

# Vibrational excitation of the $C^3\Pi_u$ state of $N_2$ by electron impact

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## Abstract

The relative differential cross-sections for electron impact excitation of  $v = 0, 1$  and  $2$  vibrational levels of the  $C^3\Pi_u$  state of the nitrogen molecule have been measured for incident energies from threshold to  $17$  eV and for  $0^\circ$  scattering angle. By considering a number of possible angular distributions for this excitation a range of differential and integral vibrational cross-sections and the total cross-section for excitation of the  $C^3\Pi_u$  state are determined. These are used in a comparison with previous results where there are considerable discrepancies. Resonant structures in excitation functions of all three vibrational levels are observed and their locations are compared with resonances obtained in different decay channels, from the literature. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Electron impact excitation of the  $C^3\Pi_u$  state of the nitrogen molecule has been the subject of continuous interest in the last two decades. The triplet  $C^3\Pi_u$  state belongs to a group of nitrogen excited states which have relatively high excitation cross-section and thus plays an important role in the Earth's atmosphere as well as in electron transport processes in nitrogen, gas discharges and plasma physics. The excited  $C^3\Pi_u$  state decays significantly via cascade:  $C^3\Pi_u \rightarrow B^3\Pi_g \rightarrow A^3\Sigma_u^+$ . The first step of this decay is a source of light emission in the visible region and the second step leads further into the metastable  $A^3\Sigma_u^+$  state. The investigation of each step requires a different experimental technique to be employed. Large discrepancies between different measurements of the  $C^3\Pi_u$  excitation, and the

need of accurate knowledge of its cross-section for modeling, have initiated the present measurements.

The differential cross-section (DCS) for excitation of the  $C^3\Pi_u$  state was first measured by Cartwright et al. [1], and renormalized by Trajmar et al. [2], at several incident electron energies from  $15$  to  $50$  eV. The integral cross-sections are published by the same authors, [3]. These cross-sections, however, show a substantial discrepancies with the data inferred from the swarm experiment by Taniguichi et al. [4]. Phelps and Pitchford [5] have proposed an increase of the total cross-sections of Trajmar et al. by a factor of  $2$  in order to achieve the agreement between calculated and measured excitation coefficients of the  $C^3\Pi_u$  state. More recent calculations by Jelenkovic and Phelps [6] have shown a noticeable improvement in this agreement when increasing the value of the integral  $C^3\Pi_u$  excitation cross-section of Cartwright et al. [3] by  $30\%$ .

Brunger and Teubner [7] have measured DCSs for  $15$ ,  $17.5$  and  $20$  eV, from  $10^\circ$  to  $90^\circ$ , and have

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obtained a significant disagreement with the previous measurements for all energies and in particular at low scattering angles. Furthermore the angular dependence of these two measurements is very different. The integral cross-section, estimated by Brunger and Teubner, is also  $\sim 30\%$  higher than the data of Cartwright et al. [3].

The most recent direct measurement of DCSs has been performed by LeClair and Trajmar [8]. They used a time of flight technique to obtain DCSs at low impact energy and  $90^\circ$  scattering angle. Their DCSs are even slightly lower than the results of Cartwright et al. [1].

Vibrational excitation of the  $C^3\Pi_u$  state has been measured by Zubek [9]. The integral cross-sections have been obtained from the emission measurements of the second positive band in the 290–410 nm spectral range, from the  $C^3\Pi_u \rightarrow B^3\Pi_g$  transition. The measurements were normalized to the absolute value for all vibrational levels and the total excitation cross-section is estimated. The total integral cross-section of Zubek is, however, in good agreement with the measurements of Trajmar et al. [2] at 15 eV, and it is  $\sim 25\%$  higher at 17 eV electron energy.

## 2. Experimental

The present measurements have been performed on a double trochoidal electron spectrometer [10]. The electrons are extracted from a directly heated hairpin tungsten cathode and a monoenergetic electron beam is selected by a trochoidal electron monochromator (TEM) device [11] and collimated into the interaction region. The electron beam is crossed at right angles with the gas beam. After the collision, electrons scattered in a forward (and backward) direction are analyzed by use of a double TEM device [10,12,13]. The first one is serving only to separate the primary electron beam from inelastically scattered electrons and the second one for the careful scattered-electron energy analysis. The inelastically scattered electrons are detected using a channel electron multiplier.

Special attention was paid to the interaction geometry. The gas is introduced into the interaction region by a one-dimensional capillary array, which

consist of nine graphite-coated glass tubes (0.2 mm ID each), positioned along the electron beam trajectory. This device enables higher signal count rate than a single tube and also allows better energy resolution [10] than in a conventional collision chamber.

The presence of the homogeneous magnetic field, needed for the spectrometer operation, is limiting our measurements only to the forward direction. The signal represents a superposition of electrons scattered at  $0^\circ$  and  $180^\circ$ , presumably within the same solid angles, at the given residual energy. The collection of the backward scattered electrons, which are reflected on the potential barrier at the monochromator exit, is expected to be very efficient, since there is no evident loss mechanism. This was demonstrated by Allan [13,14] in a separate time of flight experiment. The  $0^\circ$  scattering signal is determined by using the ratio of forward DCS to backward DCS for each considered angular distribution. The magnetic field and the spectrometer geometry determine the transmission of the experiment to be proportional to the inverse of the scattered electrons residual energy. This has been demonstrated and discussed earlier [10,12–14].

Particular care is devoted to background signal elimination, electrode voltage stabilization and the spectrometer tuning procedure. In this way a high energy resolution has been obtained, below 25 meV full width at half maximum (FWHM).

## 3. Results and discussion

The relative DCSs at zero degrees for excitation of the  $v = 0, 1$  and  $2$  vibrational levels of the  $C^3\Pi_u$  state of the nitrogen molecule have been measured. The electron energy is calibrated against the sharp resonant structure at 11.49 eV in the  $v = 0$  excitation channel and is estimated to be accurate within 20 meV. The data are corrected to the  $1/E_r$  residual energy dependence of the spectrometer transmission [10,12–14]. Our measurements are placed on an absolute scale by simultaneous measurements of the DCS for vibrational excitation of the  $v = 1$  level of the ground state of  $N_2$ , via the  $^2\Pi_g$  resonance [10], at 1.71 eV residual electron energy. This is performed under the assumption that the angular distri-

bution of the scattered electrons is isotropic or symmetric around  $90^\circ$ , i.e. has a same values at  $0^\circ$  and  $180^\circ$  (same as the  $^2\Pi_g$  resonance). This assumption will be discussed in Section 3.1. The present results are shown in Fig. 1.

The threshold energies for all three vibrational levels agree well with the existing data from the literature. The cross-section maxima are slightly shifted toward higher energies with increasing vibrational level  $v$ , and they all lie between 14 and 14.5 eV. The DCSs at the maximum are 2.35, 1.60 and  $0.82 \times 10^{-18} \text{ cm}^2 \text{ sr}^{-1}$ , respectively.

A sharp resonant peak at 11.49 eV in the  $v=0$  excitation channel belongs to the  $v=0$  level of the well-known ‘window’ type resonance  $[\text{N}_2^+ \text{X}^2\Sigma_g^+ (3s\sigma_g)^2 2\Sigma_g^+]$ , which has been assigned in previous measurements — in the electron transmission experiment [15], and in the  $a^1\Pi_g$  [16] and the  $\text{B}^3\Pi_g$  [17] excitation measurements.

A change of the slope, i.e. a weak bump just above 12.5 eV, in the  $v=0$  DCS curve, can be associated to the  $^2\Pi_u$  core excited resonances, seen by Mazeau et al. [16] at 12.54 and 12.78 eV electron energy in the  $v=0$  excitation channel of the  $\text{C}^3\Pi_u$  state, the last one being very weak. These two energies are also shown in the figure.

At the higher electron energies, additional structure is clearly seen in the energy region from 12.9 to 14.6 eV, in all vibrational levels. It consists of a series of peaks separated by  $\sim 230 \text{ meV}$  from each other. This separation gradually decreases with in-

creasing electron energy. However, the beginning of the structure is shifted toward higher energies for each consecutive vibrational level by about one feature, i.e. the first peak is missing.

In order to explain the origin of this resonant structure we have searched primarily for the resonances in the energy range from 12.9 to 14.6 eV observed in previous measurements. In the electron transmission measurements, Sanche and Schulz [15] assigned two short bands, in the above energy region, as ‘c’ and ‘d’, which start at 13.0 and 13.88 eV, respectively. Band ‘c’ with the average spacing of 230 meV was associated to the  $\text{A}^2\Pi_u$  state of  $\text{N}_2$  as a grandparent.

In the DCS measurements of the  $\text{E}^3\Sigma_g^+$ ,  $a''^1\Sigma_g^+$  and  $\text{C}^3\Pi_u$  states, Mazeau et al. [16] have observed core excited resonant series in various exit channels. They start at 12.98 eV and have an average energy spacing of 228 meV. This series was assigned as band ‘b’, although it energetically corresponds to the band ‘c’, previously assigned by Sanche and Schulz [15]. Due to its angular behavior in the  $\text{E}^3\Sigma_g^+$  and in the  $\text{C}^3\Pi_u$  exit channel this resonant contribution is associated to a  $^2\Sigma_u^+$  symmetry of a core excited Feshbach resonance. Mazeau et al. suggested the H state of  $\text{N}_2$  as a parent state for this resonance because of its energy position and the average spacing between vibrational levels.

In the total cross-section measurements of the metastable  $\text{A}^3\Sigma_u^+$  production, performed by Lawton and Pichanick [18], band ‘c’ is also observed as the resonant contribution in the excitation function.

In a combined transmission and photon emission experiment Golden et al. [19] have observed two distinct series ‘c + d’ which energetically overlap between each other in the whole region from 13 to 14.5 eV.

High-sensitivity measurements of excitation functions of metastable states in  $\text{N}_2$  performed by Newman et al. [17] have provided a number of resonances in the considered energy region, classified as series ‘b’ and ‘d’.

The energy positions of the observed structure from cited measurements are summarized in Table 1. They all agree well with each other. The energy positions of the vibrational levels of the  $^2\Sigma_u^+$  Feshbach resonance, band ‘b’ [16], are indicated by the vertical bars in Fig. 1. As it can be seen, the energy

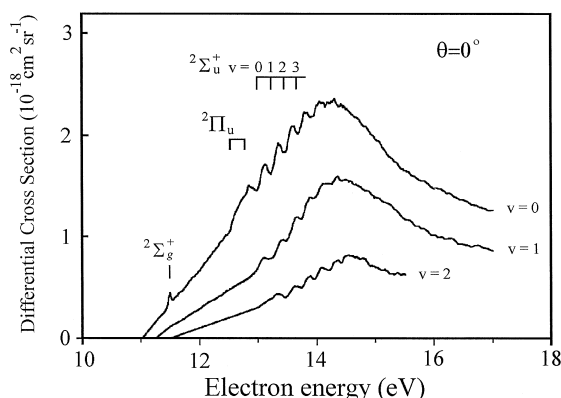


Fig. 1. Differential cross-sections at zero degree for excitation of the  $v=0, 1$  and  $2$  vibrational levels of the  $\text{C}^3\Pi_u$  state of  $\text{N}_2$  (see text).

Table 1

Observed resonances of the nitrogen molecule in the 13–15 eV energy region

Sanche and Schulz [15] Transmission experiment	Mazeau et al. [16] Excitation $a''^1\Sigma_g^+ v = 0$	Golden et al. [19] Transmission/Light emission	Newman et al. [17] Metastable excitation	Present results DCS		
				$C^3\Pi_u$		
				$v = 0$	$v = 1$	$v = 2$
13.00 'c'	12.98 'b'	12.98 'c + d'	12.992 'b + d'	12.98		
13.23	13.20	13.20	13.23	13.21	13.21	
13.50	13.43	13.41	13.459	13.45	13.47	13.47
13.70	13.66	13.65	13.684	13.68	13.72	13.73
13.88 'd'		13.94	13.872	13.92	13.94	13.95
14.12		14.14	14.109	14.15	14.18	14.18
14.36		14.34	14.343	14.38	14.40	14.42
14.57		14.54	14.574			14.62

positions of these levels correspond to minima in the present DCS data, with an excellent agreement over all three vibrational levels. We believe this situation is the consequence of the Fano profile of resonant scattering, with the actual phase shift equal to  $\pi$ . Another explanation due to the flux going into the resonance is not likely since it cannot explain the shift of the structure with increasing vibrational level. Thus, we can associate the structures in our spectra to the  $^2\Sigma_u^+$  Feshbach resonance. Moreover, Mazeau et al. [16] have already seen the  $v = 0$  vibrational level of the  $^2\Sigma_u^+$  resonance in the  $v = 0$  excitation channel of the  $C^3\Pi_u$  state and it agrees with our value of 12.98 eV. The energy positions of the structure estimated from our measurements are also listed in the table and the agreement with the previous results is remarkable.

The shift of the observed structure with the vibrational levels, toward higher energies, in our measurements, we believe, is related to the Franck–Condon overlap integrals between vibrational levels of the resonant and the  $C^3\Pi_u$  state.

### 3.1. Differential excitation cross-sections

As it is pointed out in Section 1, the existing total (summed over vibrational levels) DCSs of Cartwright et al. [1] and Brunger and Teubner [7] differ significantly, in particular at low scattering angles. At 15 eV and  $0^\circ$  the total DCS of Cartwright et al. is  $0.71 \times 10^{-18} \text{ cm}^2 \text{ sr}^{-1}$  and for the same energy the data of Brunger and Teubner can be extrapolated to a zero degree value of  $\sim 5.6 \times 10^{-18} \text{ cm}^2 \text{ sr}^{-1}$ . They

therefore differ by a factor of  $\sim 8$ . Furthermore the angular dependence of these two measurements is very different, while the first increases significantly in the whole range from  $0^\circ$  to  $180^\circ$  (measured from  $5^\circ$  to  $138^\circ$ ) the data of Brunger and Teubner are almost uniform, even with a slight decrease from  $20^\circ$  to  $90^\circ$ . The same discrepancy exists for other electron energies as well, since the overall behavior of the measured DCS does not change significantly with the energy. The data of Brunger and Teubner are restricted to the angular range from  $10^\circ$  to  $90^\circ$ .

Since only the total DCSs are measured, we consider the angular distributions to be of the same form for all vibrational levels. This can be supported by the fact that the angular distribution is determined by the final electronic state symmetry, in the absence of the resonant contribution.

For the purpose of normalization of our measurements, we have considered three possible angular distributions of the scattered electrons: (1) an isotropic distribution which is a reconcilable solution between the two existing sets of measurements at low angles, where one increases and other decreases in the range from  $20^\circ$  to  $90^\circ$ ; (2) a distribution obtained by fitting existing data of Brunger and Teubner, symmetrically extrapolated around  $90^\circ$ , by a polynomial of the sixth order; and (3) a distribution obtained by fitting the data of Cartwright et al. also by a polynomial. We should note that in the case (2) the extrapolated part in the range  $90^\circ$  to  $180^\circ$  has a very similar form to the data of Cartwright et al.

The cases (1) and (2) give the same result for the normalization procedure, assuming equal values of

the DCS in the forward and backward directions, and the obtained results are already shown in Fig. 1. For the case (3) the ordinate needs to be multiplied by 0.25 since the backward contribution is  $\sim 7$  times larger than the forward. This discrepancy, however, cancels out partially with the angular distribution, when the integral cross-sections are to be determined.

The total  $C^3\Pi_u$  electronic DCS vs. energy, at  $0^\circ$ , is obtained from the partial cross-sections as a sum over all vibrational levels. The contribution of the  $v = 3$  vibrational level is estimated to  $\sim 5\%$  of the  $v = 0$  cross-section, and thus neglected. The maximum of the cross-section is  $4.7 \times 10^{-18} \text{ cm}^2 \text{ sr}^{-1}$  at an electron energy of 14.3 eV. Our total electronic DCS, for cases (1) and (2), at 15 eV is  $4.1 \times 10^{-18} \text{ cm}^2 \text{ sr}^{-1}$  with an estimated error of 23% (the error is obtained as a quadrature sum of 20% uncertainty [20] of absolute measurements of  $^2\Pi_g$  resonant excitation to which we have calibrated our data and 12% as one standard deviation of ten independent cross-section measurements). This value can be compared with the existing results of  $0.71 \times 10^{-18} \text{ cm}^2 \text{ sr}^{-1}$  of Cartwright et al. [1] and  $5.6 \times 10^{-18} \text{ cm}^2 \text{ sr}^{-1}$  of Brunger and Teubner [7]. The present value lies between these two values, although it is closer to the result of Brunger and Teubner. For the case (3) the value obtained at 15 eV and  $0^\circ$  is  $1.02 \times 10^{-18} \text{ cm}^2 \text{ sr}^{-1}$ , still  $\sim 30\%$  higher than the value of Cartwright et al. [1].

### 3.2. Integral excitation cross-sections

Due to the large discrepancy in the overall angular behavior of the two previous measurements it is a very difficult task to infer reliable integral cross-sections with the available data. The three cases discussed in Section 3.1 will be considered here again.

However, some further assumptions need to be adopted. Firstly, we have already supposed that the angular distribution is the same for all vibrational levels, since the distribution is determined by the final electronic state symmetry, in the absence of the resonant contribution. Secondly, the angular distribution is assumed to be independent of the electron energy, which is true if only one, direct, process is involved. In the excitation of the  $C^3\Pi_u$  state, in the energy range from threshold to 17 eV, both direct

and resonant processes are involved, and they are likely to have the different angular behavior. Mazeau et al. [16] observed  $^2\Sigma_u^+$  resonant contributions only at low scattering angles in the  $C^3\Pi_u$  exit channel. Since, from our measurements, resonant contributions can be estimated to  $\sim 10\%$  of the DCS, and it is lower or disappears for other scattering angles, it should not significantly influence the overall integral cross-section. Under these assumptions we can consider the constant ratios of differential and integral cross-sections for different vibrational levels and for all measured energies.

Considering case (1) of isotropic angular distribution, the integral cross-section can be easily obtained by multiplying the DCS from Fig. 1 by  $4\pi$ . Using the extrapolated angular dependence of the DCS of the  $C^3\Pi_u$  state at 15 eV, measured by Brunger and Teubner [7], under the above assumptions, i.e. considered case (2), and our DCS value at  $0^\circ$ , we have estimated the integral cross-sections for all three vibrational levels. They are  $\sim 14\%$  lower than in the case (1). The estimated DCS values of case (3) and the corresponding angular distribution give after integration cross-sections which are 10% higher than in the case (1). All three considered cases give integral cross-sections which agree with each other within 24%, which is significant bearing in mind the discrepancy between existing DCS measurements.

The obtained integral cross-sections for the  $v = 0, 1$  and 2 vibrational levels of the  $C^3\Pi_u$  state of  $N_2$  have the same form as the curves presented in Fig. 1. We will choose as the representative our data of case (1). The cross-section maxima are estimated to be 2.91, 2.03 and  $1.04 \times 10^{-17} \text{ cm}^2$ , respectively. These cross-sections can be compared directly with the results obtained in a photon emission experiment by Zubek [9]. A general shape of the two sets of curves is similar, but our values are somewhat higher than those obtained by Zubek, by  $\sim 25\%$  near the maximum. The difference is larger at lower electron energies. The energy positions of the corresponding maxima are very close. Due to the lower energy resolution (over 100 meV) none of the presently observed structure is present in Zubek's results.

Zubek [9] has discussed in his paper the non Franck–Condon behavior of this excitation processes, based on the ratios of observed integral vibrational cross-sections at the same electron energy. The

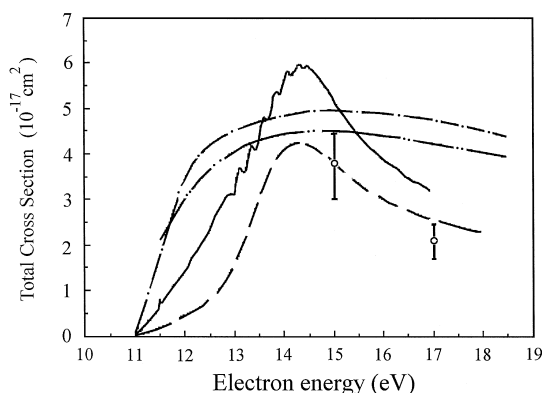


Fig. 2. Total integral cross-sections for excitation of the  $C^3\Pi_u$  electronic state: —, present data; ---, Zubek [9]; ○, Trajmar et al. [2]; - · -, Cartwright [21,23]; - - - -, Chung and Lin [22].

same conclusion can be inferred from our results. It is particularly evident at  $\sim 13.5$  eV, where the resonant contribution is expressed. Our measurements have identified this resonant, i.e. indirect contribution, and thus we can explain this non Franck–Condon behavior by its presence. We should note also that all existing theoretical studies [21–23] were based on the Franck–Condon approximation and considered only the direct process of excitation.

The total absolute uncertainty of our measurements is estimated to be 38% and consists of 1% due to the counting statistics, 23% due to the normalization procedure and 14% due to the choice of the angular distribution of the scattered electrons and integration procedure.

The total integral cross-section for excitation of the  $C^3\Pi_u$  electronic state, obtained as a sum over  $v=0, 1$  and 2 vibrational levels ( $v=3$  is again neglected) is presented in Fig. 2, represented by the results considered under case (1). The maximum of the cross-section is  $5.9 \times 10^{-17} \text{ cm}^2$  at an electron energy of 14.3 eV. In the same figure our total integral cross-section is compared with the measurements of Zubek [9] and Trajmar et al. [2] and with the theoretical predictions of Cartwright [21,23] and Chung and Lin [22].

Both theories are based on the Born–Ochkur–Rudge exchange approximation, are insensitive to the observed structure and disagree significantly near the threshold from the experimental data, but agree reasonably well at the cross-section maximum. The

three sets of measurement are in a good agreement regarding the relative shape of the cross-section. However, our data are higher over the whole energy range than the results of Trajmar et al. [2] and Zubek [9]. Near the cross-section maximum our DCSs are  $\sim 30$ – $35\%$  higher. This is in a good agreement with the recommendation of Phelps and Pitchford [5] and with the calculations of Jelenkovic and Phelps [6] who propose an increase of the previous cross-sections by  $\sim 30\%$  in order to achieve better agreement with the measured excitation coefficients of the  $C^3\Pi_u$  state.

#### 4. Conclusions

Relative differential cross-sections for electron impact excitation of the  $v=0, 1$  and 2 vibrational levels of the  $C^3\Pi_u$  state of the nitrogen molecule have been measured by using the double trochoidal electron spectrometer. Obtained spectra are normalized and compared to previous experimental and theoretical results. The total integral cross-section is found to be  $\sim 30$ – $35\%$  higher than in the previous measurements. The contribution of the  $^2\Sigma_u^+$  Feshbach resonance has been observed in the excitation functions of all three vibrational levels.

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