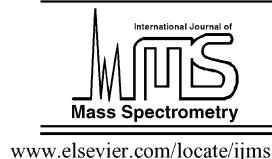




ELSEVIER

International Journal of Mass Spectrometry 223–224 (2003) 205–215



www.elsevier.com/locate/ijms

Low-energy electron collisions in nitrogen oxides: a comparative study

Antonio Zecca ^a, Grzegorz P. Karwasz ^{a,*}, Roberto S. Brusa ^a, Tomasz Wróblewski ^b

^a Dipartimento di Fisica, Istituto Nazionale per la Fisica della Materia, Università di Trento, I-38050 Povo TN, Italy

^b Institute of Physics, Pomeranian Pedagogical Academy, PL-76200 Szczecin, Poland

Received 15 January 2002; accepted 4 April 2002

Abstract

Cross-sections for low-energy electron scattering in nitric oxide (NO), nitrous oxide (N_2O) and nitrogen dioxide (NO_2) are discussed. We compare earlier and recent cross-sections derived from beam and swarm experiments for elastic, vibrational, electronic excitation, ionization, electron attachment phenomena. The importance of resonant scattering at low energies is stressed for all three targets. (Int J Mass Spectrom 223–224 (2003) 205–215)

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nitrogen oxide; Electron scattering

1. Introduction

Nitrogen oxides prove to be of essential importance for a number of biological processes. Nitrous oxide (N_2O) is the laughing gas, used as an anesthetic. Nitric oxide (NO) is noxious because of its extra electron compared to N_2 , making it highly chemically reactive. Recently [1], much attention has been devoted to NO due to its possible role in neurotransmitters. Traffic-born NO transforms easily to nitrogen dioxide (NO_2), which is also toxic (the toxicity limit 30 mg/m³). In general, studies of all the three nitrogen oxides considered are important for environmental sciences: NO and NO_2 are traffic pollutants and the presence of biogenic N_2O influences the infrared absorption in the Earth atmosphere [2]. N_2O is a linear molecule (with N–N distance of 1.126 Å and

N=O bond of 1.186 Å); NO_2 is a bent molecule with 1.188 Å bond length and 134° apex angle.

Electron collisions in NO and N_2O were studied already in pioneer research [3–6] proving existence of resonances, i.e., temporary negative ion states of these molecules. These states manifest themselves in different scattering channels: in the total cross-section, vibrational excitation, dissociative attachment. Cross-sections measurements from earlier works for all the three oxides were reviewed in our previous works [7,8]. Recently, new, high resolution measurements have been performed on total [9], elastic and vibrational [10], electronic excitation [11,12], ionization [13,14] and electron attachment [15,16] in NO. New data have been published for elastic [17,18], vibrational [18], electron attachment [19,20] processes in N_2O and ionization in NO_2 [13]. Nevertheless, cross-sections show still some “white spots” for all the three gases, and in particular for NO_2 .

* Corresponding author. E-mail: karwasz@science.unitn.it

In this work we compare total and partial cross-sections for the three molecules, looking for similarities which could arise from a similar atomic composition.

2. Total cross-section

In spite of the great importance of the molecules considered, total cross-sections were measured only in a few laboratories. The data of Zecca and co-workers cover the energy range below 10 eV for NO and N₂O [6] and above 100 eV for NO [21] and NO₂ [22], the intermediate range is covered by data of Szymkowski et al. [23–26]. For N₂O, additional measurements by Kwan et al. [27] exist at 1–500 eV and by Xing et al. [28] at 600–4250 eV. Recommended total cross-sections based on all these experiments for NO, N₂O and NO₂, are shown in Figs. 1–3, respectively.

The total cross-section rises towards zero energy in all the three targets because of the direct (non-resonant) rotational excitation induced by the permanent dipole moment of the molecules (0.153 Debye (D) for NO, 0.167 D for N₂O and 0.29 D for

NO₂). However, due to different inertia moments, the rise of TCS is well visible for N₂O already at 0.4 eV [4] while for NO only below 0.1 eV [6].

Early measurements of total cross-sections [6] performed with 30 meV energy resolution showed in NO a resonant, vibrational-like structure in the 0.2–2 eV energy range. Recent measurements from Canberra laboratory [6,29] with a resolution of 3 meV confirmed the average values of those [6] measurements but showed that the resonant structure is much deeper, with more than 50% “modulation” of the average value (see Fig. 1). We recall a similarly sharp, comb-like structure in O₂ total cross-section at 0.2–1 eV, but with a much smaller (25%) modulation [29].

In N₂O, the resonant maximum [4,6,23] is placed at a higher energy (2.3 eV) than the resonance in NO and is structureless, resembling the one in CO₂ at 3.9 eV [30–32]. It has been identified already in early theoretical works [33] that this rise in the total (and elastic, vibrational) cross-section is due to formation of a temporarily negative N₂O[−] molecular ion, by capturing of the incoming electron within the effective scattering potential barrier of the molecule

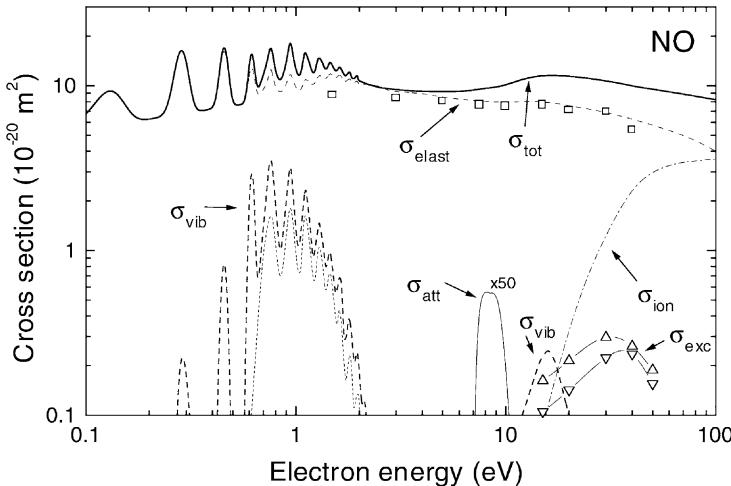


Fig. 1. Total and partial cross-sections in NO. Total, recommended cross-sections, this work. Elastic: broken line, semiempirical model of Josić et al. [43] below 3 eV and present analysis at 3–100 eV; squares, experimental points of Mojarrabi et al. [10] (normalized by a factor 1.1 in present work). Vibrational: semiempirical model of Josić et al. [43] below 3 eV, only $\nu = 1$ (upper curve) and $\nu = 2$ (lower curve) modes are shown; experimental Mojarrabi et al. [10]. Electronic excitation, Brunger et al. [12], triangles, sum of excitation to valence states; inverted triangles, sum of Rydberg states. Ionization: Iga et al. [14], apart from near-to-threshold values which are from [58]. Dissociative attachment [62].

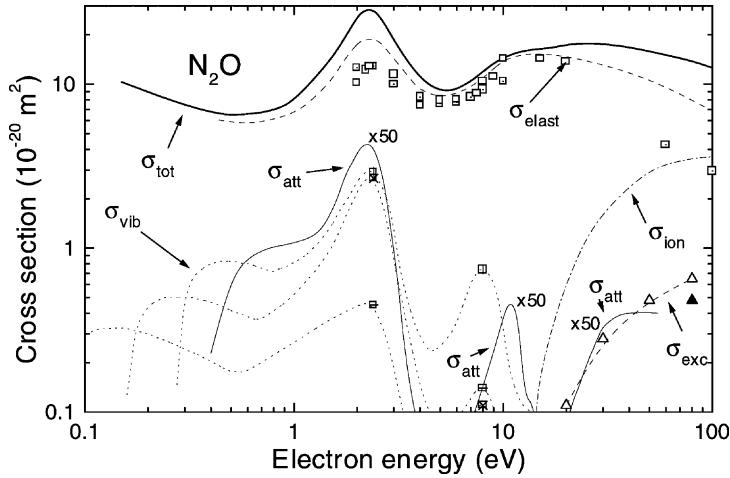


Fig. 2. Total and partial cross-sections in N_2O . Total, recommended cross-sections, this work. Elastic, broken line, semiempirical evaluation, present work and [8], open squares, Canberra laboratory data [18], dotted squares, Tokyo laboratory data [18]. Vibrational, broken line, present semiempirical evaluation using data from [18,45] and the Born approximation, from upper to lowest curve (1 0 0), (0 1 0) and (0 0 1) modes; experimental data at 2.3 and 8 eV are from Canberra laboratory [18], crossed squares the (0 1 0) mode, vertically barred squares the (1 0 0) mode, horizontally barred squares the (0 0 1) mode. Electronic excitation: open triangles, numerical integration [8] of differential cross-sections for the $\text{D}^1\Sigma^+$ state [54]; full triangle, normalization of data from [54] by Marinković et al. [54]. Ionization: Iga et al. [14], apart from near-to-threshold values which are from [58]. Dissociative attachment [62].

in its fundamental electronic mode (“shape” resonance). At the resonance position (2.3 eV) the total cross-section exceeds the values in the neighborhood (4.0 eV) by a factor of three [23]. In NO_2 the only existing, to our knowledge, low-energy data

[26] do not show any sharp peaks in the low-energy region.

In the 5–20 eV range the total cross-sections in the three targets vary slowly and assume similar values ($(8\text{--}15) \times 10^{-20} \text{ m}^2$). At high energies it was shown

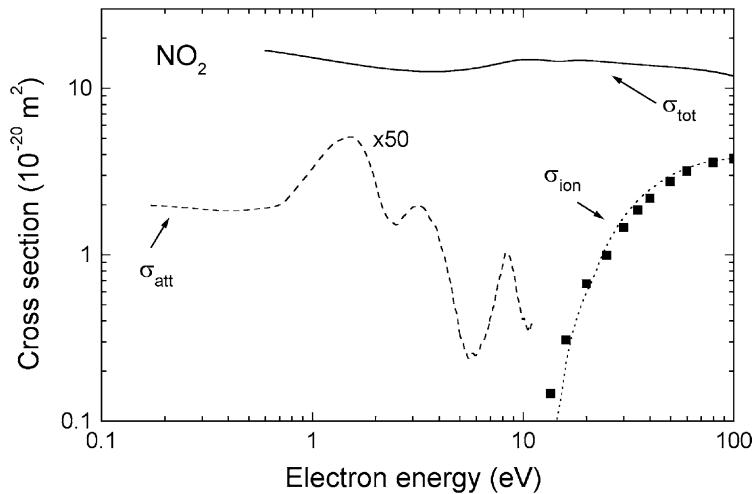


Fig. 3. Total and partial cross-sections in NO_2 . Total, recommended cross-sections, this work. Ionization: points, Lindsay et al. [13], line, semiempirical model [61]. Dissociative attachment [69].

[34,35] that a kind of additivity rule can be applied to calculate total cross-sections. The model [35] sums effective “geometrical” cross-sections of atoms, taking into account effects of geometrical shadowing in molecules. The agreement between the calculation [35] and the data from different laboratories [21,22,27,28] is within experimental errors for all the three targets.

3. Elastic scattering

Elastic (differential and integral) cross-sections in NO at 1.5–40 eV have been recently measured by Buckman and co-workers [10] (see Fig. 3). The integral value in NO at 3 eV [10] agrees well with the total one [24], being only 10% lower. Below 1 eV, i.e., in the region of the low-energy resonance, we are only aware of relative differential measurements of Tronc et al. [36]. The data from that paper, normalized in arbitrary way and at a chosen energy of 0.87 eV are shown in Fig. 3a and compared with the elastic cross-sections in N₂O at 2.3 eV [18]. As seen from the figure, the general shape in NO and in N₂O in the region of the resonance is surprisingly similar. Unfortunately, we are not aware of elastic cross-section measurements for NO₂.

At 1.5–3 eV, the differential cross-section in NO [10] show an unusual for polar molecules dependence, falling towards low angles, similar to that in N₂O above the resonance energy (see Fig. 3b). At 10–30 eV the differential cross-section shows a minimum at 90°, similar to those in other diatomic molecules at these energies (see [7]). The integral cross-section shows a weak maximum at 15 eV [10].

For N₂O integral cross-sections coming from Tokyo (1.5–100 eV) [17] and Canberra (2–20 eV) [18] laboratories have been published [18] recently. The integral cross-section shows a similar maximum at 2.3 eV as the total one. Some uncertainty exists on absolute values of integral cross-sections in N₂O—the sum for the elastic and vibrational scattering from [18] is by 1/3 lower than the total value [23,27] (see Fig. 2). At high energies a similar discrepancy exists: the in-

tegral cross-section given by Kitajima et al. [18] at 100 eV is by 50% lower than the value evaluated in our previous work [8] obtained by numerical integration of the differential data of Kitajima et al. [17]. These discrepancies can be caused by some arbitrariness in extrapolating differential cross-sections towards small angles—differential cross-sections both at 2.3 eV and at high energies are forward centered. In Fig. 2, we present the two recent (Tokyo and Canberra) experimental datasets [18] together with our semiempirical evaluation.

A special experimental interest has been devoted to differential cross-sections in the region of the shape resonance in N₂O [18]. It is known for other shape resonances, like the one at about 2.1 eV in N₂, that the differential cross-sections vary quickly with energy through the resonance, see for example, a comparative study in [9]. At energies 1.5–3 eV the differential cross-sections in N₂O show a dominant p-wave scattering, with a minimum at about 90°. At energies above the resonance energy, the differential cross-sections at 60–90° are almost equal to that at 2.3 eV but start to fall at low scattering angles and above 90° (compare Fig. 3a and b). Note also close values of differential cross-sections above the resonance energies in NO (at 3 eV) and N₂O (at 5 eV).

4. Vibrational excitation

The knowledge of the vibrational cross-sections in NO is needed for modeling low-temperature plasmas and atmospheric processes involving the recombination of the NO⁺ ion [37,38]. In particular, the high recombination coefficients for NO⁺ ions in afterglow plasmas indicate big values of the vibrational cross-sections. Transfer of the vibrational energy from NO⁺ ions to different atomic and molecular species was recently studied in detail by Lindinger and co-workers [39,40].

The resonant structure in the very low-energy vibrational cross-section in NO was already observed in early works [36,41] but no absolute values were given. Teillet-Billy and Fiquet-Fayard [42] analyzing

vibrational cross-section measurements of Tronc et al. [36] predicted the overlapping of resonances between 0 and 2 eV and reported an experimental integral cross-section of as much as $4.4 \times 10^{-16} \text{ m}^2$ for $\nu = 1$ at 0.9 eV. In a recent work [43], a semiempirical analysis showed that in order to reproduce the electron-drift coefficients at intermediate reduced electric fields [44], it is necessary to assume high values of the vibrational cross-sections in the region of the resonance (up to 30% of the total cross-section in the peaks between 0.6 and 1.2 eV). Josić et al. [43] considered two distinct characters of the overlapping resonances. For the first one they assumed a well-separated vibrational structure, similar to that observed for the ${}^2\Pi_g$ resonance in O₂, and high scaling (by a factor of 1/4 to 1/5) between successive vibrational channels; for the second one—broader peaks scaling by a factor of 0.8 approximately, similarly to that in the ${}^2\Pi_g$ resonance in N₂.

Recently, absolute values for $\nu = 1$ and $\nu = 2$ excitations at 7.5–40 eV in NO have been measured in Canberra laboratory [10]. A maximum of the vibrational cross-section is observed at 15 eV, where its contribution is about 4% of the elastic one and partitioning between for $\nu = 1$ and $\nu = 2$ modes is 4:1 [10].

The N₂O vibrational cross-sections shows a structureless maximum around 2.3 eV [45], with symmetric stretch (1 0 0) and bending (0 1 0) modes dominating (integral cross-section equal to 2.9×10^{-20} and $2.7 \times 10^{-20} \text{ m}^2$, respectively [18]) (see Fig. 2). Differential cross-sections at 2.4 eV for stretching (1 0 0) and (0 0 1) modes show a p-wave character with a minimum at 90°, while that for the bending mode a maximum at 90° [18].

Andrić and Hall [46] at 2.4 eV observed in N₂O overtones ($n\ 0\ 0$) and ($n\ 0\ 1$) up to $n = 12$. These authors stressed that angular dependencies for the (0 1 0) and (1 1 0) modes remain the same across the resonance (1.4–3.1 eV) while for the (1 0 0) and (2 0 0) levels change passing from the 1.4–1.85 to 2.3–3.1 eV energy range. According to Andrić and Hall this indicates the existence of two distinct resonant states overlapping in the 1.4–2.3 eV energy range. This the-

sis has been recently verified by a common Innsbruck, Berlin experiment on dissociative attachment [16], although the assignment of the states is different, as will be discussed later on. We recall from early data [45] that the cross-section for the (0 0 1) mode at 40° scattering angle varies little from 0.7 to 2.3 eV, in contrast to the (1 0 0) and (0 1 0) modes which are much lower at 1 V than at 2.3 eV; this feature is qualitatively reproduced in Fig. 2. The vibrational cross-section at the resonant maximum in N₂O amounts to as much as 50% of the elastic cross-sections [18]. This resembles proportions observed for the ${}^2\Pi$ resonance at 3.9 eV in CO₂ [47], isoelectronic with N₂O.

The vibrational excitation in N₂O shows another maximum at 8 eV [46] with the sum of three fundamental modes amounting to 1/10 of the integral elastic cross-section [18] and a significant enhancement of the (1 0 0) mode only (see Fig. 2).

In NO₂ an enhancement of vibrational excitation has been observed below 2 eV [48]. In the differential cross-section for symmetric stretching ($n\ 0\ 0$) modes a broad maximum centered at about 1 eV with a vibrational structure superimposed is seen while a similar enhancement for the bending (0 1 0) mode vanishes out above 1.3 eV [49]. This different behavior of the modes suggests presence of two resonant states at low energies. Data of [49] indicate that at 0.65 eV the vibrational excitation constitutes about 1/8 of the elastic cross-section.

For comparison with resonant scattering, we have evaluated vibrational cross-sections in NO and N₂O at energies below 1 eV with the Born approximation (see [7]), using transition dipole moments for vibrational excitation from [50], the calculated integral cross-sections are shown in Fig. 2 for N₂O. The vibrational cross-section for $\nu = 1$ excitation in NO evaluated in this way reaches a maximum of $0.11 \times 10^{-20} \text{ m}^2$ at 0.4 eV while in N₂O the sum of three fundamental modes—a similar value of $1.35 \times 10^{-20} \text{ m}^2$ at the same energy. In N₂O at the 8 eV resonance [18] the cross-sections for (0 1 0) and (1 0 0) modes exceed by a factor of 10 Born's values but the (0 0 1) mode is equal to it (see Fig. 2).

5. Electron excitation

Recently an extensive study of differential and integral cross-sections in NO was performed for as many as 22 valence and Rydberg states at 15–50 eV [11,12]. It has been found that the integral cross-sections for all these states reach maxima at energies 30–40 eV, but their amplitudes are small (the highest, for the $L^2\Pi$ state, amounting to $0.14 \times 10^{-20} \text{ m}^2$). In Fig. 1, we present separately the summed cross-sections for the valence and Rydberg states. The energy dependencies for these sums are similar, but two of the valence states, dipole-forbidden ($a^4\Pi$ and $b^4\Sigma^-$) fall quickly with energy above 30 eV. The overall electron excitation cross-sections amounts to as little as 5% of TCS at 30 eV.

In the case of N₂O we are not aware of such a complete study of the electronic excitation. A supplementary way of evaluating electronic excitation cross-sections for optically allowed transitions are the measurements of photoabsorption [51,52] and optical emission [53]. In Fig. 4, we compare photoabsorption cross-sections for NO and N₂O obtained

by an absolute method, using zero energy differential cross-sections for electron scattering [51,52]. In both gases the main part of the overall photoabsorption cross-section falls above the ionization threshold. In N₂O, the excitation into the D¹ Σ^+ state is the most prominent structure below the ionization threshold; in its maximum it exceeds by a factor of 10 the maximum for the C² Π state in NO (we recall the cross-section value of $0.047 \times 10^{-20} \text{ m}^2$ at 40 eV for the latter state in NO [12]).

The differential cross-sections for C¹ Π and D¹ Σ^+ states were measured by Marinković et al. [54] at 20–80 eV collision energies. These authors, performing successively the normalization of their differential cross-sections [54] to the photoabsorption data, reported for the state an integral cross-section of $0.48 \times 10^{-20} \text{ m}^2$ at 80 eV collision energy [55]. By numerical integration of the differential cross-sections of Marinković et al. [54] we evaluate the upper limit for the D¹ Σ^+ state as $0.68 \times 10^{-20} \text{ m}^2$ at 80 eV. The D¹ Σ^+ state is repulsive, leading to dissociation into N₂ (X¹ Σ_g^+) molecule and an O (¹S) atom. Measurements of the electronic dissociation cross-sections

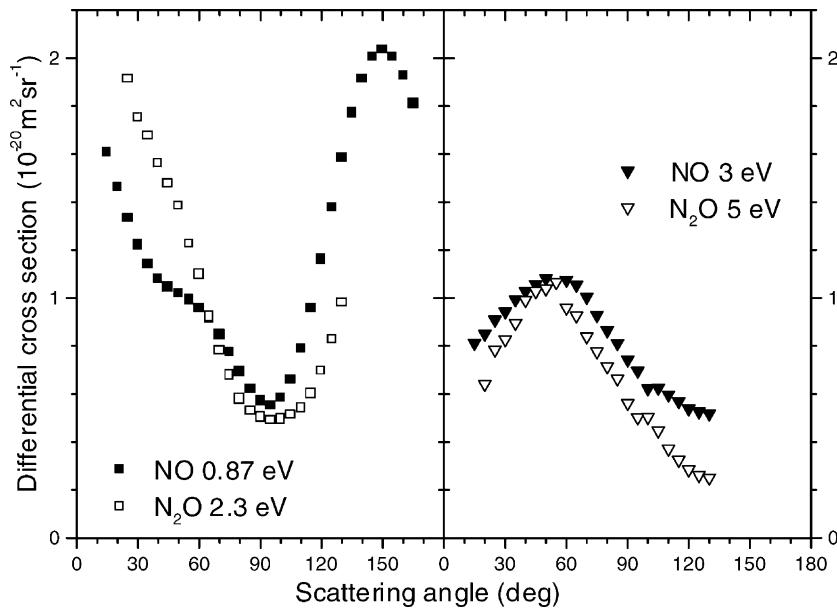


Fig. 4. Comparison of elastic differential cross-section at the resonance and above the resonance position in NO and N₂O. N₂O at 2.3 and 5 eV and NO at 3 eV, absolute data from Canberra laboratory [10,18], NO at 0.87 eV, Tronc et al. [36] normalized in this work.

gave a value $0.21 \times 10^{-20} \text{ m}^2$ for the O (${}^1\text{S}$) atom yield [56]. The cross-sections for the $\text{C}^1\Pi$ excitation derived from measurements of Marinković et al. [54] is much smaller than that for the $\text{D}^1\Sigma^+$ state, amounting to $0.015 \times 10^{-20} \text{ m}^2$ at 80 eV. All these different evaluations suggest that the electronic excitation cross-section in N_2O contributes, at most, to 5% of the total cross-section at 80 eV, similarly as in the case of NO.

In NO_2 we regret lack of data, apart from the photoabsorption cross-section measured by electron scattering method [57]. These data indicate low values of electronic excitation cross-sections—the main part of photoabsorption falls above the ionization threshold. A broad peak extending from about 2 eV to about 4.5 eV amounts in its maximum to as little as $0.8 \times 10^{-22} \text{ m}^2$. The highest peak in NO_2 below the ionization threshold is placed at 9.7 eV amounts to $0.44 \times 10^{-20} \text{ m}^2$, much less than the peak value for the $\text{D}^1\Sigma^+$ state in N_2O .

6. Ionization

Total ionization cross-sections presented in Figs. 1–3 and taken from recent measurements ([14] for NO and N_2O and from [13] for NO_2) agree well with early data [58,59] and recent semiempirical models [60,61]. In N_2O the data of Iga et al. [14] are by merely 5% higher than those of Rapp and Englander-Golden [58] and in NO by 18% at the most.

In spite of expected differences, the total ionization cross-section assumes similar values in the maximum for the two targets $-3.61 \times 10^{-20} \text{ m}^2$ at 100 eV for N_2O and $3.57 \times 10^{-20} \text{ m}^2$ for NO [16] and 3.75 for NO_2 [13]. Partitioning into separate ionization channels for the three molecules at 100 and 1000 eV is shown in Fig. 5. In NO and N_2O the formation of the parent ion is dominant in the whole energy range studied [14] but in N_2O it constitutes a smaller part of the total ionization (54% for N_2O and 81% for NO at 100 eV). In NO_2 the dominant ion from the threshold

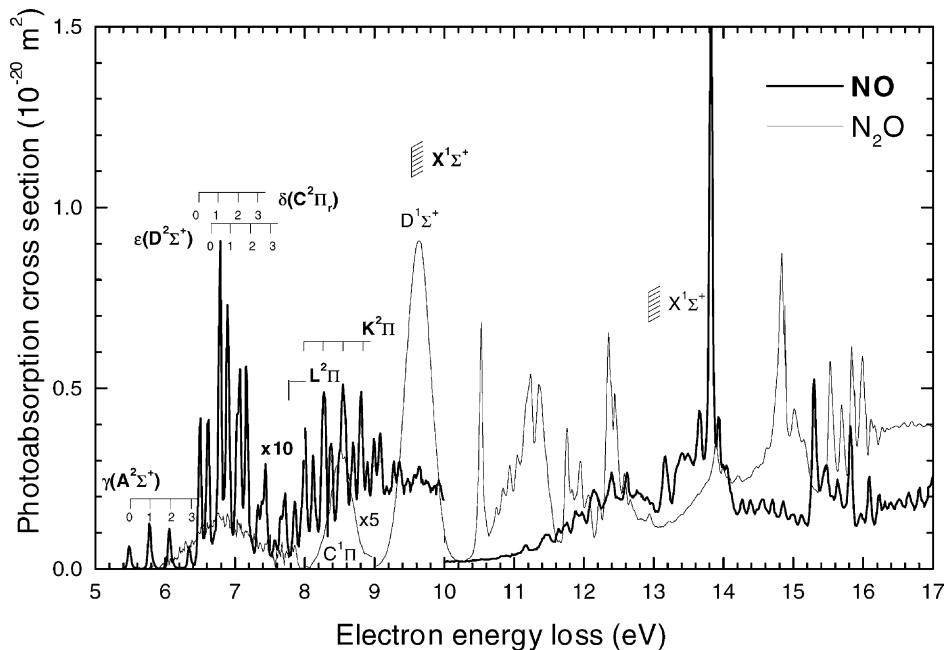


Fig. 5. Zero-angle electron energy loss spectra in NO (electronic-state symbols are in bold) and N_2O (electronic-state symbols in normal font), corresponding to the photoabsorption cross-sections, from experiments by Chan et al. [51,52]. Between 5 and 8 eV the N_2O curve is multiplied by a factor of 100 (not signed on the figure). Thresholds for the ground-state ionization are shown (for NO in bold symbol).

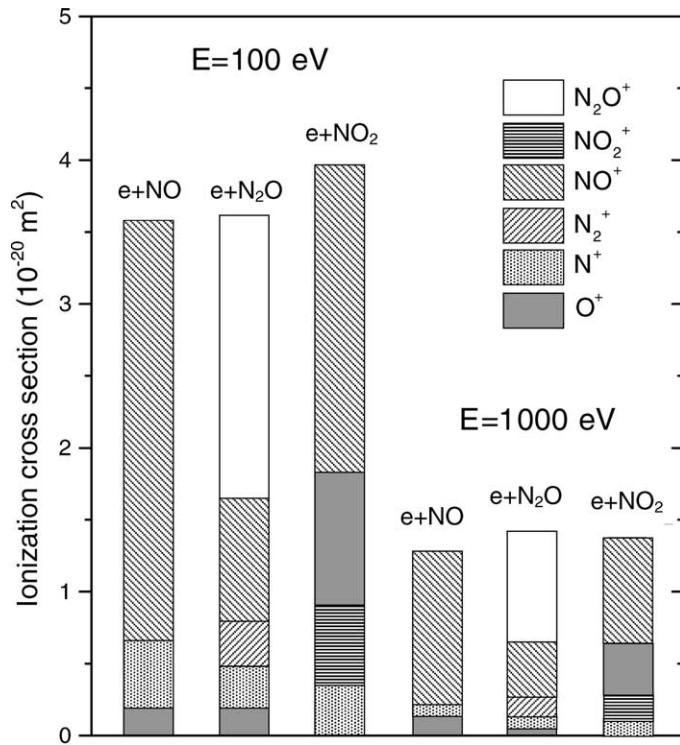


Fig. 6. Partial cross-sections for electron-impact ionization in NO [14], N₂O [14] and NO₂ [13] at 100 and 1000 eV.

up to 1000 eV is NO⁺ [13] which is formed almost in the same amount as in ionization of NO; the parent ionization in NO₂ constitutes less than 25% of the total ionization cross-section (Fig. 6).

7. Dissociative attachment

Dissociative attachment in NO and N₂O was already studied by Rapp and Briglia [62]. More recently, three laboratories performed measurements on both molecules: in Innsbruck [15,16,19], in Berlin [16,20] and Pasadena [63].

In NO a double peak was observed by Rapp and Briglia [62], corresponding to dissociation in two excited states of atomic N (²D and ²P). More recently, a discovery of a new channel corresponding to dissociation into a ground-state N (⁴S) atom was announced [63] but has not been confirmed by successive works from Innsbruck laboratory [15,16]. We are not aware

of detection of any stable and/or metastable parent NO⁻ anions which *could be* formed at low energies (note a small, but positive value of the electron affinity in NO (0.033 eV), as measured in a recent scattering experiment [9]).

In N₂O a peak for O⁻ formation at 2.3 eV and a shoulder at about 0.7 eV was observed already in early works [5,62,64]. Chantry [64] noticed that the 2.3 eV peak does not depend on the gas temperature while the 0.7 eV shoulder rises and shifts to lower energies with temperature. As shown recently [20], a threshold peak appears with rising the gas temperature, merging at high temperatures (675 K) with the low-energy shoulder. In the N₂O resonant peak the dissociative attachment constitutes as much as 0.3% of the total cross-section, compared, for example, to a maximum of 0.04% in CH₄ (see [8]).

Rapp and Briglia [62] reported in N₂O another broad peak extending from about 7 to 14 eV and then a rise of the cross-section above 20 eV (see Fig. 2).

Krishnakumar and Srivastava [65] reported three very weak peaks at 5.4, 8.1 and 13.2 eV. Sanche and co-workers [66] in studies of condensed N₂O observed essentially a similar picture to that of Rapp and Briglia but shifted to somewhat lower energies (due to the polarization interaction with the solid-state matrix). Existence of anion states at 7.0, 9.0, 15.9 and possibly 12.5 eV was deduced [66] but only the 9 eV peak and 7 eV shoulder are directly visible in the O⁻ current. In recent experiments from Innsbruck [19,20] only a smooth rising of the O⁻ signal from 5 to 20 eV was observed.

NO₂ forms stable negative parent ions (the vertical electron affinity is 2.27 eV) and shows a reach pattern of dissociative attachment: the yields for O⁻, NO⁻ and O₂⁻ ions reach their maxima at 1.8, 3.2 and 4.4 eV, respectively [67] and the relative intensities scale as 1000:3:10 [68]. The most recent data [69] show somewhat different energy position of peaks but also testify existence of overlapping resonant states. According to these recent data [69] electron attachment amounts in its maximum to as much as 0.6% of the total cross-section.

8. Resonances

The existence of resonant states can be observed in different channels. Resonant structures in NO are visible in vibrational excitation, elastic and total cross-sections [36,6,24]. In particular in the vibrational channel the lowest-energy NO resonance manifests itself as a series of narrow peaks below 1.5 eV (see Fig. 1). However, the complex picture observed in NO indicates an overlap of more than one resonant state. In fact, as the NO⁻ ion is isoelectronic with O₂ molecule, one can expect similar electronic excitation energies for both of them. We recall very low thresholds for electronic excitation in O₂, 0.98 eV for the a¹Δ_g state and 1.63 eV for the b¹Σ_g⁺ state and also a long (75 min) lifetime for the a¹Δ_g state. Teillet-Billy and Fiquet-Fayard [42] predicted three resonant states in NO, the lowest one related to the molecule in its ground electronic state ³Σ⁻ and

next two related to core-excited configurations; they placed the ground-state resonance at zero energy and the excited ¹Δ state at 0.75 eV. Josić et al. [43] in a recent semiempirical work placed the onset of the shape, O₂-like resonance at the electron affinity value (-0.03 eV [29]) and of the second, N₂-like resonance at +0.65 eV; in spite of the vicinity of these states they can be well separated in the total cross-section spectrum. At higher energies in NO already early electron transmission spectra evidenced resonant phenomena in the 5–18 eV energy range [70,71], attributed to some core-excited states. These states have received very little theoretical attention.

In N₂O it is not quite clear if one or two resonances should be attributed to the structures seen in total, elastic, vibrational and attachment cross-sections below 4 eV. An indication for two resonances would be a different behavior vs. gas temperature of the two peaks and/or structures seen in the dissociative attachment, as discussed above. The early theoretical work of Bardsley [33], together with measurements of the O⁻ angular distributions [72] and vibrational excitation [45], placed the ²Π N₂O⁻ resonant state at 0.7 eV while the ²Σ state at 2.3 eV. Andrić and Hall [46], analyzing the vibrational-excitation angular distributions, reversed this order and deduced that in the region 1.4–1.85 eV only the ²Σ state is accessible while at 2.4–3 eV both ²Σ and ²Π state are present and contribute to the vibrational excitation in the proportions 1:2, respectively. Recent calculations [73–75] indicate the presence of only the ²Π state around 2 eV. As reviewed by Sanche and co-workers [66], the double behavior of the 0.7–2.3 eV structure can result from splitting of the ²Π state in its energy minimal, bent geometry into two A' and A'' configurations: the formation of the A'²Π NO⁻ anion state is enhanced by the vibrational excitation while the formation of the A''²Π NO⁻ state does not depend on the vibrational state (i.e., gas temperature). In this sense the A'²Π NO⁻ state could be considered to be a Feshbach, i.e., excited-state resonance.

In N₂O at higher energies, the recent calculations [17,73] placed the ²Σ shape resonance at 8 eV. As discussed before, it has been observed as a slight

enhancement of the vibrational [18] and in the dissociative cross-section [19,62] (see Fig. 2). Some core-excited resonant states in N₂O were observed also between 10 and 13 eV [70].

Also in NO₂ some overlapping resonances were discovered in the low-energy region. Presence of two states was deduced from detailed studies of the vibrational excitation [49]—a long-lived ¹A₁ shape resonance below 1 eV and an intermediate lifetime ³B₁ shape resonance above 1.1 eV. The presence of these resonances was not observed in the total cross-section [26] but produces well visible structures in electron transmitted current [48]. The recent, pioneer calculation [76] for NO₂ show enhancement of elastic cross-section at about 14 eV but does not cover the region of low-energy resonant structures in the vibrational excitation.

9. Remarks

Analysis of electron scattering cross-sections shows some similarities between the nitrogen oxides, NO, N₂O and NO₂. All of them show a strong resonant scattering at low energies—NO between 0 and 2 eV, N₂O between 1 and 5 eV. For NO the resonant part of the total cross-sections exceeds the non-resonant background by a factor of about 1.5, in N₂O by a factor of 2, in NO₂ no data is available. A common feature is also a high contribution from the vibrational excitation in the region of the low-energy resonance. Experimental data for NO [18] indicate that the vibrational excitation cross-section at 2.4 eV equals to the resonant part of the elastic cross-section. The same indication at 0.75 and 0.91 eV comes from the early measurements [36] and from the recent semiempirical work [43].

In all three molecules two resonant states present at low energies partially overlap. In NO the ground-state (shape) resonant overlaps with one or two electronic core-excited states. In N₂O it seems that the resonance involving the molecule in excited bending vibrational modes behaves differently from the resonance involving stretching modes. It was especially well evidenced in recent measurements of electron

attachment to vibrational excited N₂O molecule [20]. The overlap of resonances in NO₂ is, probably, the reason that no sharp structures were observed in total cross-section data [26].

In NO and N₂O a rise of the vibrational excitation and a peak in the dissociative attachment (the later also in NO₂), due to resonant scattering, are observed between 5 and 15 eV. For all three molecules the cross-sections for electronic excitations are very low. In N₂O the magnitude of the vibrational cross-section at 8 eV exceeds the maximum of the dominant electronic excitation (see Fig. 2), in NO the vibrational peak at 15 eV equals to the sum of all valence electronic excitations (see Fig. 1). The magnitudes of the dissociative attachment cross-sections in these intermediate-energy peaks are similar for all three molecules -1.1×10^{-22} , 0.9×10^{-22} , and $1.0 \times 10^{-22} \text{ m}^2$ for NO, N₂O and NO₂, respectively. Apart from vibrational excitation, some more, absolute measurements on electron attachment at low energies in N₂O, NO and NO₂ would be desirable.

References

- [1] S.H. Snyder, D.S. Bredt, Sci. Am. (1992) 68.
- [2] P. Crutzen, J. Geophys. Res. 76 (1971) 7311.
- [3] E. Brüche, Ann. Phys. (Leipzig) 83 (1927) 1065.
- [4] C. Ramsauer, R. Kollath, Ann. Phys. 7 (1930) 176.
- [5] G.J. Schulz, J. Chem. Phys. 34 (1961) 1778.
- [6] A. Zecca, I. Lazzizzeri, M. Krauss, C.E. Kuyatt, J. Chem. Phys. 61 (1974) 4560.
- [7] A. Zecca, G.P. Karwasz, R.S. Brusa, La Rivista Nuovo Cimento 19 (3) (1996) 1.
- [8] G.P. Karwasz, A. Zecca, R.S. Brusa, La Rivista Nuovo Cimento 24 (1) (2001) 1.
- [9] D.T. Alle, M.J. Brennan, S.J. Buckman, J. Phys. B 29 (1996) L277.
- [10] B. Mojarrabi, R.J. Gulley, A.G. Middleton, D.C. Cartwright, P.J.O. Teubner, S.J. Buckman, M.J. Brunger, J. Phys. B 28 (1995) 487.
- [11] B. Mojarrabi, L. Campbell, P.J.O. Teubner, M.J. Brunger, D.C. Cartwright, Phys. Rev. A 54 (1996) 2977, errata in Phys. Rev. A 58 (1998) 1609.
- [12] M.J. Brunger, L. Campbell, D.C. Cartwright, A.G. Middleton, B. Mojarrabi, P.J.O. Teubner, J. Phys. B 33 (2000) 783.
- [13] B.G. Lindsay, M.-A. Mangan, H.C. Staub, R.F. Stebbings, J. Chem. Phys. 112 (2000) 9404.
- [14] I. Iga, M.V.V.S. Rao, S.K. Srivastava, J. Geophys. Res. 101 E (1996) 9261.

- [15] G. Denifl, D. Muigg, A. Stamatovic, T.D. Märk, Chem. Phys. Lett. 288 (1998) 105.
- [16] Y. Chu, G. Senn, P. Scheier, A. Stamatovic, F. Brüning, S. Matejcik, E. Illenberger, Phys. Rev. A 57 (1998) R697.
- [17] M. Kitajima, Y. Sakamoto, S. Watanabe, T. Suzuki, T. Ishikawa, H. Tanaka, M. Kimura, Chem. Phys. Lett. 309 (1999) 414.
- [18] M. Kitajima, Y. Sakamoto, R.J. Gulley, M. Hoshino, J.C. Gibson, H. Tanaka, S.J. Buckman, J. Phys. B 33 (2000) 1687.
- [19] G. Hanel, T. Fiegele, A. Stamatovic, T.D. Märk, Int. J. Mass Spectrom. 205 (2001) 65.
- [20] F. Brüning, S. Matejcik, E. Illenberger, Y. Chu, G. Senn, D. Muigg, G. Denifl, T.D. Märk, Chem. Phys. Lett. 292 (1998) 177.
- [21] G. Dalba, P. Fornasini, R. Grisenti, G. Ranieri, A. Zecca, J. Phys. B 13 (1980) 4695.
- [22] A. Zecca, J.C. Nogueira, G.P. Karwasz, R.S. Brusa, J. Phys. B 28 (1995) 477.
- [23] C. Szmytkowski, G. Karwasz, K. Maciąg, Chem. Phys. Lett. 107 (1984) 481.
- [24] C. Szmytkowski, K. Maciąg, J. Phys. B 24 (1991) 4273.
- [25] C. Szmytkowski, G. Karwasz, K. Maciąg, Phys. Scripta 54 (1996) 271.
- [26] C. Szmytkowski, K. Maciąg, Krzysztofowicz, Chem. Phys. Lett. 190 (1992) 141.
- [27] C.K. Kwan, Y.-F. Hsieh, W.E. Kauppila, S.J. Smith, T.S. Stein, M.N. Uddin, Phys. Rev. Lett. 52 (1984) 1417.
- [28] S.L. Xing, F. Zhang, L.Q. Yau, C.Q. Yu, K.Z. Xu, J. Phys. B 30 (1987) 2867.
- [29] S.J. Buckman, D.T. Alle, M.J. Brennan, P.D. Burrow, J.C. Gibson, R.J. Gulley, M. Jacka, D.S. Newman, A.R.P. Rau, J.P. Sullivan, K.W. Trantham, Aust. J. Phys. 52 (1999) 473.
- [30] C.K. Kwan, Y.-F. Hsieh, W.E. Kauppila, S.J. Smith, T.S. Stein, M.N. Uddin, M.S. Dababneh, Phys. Rev. A 27 (1983) 1328.
- [31] S.J. Buckman, M.T. Elfordt, D.S. Newman, J. Phys. B 20 (1987) 5178.
- [32] C. Szmytkowski, A. Zecca, G. Karwasz, S. Oss, K. Maciąg, B. Marinković, R.S. Brusa, R. Grisenti, J. Phys. B 20 (1987) 5817.
- [33] J.N. Bardsley, J. Chem. Phys. 58 (1969) 3384.
- [34] K.N. Joshipura, P.M. Patel, J. Phys. B 29 (1996) 3925.
- [35] A. Zecca, R. Melissa, R.S. Brusa, G.P. Karwasz, Phys. Lett. A 257 (1999) 75.
- [36] M. Tronc, A. Huett, M. Landau, F. Pochou, J. Reinhardt, J. Phys. B 8 (1975) 1160.
- [37] O. Eichwald, M. Yousfi, A. Hennad, M.D. Benabdessadok, J. Appl. Phys. 82 (1997) 4781.
- [38] T. Mostafaoui, S. Laubé, G. Gautier, C. Rebrion-Rowe, B.R. Rowe, J.B.A. Mitchell, J. Phys. B 32 (1999) 5247.
- [39] V.A. Zenevich, W. Lindinger, S.K. Pogrebny, M. Cacciatore, G.D. Billing, J. Chem. Phys. 102 (1995) 6669.
- [40] A. Hansel, N. Oberhofer, W. Lindinger, V.A. Zenevich, G.B. Billing, Int. J. Mass Spectrom. 185–187 (1999) 559.
- [41] D. Spence, G.J. Schulz, Phys. Rev. A 33 (1971) 1968.
- [42] D. Teillet-Billy, F. Fiquet-Fayard, J. Phys. B 10 (1977) L11.
- [43] L. Josić, T. Wróblewski, Z.L. Petrović, J. Mechlińska-Drewko, G.P. Karwasz, Chem. Phys. Lett. 350 (2001) 318.
- [44] J. Mechlińska-Drewko, W. Roznerski, Z.L. Petrović, G.P. Karwasz, J. Phys. D 32 (1999) 2746.
- [45] R. Azria, S.F. Wong, G.J. Schulz, Phys. Rev. A 11 (1975) 1309.
- [46] L. Andrić, R.I. Hall, J. Phys. B 17 (1984) 2713.
- [47] J.C. Gibson, M.A. Green, K.W. Trantham, S.J. Buckman, P.J.O. Teubner, M.J. Brunger, J. Phys. B 32 (1999) 231.
- [48] L. Sanche, G.L. Schulz, J. Chem. Phys. 58 (1973) 479.
- [49] C. Benoit, R. Abouaf, Chem. Phys. Lett. 177 (1991) 573.
- [50] D.M. Bishop, L.M. Cheung, J. Phys. Chem. Ref. Data 11 (1982) 119.
- [51] W.F. Chan, G. Cooper, C.E. Brion, Chem. Phys. 180 (1994) 77.
- [52] W.E. Chan, G. Cooper, C.E. Brion, Chem. Phys. Lett. 179 (1993) 111.
- [53] J.M. Ajello, K.D. Pang, B.O. Franklin, S.K. Howell, N.J. Bowring, J. Geophys. Res. 94 (1989) 9093.
- [54] B. Marinković, C. Szmytkowski, V. Pejčev, D. Filipović, L. Vušković, J. Phys. B 19 (1986) 2365.
- [55] B. Marinković, R. Panajotović, Z.D. Pešić, D. Filipović, Z. Felfi, A.Z. Msezane, J. Phys. B 32 (1999) 1949.
- [56] L.R. LeClair, J.W. McConkey, J. Chem. Phys. 99 (1993) 4566.
- [57] J.W. Au, C.E. Brion, Chem. Phys. 218 (1997) 109.
- [58] D. Rapp, P. Englander-Golden, J. Chem. Phys. 43 (1965) 1464.
- [59] E. Märk, T.D. Märk, Y.B. Kim, K. Stephan, J. Chem. Phys. 75 (1981) 4446.
- [60] H. Deutsch, K. Becker, T.D. Märk, Int. J. Mass Spectrom. Ion Process. 167/168 (1997) 503.
- [61] Y.-K. Kim, W. Hwang, N.M. Weinberger, M.A. Ali, M.E. Rudd, J. Chem. Phys. 106 (1997) 1026.
- [62] D. Rapp, D.D. Briglia, J. Chem. Phys. 43 (1965) 1480.
- [63] O.J. Orient, A. Chutjian, Phys. Rev. A 74 (1995) 130.
- [64] P.J. Chantry, J. Chem. Phys. 51 (1969) 3369.
- [65] E. Krishnakumar, S.K. Srivastava, Phys. Rev. A 41 (1990) 2445.
- [66] A.D. Bass, M. Lezius, P. Ayotte, L. Parenteau, P. Cloutier, L. Sanche, J. Phys. B 30 (1997) 3527.
- [67] R. Abouaf, R. Paineau, F. Fiquet-Fayard, J. Phys. B 9 (1976) 303.
- [68] J.A.D. Stockdale, R.N. Compton, G.S. Hurst, P.W. Reinhardt, J. Chem. Phys. 50 (1969) 2176.
- [69] S.A. Rangwala, E. Krishnakumar, S.V.K. Kumar, in: Y. Itikawa, et al. (Eds.), Proceedings of the XXI International Conference on Physics of Electronic and Atomic Collisions, Sendai, 1999, p. 342 (abstract).
- [70] G.J. Schulz, Rev. Mod. Phys. 45 (1973) 423.
- [71] L. Sanche, G.J. Schulz, Phys. Rev. A 6 (1972) 69.
- [72] M. Tronc, F. Fiquet-Fayard, C. Schermann, R. Hall, J. Phys. B 10 (1977) L459.
- [73] C. Winstead, V. McKoy, Phys. Rev. A 57 (1998) 3589.
- [74] L.A. Morgan, C.J. Gillan, J. Tenysson, X. Chen, J. Phys. B 30 (1997) 4087.
- [75] B.K. Sarpal, K. Pfingst, B.M. Nestmann, S.D. Peyerimhoff, J. Phys. B 29 (1996) 1877.
- [76] R. Curik, F.A. Gianturco, R.R. Lucchese, N. Sanna, J. Phys. B 34 (2001) 59.