collector M from entering the interaction region. Photons emitted from the collision region are transmitted via a quartz lightguide and focused on the entrance slit of an 0.5 m optical monochromator equipped with a cooled 9813 QB photomultiplier at its exit slit. The magnetic field, of strength 6×10^{-3} T, is produced by a pair of coils which allow for accurate alignment of the direction of the field with respect to the electron spectrometer symmetry axis. This alignment was checked each time the spectrometer was placed in the vacuum system. This was an important part of the measurements to ensure that the shape of the obtained excitation function was not dependent on the magnetic field strength. It also ensured that the electron current in the interaction region was constant to within better than 3% over the incident energy range from 11 to 20 eV. The measurements were carried out for a pressure range in the collision region which gave linear dependence between detected photons intensity and target pressure. It was also ensured that the detected photon intensity increased linearly with the electron beam current.

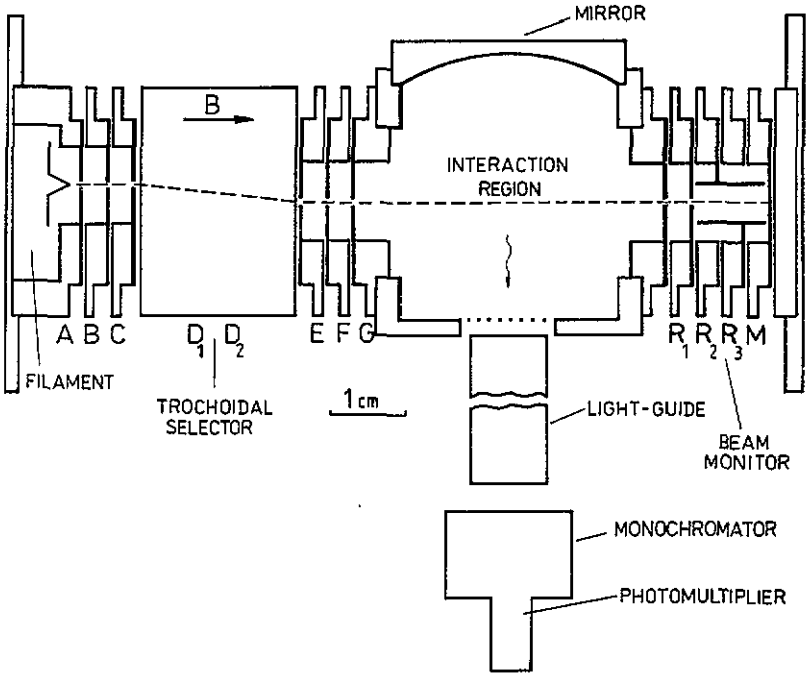

Figure 1. Schematic diagram of the electron impact spectrometer. The trochoidal selector, interaction region and electron beam monitor are shown to scale, which is indicated in the figure.

The incident electron beam energy was calibrated to within 30 meV against the position of the resonance structure at 11.50 eV (Newman *et al* 1983) observed in the excitation function.

The spectrometer was used in two modes of operation. In the first mode, for the fixed incident electron energy the wavelength of the detected light was varied and this produced the optical spectra of the fluorescence emitted by the molecules. These spectra were corrected for the change of the relative sensitivity of the photon detection system with the wavelength. In the second mode of operation the wavelength of the detected photons was fixed and equal to one of the spectral lines and the incident electron energy was ramped. The photon yield was then measured as a function of electron energy producing an excitation function.

The excitation functions studied by magnetically collimated electron beams may be distorted due to the collision path length dependence on the electron energy as a result of the helical motion of electrons. The pathlength is equal to $l_0/\cos\alpha$, where l_0 is the distance between the entrance and exit into the collision region and α is the angle between the electron velocity and the magnetic field. The increase of the path length in the present experiment in the energy range 10–20 eV is estimated to be less than 0.5% and this value also includes the effect of non-uniformity of the magnetic field along the collision path. This estimate together with the fact that the incident current at the interaction region was constant to better than 3% allowed the measured excitation function to be used without any further correction for the transmission variation of the electron monochromator.

In the present measurements no correction has been applied for the degree of polarization of the detected radiation. It has been found previously (Burns *et al* 1969) that

the polarization of light of the second positive system for various electron energies is only about 1% or less.

3. Results and discussion

3.1. Fluorescence spectrum

An electron impact fluorescence emission spectrum measured in the wavelength range 290–410 nm for an incident energy of 14.25 eV is shown in figure 2. Several lines of the second positive system have been identified corresponding to the $v'=0, 1, 2$ of the $C\,^3\Pi_u$ state. The intensities of the observed transitions enable the relative emission cross

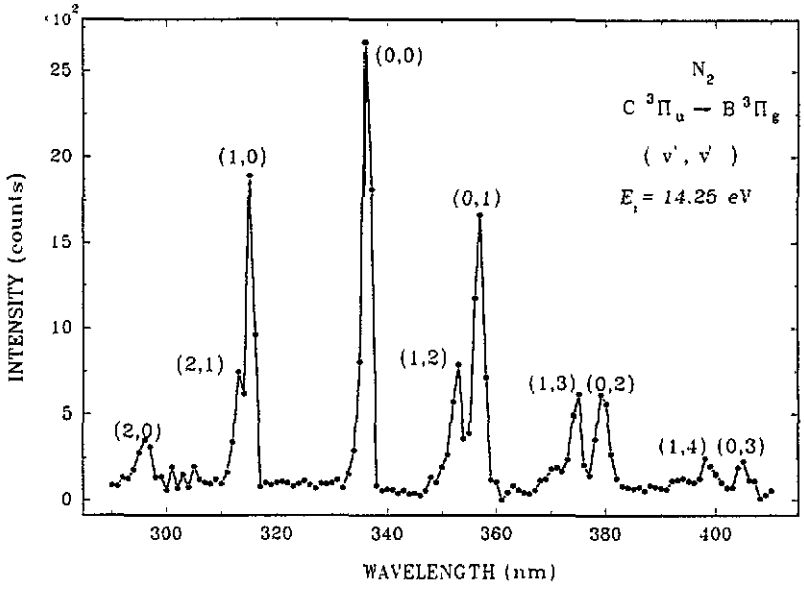

Figure 2. Fluorescence emission spectrum of the $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ second positive band of N_2 obtained in the wavelength region 290 to 410 nm at an incident electron energy of 14.25 eV. Vibrational transitions (v', v'') are indicated on the spectrum.

sections to be determined. The resonance trapping of radiation in the interaction region has a low probability as the only allowed transition from the $C\,^3\Pi_u$ state is to the $B\,^3\Pi_g$ state producing the second positive system. Also there is little or no cascade contribution to the $C\,^3\Pi_u$ state (Shaw and Campos 1983).

3.2. Emission cross section of the (0, 0) line

The excitation function of the emission from the (0, 0) line (337 nm) has been measured in the energy region from threshold at 11.03 eV to 17.8 eV and it has been normalized to the absolute emission cross section at its maximum at 14.1 eV. The maximum value of the cross section has been determined previously in five independent absolute measurements by calibration using either a tungsten-ribbon standard lamp (Jobe *et al* 1967, Aarts and de Heer 1969) or by comparison to the cross section of the (0, 0) line of the first negative band of N_2^+ (Burns *et al* 1969, Shemansky and Broadfoot 1971b)

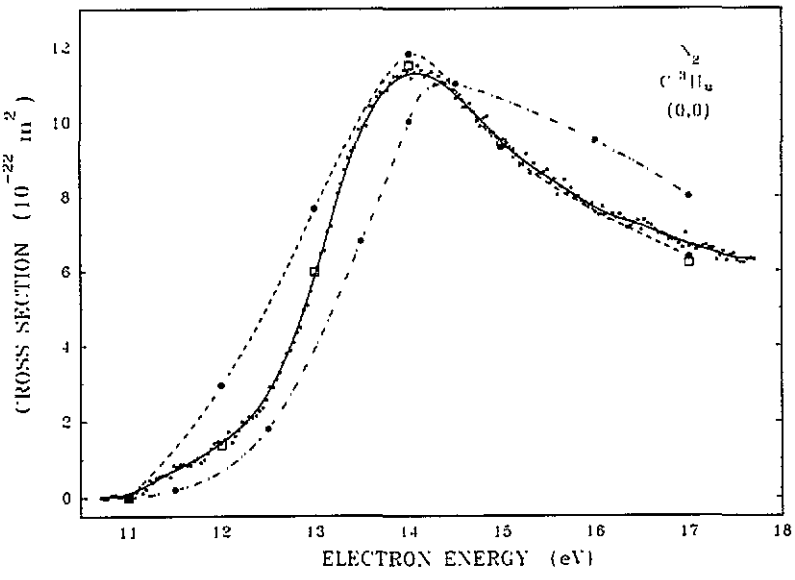

Figure 3. Normalized emission cross section of the (0, 0) (337 nm) line of the $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ second positive band of N_2 obtained in the energy region 11 to 17.5 eV. Present results, ——; Aarts and de Heer (1969), □; Burns *et al* (1969), - - ● - -; Imami and Borst (1974), - ● · · -.

and $5^1S \rightarrow 2^1P$ line of He (Shaw and Campos 1983). The average value of these determinations is equal to 11.28×10^{-22} m^2 with a standard deviation of 0.29×10^{-22} m^2 (less than 3% of the value) and the present data are normalized to that value. The present cross section is compared with other published data in figure 3 and a list of the obtained values is included in table 1. The present results are in very good agreement with the cross section measurements of Aarts and de Heer (1969). The results of Burns *et al* (1969) and Imami and Borst (1974) differ from the present results in respect to the energy variation of the cross section which could be due to their lower energy resolution (~1 eV) and less accurate electron beam energy calibration.

3.3. Cross sections for excitation of the $v' = 0, 1, 2$ vibrational levels

Cross sections for excitation of the $v' = 0, 1, 2$ vibrational levels of the $C\,^3\Pi_u$ state have been determined from the relative intensities of the fluorescence spectrum of figure 2 and the calibrated emission cross section of figure 3. Assuming that there are no secondary processes the light intensity measured for a spectral line of the $v' \rightarrow v''$ transition corresponding to excitation of the v' level at an energy E is given by

$$I_{v'v''}(E) = I_e n l \sigma_{v'}(E) A_{v'v''} \tau_{v'} \eta(\lambda) \tag{1}$$

where I_e is the incident electron current, n is the gas density, l is the excitation pathlength observed by the photon collecting system, $\sigma_{v'}$ is the excitation cross section for level v', $A_{v'v''}$ is the transition probability, $\tau_{v'}$ is the mean lifetime of level v' and $\eta(\lambda)$ is the quantum efficiency of the optical detection system for wavelength λ. The emission

Table 1. Excitation vibrational $v=0, 1, 2$ and electronic cross sections of the $C\,^3\Pi_u$ state and emission cross section of the (0, 0) line (337 nm) of the second positive band of nitrogen.

Energy (eV)	Cross section (10^{-22} m^2)				
	$v=0$	$v=1$	$v=2$	Electronic	(0, 0)
11.25	0.78	0.14	0.027	0.74	0.40
11.50	1.42	0.46	0.075	1.95	0.72
11.75	2.03	0.85	0.16	2.99	1.10
12.00	2.83	1.23	0.24	4.55	1.44
12.25	3.89	1.51	0.29	5.85	1.95
12.50	5.42	1.86	0.34	7.98	2.76
12.75	7.96	2.46	0.44	11.0	4.05
13.00	11.5	3.59	0.68	16.0	5.86
13.25	15.7	5.78	1.13	22.9	7.95
13.50	19.3	8.74	1.84	30.5	9.75
13.75	21.3	11.6	2.78	36.9	10.8
14.00	22.3	13.6	3.89	40.8	11.3
14.25	21.9	14.3	4.95	42.4	11.2
14.50	21.0	14.3	5.73	41.9	10.7
14.75	19.8	13.7	6.06	40.1	10.1
15.00	18.6	12.7	5.92	37.9	9.47
15.50	16.7	11.2	5.02	33.3	8.50
16.00	15.1	9.73	4.37	29.9	7.69
16.50	14.2	8.97	3.84	27.4	7.21
17.00	13.2	8.32	3.36	25.6	6.72
17.50	12.5	7.87		24.0	6.35

cross section is given by

$$\sigma_{v'}^{\mathrm{em}}(E)=\sigma_{v'}(E)A_{v'v''}\tau_{v'}. \tag{2}$$

From (1) and the measured intensities $I_{v'v''}$ of figure 2, using $A_{v'v''}$ and $\tau_{v'}$ given by Lofthus and Krupenie (1977), the relative values of $\sigma_{v'}$ for $v'=0, 1, 2$ have been determined at 14.25 eV. Using (2) and the emission cross section of the (0, 0) line (figure 3) this allowed the absolute cross sections for $v'=0, 1, 2$ levels to be obtained. These values have been used to normalize the excitation functions measured for the (0, 0) line at 337 nm, the (1, 0) line at 315.8 nm and the (2, 1) line at 313.5 nm yielding the excitation cross sections in the energy region from threshold to about 17.5 eV which are presented in figure 4 and listed in table 1.

The errors in the obtained cross sections are due to the quoted uncertainties in the emission cross section of the (0, 0) line, in the product of $A_{00}\tau_0$ for the $v'=0$ level and in the determination of the $\sigma_{v'}$ cross sections ratio. A critical review of the A_{00} and τ_0 values in the literature (Johnson and Fowler 1970, Shemansky and Broadfoot 1971a, Loftus and Krupenie 1977, see also Werner *et al* 1984 for a discussion of recent lifetime measurements) shows that these are known with a maximum error of 20–25% and in the case of transition probabilities this is a result of the difficulties in detected intensities calibration techniques. However the product $A_{00}\tau_0$ is obtained with higher accuracy as the values calculated from the above determinations differ by less than 6%. This value is taken as a maximum error for the product $A_{00}\tau_0$. The cross section ratio has been obtained with an error (standard deviation) of 3.5%. These estimates give a total error (standard deviation) of 4.5, 5.5 and 5.0% for the $v'=0, 1, 2$ cross sections respectively.

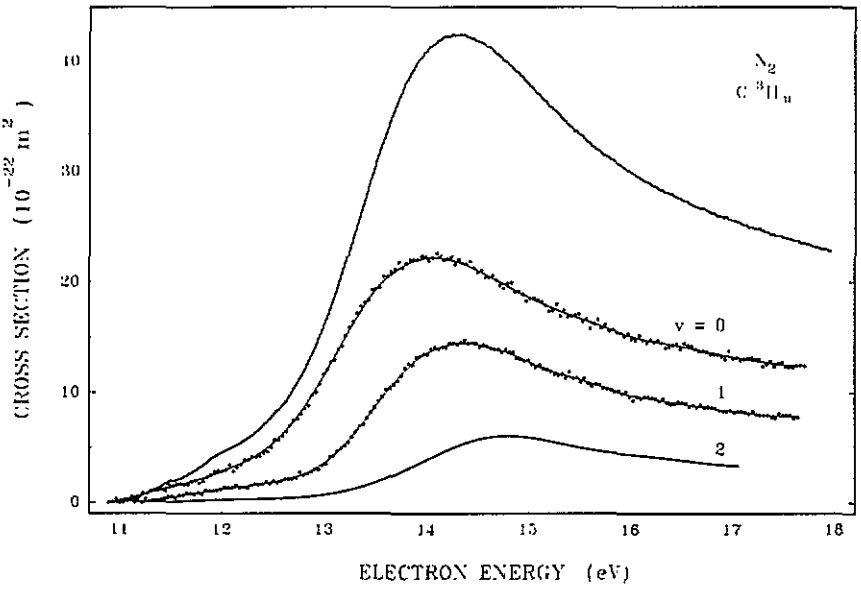

Figure 4. Total cross sections for excitation of the v = 0, 1, 2 vibrational levels and the electronic cross section of the $C\,^3\Pi_u$ state of N_2 obtained in the energy region 11 to 17.5 eV.

As can be seen from figure 4 the vibrational cross sections rise nearly linearly from threshold and display a broad maximum between 14 and 15 eV which position shifts to higher energies with increasing v'. The ratios of the $v' = 1$ and 2 cross section to that of $v' = 0$ vary with electron energy and are close to the Franck–Condon factors ratios for the $X\,^1\Sigma_g^+ \rightarrow C\,^3\Pi_u$ transition equal to 1:0.558:0.193 only close to the energy of 14 eV. For the remaining energies they deviate from those values most significantly below 13.5 eV, indicating non-Franck–Condon behaviour of the excitation. Previously the Franck–Condon approximation has been applied in the calculation of $C\,^3\Pi_u$ excitation (Cartwright 1970, Chung and Lin 1972) and also in the experimental studies of the electronic cross section (Cartwright *et al* 1977a, Brunger and Teubner 1990).

There are no previous measurements of the vibrational excitation cross sections of the $C\,^3\Pi_u$ state in the energy region from threshold to 6.5 eV above. Bauer and Bartley (1965) calculated the $v' = 0$ cross section in the classical approach obtaining a maximum cross section about 35% lower than the present experimental data.

3.4. Cross section for excitation of the $C\,^3\Pi_u$ state

An excitation function of the $C\,^3\Pi_u$ state has been measured by replacing the optical monochromator with a wide-band filter transmitting in the 240–400 nm spectral region. This filter transmits 93% of the intensity emitted within the second positive band. The excitation function has been normalized at 14.25 eV to a value of 42.4×10^{-22} m^2 obtained by summing the vibrational cross sections including $v' = 3$, which is estimated to be 5% of that for $v' = 0$. This total electronic cross section is also shown in figure 4 and listed in table 1. Its error (standard deviation) in the present determination is estimated to be 3.5%. The shape of the energy dependence of this cross section is in excellent agreement over the whole energy range with the sum of the measured vibrational cross sections which supports the use of the wide-band filter.

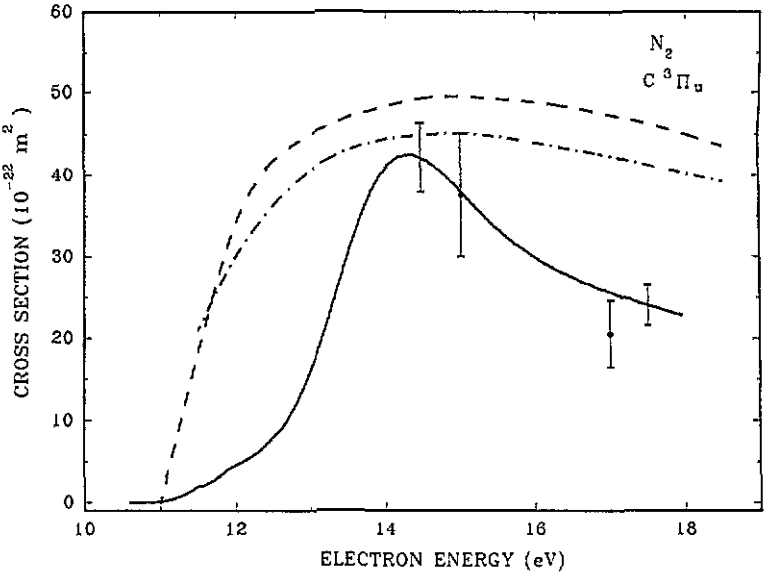

Figure 5. Total electronic cross section for excitation of the $C\ ^3\Pi_u$ state of N_2 obtained in the energy region 11 to 18 eV. Present results, ——; Trajmar *et al* (1983), ●; Cartwright (1970, 1972), – –; Chung and Lin (1972), – · –. The maximum error of three standard deviations is indicated for the present results.

The electronic cross section is compared with the only previous measurement of Trajmar *et al* (1983) and the results of theoretical calculations in figure 5. At 15 eV the present cross section coincides with Trajmar's value. However, at 17 eV it is about 25% higher and it can be estimated that approximately the same difference exists at 20 eV. The present cross section reaches a maximum of 42.5×10^{-22} m^2 at 14.3 eV which is in good agreement with the estimates given by Itikawa *et al* (1986). The $C\ ^3\Pi_u$ cross section has been calculated in the Born–Ochkur–Rudge exchange approximation from threshold to 40 eV by Cartwright (1970, 1972) and Chung and Lin (1972). The theoretical cross sections agree reasonably well in the magnitude of the maximum with the experimental curve but show a much weaker energy dependence. It is generally accepted that first-order theories when applied to the calculation of excitation cross sections show serious limitations, especially in the near-threshold region. It is also interesting to note that in these calculations the Franck–Condon approximation has been used which for the present case would overestimate the electronic cross section below 14 eV by up to about 20%. Fliflet *et al* (1979) have calculated the $C\ ^3\Pi_u$ cross section in the distorted-wave approximation from 15 to 50 eV and for the present energy range, the cross section is about a factor of two higher than the experimental results.

4. Conclusions

The total electronic cross section and cross sections for excitation of $v = 0, 1, 2$ vibrational levels of the $C\ ^3\Pi_u$ state of N_2 have been obtained in the energy region from threshold at 11.03 eV to 17.5 eV. These cross sections have been determined from measurements of the fluorescence of the second positive band of N_2 using emission cross sections of the (0, 0) line (337 nm) whose absolute value is known from several

previous studies. The present results show that there is acceptable consistency between total electronic cross sections obtained from emission and electron scattering studies and do not support recent suggestions made during studies of excitation coefficient of the $C\,^3\Pi_u$ state. Strong non-Franck–Condon excitation of vibrational levels in the present near-threshold region has been observed.

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