

Total cross section for electron impact on nitrogen monoxide

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Abstract. The absolute total electron scattering cross section for nitrogen monoxide has been measured in a transmission experiment in the energy range 0.5–160 eV. Two distinct features in the energy dependence of the cross section have been observed: an oscillatory structure below 2 eV and a very broad hump with a maximum close to 16 eV. Comparison is made with other experimental results.

1. Introduction

The total cross section is until now the most precisely, absolutely measured quantity describing electron (positron)–atom/molecule scattering. It has practical application for modelling processes in all reactive particle ensembles where free electrons/positrons are present. Experimental total cross sections serve also as one of the tests of theoretical calculations.

Unfortunately, in spite of the need for very accurate total cross sections and a long tradition of their measurement, the available experimental data have mainly been taken at very limited energy ranges, usually for the simplest targets. On the other hand, for those targets for which more than one measurement was performed, the disagreement between data available from different laboratories quite often considerably exceeds the declared experimental uncertainties.

In the particular case of nitrogen monoxide there are relatively few electron scattering experiments and much less has been done theoretically.

To date, most electron impact experimental studies in NO have concentrated on ionization processes (Hagstrum and Tate 1941, Hagstrum 1951, Cloutier and Schiff 1959, Rapp and Englander-Golden 1965, Rapp and Briglia 1965, Hierl and Franklin 1967, Kadota and Kaneko 1977) and on dissociative electron attachment to the NO molecule (see the above references, Frost and McDowell 1958, Dorman 1966, Chantry 1968, Van Brunt and Kieffer 1974, Mazeau *et al* 1978, Krishnakumar and Srivastava 1988).

Strong resonant effects in e^- -NO scattering have been observed in low-energy transmission functions by Boness and Hasted (1966), Ehrhardt and Willmann (1967), Boness *et al* (1968), Hasted and Awan (1969), Zecca *et al* (1974) and in the backscattered current by Burrow (1974). More detailed experimental studies of the resonant scattering below 3 eV were performed by Spence and Schulz (1971) and Tronc *et al* (1975).

Semi-empirical calculations of Koike (1975) showed that the observed features can be explained in terms of the transient vibrationally excited negative ionic states. Using a simple formalism Teillet-Billy and Fiquet-Fayard (1977) have analysed resonant structures obtained by Tronc *et al* (1975) and estimated spectroscopic constants of the two lowest resonances. The resonance positions and widths calculated by Tennyson

and Noble (1986) by applying the *R*-matrix method are in the best agreement with measurements of Tronc *et al* (1975).

Further resonant effects at impact energies up to about 20 eV were observed in transmission spectroscopy by Sanche and Schulz (1972) and in high-resolution experiments by Greteau *et al* (1977, 1979a, b). More recently, Tronc *et al* (1980), King *et al* (1980) and Camilloni *et al* (1987) have studied the inner-shell excited states of NO. Experiments on the radiative electron impact excitation of NO (Stone and Zipf 1972, Povch *et al* 1972, Imami and Borst 1975) were partly stimulated by the role of nitrogen monoxide in an auroral display.

The only absolute electron scattering total cross sections for nitrogen monoxide were measured by Brüche (1927) between 1 and 49 eV and from 121 to 1444 eV by Dalba *et al* (1980). In both experiments the Ramsauer technique was employed. At energies below 10 eV, Zecca *et al* (1974) have obtained a relative cross section which, after normalization, was put on an absolute scale.

In the present work, we have measured absolute total electron scattering cross sections of NO for incident energies from 0.5 to 160 eV using a linear non-magnetic transmission method. The results are compared with other total cross section measurements available in the energy range of interest.

2. Experimental

The most often employed technique for determination of the total cross section is the transmission method. In this method the experimental procedure is based on the relation between the total scattering cross section $\sigma(E)$ and the attenuation of a projectile beam of given energy E passing through the target under study. To the first approximation it is given by Bouguer-de Beer-Lambert law

$$I_n(E) = I_0(E) \exp(-nL\sigma(E))$$

where I_0 is the incident particle beam intensity, I_n is the intensity after its passage through the target region of length L , n is the target gas density.

The conceptually simple problem of total cross section determination becomes a difficult task when one wishes to obtain data of great accuracy. Inevitable factors, due to which the measured total cross section systematically differs from the exact value, depend on the method employed (Bederson and Kieffer 1971), while the degree of these divergences depends on the particular experimental arrangement.

One of the essential sources of erroneous results in all transmission experiments, which systematically lowers the measured cross sections, is an imperfect discrimination against projectiles scattered in the small-angle forward direction due to finite angular resolution of the detector system. For electron scattering this effect increases with impact energy. Another serious problem is the correct estimation of the effective path length of the projectile in a target of usually inhomogeneous density.

In the reported experiment an electron beam was energy selected ($\Delta E = 60$ meV FWHM) before entering the scattering chamber by a 127° electrostatic cylindrical deflector. The electrons which succeeded in leaving the scattering volume through the exit orifice were directed into a Faraday cup. To reduce the number of inelastically scattered electrons which might be accepted by the collector, together with transmitted electrons, a retarding field was applied before the Faraday cup detector. This enabled us to discriminate electrons with a kinetic energy difference of 0.1 eV in the case of low impact energies and 0.5 eV at the highest applied energies.

As a reference point for the absolute electron energy scale, we have chosen the oscillatory resonance structure visible in the transmission current at around 2.3 eV when some N₂ was admitted to nitrogen monoxide. The overall accuracy of this calibration was estimated to be ± 60 meV.

For the effective absorption length L we adopted the geometrical distance (30.5 mm) between entrance and exit orifices of the scattering cell. Calculations, similar to that of Nelson and Colgate (1973), show that this estimation may be correct within the limit of 0.5%.

The gas effusing through orifices of the scattering chamber into the region of the electron optics affects the primary electron beam and in consequence the measured total cross section. To avoid these variations, gas was let alternately into the scattering cell and the outer vacuum volume in such a way that the electron optics was exposed to the same partial pressure of the target gas when I_0 and I_n were measured. The pressure outside the scattering cell (<0.2 mPa) was always three orders of magnitude lower than the pressure in the cell.

The density n of the target was derived from the gas pressure readings, taken with the capacitance manometer and corrected for the thermal transpiration effect (Poulter *et al* 1983). The values of n never exceeded 5×10^{19} molecules/m³ which ensures that multiple scattering events can be ignored.

The measurements were performed at a given electron energy for a series of runs at various target gas pressures and different sets of voltages on the electron optics. We found that the measured total cross sections obtained at the same energy were independent, within the statistical experimental uncertainties, of the applied pressures of the gas, the electron current (10–100 pA), and the electron beam controlling parameters.

The present experiment was carried out on the same apparatus (with minor changes) as has already been intensively used for total cross section measurements and more experimental details can be found elsewhere (Szmytkowski *et al* 1984, 1987).

The final total cross sections at particular energies presented in this work are the weighted means of the average of about 40 to 100 cross sections from different series of individual runs for the same energy.

The statistical uncertainties based on the reproducibility (one standard deviation of weighted mean values) are about 5% below 0.9 eV, less than 3% between 0.9 and 2 eV and never exceed 2% above 2 eV.

The resulting estimation of the overall systematic uncertainty (square root of the quadratic sum of the individual uncertainties of all measured quantities) gives values up to 5% under 1.5 eV, decreasing below 3% between 3 and 50 eV and increasing again up to 4% at the highest applied energies.

The relatively large uncertainties at the lowest energies are mainly related to the shape of the total cross section function below 2 eV, where any small drift in energy causes a relatively large change in cross section.

The nitrogen monoxide, from Matheson Gas Product Company, was 0.999 pure and no further purification was performed.

3. Results

The absolute total cross sections for e⁻-NO scattering obtained in the present experiment are displayed in figure 1. They are compared with the experimental absolute data

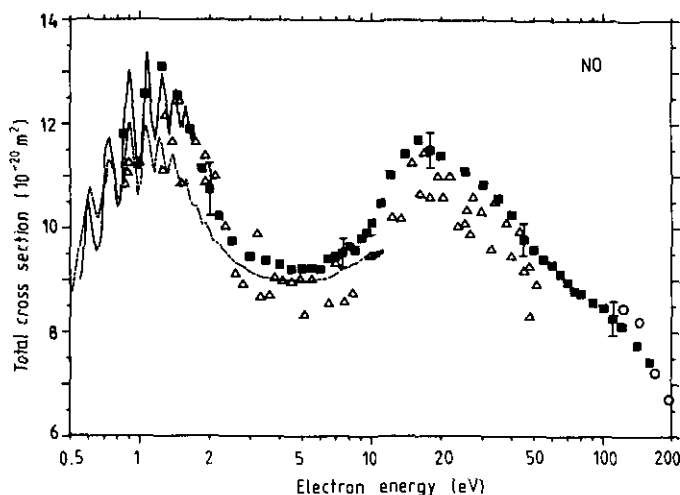


Figure 1. The total cross section for electron impact of NO. Experimental absolute data: Brüche (1927) (open triangles), Dalba *et al* (1980) (open circles), present (full squares and full curve) and normalized data: Zecca *et al* (1974) (broken curve). The bars, at some selected points, correspond to the direct sum of statistical and overall systematical experimental uncertainty.

of Brüche (1927) and with the normalized results of Zecca *et al* (1974). From the high-energy absolute measurements of Dalba *et al* (1980) we selected for comparison only the lowest-energy points which overlap the present energy range.

The most striking feature of the measured cross section is an oscillatory structure at an incident energy below 2 eV. This part of the cross section energy dependence (full curve in figure 1) is an average obtained from a series of runs during which the target gas pressure in the collision chamber was constant while the electron energy was swept over the range of interest.

Similar oscillations below 2 eV have already been observed in prior transmission spectra (Boness and Hasted 1966, Boness *et al* 1968, Hasted and Awan 1969, Spence and Schulz 1971, Burrow 1974, Zecca *et al* 1974) and in vibrational excitation functions (Ehrhardt and Willmann 1967, Tronc *et al* 1975). The structure was attributed (Tronc *et al* 1975) to the vibrational series of NO^- shape resonant states formed in this energy range. These short-lived negative ions belong to a three-member multiplet of $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$ symmetries, respectively. Visible variations of intensities of oscillations, peak spacings and, to some extent, the shape of the background on which oscillations are superimposed, may be partly associated with interference effects between overlapping vibrational series of successive resonant states.

There is quite good accord with respect to the positions of maxima in oscillatory structures between the present experiment, the results of Zecca *et al* (1974) and other transmission measurements. The magnitude of the oscillations in the Zecca *et al* curve is, however, noticeably smaller than in the present total cross section. This discrepancy is intriguing because it cannot be explained only by the difference in the energy resolutions of compared experiments as they were almost the same. The absence of the vibrational structure in Brüche's total cross section is a result of a much wider impact energy spread in that experiment which completely smeared out oscillations. The non-oscillating part of the Zecca *et al* cross section is lower than in the present

results over the whole energy of overlap. The reason for this discrepancy might be the normalization procedure applied in their experiment.

The next prominent feature of the e^- -NO scattering cross section is the very broad structureless maximum centred around 16 eV. Similar enhancements of the total cross sections, close to 10 eV, have been observed for many targets. Transmission experiments of Sanche and Schulz (1972), investigations of nitrogen monoxide excitation by electron impact (Stone and Zipf 1972, Povch *et al* 1972, Imami and Borst 1975, Greteau *et al* 1977, 1979a, b) and on electron dissociative attachment (Mazeau *et al* 1978, Krishnakumar and Srivastava 1988) gave evidence that a large number of weak processes, among them also resonant ones, can be responsible for the observed increase of the cross section in this energy range.

For energies above 16 eV up to 160 eV the total cross section decreases with energy as $E^{-0.2}$. A slight change of the slope of the experimental total cross section between 90 and 130 eV coincides with the maximum in ionization total cross section (Rapp and Englander-Golden 1965). The role of ionization gradually increases with energy and at energies ranging upwards from about 70 eV at least one third of the total cross section is due to the ionization processes. Measurements of Dalba *et al* (1980) show that at high energies the total cross section falls off as a function of impact energy in the order of $E^{-0.7}$.

At the highest investigated energies our results are lower than the data of Dalba *et al* (1980). This difference (within combined uncertainties of both experiments) might be partly associated with slightly poorer angular discrimination of scattered electrons in the present experiment. To estimate this effect, we used the only available experimental data of Kubo *et al* (1981) on differential elastic cross sections. For the present apparatus, with a detector acceptance angle of 1 msr, we found the relative small-angle lowering of the total cross section at 20 eV to be less than 0.3%. Because, at present, there are no differential cross sections for e^- -NO scattering at higher energies at our disposal, one can only speculate about the possible contribution of this effect near 100 eV. Calculations carried out for N₂O (Szymkowski *et al* 1989), a molecule with

Table 1. Measured absolute total cross sections (TCS) for electron impact of NO in units of 10^{-20} m².

Energy (eV)	TCS	Energy (eV)	TCS	Energy (eV)	TCS
0.85	11.8	6.5	9.41	35	10.5
1.05	12.6	7.0	9.46	40	10.3
1.25	13.1	7.5	9.52	45	9.79
1.45	12.5	8.0	9.65	50	9.59
1.65	11.9	8.5	9.68	55	9.40
1.85	11.1	9.0	9.81	60	9.30
2.0	10.7	9.5	9.92	65	9.12
2.2	10.2	10	10.1	70	8.96
2.5	9.75	11	10.5	75	8.80
3.0	9.45	12	11.0	80	8.75
3.5	9.38	14	11.4	90	8.58
4.0	9.30	16	11.7	100	8.48
4.5	9.21	18	11.5	110	8.29
5.0	9.22	20	11.4	120	8.13
5.5	9.23	25	11.1	140	7.76
6.0	9.21	30	10.8	160	7.44

comparable permanent dipole moment to that of NO, indicate that near 100 eV detection of forward scattered electrons in the present experiment can lower the measured cross sections by less than 1%. This value is considerably lower than the observed discrepancy.

The results of Brüche (1927) are systematically lower, by on average 8%, than the present results in the energy range 2.5–49 eV. Although differences are within the limits of combined experimental uncertainties, it is believed that they are real. Most of the recent results for other targets exceed to the same degree the pioneering measurements of Brüche.

In table 1 we have given our e^- -NO total cross sections for selected energies.

To the best of the authors' knowledge, up to the present day, no theoretical calculations of the total electron scattering cross section by NO have been published which could enable comparison with our experimental results.

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