

A study of electron impact excitation of the $A^2\Sigma^+$ state of nitric oxide in the near-threshold energy range

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Abstract

Excitation of the Rydberg $A^2\Sigma^+$ state of nitric oxide has been studied by electron impact in the energy region from threshold to 15 eV using an optical method. Absolute emission cross-sections of 13 bands of the γ -system ($A^2\Sigma^+ \rightarrow X^2\Pi_r$ transition) and integral cross-sections for excitation of the $v = 0$ and 1 vibrational levels of the $A^2\Sigma^+$ state have been determined. Emission spectra of nitric oxide have been also obtained for selected values of incident electron energy. © 2001 Published by Elsevier Science B.V.

1. Introduction

Nitric oxide (NO) is identified in physical and chemical processes observed in the Earth's thermosphere [1] and also plays a significant role in human physiology. In the thermosphere nitric oxide is produced through ionization and dissociation of the major atmospheric species (N_2 , O_2) and its γ -system ($A^2\Sigma^+ \rightarrow X^2\Pi_r$ transition) is detected in the dayglow and twilight spectra of the atmosphere in the UV wavelength region. The $v' = 0$ progression of the γ -system is observed in the night airglow of the thermosphere and here the process responsible for the emission is the inverse pre-dissociation of the $C^2\Pi_r$ state [2].

Nitric oxide is also a source of short wavelength infrared emission from the ground $X^2\Pi_r$ state vibrational–rotational levels which participate in the thermal balance of the thermosphere. The in-

tensity of the infrared radiation increases in the polar regions during auroral activity as a result of increased production of nitric oxide by impact of auroral electrons [3,4]. It is expected that the infrared radiation is emitted from vibrational levels having extended distribution which are populated by cascading decay of higher-lying electronic states excited by impact of secondary electrons [5]. To model above phenomena appearing in the thermosphere a set of well established molecular parameters of nitric oxide such as photon absorption and electron impact cross-sections and radiative transition probabilities are of high relevance. The present work is motivated by a requirement for these molecular data and its aim is also to study electron impact excitation phenomena in molecules in the threshold region.

In this work we have obtained absolute integral cross-sections for excitation of the $v = 0$ and 1 vibrational levels of the Rydberg $(3s\sigma)A^2\Sigma^+$ state from measurements of emission cross-sections of the $(0, v'')$ and $(1, v'')$ bands of the γ -system. The integral cross-sections have been determined in the

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electron energy range up to 15 eV. Previously excitation of nitric oxide by electron collisions has been investigated in a limited number of studies. The most extensive measurements of the emission cross-sections have been made by Povch et al. [6] who obtained cross-sections for a number of the γ -bands and the β -bands ($B^2\Pi_r \rightarrow X^2\Pi_r$ transition) and also for five other emission systems in a wider energy range from threshold to 300 eV. Using these results Skubenich et al. [7] determined integral electronic cross-sections in the same energy range for excitation of the $A^2\Sigma^+$, $B^2\Pi_r$, $B'^2\Delta$, $F^2\Delta$ and $b^4\Sigma^-$ states. Imami and Borst [8] reported emission cross-sections for several γ -bands from close to threshold to 1000 eV. It is interesting to note that the results of [6,8] disagree in the shape of the energy dependence of the reported cross-sections. Also these studies in the near-threshold energy range presented results with low electron energy resolution. Other studies have been carried out for selected values of incident electron energy. Brunger et al. [9] determined integral cross-sections for nine Rydberg and valence states of nitric oxide in the energy region 15–50 eV from their measured differential cross-sections [10]. Ajello et al. [11] obtained emission cross-sections for the γ - and ε -bands at 200 eV while Van Sprang [12] measured γ -bands emission cross-sections at 300 eV. Energy loss spectra have been also measured for low and intermediate incident electron energy [13–16]. The only published theoretical work on electron impact excitation of nitric oxide presents the distorted wave calculations of differential cross-sections of the $A^2\Sigma^+$, $C^2\Pi_r$ and $D^2\Sigma^+$ states for the electron energies between 12.5 and 50 eV [17].

2. Experimental

In the measurements an electron spectrometer has been used which contains a trochoidal selector to produce energy selected incident electron beam. The electron beam leaving selector is accelerated into the collision region through a set of two apertures. Molecular fluorescence produced in the collision region is analyzed by a 0.25 m Ebert grating monochromator and is detected by a

cooled photomultiplier. More details on the construction of the spectrometer are given in [18].

The excited optical lines have been identified by recording emission spectra of nitric oxide at fixed incident electron energy. Measurements of excitation functions of the observed optical lines have been performed with the electron energy spread of 130 meV and electron beam intensity of about 20 nA. The measured photon counting rate which is proportional to the emission cross-section of a given optical band was in the range of $1\text{--}2\text{ s}^{-1}$ at the resolution ($\Delta\lambda/\lambda$) of 0.007 of the optical detection channel. The incident electron current as measured by a beam monitor was constant to better than 5% and no corrections have been applied to the obtained excitation functions for the energy variation in the transmission of the electron beam source. The gas pressure in the collision region measured by a baratron was below 4×10^{-2} Pa to maintain its linear dependence with the detected photon intensity. The wavelength variation of the relative sensitivity of the photon detection system has been established using the molecular branching ratio method and the measured relative bands intensities of the second positive system of nitrogen, fourth positive system of carbon monoxide and the γ -system of nitric oxide together with their known transition probabilities. The relative sensitivity curve obtained in the 185–300 nm wavelength range is shown in Fig. 1 together with an emission spectrum. No correction for polarization of the detected fluorescence of nitric oxide has been applied as it has been found in [19] that the polarization of the γ -lines is small and less than 2% when rotational structure of the bands is not resolved.

Absolute emission cross-sections have been determined for the γ -bands of $(0, v'')$ and $(1, v'')$ progressions at an energy of 7.2 eV by normalizing the photon intensities of the $(0, 1)$ and $(1, 0)$ bands to that of the $(0, 0)$ band of the second positive system of nitrogen at 14.1 eV and using its emission cross-section determined previously [18]. The cross-sections of remaining bands of both progressions were determined from relative intensities obtained in emission spectrum of Fig. 1. The integral cross-sections for excitation of the $v = 0$ and 1 vibrational levels of the $A^2\Sigma^+$ state at 7.2 eV are

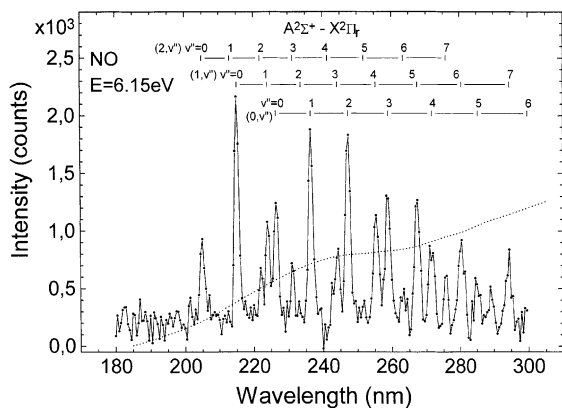


Fig. 1. Emission spectrum of nitric oxide obtained at an incident electron energy of 6.15 eV with an optical resolution of 0.007. A constant background has been subtracted from the original spectrum. The spectrum is not corrected for the wavelength variation of the sensitivity of optical detection channel, which is shown by the dashed line.

equal to the sum of the corresponding emission cross-sections which has been corrected for the contribution of emission to higher $v'' = 6$ –10 levels. The energy dependence of the $v = 0$ and $v = 1$ integral cross-sections has been obtained from measurements of excitation functions of the (0,1) line at 236.6 nm and the (1,0) line at 215.1 nm. These excitation functions have been normalized to the absolute integral cross-sections at the energy of 7.2 eV.

The incident electron energy has been calibrated to within ± 30 meV against the position of the $^2\Sigma^+$ resonance structure at 10.04 eV in carbon monoxide observed in mixture with nitric oxide. The wavelength in the emission spectra has been established to within ± 0.2 nm by detecting the (0,0) line of the second positive system in nitrogen at 337.0 nm. Statistical uncertainties (standard deviations) in the measured cross-sections have been determined with the help of error propagation method taking into account uncertainties in the measured photon intensities (major contribution to the final error), in the pressure ratio of nitric oxide to nitrogen in the collision region, incident current intensities, relative sensitivity of the optical detection channel and the uncertainty in the calibration emission cross-section of nitrogen [18]. The error in the emission and integral cross-sections

measured at 7.2 eV is taken to be equal to three standard deviations and is 30%.

3. Results and discussion

3.1. Emission spectra

Emission spectra of nitric oxide recorded at two incident electron energies, 6.15 and 12 eV are shown in Figs. 1 and 2 respectively. In Fig. 1 the observed (v', v'') emission bands correspond clearly to three progressions of $v' = 0, 1$ and 2 of the γ -system ($A^2\Sigma^+ \rightarrow X^2\Pi_r$ transition). Here the incident electron energy is below that of higher v' vibrational levels of the $A^2\Sigma^+$ state and other Rydberg states of nitric oxide. The relative intensities of the bands in the $v' = 0$ and 1 progressions when corrected for sensitivity variation of the optical detection channel are used in Section 3.2 to determine the emission cross-sections of the observed bands.

The above three progressions also give main contribution to the emission spectrum of Fig. 2. In the wavelength range from 190 to 240 nm we detect less intense bands corresponding to the ϵ -system ($D^2\Sigma^+ \rightarrow X^2\Pi_r$ transition). Several individual ϵ -bands can be distinguished in the main spectrum of Fig. 2 obtained with optical resolution of 0.010 and also in the spectrum presented in the inset measured with higher resolution of 0.007.

3.2. Emission cross-sections of the γ -bands

Emission cross-sections of 13 bands of the $v' = 0$ and 1 progressions of the γ -system measured at an electron energy of 7.2 eV are shown in Table 1. Our results are compared with the cross-sections obtained in low energy region (≤ 10 eV) in previous optical excitation studies [6,8]. The present values of the cross-sections agree with that found in [6] at an energy of 9.5 eV for most of the transitions except that of the (1,0) and (1,1) lines. However result of [8] for the (1,0) line indicate higher value of its emission cross-section than obtained in [6] in agreement with our measurements. In last two columns of Table 1 we compare our cross-sections with the corresponding relative transition proba-

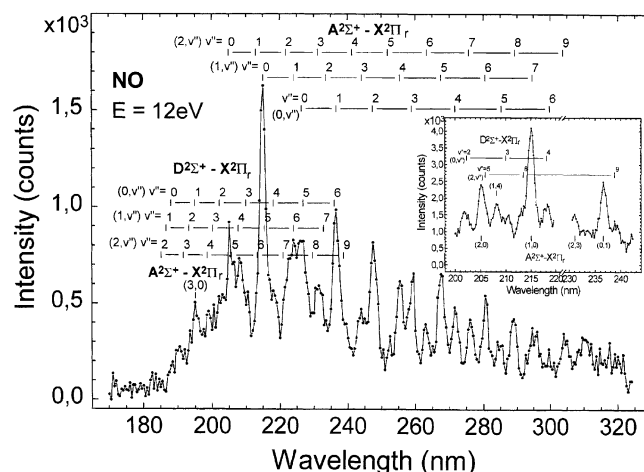


Fig. 2. Emission spectrum of nitric oxide obtained at an incident electron energy of 12 eV with an optical resolution of 0.010 (main spectrum) and 0.007 (inset). A constant background has been subtracted from original spectra. The spectra are not corrected for the wavelength variation of the sensitivity of optical detection channel.

Table 1

Emission cross-sections in units of 10^{-22} m^2 for (v', v'') bands of the γ -system ($A^2\Sigma^+ - X^2\Pi_r$) of nitric oxide

Vibrational transition (v', v'')	Wavelength ^a (nm)	Emission cross-section				Transition probability ^a (relative)
		Present 7.2 eV	9.5 eV [6]	10 eV [8]	Present (relative)	
(0,0)	226.5	0.203	0.13		0.772	0.729
(0,1)	236.6	0.263	0.27	0.16	1	1
(0,2)	247.4	0.231	0.26	0.13	0.878	0.817
(0,3)	259.1	0.149	0.18		0.567	0.520
(0,4)	271.7	0.081	0.09		0.308	0.284
(0,5)	285.4	0.049	0.042		0.186	0.140
(1,0)	215.1	0.698	0.087	0.56	1	1
(1,1)	224.2	0.221	0.063		0.317	0.250
(1,2)	233.9					0.002
(1,3)	244.3	0.102	0.12		0.146	0.137
(1,4)	255.4	0.156	0.17		0.223	0.237
(1,5)	267.5	0.174	0.16	0.105	0.249	0.225
(1,6)	280.5	0.104	0.12		0.149	0.162
(1,7)	294.6	0.065	0.064		0.094	0.098

^a Ref. [20].

bilities of [20]. Within each progression our relative cross-sections evolve with the v'' quantum number in good agreement with the relative transition probabilities.

3.3. Excitation of the $v = 0$ and 1 vibrational levels

The integral cross-sections for excitation of the $v = 0$ and 1 levels of the $A^2\Sigma^+$ state measured in the energy region below 8 eV are shown in Fig. 3.

The values of the cross-sections used in the normalization we present in Table 2. For both vibrational levels the cross-sections increase fast with energy above threshold and each curve displays two narrow resonance peaks. The lower intensity structures at 5.72 and 5.99 eV (b-series) and the higher intensity structures at 6.46 and 6.74 eV (d-series) occur from the decay of the $(3s\sigma)(3p\pi)^3\Pi$ and the $(3p\pi)(3p\sigma)^3\Pi$ Feshbach resonances respectively. These resonances have been previously

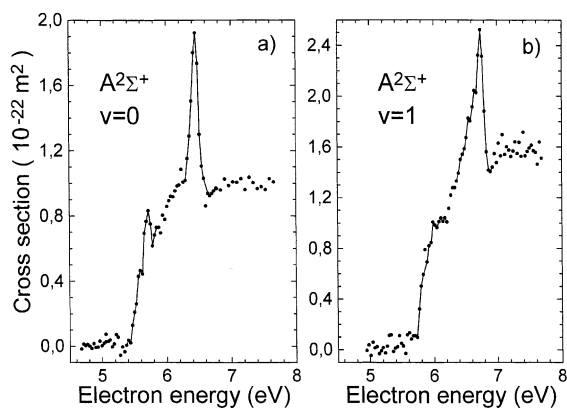


Fig. 3. Cross-sections for excitation of (a) $v = 0$ and (b) $v = 1$ vibrational levels of the $A^2\Sigma^+$ state of nitric oxide obtained in the electron energy region from threshold to 8 eV.

studied in differential cross-sections measurements and the $\Delta v = 1$ and 0 propensity rules in their decay to the $A^2\Sigma^+$ state have been well established for the b-series and d-series respectively [21]. The energy positions of the resonance peaks observed in the integral cross-sections agree to within less than 20 meV with that obtained in the differential cross-sections measurements of [21]. The ratio of the vibrational cross-sections at 7.2 eV as it is seen from Table 2 is in very good agreement with the ratio of the Franck–Condon (F–C) factors determined in recent electron energy loss measurements of [10].

Previous optical excitation studies of nitric oxide [6,7,11] reported cascading contributions to the excitation of the $A^2\Sigma^+$ state which can originate from higher-lying Rydberg states with $\Delta v = 0$ vibrational transitions. In the electron energy loss studies excitation of the following states, $C^2\Pi_r$, $D^2\Sigma^+$, $E^2\Sigma^+$, $H^2\Sigma^+$ and $H'^2\Pi$ have been observed [9,14–16] and these states may decay to the $A^2\Sigma^+$

state by photon emission [22] giving an apparent increase of its measured emission cross-section. In the energy region below 7.4 eV two states, the $C^2\Pi_r$ and $D^2\Sigma^+$ are excited. The $C^2\Pi_r$ state is known to be pre-dissociated by the $a^4\Pi$ state and its $v' = 0$ and 1 emission yields are low [11,23]. In effect we do not observe any emission lines of the δ -system ($C^2\Pi_r \rightarrow X^2\Pi_r$ transition) in our spectrum of Fig. 2. This spectrum on the other hand contains lines of the ε -system ($D^2\Sigma^+ \rightarrow X^2\Pi_r$ transition) which have however much lower intensities than the lines of the γ -system. The $D^2\Sigma^+$ state decays also to the $A^2\Sigma^+$ state (Feast 1 system) but the decay rate is about 2.5 times lower than that for the decay to the ground $X^2\Pi_r$ state [24]. These facts indicate that the cascading contributions of these two states to the cross-sections presented in Fig. 3 will be small. Small cascading contributions of the $D^2\Sigma^+$ state to the spectra of Fig. 3 is also supported by the absence of higher vibrational members of the d-series resonances in the excitation cross-sections of the $v = 0$ and 1 levels of the $A^2\Sigma^+$ state for example the 7.02 eV resonance in the $v = 1$ cross-section (Fig. 3b) which has been observed to decay with high intensity to the $v = 1$ level of the $D^2\Sigma^+$ state [21].

The energy dependence of the $v = 0$ cross-section of the $A^2\Sigma^+$ state (Fig. 3a) can be compared with that of the first Rydberg state $(3s\sigma)b^3\Sigma^+$ of carbon monoxide obtained in [25]. The $b^3\Sigma^+$ cross-section within 1 eV above threshold shows a strong resonance peak followed by a second lower intensity peak both having measured widths of about 0.4 eV. These two structures are attributed to core-excited shape resonances decaying to the $b^3\Sigma^+$ state and the lower-lying resonance has $(3s\sigma)(3p\pi)^2\Pi$ configuration build on the same electron pair as that of the b-series resonance in nitric oxide. The difference between near-threshold excitation of the $A^2\Sigma^+$ and $b^3\Sigma^+$ states is explained at least partly by a higher binding energy of the $(3s\sigma)(3p\pi)$ electron pair to its ion core in nitric oxide than in carbon monoxide. Thus the $^3\Pi$ resonance of NO^- appears below the $A^2\Sigma^+$ state and is a Feshbach resonance which can not decay to its parent state. Higher binding energy of the $NO^+X^1\Sigma^+$ ion core is associated with its closed-shell electronic structure.

Table 2

Integral cross-sections for excitation of the $A^2\Sigma^+$ state of nitric oxide at an energy of 7.2 eV

Vibrational level	Cross-section $\times 10^{-22} \text{ m}^2$	Cross-section ratio	F–C factors ^a ratio
$v = 0$	1.00	0.63	0.580
$v = 1$	1.58	1	1

^a Ref. [10].

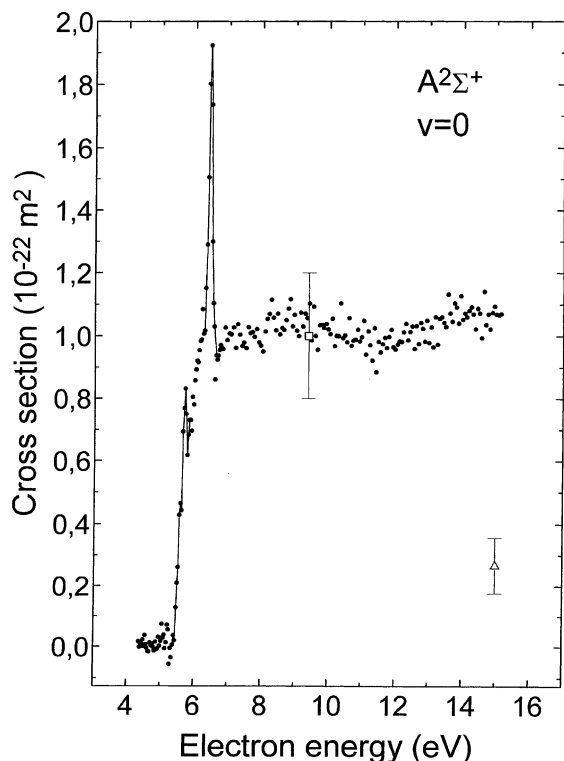


Fig. 4. Cross-sections for excitation of the $v=0$ vibrational level of the $A^2\Sigma^+$ state of nitric oxide obtained in the electron energy region from threshold to 15 eV: (●) present results, (□) Skubenich et al. [7], (Δ) deduced from Brunger et al. [9] (see text for details).

We have also obtained cross-section for excitation of the $v=0$ vibrational level of the $A^2\Sigma^+$ state in a wider energy range up to 15 eV which is shown in Fig. 4. Here we also plot the cross-section of Skubenich et al. [7] measured at 9.4 eV and an estimate of vibrational cross-section at 15 eV deduced from the integral electronic cross-section of Brunger et al. [9] ($1.223 \times 10^{-22} \text{ m}^2$) which has been multiplied by F–C factor for excitation of the $v=0$ level ($q=0.2173$) taken from [10]. Our cross-section which above 8 eV displays weak variations with energy is in very good agreement with the value of Skubenich et al., but exceeds the cross-section derived from Brunger et al. [9] by a factor of about 3. This difference at 15 eV in our measured cross-section could be an evidence for strong cascading contribution. That contribution will increase with electron energy above 7.4 eV as a result

of increasing number of contributing states and of an increase of their excitation cross-sections with energy which could be anticipated from behavior of the cross-sections of Brunger et al. [9] reported at and above 15 eV and also is observed for the $D^2\Sigma^+$ state in our measurements of excitation function of the (1,4) band at 208 nm of the ϵ -system. Povch et al. [6] in their studies of γ -bands excitation have discussed cascading from higher-lying Rydberg states to explain maxima observed at 15 eV in their excitation functions. We also consider that above about 12 eV at our present spectral resolution there is a small contribution of higher bands of the ϵ -system e.g. (0,6), (1,7) and (2,9) to the measured excitation function of the (0,1) γ -band. The increasing cascading contribution to the cross-section of Fig. 4 would further imply that the direct excitation cross-section of the $A^2\Sigma^+$ state decreases with energy above about 8 eV.

4. Conclusions

We have presented the first determination of the integral cross-sections for excitation of the $v=0$ and 1 vibrational levels of the Rydberg $A^2\Sigma^+$ state of nitric oxide in the near-threshold energy region. It has been found that excitation cross-sections of both vibrational levels does not show formation of core-excited shape resonances which is a typical mechanism for excitation in the corresponding Rydberg states of carbon monoxide and nitrogen.

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