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# Calculation of electron impact inelastic cross sections and rate coefficients for diatomic molecules. Application to air molecules

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## Abstract

A method based upon the modified Weighted Total Cross Section (WTCS) theory for the determination of electron impact excitation, ionization and dissociation cross sections and rate coefficients is proposed. An application to the main electronic states of diatomic molecules of the air ( $O_2$ ,  $N_2$  and  $NO$ ) and the corresponding ions ( $O_2^+$ ,  $N_2^+$  and  $NO^+$ ) is given. The reaction rate coefficients were calculated using one and two kinetic temperatures ( $\theta_e$  and  $\theta_g$  for electrons and heavy particles, respectively) and were fitted in the Arrhenius form in the range 1500–15 000 K. This method can be easily extended to any diatomic molecule.  
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*Keywords:* Cross sections; Excited molecular species; Air

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## 1. Introduction

The chemistry of the electronic states is generally not well known for molecular plasmas. Mostly, the only experimentally available quantities are cross sections between fundamental and radiative electronic states. An electron beam impacts a gas at room temperature, producing excited or ionized radiative molecular states. The intensity of radiative deexcitation can be related to the initial collisional inelastic cross section (optical cross section). With this method, cross sections for initial states different from the fundamental or non-radiative final states are very difficult to access. The lack of experimental data is even greater for dissociative processes involving a particular electronic state.

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Nevertheless, predicting the inelastic exchanges occurring in a given chemical species requires knowledge of the whole set of cross sections or rate coefficients connecting the different electronic states between them [1, 2].

A very small number of papers deal with this problem. Concerning air molecules, Bacri and Médani [3], Slinker and Ali [4], Morrill et al. [5], Huo and McKoy [6] and Park [7] can be mentioned. Slinker and Ali [4] and Morrill et al. [5] used experimental cross sections at 300 K and a monothermal Maxwellian distribution function to calculate the rate coefficients. More recently, Huo and McKoy [6] carried out a quantum mechanical calculation to determine the excitation rate coefficients for the singlet and triplet excited states of  $N_2$ , using a state-of-the-art multichannel Schwinger variational method. In its principle, Park's method [7] is relatively close to the one proposed by Bacri and Médani [3]. One of the main differences comes from the radial dependence of the elementary cross section: it was calculated for each rotational transition by Bacri and Médani and using Franck Condon factors by Park. Unfortunately, Park's results are not available in the literature.

Consequently, it seems necessary to publish a complete and reliable set of reaction rate coefficients  $K_{T_1}^{T_2}$  for excitation, ionization and dissociation by electron impact. The Weighted Total Cross Section (WTCS) method used in this work is based upon a summation of the contributions coming from each rovibrational state to the cross section, owing to the probability for the molecule to be in this given state. This method was developed by Bacri and Médani [3] and first applied to  $N_2$  and  $N_2^+$  [8, 9]. It was then extended to other air molecules  $O_2$  [10] and  $NO$  [11]. For these species, some of the simplifying assumptions made for  $N_2$  (number of rotational and vibrational states taken into account, stability area boundaries for the different electronic states) led to questionable results.

Another important property of some electronic states of  $O_2$  and  $NO$  is their strong predissociation [12]. This effect is considered in the present work for the calculation of electron impact dissociation cross sections and rate coefficients (see also Ref. [13]).

## 2. Weighted total cross section (WTCS) determination

### 2.1. Method

For a diatomic molecule, an energy level  $|T_e, v, J\rangle$  belonging to an electronic state defined by the energy term  $T_e$ , is characterized by the vibrational and rotational quantum numbers  $v$  and  $J$ . The potential energy of this level depends on the internuclear separation  $r$ . In this work, these energies are approximated using Morse's well-known potential function [12].

$$u(T_e, v, J, r) = T_e + G(v) + (D_e - G(v))[1 - \exp(-\beta_0(r - r_e))]^2 + \frac{h}{8\pi^2\mu c} \frac{J(J+1)}{r^2}. \quad (1)$$

$G(v)$  is the vibrational energy and  $\beta_0 = 2.43534 \times 10^7 (\mu_A \omega_e x_e)^{0.5}$ .

$\mu_A$  is the reduced mass of the molecule expressed in atomic mass units and  $D_e$  is the dissociation energy of the electronic state  $T_e$ . The spectroscopic molecular constants used in this work were taken from the literature [14–18] and are compiled in Tables 1–3.

Table 1  
Spectroscopic constants of NO and NO<sup>+</sup> electronic states

State	$T_e$ (cm <sup>-1</sup> )	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$\omega_e y_e$ (cm <sup>-1</sup> )	$r_e$ (10 <sup>-8</sup> cm)	$D_0$ (cm <sup>-1</sup> )
NO <sup>+</sup> A <sup>1</sup> Π	148 193.12	1601.93	20.207		1.19310	21 319.34
NO <sup>+</sup> b <sup>1</sup> Σ <sup>-</sup>	142 441.4	1284.00	10.700		1.29000	27 143.06
NO <sup>+</sup> b <sup>3</sup> Π	133 961.4	1710.00	14.000		1.17500	35 623.06
NO <sup>+</sup> a <sup>3</sup> Σ <sup>+</sup>	126 911.4	1293.00	15.100		1.28400	35 240.56
NO <sup>+</sup> X <sup>1</sup> Σ <sup>+</sup>	74 721.4	2376.42	16.262		1.06322	87 430.56
NO F <sup>2</sup> Δ	61 800.00	2394.00	20.000		1.06700	
NO B <sup>1</sup> Δ	60 364.20	1217.40	15.610		1.30200	11 257.06
NO C <sup>2</sup> Π	52 126.00	2395.00	15.000		1.06200	
NO B <sup>2</sup> Π	45 913.60	1037.20	7.700	0.1000	1.41670	25 707.66
NO A <sup>2</sup> Σ <sup>+</sup>	43 965.70	2374.31	16.106	- 0.0465	1.06340	
NO X <sup>2</sup> Π	0.00	1904.20	14.075	0.0070	1.15077	52 393.26

Table 2  
Spectroscopic constants of O<sub>2</sub>, O<sub>2</sub><sup>+</sup> and O<sub>2</sub><sup>-</sup> electronic states

State	$T_e$ (cm <sup>-1</sup> )	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$\omega_e y_e$ (cm <sup>-1</sup> )	$r_e$ (10 <sup>-8</sup> cm)	$D_0$ (cm <sup>-1</sup> )
O <sub>2</sub> <sup>+</sup> b <sup>4</sup> Σ <sub>g</sub> <sup>-</sup>	146 556	1196.91	17.13		1.280	20 408
O <sub>2</sub> <sup>+</sup> A <sup>2</sup> Π <sub>u</sub>	137 435	898.17	13.57		1.408	13 662
O <sub>2</sub> <sup>+</sup> a <sup>4</sup> Π <sub>u</sub>	129 889	1035.53	10.32		1.382	21 208
O <sub>2</sub> <sup>+</sup> X <sup>2</sup> Π <sub>g</sub>	97 365	1905.13	16.28		1.117	53 732
O <sub>2</sub> B <sup>3</sup> Σ <sub>u</sub> <sup>-</sup>	49 358.1	709.06	10.61	- 0.0592	1.604	7770
O <sub>2</sub> A <sup>3</sup> Σ <sub>u</sub> <sup>+</sup>	35 007.1	799.08	12.16	- 0.5500	1.521	6253
O <sub>2</sub> b <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	13 120.9	1432.67	13.93	- 0.0143	1.227	28 139
O <sub>2</sub> a <sup>1</sup> Δ <sub>g</sub>	7882.4	1509.30	12.90		1.216	33 378
O <sub>2</sub> X <sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	0.0	1580.20	11.98	0.0475	1.207	41 260
O <sub>2</sub> <sup>-</sup> X <sup>2</sup> Π <sub>g</sub>	- 3550	1089	12.1		1.34	33 400.6

Table 3  
Spectroscopic constants of N<sub>2</sub> and N<sub>2</sub><sup>+</sup> electronic states

State	$T_e$ (cm <sup>-1</sup> )	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$\omega_e y_e$ (cm <sup>-1</sup> )	$r_e$ (10 <sup>-8</sup> cm)	$D_0$ (cm <sup>-1</sup> )
N <sub>2</sub> <sup>+</sup> C <sup>2</sup> Σ <sub>u</sub> <sup>+</sup>	190 209.5	2071.51	9.29	- 0.4333	1.263	24 954
N <sub>2</sub> <sup>+</sup> B <sup>2</sup> Σ <sub>u</sub> <sup>+</sup>	151 233.5	2419.84	23.19		1.078	44 708
N <sub>2</sub> <sup>+</sup> A <sup>2</sup> Π <sub>u</sub>	134 683.9	1903.53	15.01		1.174	61 256
N <sub>2</sub> <sup>+</sup> X <sup>2</sup> Σ <sub>g</sub> <sup>+</sup>	125 667.5	2207.00	16.10	- 0.0400	1.116	70 273
N <sub>2</sub> C <sup>3</sup> Π <sub>u</sub>	88 977.8	2047.18	28.45	2.0883	1.149	8960
N <sub>2</sub> B <sup>3</sup> Π <sub>g</sub>	59 306.8	1733.39	14.12	- 0.0569	1.213	38 631
N <sub>2</sub> A <sup>3</sup> Σ <sub>g</sub> <sup>+</sup>	49 754.8	1460.64	13.87	- 0.0103	1.287	28 959
N <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	0.0	2358.57	14.32	- 0.0023	1.098	78 714

In the most general case, WTCS have to be calculated as functions of four temperatures  $\theta_e$ ,  $\theta_g$ ,  $\theta_v$  and  $\theta_r$ , i.e. the electron kinetic, molecule kinetic, vibrational and rotational temperatures respectively. But, considering that in quasi-thermal air plasmas, owing to the fast energy transfer between the translational motion of the free electrons and the vibrational motion of the molecules,  $\theta_e$  and  $\theta_v$  are generally assumed to be similar [19–20]. In the same way, a very small number of heavy particle collisions are necessary to equilibrate the rotational levels with molecule kinetic temperature. Then, the hypothesis  $\theta_g = \theta_r$  is assumed to be valid.

In this case, WTCS for transition from electronic state  $T_1$  to state  $T_2$  is obtained summing all initial and final rovibrational levels:

$$Q_{T_1}^{T_2}(\varepsilon, \theta_e, \theta_g) = \sum_{v_1=0}^{v_L(T_1)} P(v_1, \theta_e) \sum_{J_1=0}^{J_L(v_1)} P(J_1, \theta_g) \int_0^\infty P(r) \sum_{v_2=0}^{v_L(T_2)} \sum_{J_2=0}^{J_L(v_2)} q_{T_1 v_1 J_1}^{T_2 v_2 J_2}(r, \varepsilon) dr. \quad (2)$$

The potential well shape allows us to define  $J_L(v)$ , the maximum value of the rotational quantum number of a given electrovibrational state  $|T_i, v\rangle$ . It is associated to the ultimate rotational level  $J$  whose potential energy curve  $U(T_i, v, J, r)$  exhibits a potential well. Similarly,  $v_L(T_i)$  is the maximum value of the vibrational quantum number  $v$  of an electronic state  $T_i$  for which the potential energy of the fundamental rotational state  $U(T_i, v, J=0, r)$  has a potential well.

$\varepsilon$  is the impinging electron kinetic energy;  $q_{T_1 v_1 J_1}^{T_2 v_2 J_2}(r, \varepsilon)$  is the elementary cross section for the studied inelastic collision corresponding to a transition from a stable rovibrational state of  $T_1$  to a stable rovibrational state of  $T_2$  (excitation or ionization processes) or to an unstable state of  $T_2 = T_1$  (dissociation).  $P(v_1, \theta_e)$  is the probability for the molecule to be in the vibrational state  $v_1$  of electronic state  $T_1$  at temperature  $\theta_e$  and  $P(J_1, \theta_g)$  is the probability for the molecule to be in the rotational state  $J_1$  of the state  $|T_1, v_1\rangle$  at temperature  $\theta_g$ .  $P(r)$  is the probability for the internuclear distance to be in the range  $r, r + dr$ ; we assume that this probability  $P(r)$  can be dealt within the approximation of the harmonic oscillator (HO) and then depends only on the value of the vibrational quantum number  $v_1$  [12, p 113]:

$$P(r) = P_{v_1}(r) = \frac{1}{2^{v_1} \cdot r_1!} \sqrt{\alpha/\pi} \exp[-\alpha(r - r_e)^2] H_{v_1}^2(\chi) \quad (3)$$

with  $\chi = \sqrt{\alpha}(r - r_e)$ ,  $\alpha = (2\pi/h)\sqrt{\mu k_0}$  and  $k_0 = (4\pi^2 c^2/N_a)\mu_a \omega_e^2$

$H_{v_1}$  is the Hermitian polynomial of the  $v_1$ th degree,  $h$  is Planck's constant,  $c$  is the speed of light,  $N_a$  is Avogadro's number,  $\mu_a$  is the reduced mass of the molecule (in atomic mass unit) and  $r_e$  is equilibrium internuclear distance.

The implied assumption of a parabolic potential rather than a Morse model for the estimation of  $P(r)$  is justified here, even for excited vibrational levels, because of the limitation upon  $r$  introduced in the summation (see Section 2.3.).

For an initial state  $|T_1, v_1, J_1\rangle$ , the product  $P(v_1, \theta_e)P(J_1, \theta_g)$  is given by

$$P(v_1, \theta_e)P(J_1, \theta_g) = \frac{1}{s(T_1, \theta_e, \theta_g)} \left[ (2J_1 + 1) \exp\left(-\frac{G(v_1)}{k\theta_e}\right) \exp\left(-\frac{F_{v_1}(J_1)}{k\theta_g}\right) \right] \quad (4)$$

where  $k$  is Boltzmann's constant;  $s(T_1, \theta_e, \theta_g)$  is the two-temperature partial partition function of electronic state  $T_1$  [21, 22]:  $s(T_1, \theta_e, \theta_g) = \theta_g/\theta_e s(T_1, \theta = \theta_e = \theta_g)$  with  $s(T_1, \theta = \theta_e = \theta_g)$  the monothermal partial partition function of electronic state  $T_1$ :

$$s(T_1, \theta = \theta_e = \theta_g) = \sum_{v_1=0}^{v_L(T_1)} \exp\left(-\frac{G(v_1)}{k\theta}\right) \sum_{J_1=0}^{J_L(v_1)} (2J_1 + 1) \exp\left(-\frac{F_{v_1}(J_1)}{k\theta}\right) \quad (5)$$

$G(v_1)$  and  $F_{v_1}(J_1)$  are the vibrational and rotational energy, respectively:

$$G(v_1) = (v_1 + \frac{1}{2})\omega_e - (v_1 + \frac{1}{2})^2 \omega_e x_e + (v_1 + \frac{1}{2})^3 \omega_e y_e, \quad (6)$$

$$F_{v_1}(J_1) = B_{v_1} J_1(J_1 + 1) - D_{v_1} J_1^2(J_1 + 1)^2 \quad (7)$$

with  $B_{v_1} = B_e - \alpha_e(v_1 + \frac{1}{2})$  and  $D_{v_1} = D_e + \beta_e(v_1 + \frac{1}{2})$ . In all cases (excitation, ionization or dissociation), the collisional transition from the  $|T_1, v_1, J_1\rangle$  state to the  $|T_2, v_2, J_2\rangle$  state will obey the Franck and Condon principle, that is with constant internuclear separation. This principle, valid for nearly instantaneous electronic collisions, cannot be applied in the case of heavy particle collisions (not studied in this paper) where the collision time may be sufficient to affect the momentum of nuclear skeleton.

### 2.1.1. Excitation and ionization

For this type of processes, the WTCS is finally written

$$\begin{aligned} Q_{T_1}^{T_2}(\varepsilon, \theta_e, \theta_g) &= \frac{1}{s(T_1, \theta_e, \theta_g)} \sum_{v_1=0}^{v_L(T_1)} \exp\left(-\frac{G(v_1)}{k\theta_e}\right) \sum_{J_1=0}^{J_L(v_1)} (2J_1 + 1) \exp\left(-\frac{F_{v_1}(J_1)}{k\theta_g}\right) \\ &\times \sum_{v_2=0}^{v_L(T_2)} \sum_{J_2=0}^{J_L(v_2)} \delta(J_2 - J_1 \pm 2) \int_0^\infty P(r) q_{T_1 v_1 J_1}^{T_2 v_2 J_2}(r, \varepsilon) dr. \end{aligned} \quad (8)$$

Kronecker's symbol  $\delta(J_2 - J_1 \pm 2)$  has been introduced in the WTCS expression in order to respect the selection rule  $J_2 = J_1 \pm 2$  established by Stein and Gerjuoy [23] into Born's approximation for collisional transitions between rotation levels. Elementary cross sections  $q_{T_1 v_1 J_1}^{T_2 v_2 J_2}(r, \varepsilon)$  are taken from Drawin [24]; different cases have to be considered (see Appendix).

### 2.1.2. Dissociation

The WTCS becomes

$$\begin{aligned} Q_{T_1}^D(\varepsilon, \theta_e, \theta_g) &= \frac{1}{s(T_1, \theta_e, \theta_g)} \sum_{v_1=0}^{v_L(T_1)} \exp\left(-\frac{G(v_1)}{k\theta_e}\right) \sum_{J_1=0}^{J_L(v_1)} (2J_1 + 1) \exp\left(-\frac{F_{v_1}(J_1)}{k\theta_g}\right) \\ &\times \int_0^\infty P(r) q_{T_1 v_1 J_1}^D(r, \varepsilon) dr. \end{aligned} \quad (9)$$

The elementary cross section  $q_{T_1 v_1 J_1}^D(r, \varepsilon)$  was, in this case, calculated (see Appendix) using Gryzinski's formulation [25] which seems to be more suitable for the treatment of transitions between stable and unstable molecular states.

## 2.2. Stability areas of electronic molecular states

### 2.2.1. Excitation and ionization

In their work, Bacri and Medani [3] limited the points of the  $U(r)$  plane corresponding to stable rovibrational levels of a given electronic state  $T_1$  by the three potential curves  $U(T_1, 0, 0, r)$ ,  $U(T_1, 0, J_L(0), r)$  and  $\Gamma(T_e, v = 0, r)$ .  $\Gamma(T_e, v, r)$  curves are obtained by interpolation from the points  $A_v^J$  ( $J$  varying from 0 to  $J_L(v)$ ). These points are the geometrical loci of the  $U(r)$  plane obtained for each  $J$  value and corresponding to the maxima of the function  $U(T_e, v, J, r)$  (cf. Fig. 1).

Excitation or ionization then represents a transition between an initial stable state  $|T_1, v_1, J_1, r\rangle$  and a final stable state  $|T_2, v_2, J_2, r\rangle$  of another electronic state.

For  $N_2$  and  $N_2^+$ , these assumptions give a relatively good agreement concerning the reaction thresholds and the maxima of the cross sections between calculated WTCS and experimental cross sections.

This method was then extended to  $O_2$  and NO molecules [10, 11]. As can be seen in Fig. 1, the previously defined stability areas could lead to undesirable dissociative excitation.

To rule out this problem, in this work we define stability areas for each electrorovibrational state  $|T_1, v, J\rangle$ . With this assumption, the lower limit of a stability area is now given by the potential energy curve  $U(T_1, v, J, r)$  and the upper limit by the horizontal asymptote passing through the  $A_v^J$  point (cf. Fig. 2).  $\Gamma(T_e, v, r)$  curves are now not necessary.

Let us consider that point D in Fig. 2 corresponds to the molecular internal energy after electron impact on  $O_2$  in its ground state. Bacri and Médani made the hypothesis that electron incident energy was transferred to the electronic cloud of the molecule, that is to say the final electronic state must be the one with the lowest rovibrational energy  $G(v) + F_v(J)$  (in Fig. 2, the final electronic state must be the b state of  $O_2$ ). In fact, this energy is only preferentially transferred to the electronic cloud of the molecule and can (with a smaller probability) contribute to populate any available electronic state. So, point D could belong to state  $O_2$  (b) or  $O_2$  (a) with the impossibility of distinguishing which state is actually preferentially formed.

Considering new stability area definitions, the initial state energy always has to be smaller than that of the final state during WTCS calculation.

### 2.2.2. Dissociation

The predissociation phenomenon, described in detail by Herzberg [12], is taken into account and allows a rotational predissociation area to be introduced for each electronic state. If a stable rotational level (with a potential well) of an electrovibrational state  $|T_1, v\rangle$  is located above the dissociation energy  $D_0$  of electronic state  $T_1$ , it can predissociate by rotation passing through another unstable rotational level of the same electronic state. As shown in Fig. 3, the stability area of an electrovibrorotational state  $|T_1, v, J\rangle$  will then be limited in its lower part by the potential energy curve of the state  $U(T_1, v, J, r)$  and its upper part by dissociation energy  $D_0$ .

With these assumptions, dissociation of electronic state  $T_1$  will occur if, from a stable level  $|T_1, v, J\rangle$  onwards, the incident electron energy is sufficient to leave the molecule in an unstable state located in the dissociation area; i.e. above the potential energy curve  $U(T_1, v = 0, J_L(v = 0), r)$  of the ultimate stable level of electronic state  $T_1$  (cf. Fig. 3). If the electron energy leaves the molecule in a stable state situated in rotational predissociation

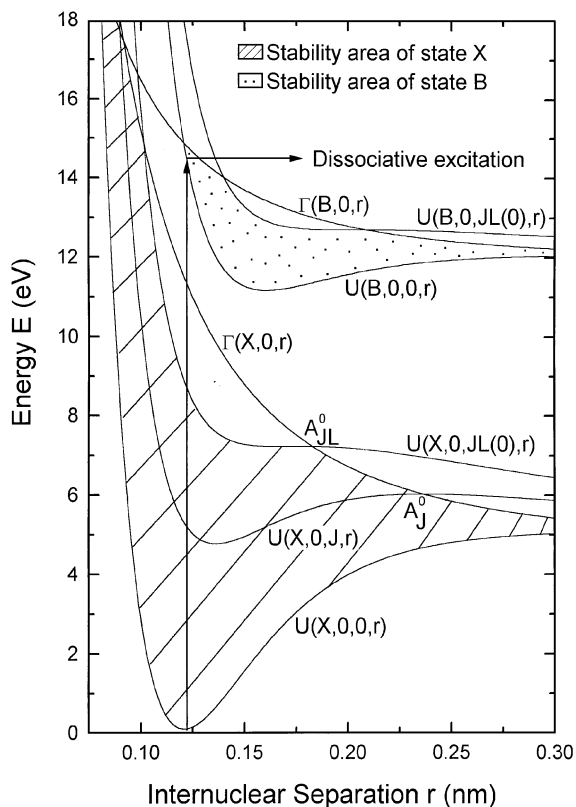


Fig. 1. Stability areas defined by Bacri and Médani [3] leading to undesirable dissociative excitation processes.

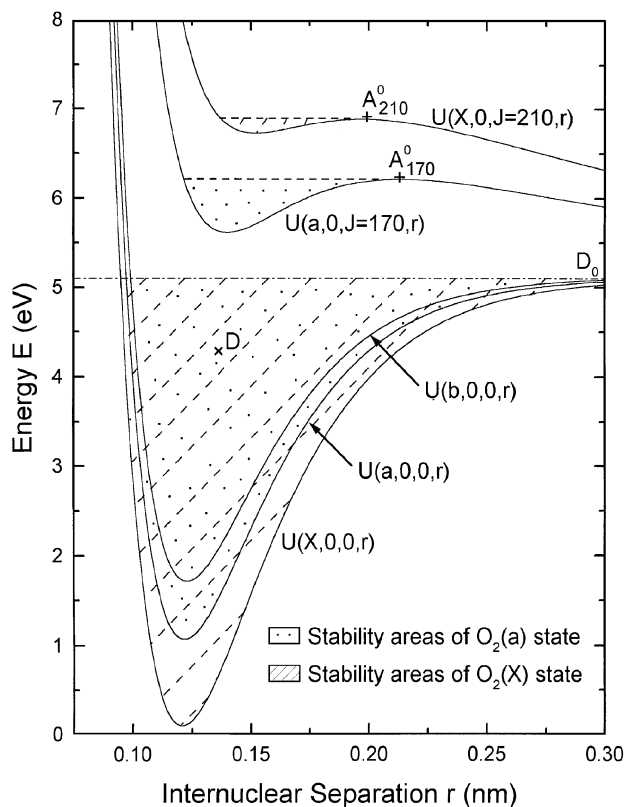


Fig. 2. Potential energy curves of  $O_2$  X, a and b states and new stability areas of  $O_2$  X and a states.

area, it could dissociate but through predissociation phenomenon which cannot be assimilated to dissociation.

Some electronic states of  $O_2$  and NO ( $O_2(B)$  for example) are also subject to electronic predissociation [12]. This phenomenon and other hypotheses concerning electron impact dissociation cross section and rate coefficient calculations for diatomic air molecules have been studied in detail in a previous paper [13].

### 2.3. Calculation assumptions

The simplifying hypotheses introduced by Bacri and Médani [3] are discussed:

- The limitation upon internuclear separations  $r$  taken into consideration during a collisional transition  $P_{v_1}(r) > 10^{-3} [P_{v_1}(r)]_{\text{Max}}$  is maintained. Physically, this assumption indicates the fact that the molecule has a high probability of having its internuclear distance located in an interval  $(r_{\text{min}}, r_{\text{max}})$  surrounding the bottom of the potential well. The fast decrease of  $P_{v_1}(r)$  outside this interval validates the assumption of the harmonic oscillator used in the calculation.

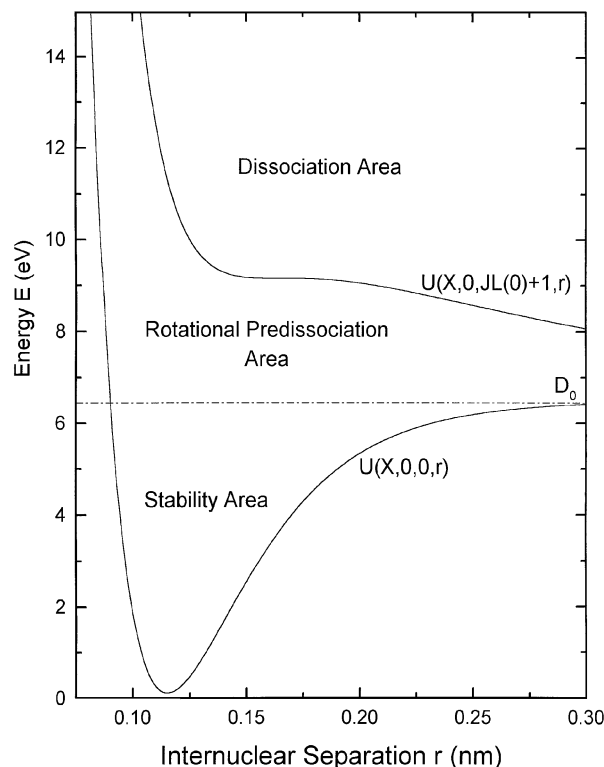


Fig. 3. Stability, rotational predissociation and dissociation areas of state NO(X).

- The restrictive condition upon vibrational and rotational level  $v_1$  and  $J_1$  for WTCS calculation  $P(v_1, \theta_e)P(J_1, \theta_g) > 10^{-3}[P(v_1, \theta_e)P(J_1, \theta_g)]_{\text{Max}}$  is suppressed. This hypothesis, required by Bacri and Médani's definitions of the stability areas, led to the highest rovibrational levels being ignored. However, even if they are less populated than lower ones, they dictate the threshold reaction value and thus the reaction rate coefficient.

#### 2.4. Determination of normalisation coefficients $\alpha_{g_1 g_2}$

Room temperature excitation and ionization cross sections have been calculated for transitions between the main electronic states of  $\text{N}_2$ ,  $\text{O}_2$ , NO or corresponding positive ions. Maximal values of these cross sections, calculated with  $\alpha_{g_1 g_2} = 1$ , were compared with available experimental results to determine the  $\alpha_{g_1 g_2}$  coefficients.

For the transitions studied in the literature, the assumed  $\alpha_{g_1 g_2}$  coefficients are the average of the deduced coefficients for each  $g_1 \rightarrow g_2$  transition.

When experimental data did not exist,  $\alpha_{g_1 g_2}$  coefficients were assumed to be identical when

*Hypothesis 1:* The transitions occur without change of spin multiplicity:  $\Delta S = 0$  ( $g_1 = g_2$ ).



*Hypothesis 2:* The transitions are such that the final states have the same spin multiplicity ( $\alpha_{g_3g_2} = \alpha_{g_1g_2}$ ).

The normalization coefficients of nitrogen, oxygen and nitric oxide are summarized in Tables 4–6, respectively.

Electron impact excitation and ionization of molecular electronic states for diatomic air molecules have been poorly studied (especially concerning nitric oxide). The assumed normalization coefficients are then questionable. They will have to be modified if new experimental cross sections are published in the future.

Table 4

Normalisation coefficients for excitation and ionization processes of  $N_2$  and  $N_2^+$

Type of transition	Transitions	References	Calculated $\alpha_{g_1g_2}$	Used $\alpha_{g_1g_2}$
Singlet–triplet	$N_2(X^1\Sigma_g^+) \rightarrow N_2(A^3\Sigma_u^+)$ $\rightarrow N_2(B^3\Pi_g)$ $\rightarrow N_2(C^3\Pi_u)$	[26–31] [26–28, 30–34] [27–28, 30–38]	$10^{-2}$ $8 \times 10^{-3}$ $4 \times 10^{-2}$	$\alpha_{13} = 2 \times 10^{-2}$
Triplet—triplet	$N_2(A^3\Sigma_u^+) \rightarrow N_2(B^3\Pi_g)$ $\rightarrow N_2(C^3\Pi_u)$ $N_2(B^3\Pi_g) \rightarrow N_2(C^3\Pi_u)$	— — —	Hypothesis 1: $\alpha_{33} = \alpha_{22}$	$\alpha_{33} = 6 \times 10^{-1}$
Doublet–doublet	$N_2^+(X^2\Sigma_g^+) \rightarrow N_2^+(A^2\Pi_u)$ $\rightarrow N_2^+(B^2\Sigma_u^+)$ $\rightarrow N_2^+(C^2\Sigma_u^+)$ $N_2^+(A^2\Pi_u) \rightarrow N_2^+(B^2\Sigma_u^+)$ $\rightarrow N_2^+(C^2\Sigma_u^+)$ $N_2^+(B^2\Sigma_u^+) \rightarrow N_2^+(C^2\Sigma_u^+)$	— [39–40] — — — —	— $6 \times 10^{-1}$ (a) — — — —	$\alpha_{22} = 6 \times 10^{-1}$
Singlet–doublet	$N_2(X^1\Sigma_g^+) \rightarrow N_2^+(X^2\Sigma_g^+)$ $\rightarrow N_2^+(A^2\Pi_u)$  $\rightarrow N_2^+(B^2\Sigma_u^+)$ $\rightarrow N_2^+(C^2\Sigma_u^+)$	[41–44] [33–34, 41, 43, 45–46] [33–34, 43–47] —	$2 \times 10^{-2}$ $10^{-2}$ $2 \times 10^{-2}$ —	$\alpha_{12} = 10^{-2}$
Triplet–doublet	$N_2(A^3\Sigma_u^+) \rightarrow N_2^+(X^2\Sigma_g^+)$ $\rightarrow N_2^+(A^2\Pi_u)$ $\rightarrow N_2^+(B^2\Sigma_u^+)$ $\rightarrow N_2^+(C^2\Sigma_u^+)$ $N_2^+(X^2\Sigma_g^+)$ $N_2^+(B^3\Pi_g) \rightarrow N_2^+(A^2\Pi_u)$ $\rightarrow$ $N_2(C^3\Pi_u) \rightarrow N_2^+(B^2\Sigma_u^+)$ $N_2^+(C^2\Sigma_u^+)$	— [42, 48–49] (b) — — — — — —	Hypothesis 2: $\alpha_{32} = \alpha_{12}$	$\alpha_{32} = 10^{-2}$

<sup>a</sup>For  $N_2^+$  excitation reactions, the only available data in the literature [39, 40] are for  $N_2^+(X, v=0) + e^- \rightarrow N_2^+(B, v=0) + e^-$

<sup>b</sup>Concerning the ionization process  $N_2(A) + e^- \rightarrow N_2^+(A) + 2e^-$ , both theoretical [48, 49] and experimental [42] studies have been reported. The authors agree to say that they do not know the initial vibrational states of  $N_2(A)$ . It is therefore impossible to determine the coefficients  $\alpha_{32}$  with certainty.

Table 5

Normalisation coefficients for excitation and ionization processes for O<sub>2</sub> and O<sub>2</sub><sup>+</sup>

Type of transition	Transitions	References	Calculated $\alpha_{g_1g_2}$	Used $\alpha_{g_1g_2}$
Triplet–singlet	O <sub>2</sub> (X <sup>3</sup> Σ <sub>g</sub> ) → O <sub>2</sub> (a <sup>1</sup> Δ <sub>g</sub> ) → O <sub>2</sub> (b <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	[50–57] [50–57]	$2 \times 10^{-3}$ $5 \times 10^{-4}$	$\alpha_{31} = 10^{-3}$
Triplet–triplet	O <sub>2</sub> (X <sup>3</sup> Σ <sub>g</sub> ) → O <sub>2</sub> (A <sup>3</sup> Σ <sub>u</sub> <sup>+</sup> ) → O <sub>2</sub> (B <sup>3</sup> Σ <sub>u</sub> <sup>−</sup> ) O <sub>2</sub> (A <sup>3</sup> Σ <sub>u</sub> <sup>+</sup> ) → O <sub>2</sub> (B <sup>3</sup> Σ <sub>u</sub> <sup>−</sup> )	[41, 51, 56, 59] [41–58] —	<sup>b</sup> $10^{-3a}$ —	$\alpha_{33} = 10^{-3}$
Singlet–singlet	O <sub>2</sub> (a <sup>1</sup> Δ <sub>g</sub> ) → O <sub>2</sub> (b <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	[60]	$6 \times 10^{-3}$	$\alpha_{11} = 6 \times 10^{-3}$
Singlet–triplet	O <sub>2</sub> (a <sup>1</sup> Δ <sub>g</sub> ), O <sub>2</sub> (b <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> ) → O <sub>2</sub> (A <sup>3</sup> Σ <sub>u</sub> <sup>+</sup> ), O <sub>2</sub> (B <sup>3</sup> Σ <sub>u</sub> <sup>−</sup> )	—	Hypothesis 2 $\alpha_{13} = \alpha_{33}^c$	$\alpha_{13} = 10^{-3}$
Triplet–doublet	O <sub>2</sub> (X <sup>3</sup> Σ <sub>g</sub> <sup>−</sup> ) → O <sub>2</sub> <sup>+</sup> (X <sup>2</sup> Π <sub>g</sub> ) → O <sub>2</sub> <sup>+</sup> (A <sup>2</sup> Π <sub>u</sub> ) O <sub>2</sub> (A <sup>3</sup> Σ <sub>u</sub> <sup>+</sup> ), O <sub>2</sub> (B <sup>3</sup> Σ <sub>u</sub> <sup>−</sup> ) → O <sub>2</sub> <sup>+</sup> (X <sup>2</sup> Π <sub>g</sub> ), O <sub>2</sub> <sup>+</sup> (A <sup>2</sup> Π <sub>u</sub> )	[41, 51, 56, 64] [41, 56, 61, 62, 64] —	$10^{-2}$ $9 \times 10^{-3}$ —	$\alpha_{32} = 10^{-2}$
Triplet–quadruplet	O <sub>2</sub> (X <sup>3</sup> Σ <sub>g</sub> <sup>−</sup> ) → O <sub>2</sub> <sup>+</sup> (a <sup>4</sup> Π <sub>u</sub> ) → O <sub>2</sub> <sup>+</sup> (b <sup>4</sup> Σ <sub>g</sub> <sup>−</sup> ) O <sub>2</sub> (A <sup>3</sup> Σ <sub>u</sub> <sup>+</sup> ), O <sub>2</sub> (B <sup>3</sup> Σ <sub>u</sub> <sup>−</sup> ) → O <sub>2</sub> <sup>+</sup> (a <sup>4</sup> Π <sub>u</sub> ), O <sub>2</sub> <sup>+</sup> (b <sup>4</sup> Σ <sub>g</sub> <sup>−</sup> )	[41, 56, 64] [41, 56, 61–64] —	$2 \times 10^{-2}$ $7 \times 10^{-3}$ —	$\alpha_{34} = 10^{-2}$
Singlet–doublet	O <sub>2</sub> (a <sup>1</sup> Δ <sub>g</sub> ), O <sub>2</sub> (b <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> ) → O <sub>2</sub> <sup>+</sup> (X <sup>2</sup> Π <sub>g</sub> ), O <sub>2</sub> <sup>+</sup> (A <sup>2</sup> Π <sub>u</sub> )	—	Hypothesis 2 $\alpha_{12} = \alpha_{32}$	$\alpha_{12} = 10^{-2}$
Singlet–quadruplet	O <sub>2</sub> (a <sup>1</sup> Δ <sub>g</sub> ), O <sub>2</sub> (b <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> ) → O <sub>2</sub> <sup>+</sup> (a <sup>4</sup> Π <sub>u</sub> ), O <sub>2</sub> <sup>+</sup> (b <sup>4</sup> Σ <sub>g</sub> <sup>−</sup> )	—	Hypothesis 2 $\alpha_{14} = \alpha_{34}$	$\alpha_{14} = 10^{-2}$
Doublet–doublet	O <sub>2</sub> <sup>+</sup> (X <sup>2</sup> Π <sub>g</sub> ) → O <sub>2</sub> <sup>+</sup> (A <sup>2</sup> Π <sub>u</sub> )	—	Hypothesis 1 $\alpha_{22} = \alpha_{33}^d$	$\alpha_{22} = 10^{-3}$
Quadruplet–quadruplet	O <sub>2</sub> <sup>+</sup> (a <sup>4</sup> Π <sub>u</sub> ) → O <sub>2</sub> <sup>+</sup> (b <sup>4</sup> Σ <sub>g</sub> <sup>−</sup> )	—	Hypothesis 1 $\alpha_{44} = \alpha_{11}^e$	$\alpha_{44} = 6 \times 10^{-3}$
Doublet–quadruplet	O <sub>2</sub> <sup>+</sup> (X <sup>2</sup> Π <sub>g</sub> ) → O <sub>2</sub> <sup>+</sup> (a <sup>4</sup> Π <sub>u</sub> ) → O <sub>2</sub> <sup>+</sup> (b <sup>4</sup> Σ <sub>g</sub> <sup>−</sup> ) O <sub>2</sub> <sup>+</sup> (A <sup>2</sup> Π <sub>u</sub> ) → O <sub>2</sub> <sup>+</sup> (b <sup>4</sup> Σ <sub>g</sub> <sup>−</sup> )	— — —	Hypothesis 2 $\alpha_{24} = \alpha_{34}$	$\alpha_{24} = 10^{-2}$
Quadruplet–doublet	O <sub>2</sub> <sup>+</sup> (a <sup>4</sup> Π <sub>u</sub> ) → O <sub>2</sub> <sup>+</sup> (A <sup>2</sup> Π <sub>u</sub> )	—	Hypothesis 2 $\alpha_{42} = \alpha_{32}$	$\alpha_{42} = 10^{-2}$

<sup>a</sup>As shown by Ali [41] and Garrett et al. [58], the total cross section at 300 K for the excitation process O<sub>2</sub>(X) + e<sup>−</sup> → O<sub>2</sub>(B) + e<sup>−</sup> partly corresponds to dissociative excitation. So, cross sections given by Garrett et al. [58] for the three following effective excitation processes: O<sub>2</sub>(X, *v* = 0, 1, 2) + e<sup>−</sup> → O<sub>2</sub>(B) + e<sup>−</sup> have been used to establish the normalisation coefficient.

<sup>b</sup>The X → A transition has also been studied [41, 51, 56, 59]. However, the cross sections given by these authors seem to be overestimated because, as shown by Ali [41], in the energy area around 4.5 eV, there is not only the A state but also the C and c states [14, 15]: the measured cross section is in fact the total excitation cross section of the A, C and c states together. So, it is not advisable to deduce the coefficient  $\alpha_{33}$  from these works.

<sup>c</sup>Unlike in Gomes et al. [10] and following Hypothesis 2, the assumption  $\alpha_{13} = \alpha_{33}$  was preferred to  $\alpha_{13} = \alpha_{31}$ .

<sup>d</sup> $\alpha_{22} = \alpha_{33}$  because, in these two cases, transitions are without change in spin multiplicity from a fundamental molecular electronic state onwards.

<sup>e</sup> $\alpha_{44} = \alpha_{11}$  because these are transitions without change in spin multiplicity between excited electronic states.

Table 6

Normalisation coefficients for excitation and ionization processes for NO and NO<sup>+</sup>

Type of transition	Transitions	References	Calculated $\alpha_{g_1 g_2}$	Used $\alpha_{g_1 g_2}$
Doublet–Doublet	NO X <sup>2</sup> Π → NO A <sup>2</sup> Σ <sup>+</sup>	[32, 65–67, 69]	$4 \times 10^{-3}$	$\alpha_{22} = 2 \times 10^{-3}$
	→ NO B <sup>2</sup> Π	[32]	$5 \times 10^{-5}$	
	→ NO C <sup>2</sup> Π	—	—	
	→ NO B' <sup>2</sup> Δ	[32, 67–68]	$10^{-4}$	
	→ NO F <sup>2</sup> Δ	[32]	$10^{-4}$	
	NO A <sup>2</sup> Σ <sup>+</sup> → NO B <sup>2</sup> Π, NO C <sup>2</sup> Π, NO B' <sup>2</sup> Δ, NO F <sup>2</sup> Δ	—	—	
	NO B <sup>2</sup> Π → NO C <sup>2</sup> Π, NO B' <sup>2</sup> Δ, NO F' <sup>2</sup> Δ	—	—	
	NO C <sup>2</sup> Π → NO B' <sup>2</sup> Δ	—	—	
	→ NO F <sup>2</sup> Δ	—	—	
	NO B' <sup>2</sup> Δ → NO F <sup>2</sup> Δ	—	—	
Doublet–singlet	NO X <sup>2</sup> Π → NO <sup>+</sup> X <sup>1</sup> Σ <sup>+</sup>	—	—	$\alpha_{21} = 9 \times 10^{-3}$
	→ NO <sup>+</sup> A <sup>1</sup> Π	[68, 70]	$9 \times 10^{-3}$	
	NO A <sup>2</sup> Σ <sup>+</sup> , NO B <sup>2</sup> Π, NO C <sup>2</sup> Π, NO B' <sup>2</sup> Δ, NO F <sup>2</sup> Δ → NO <sup>+</sup> X <sup>1</sup> Σ <sup>+</sup> , NO <sup>+</sup> A <sup>1</sup> Π	—	—	
Doublet–triplet	NO X <sup>2</sup> Π, NO A <sup>2</sup> Σ <sup>+</sup> , NO B <sup>2</sup> Π, NO C <sup>2</sup> Π, NO B' <sup>2</sup> Δ, NO F <sup>2</sup> Δ → NO <sup>+</sup> a <sup>3</sup> Σ <sup>+</sup> , NO <sup>+</sup> b <sup>3</sup> Π, NO <sup>+</sup> b' <sup>3</sup> Σ <sup>−</sup>	—	<sup>a</sup>	$\alpha_{23} = 2 \times 10^{-2}$
Singlet–singlet	NO <sup>+</sup> X <sup>1</sup> Σ <sup>+</sup> → NO <sup>+</sup> A <sup>1</sup> Π	—	Hypothesis 1 $\alpha_{11} = \alpha_{22}$	$\alpha_{11} = 2 \times 10^{-3}$
Triplet–triplet	NO <sup>+</sup> a <sup>3</sup> Σ <sup>+</sup> → NO <sup>+</sup> b <sup>3</sup> Π	—	Hypothesis 1	$\alpha_{33} = 2 \times 10^{-3}$
	→ NO <sup>+</sup> b' <sup>3</sup> Σ <sup>−</sup>	—	$\alpha_{33} = \alpha_{22}$	
Singlet–triplet	NO <sup>+</sup> b <sup>3</sup> Π → NO <sup>+</sup> b' <sup>3</sup> Σ <sup>−</sup>	—		
	NO <sup>+</sup> X <sup>1</sup> Σ <sup>+</sup> → NO <sup>+</sup> a <sup>3</sup> Σ <sup>+</sup> , NO <sup>+</sup> b <sup>3</sup> Π, NO <sup>+</sup> b' <sup>3</sup> Σ <sup>−</sup>	—	Hypothesis 2 $\alpha_{13} = \alpha_{23}$	$\alpha_{13} = 2 \times 10^{-2}$
Triplet–singlet	NO <sup>+</sup> a <sup>3</sup> Σ <sup>+</sup> , NO <sup>+</sup> b <sup>3</sup> Π, NO <sup>+</sup> b' <sup>3</sup> Σ <sup>−</sup> → NO <sup>+</sup> A <sup>1</sup> Π	—	Hypothesis 2 $\alpha_{31} = \alpha_{21}$	$\alpha_{31} = 9 \times 10^{-3}$

<sup>a</sup>Using a technique developed by Sarrette [71] and from the total ionization cross section of Kim et al. [72], it was possible to calculate the coefficient  $\alpha_{23} = 2 \times 10^{-2}$  for doublet–triplet ionization processes.

## 2.5. Reaction rate coefficient calculation

If the energy distribution function of the electrons is assumed to be Maxwellian, the two-temperature ( $\theta_e$  and  $\theta_g$ ) reaction rate coefficient is written as

$$K_{T_1}^{T_2}(\theta_e, \theta_g) = 2 \left( \frac{2}{\pi m_e} \right)^{0.5} (k\theta_e)^{-1.5} \int_0^\infty \varepsilon Q_{T_1}^{T_2}(\varepsilon, \theta_e, \theta_g) \exp\left(-\frac{\varepsilon}{k\theta_e}\right) d\varepsilon \quad (10)$$

where  $m_e$  is the mass of the electron. One-temperature reaction rates are obtained with the assumption  $\theta_e = \theta_g = \theta$ . That is to say that the one-temperature WTCS,  $Q_{T_1}^{T_2}(\varepsilon, \theta)$ , has to be used to calculate the reaction rate coefficients.

3. Results

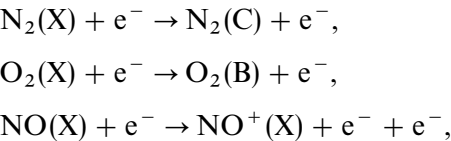
3.1. One-temperature reaction rate coefficients

For the electronic states of the diatomic air molecules considered ( $O_2$ ,  $N_2$ ,  $NO$ ,  $O_2^+$ ,  $N_2^+$  and  $NO^+$ ), the reaction rate coefficients for electron impact excitation, ionization and dissociation were fitted in the Arrhenius form ( $K(\text{cm}^3 \text{s}^{-1}) = a\theta^b \exp(-c/\theta)$  with  $\theta$  in Kelvin).

The fitting coefficients  $a$ ,  $b$  and  $c$  of electron impact dissociation are given in Table 7. They are summarized in Tables 8–10 for excitation processes of nitric oxide, oxygen and nitrogen, respectively, and in Tables 11–13 for ionization of  $NO$ ,  $O_2$  and  $N_2$ , respectively.

3.2. Two-temperature ( $\theta_e$  and  $\theta_g$ ) reaction rate coefficients

These rate coefficients were calculated with  $\theta_e$  and  $\theta_g$  in the range 2000–14 000 K. It was impossible to show here all our two-temperature results concerning diatomic air molecules. The rate coefficients for the three following processes



are presented as examples in Tables 14–16, respectively. Other two-temperature rate coefficients may be obtained from the authors upon request.

Table 7  
Fittings of the dissociation rate coefficients in the Arrhenius form:  $K_{T_1}(\theta)$  ( $\text{cm}^3 \text{s}^{-1}$ ) =  $a\theta^b \exp(-c/\theta)$  with  $\theta$  in Kelvin

State	<i>a</i>	<i>b</i>	<i>c</i> (K)	State	<i>a</i>	<i>b</i>	<i>c</i> (K)	State	<i>a</i>	<i>b</i>	<i>c</i> (K)
O <sub>2</sub> X	5.76 × 10 <sup>−22</sup>	3.52	59 369.8	N <sub>2</sub> X	4.11 × 10 <sup>−33</sup>	6.16	113 263.0	NOX	1.74 × 10 <sup>−26</sup>	4.52	75 389.6
O <sub>2</sub> a	9.42 × 10 <sup>−21</sup>	3.17	48 028.2	N <sub>2</sub> A	6.61 × 10 <sup>−20</sup>	2.98	41 669.6	NOB	3.56 × 10 <sup>−15</sup>	1.90	36 991.2
O <sub>2</sub> b	2.94 × 10 <sup>−19</sup>	2.81	40 561.7	N <sub>2</sub> B	4.50 × 10 <sup>−23</sup>	3.73	55 586.8	NOB′	2.33 × 10 <sup>−15</sup>	1.95	16 198.0
O <sub>2</sub> A	3.49 × 10 <sup>−13</sup>	1.49	8997.6	N <sub>2</sub> C	5.14 × 10 <sup>−21</sup>	3.27	12 892.7	NO <sup>+</sup> X	8.02 × 10 <sup>−33</sup>	6.16	125 805.4
O <sub>2</sub> B	2.30 × 10 <sup>−13</sup>	1.54	11 180.4	N <sub>2</sub> <sup>+</sup> X	8.02 × 10 <sup>−31</sup>	5.54	101 117.1	NO <sup>+</sup> a	4.11 × 10 <sup>−16</sup>	2.07	50 708.3
O <sub>2</sub> <sup>+</sup> X	1.98 × 10 <sup>−26</sup>	4.50	77 315.9	N <sub>2</sub> <sup>+</sup> A	8.27 × 10 <sup>−26</sup>	4.38	88 142.4	NO <sup>+</sup> b	3.24 × 10 <sup>−23</sup>	3.70	51 258.7
O <sub>2</sub> <sup>+</sup> a	2.90 × 10 <sup>−15</sup>	1.88	30 516.6	N <sub>2</sub> <sup>+</sup> B	2.58 × 10 <sup>−32</sup>	5.81	64 328.3	NO <sup>+</sup> b′	8.36 × 10 <sup>−18</sup>	2.46	39 056.6
O <sub>2</sub> <sup>+</sup> A	7.25 × 10 <sup>−13</sup>	1.35	19 658.5	N <sub>2</sub> <sup>+</sup> C	1.31 × 10 <sup>−28</sup>	4.93	35 906.8	NO <sup>+</sup> A	1.84 × 10 <sup>−20</sup>	3.05	30 780.4
O <sub>2</sub> <sup>+</sup> b	8.12 × 10 <sup>−16</sup>	2.02	29 365.4								
O <sub>2</sub> <sup>+</sup> X	2.40 × 10 <sup>−09</sup>	0.49	48 060.7								

Table 8

Fittings of NO and NO<sup>+</sup> excitation rate coefficients in the Arrhenius form:  $K_{T_1}^{T_2}(\theta)$  (cm<sup>3</sup> s<sup>-1</sup>) =  $a\theta^b \exp(-c/\theta)$  with  $\theta$  in Kelvin

Transition	<i>a</i>	<i>b</i>	<i>c</i> (K)	Transition	<i>a</i>	<i>b</i>	<i>c</i> (K)
NO X → NO A	$2.75 \times 10^{-12}$	0.51	53 387.3	NO C → NO F	$1.03 \times 10^{-04}$	- 1.53	18 319.0
NO X → NO B	$3.17 \times 10^{-11}$	0.36	58 124.2	NO B' → NO F	$7.15 \times 10^{-09}$	- 0.87	6407.6
NO X → NO C	$1.03 \times 10^{-10}$	0.09	66 320.9	NO <sup>+</sup> X → NO <sup>+</sup> a	$5.28 \times 10^{-13}$	1.13	56 955.3
NO X → NO B'	$5.64 \times 10^{-07}$	- 0.68	83 492.5	NO <sup>+</sup> X → NO <sup>+</sup> b	$6.49 \times 10^{-10}$	0.44	73 869.9
NO X → NO F	$7.30 \times 10^{-08}$	- 0.70	83 624.4	NO <sup>+</sup> X → NO <sup>+</sup> b'	$1.36 \times 10^{-09}$	0.35	81 359.4
NO A → NO B	$4.79 \times 10^{-08}$	- 0.62	18 838.5	NO <sup>+</sup> X → NO <sup>+</sup> A	$1.85 \times 10^{-10}$	0.37	94 519.6
NO A → NO C	$2.72 \times 10^{-07}$	- 0.80	15 549.8	NO <sup>+</sup> a → NO <sup>+</sup> b	$7.36 \times 10^{-15}$	1.11	7562.3
NO A → NO B'	$1.06 \times 10^{-05}$	- 1.29	26 096.9	NO <sup>+</sup> a → NO <sup>+</sup> b'	$7.79 \times 10^{-09}$	- 0.23	25 194.8
NO A → NO F	$3.03 \times 10^{-04}$	- 1.59	30 403.1	NO <sup>+</sup> a → NO <sup>+</sup> A	$7.89 \times 10^{-08}$	- 0.41	28 865.2
NO B → NO C	$6.61 \times 10^{-09}$	- 0.65	13 462.9	NO <sup>+</sup> b → NO <sup>+</sup> b'	$2.07 \times 10^{-12}$	0.52	11 384.3
NO B → NO B'	$1.43 \times 10^{-08}$	- 0.44	19 067.4	NO <sup>+</sup> b → NO <sup>+</sup> A	$6.21 \times 10^{-06}$	- 0.91	23 615.8
NO B → NO F	$1.87 \times 10^{-07}$	- 1.20	16 318.8	NO <sup>+</sup> b' → NO <sup>+</sup> A	$3.92 \times 10^{-08}$	- 0.47	11 053.1
NO C → NO B'	$6.29 \times 10^{-05}$	- 1.58	18 650.4				

Table 9

Fittings of O<sub>2</sub> and O<sub>2</sub><sup>+</sup> excitation rate coefficients in the Arrhenius form:  $K_{T_1}^{T_2}(\theta)$  (cm<sup>3</sup> s<sup>-1</sup>) =  $a\theta^b \exp(-c/\theta)$  with  $\theta$  in Kelvin

Transition	<i>a</i>	<i>b</i>	<i>c</i> (K)	Transition	<i>a</i>	<i>b</i>	<i>c</i> (K)
O <sub>2</sub> X → O <sub>2</sub> a	$6.20 \times 10^{-10}$	- 0.12	12 498.7	O <sub>2</sub> b → O <sub>2</sub> B	$3.42 \times 10^{-02}$	- 2.09	54 845.7
O <sub>2</sub> X → O <sub>2</sub> b	$4.68 \times 10^{-08}$	- 0.52	20 884.1	O <sub>2</sub> A → O <sub>2</sub> B	$1.15 \times 10^{-10}$	0.03	21 366.3
O <sub>2</sub> X → O <sub>2</sub> A	$1.64 \times 10^{-03}$	- 1.70	48 941.0	O <sub>2</sub> <sup>+</sup> X → O <sub>2</sub> <sup>+</sup> a	$6.97 \times 10^{-09}$	- 0.15	40 020.0
O <sub>2</sub> X → O <sub>2</sub> B	$6.03 \times 10^{-04}$	- 1.51	70 974.3	O <sub>2</sub> <sup>+</sup> X → O <sub>2</sub> <sup>+</sup> A	$9.72 \times 10^{-08}$	- 0.61	52 156.6
O <sub>2</sub> a → O <sub>2</sub> b	$1.77 \times 10^{-10}$	0.18	9063.7	O <sub>2</sub> <sup>+</sup> X → O <sub>2</sub> <sup>+</sup> b	$2.51 \times 10^{-07}$	- 0.40	65 443.1
O <sub>2</sub> a → O <sub>2</sub> A	$1.33 \times 10^{-01}$	- 2.36	39 700.1	O <sub>2</sub> <sup>+</sup> a → O <sub>2</sub> <sup>+</sup> A	$1.20 \times 10^{-03}$	- 1.53	15 253.9
O <sub>2</sub> a → O <sub>2</sub> B	$4.34 \times 10^{-02}$	- 2.09	61 778.8	O <sub>2</sub> <sup>+</sup> a → O <sub>2</sub> <sup>+</sup> b	$1.34 \times 10^{-11}$	0.49	20 323.6
O <sub>2</sub> b → O <sub>2</sub> A	$1.17 \times 10^{-01}$	- 2.39	33 034.0	O <sub>2</sub> <sup>+</sup> A → O <sub>2</sub> <sup>+</sup> b	$1.31 \times 10^{-11}$	0.44	10 571.9

Table 10

Fittings of N<sub>2</sub> and N<sub>2</sub><sup>+</sup> excitation rate coefficients in the Arrhenius form:  $K_{T_1}^{T_2}(\theta)$  (cm<sup>3</sup> s<sup>-1</sup>) =  $a\theta^b \exp(-c/\theta)$  with  $\theta$  in Kelvin

Transition	<i>a</i>	<i>b</i>	<i>c</i> (K)	Transition	<i>a</i>	<i>b</i>	<i>c</i> (K)
N <sub>2</sub> X → N <sub>2</sub> A	$5.48 \times 10^{-11}$	0.55	57 700.3	N <sub>2</sub> <sup>+</sup> X → N <sub>2</sub> A	$8.70 \times 10^{-14}$	1.46	8750.3
N <sub>2</sub> X → N <sub>2</sub> B	$1.89 \times 10^{-10}$	0.50	75 287.5	N <sub>2</sub> <sup>+</sup> X → N <sub>2</sub> <sup>+</sup> B	$1.52 \times 10^{-10}$	0.75	33 501.1
N <sub>2</sub> X → N <sub>2</sub> C	$8.86 \times 10^{-04}$	- 1.13	124 965.8	N <sub>2</sub> <sup>+</sup> X → N <sub>2</sub> <sup>+</sup> C	$6.58 \times 10^{-09}$	0.41	85 038.3
N <sub>2</sub> A → N <sub>2</sub> B	$6.47 \times 10^{-13}$	1.25	9229.0	N <sub>2</sub> <sup>+</sup> A → N <sub>2</sub> <sup>+</sup> B	$2.35 \times 10^{-15}$	1.80	11 953.0
N <sub>2</sub> A → N <sub>2</sub> C	$2.85 \times 10^{-09}$	0.28	46 655.0	N <sub>2</sub> <sup>+</sup> A → N <sub>2</sub> <sup>+</sup> C	$1.32 \times 10^{-07}$	0.11	78 403.3
N <sub>2</sub> B → N <sub>2</sub> C	$1.15 \times 10^{-03}$	- 0.99	44 385.4	N <sub>2</sub> <sup>+</sup> B → N <sub>2</sub> <sup>+</sup> C	$3.86 \times 10^{-09}$	0.34	49 622.8

Table 11

Fittings of NO ionization rate coefficients in the Arrhenius form:  $K_{T_1}^{T_2}(\theta)$  ( $\text{cm}^3 \text{s}^{-1}$ ) =  $a\theta^b \exp(-c/\theta)$  with  $\theta$  in Kelvin

Transition	<i>a</i>	<i>b</i>	<i>c</i> (K)	Transition	<i>a</i>	<i>b</i>	<i>c</i> (K)
NO X → NO <sup>+</sup> X	$4.49 \times 10^{-14}$	1.13	95 091.7	NO C → NO <sup>+</sup> X	$4.13 \times 10^{-07}$	− 0.35	34 906.4
NO X → NO <sup>+</sup> a	$8.76 \times 10^{-13}$	0.92	176 367.4	NO C → NO <sup>+</sup> a	$1.03 \times 10^{-14}$	1.23	102 939.0
NO X → NO <sup>+</sup> b	$1.94 \times 10^{-11}$	0.57	193 172.9	NO C → NO <sup>+</sup> b	$1.04 \times 10^{-12}$	0.74	112 953.6
NO X → NO <sup>+</sup> b'	$6.17 \times 10^{-12}$	0.67	199 142.3	NO C → NO <sup>+</sup> b'	$9.33 \times 10^{-14}$	0.94	126 544.4
NO X → NO <sup>+</sup> A	$1.41 \times 10^{-10}$	0.26	213 309.7	NO C → NO <sup>+</sup> A	$1.68 \times 10^{-12}$	0.56	133 924.2
NO A → NO <sup>+</sup> X	$1.36 \times 10^{-07}$	− 0.23	46 605.8	NO B' → NO <sup>+</sup> X	$4.26 \times 10^{-15}$	1.34	14 183.2
NO A → NO <sup>+</sup> a	$1.63 \times 10^{-13}$	0.99	112 686.3	NO B' → NO <sup>+</sup> a	$3.32 \times 10^{-14}$	1.24	94 034.2
NO A → NO <sup>+</sup> b	$5.43 \times 10^{-12}$	0.62	124 299.2	NO B' → NO <sup>+</sup> b	$3.87 \times 10^{-18}$	2.05	97 574.5
NO A → NO <sup>+</sup> b'	$9.45 \times 10^{-13}$	0.74	135 980.5	NO B' → NO <sup>+</sup> b'	$1.23 \times 10^{-13}$	1.05	117 057.5
NO A → NO <sup>+</sup> A	$9.96 \times 10^{-12}$	0.42	144 942.4	NO B' → NO <sup>+</sup> A	$4.63 \times 10^{-17}$	1.70	120 200.9
NO B → NO <sup>+</sup> X	$5.24 \times 10^{-12}$	0.54	22 788.9	NO F → NO <sup>+</sup> X	$6.67 \times 10^{-07}$	− 0.43	20 145.3
NO B → NO <sup>+</sup> a	$6.64 \times 10^{-15}$	1.37	108 170.0	NO F → NO <sup>+</sup> a	$8.66 \times 10^{-17}$	1.66	92 712.9
NO B → NO <sup>+</sup> b	$9.23 \times 10^{-18}$	1.88	108 088.5	NO F → NO <sup>+</sup> b	$1.02 \times 10^{-13}$	0.90	100 718.0
NO B → NO <sup>+</sup> b'	$4.51 \times 10^{-14}$	1.13	132 080.0	NO F → NO <sup>+</sup> b'	$1.36 \times 10^{-15}$	1.30	116 677.3
NO B → NO <sup>+</sup> A	$9.65 \times 10^{-18}$	1.80	130 416.9	NO F → NO <sup>+</sup> A	$5.64 \times 10^{-14}$	0.84	121 886.7

Table 12

Fittings of O<sub>2</sub> ionization rate coefficients in the Arrhenius form:  $K_{T_1}^{T_2}(\theta)$  ( $\text{cm}^3 \text{s}^{-1}$ ) =  $a\theta^b \exp(-c/\theta)$  with  $\theta$  in Kelvin

Transition	<i>a</i>	<i>b</i>	<i>c</i> (K)	Transition	<i>a</i>	<i>b</i>	<i>c</i> (K)
O <sub>2</sub> X → O <sub>2</sub> <sup>+</sup> X	$3.65 \times 10^{-14}$	1.16	130 102.0	O <sub>2</sub> b → O <sub>2</sub> <sup>+</sup> A	$5.17 \times 10^{-09}$	− 0.15	178 013.5
O <sub>2</sub> X → O <sub>2</sub> <sup>+</sup> a	$1.89 \times 10^{-10}$	0.31	183 169.9	O <sub>2</sub> b → O <sub>2</sub> <sup>+</sup> b	$2.96 \times 10^{-10}$	0.16	193 117.9
O <sub>2</sub> X → O <sub>2</sub> <sup>+</sup> A	$1.15 \times 10^{-08}$	− 0.14	194 852.8	O <sub>2</sub> A → O <sub>2</sub> <sup>+</sup> X	$1.09 \times 10^{-24}$	3.44	96 481.5
O <sub>2</sub> X → O <sub>2</sub> <sup>+</sup> b	$6.19 \times 10^{-10}$	0.17	210 535.6	O <sub>2</sub> A → O <sub>2</sub> <sup>+</sup> a	$1.86 \times 10^{-17}$	1.83	132 765.8
O <sub>2</sub> a → O <sub>2</sub> <sup>+</sup> X	$8.87 \times 10^{-15}$	1.21	118 458.0	O <sub>2</sub> A → O <sub>2</sub> <sup>+</sup> A	$2.49 \times 10^{-15}$	1.33	145 388.8
O <sub>2</sub> a → O <sub>2</sub> <sup>+</sup> a	$8.68 \times 10^{-11}$	0.31	173 011.0	O <sub>2</sub> A → O <sub>2</sub> <sup>+</sup> b	$1.59 \times 10^{-19}$	2.27	156 744.5
O <sub>2</sub> a → O <sub>2</sub> <sup>+</sup> A	$4.90 \times 10^{-09}$	− 0.13	184 733.7	O <sub>2</sub> B → O <sub>2</sub> <sup>+</sup> X	$5.73 \times 10^{-26}$	3.76	77 005.0
O <sub>2</sub> a → O <sub>2</sub> <sup>+</sup> b	$2.60 \times 10^{-10}$	0.18	200 019.5	O <sub>2</sub> B → O <sub>2</sub> <sup>+</sup> a	$1.07 \times 10^{-19}$	2.38	109 539.5
O <sub>2</sub> b → O <sub>2</sub> X	$5.83 \times 10^{-15}$	1.23	110 703.5	O <sub>2</sub> B → O <sub>2</sub> <sup>+</sup> A	$4.71 \times 10^{-17}$	1.76	122 778.5
O <sub>2</sub> b → O <sub>2</sub> <sup>+</sup> a	$1.03 \times 10^{-10}$	0.28	166 337.0	O <sub>2</sub> B → O <sub>2</sub> <sup>+</sup> b	$2.21 \times 10^{-21}$	2.72	134 636.7

Table 13

Fittings of N<sub>2</sub> ionization rate coefficients in the Arrhenius form:  $K_{T_1}^{T_2}(\theta)$  ( $\text{cm}^3 \text{s}^{-1}$ ) =  $a\theta^b \exp(-c/\theta)$  with  $\theta$  in Kelvin

Transition	<i>a</i>	<i>b</i>	<i>c</i> (K)	Transition	<i>a</i>	<i>b</i>	<i>c</i> (K)
N <sub>2</sub> X → N <sub>2</sub> <sup>+</sup> X	$8.58 \times 10^{-12}$	0.72	184 300.2	N <sub>2</sub> B → N <sub>2</sub> <sup>+</sup> X	$1.60 \times 10^{-13}$	1.00	87 863.1
N <sub>2</sub> X → N <sub>2</sub> <sup>+</sup> A	$1.54 \times 10^{-13}$	1.11	187 758.5	N <sub>2</sub> B → N <sub>2</sub> <sup>+</sup> A	$1.01 \times 10^{-11}$	0.62	107 537.3
N <sub>2</sub> X → N <sub>2</sub> <sup>+</sup> B	$1.80 \times 10^{-12}$	0.81	217 667.8	N <sub>2</sub> B → N <sub>2</sub> <sup>+</sup> B	$1.27 \times 10^{-15}$	1.36	113 666.1
N <sub>2</sub> X → N <sub>2</sub> <sup>+</sup> C	$1.51 \times 10^{-13}$	0.94	262 404.0	N <sub>2</sub> B → N <sub>2</sub> <sup>+</sup> C	$1.45 \times 10^{-11}$	0.42	189 136.4
N <sub>2</sub> A → N <sub>2</sub> <sup>+</sup> X	$5.48 \times 10^{-16}$	1.43	93 478.3	N <sub>2</sub> C → N <sub>2</sub> <sup>+</sup> X	$2.43 \times 10^{-15}$	1.52	52 847.1
N <sub>2</sub> A → N <sub>2</sub> <sup>+</sup> A	$5.45 \times 10^{-15}$	1.25	111 483.2	N <sub>2</sub> C → N <sub>2</sub> <sup>+</sup> A	$7.00 \times 10^{-15}$	1.40	64 344.5
N <sub>2</sub> A → N <sub>2</sub> <sup>+</sup> B	$6.03 \times 10^{-18}$	1.77	122 005.4	N <sub>2</sub> C → N <sub>2</sub> <sup>+</sup> B	$2.30 \times 10^{-18}$	2.09	82 522.5
N <sub>2</sub> A → N <sub>2</sub> <sup>+</sup> C	$1.11 \times 10^{-12}$	0.63	203 145.8	N <sub>2</sub> C → N <sub>2</sub> <sup>+</sup> C	$7.90 \times 10^{-18}$	1.84	142 103.0

Table 14

Excitation rate coefficients ( $\text{cm}^3 \text{s}^{-1}$ ) for the production of  $\text{N}_2(\text{C}^3\Pi_u)$  state from the ground electronic state of  $\text{N}_2$  by electron impact

$\theta_e$ (K)	$\theta_g$ (K)						
	2000	4000	6000	8000	10 000	12 000	14 000
2000	1.227(−34)	1.215(−34)	1.182(−34)	1.135(−34)	1.081(−34)	1.025(−34)	9.697(−35)
4000	1.943(−21)	1.867(−21)	1.769(−21)	1.662(−21)	1.556(−21)	1.455(−21)	1.363(−21)
6000	4.970(−17)	4.694(−17)	4.386(−17)	4.076(−17)	3.784(−17)	3.517(−17)	3.277(−17)
8000	7.513(−15)	7.018(−15)	6.503(−15)	6.005(−15)	5.548(−15)	5.139(−15)	4.774(−15)
10 000	1.444(−13)	1.339(−13)	1.234(−13)	1.135(−13)	1.046(−13)	9.661(−14)	8.961(−14)
12 000	9.908(−13)	9.141(−13)	8.391(−13)	7.697(−13)	7.075(−13)	6.527(−13)	6.046(−13)
14 000	3.785(−12)	3.478(−12)	3.184(−12)	2.915(−12)	2.675(−12)	2.465(−12)	2.282(−12)

Note: The number inside parenthesis corresponds to power of 10.

Table 15

Excitation rate coefficients ( $\text{cm}^3 \text{s}^{-1}$ ) for the production of  $\text{O}_2(\text{B}^3\Sigma_u^-)$  state from the ground electronic state of  $\text{O}_2$  by electron impact

$\theta_e$ (K)	$\theta_g$ (K)						
	2000	4000	6000	8000	10 000	12 000	14 000
2000	2.376(−24)	2.206(−24)	1.988(−24)	1.781(−24)	1.601(−24)	1.448(−24)	1.319(−24)
4000	4.619(−17)	3.986(−17)	3.436(−17)	2.993(−17)	2.640(−17)	2.357(−17)	2.126(−17)
6000	1.214(−14)	1.012(−14)	8.551(−15)	7.358(−15)	6.438(−15)	5.713(−15)	5.131(−15)
8000	1.846(−13)	1.509(−13)	1.261(−13)	1.078(−13)	9.393(−14)	8.310(−14)	7.446(−14)
10 000	9.004(−13)	7.271(−13)	6.039(−13)	5.141(−13)	4.466(−13)	3.944(−13)	3.528(−13)
12 000	2.516(−12)	2.015(−12)	1.666(−12)	1.414(−12)	1.226(−12)	1.081(−12)	9.664(−13)
14 000	5.161(−12)	4.108(−12)	3.385(−12)	2.867(−12)	2.483(−12)	2.188(−12)	1.954(−12)

Note: The number inside parenthesis corresponds to power of 10.

Table 16

Ionization rate coefficients ( $\text{cm}^3 \text{s}^{-1}$ ) for the production of  $\text{NO}^+(\text{X}^1\Sigma_g^+)$  state from the ground electronic state of  $\text{NO}$  by electron impact

$\theta_e$ (K)	$\theta_g$ (K)						
	2000	4000	6000	8000	10 000	12 000	14 000
2000	5.624(−31)	5.588(−31)	5.427(−31)	5.198(−31)	4.943(−31)	4.685(−31)	4.437(−31)
4000	2.514(−20)	2.409(−20)	2.285(−20)	2.157(−20)	2.033(−20)	1.918(−20)	1.811(−20)
6000	1.306(−16)	1.224(−16)	1.144(−16)	1.071(−16)	1.004(−16)	9.437(−17)	8.893(−17)
8000	1.069(−14)	9.889(−15)	9.177(−15)	8.549(−15)	7.995(−15)	7.504(−15)	7.066(−15)
10 000	1.586(−13)	1.457(−13)	1.347(−13)	1.252(−13)	1.170(−13)	1.097(−13)	1.034(−13)
12 000	9.874(−13)	9.032(−13)	8.333(−13)	7.741(−13)	7.231(−13)	6.787(−13)	6.395(−13)
14 000	3.726(−12)	3.401(−12)	3.135(−12)	2.912(−12)	2.721(−12)	2.555(−12)	2.409(−12)

Note: The number inside parenthesis corresponds to power of 10.

## 4. Comparison with previous works

### 4.1. Cross sections at 300 K

The present cross section calculation for the process  $O_2(X) + e^- \rightarrow O_2^+(X) + e^- + e^-$  is presented in Fig. 4. Ionization cross sections of  $O_2(X)$  taken from Phelps [51], Ali [41] and Doering and Yang at 100 eV [64] are also given. Our cross section is located between those of Ali and Phelps and the agreement is particularly good with the measurement of Doering and Yang.

### 4.2. Reaction rate coefficients

Concerning nitric oxide, the total ionization rate coefficient of Slinker and Ali [4] is, to our knowledge, the only published data.

In Fig. 5, our rate coefficient for electron impact excitation of the transition  $O_2(X \rightarrow a)$  is compared with that of Slinker and Ali [4] and with the WTCS calculation made by Gomes et al. [10] using Bacri and Médani's assumptions [3]. The agreement between our result and Ali's is satisfactory. More experimental data are available for excitation processes in nitrogen. Slinker and Ali [4] and Morrill et al. [5] give reaction rate coefficients for the reactions  $X \rightarrow A$ ,  $X \rightarrow B$  and  $X \rightarrow C$ . These authors report very close results because they used the same set of cross sections for their calculations. As can be seen in Fig. 6, the agreement between our results and those of Morrill et al. for the process  $N_2(X) + e^- \rightarrow N_2(C) + e^-$  is acceptable (rate coefficients of Bacri and Médani [9] and of Huo and Mc Koy [6] at  $\theta_e = 8000$  K are also shown).

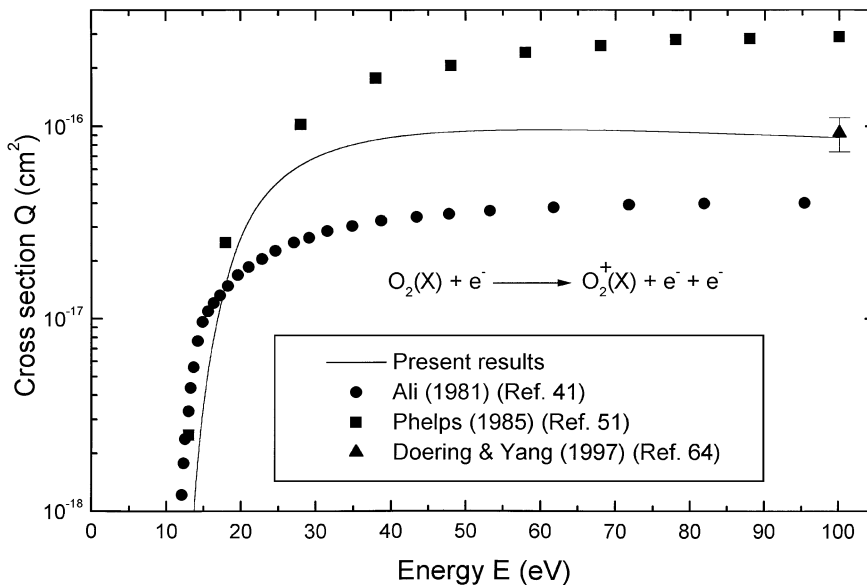


Fig. 4. Comparison between our cross section at 300 K and the literature values for electron impact ionization of  $O_2(X)$ .



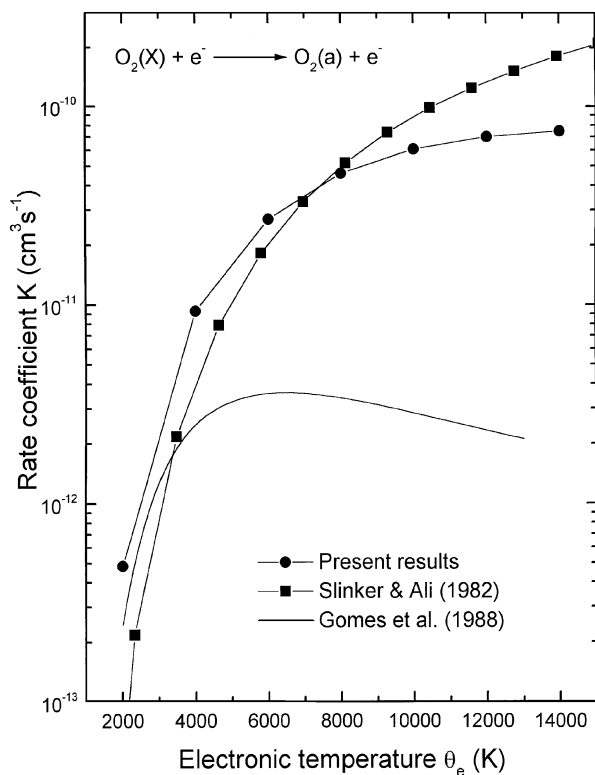


Fig. 5. Comparison between our rate coefficient and the literature values for electron impact excitation of  $O_2(X)$  to  $O_2(a)$ .

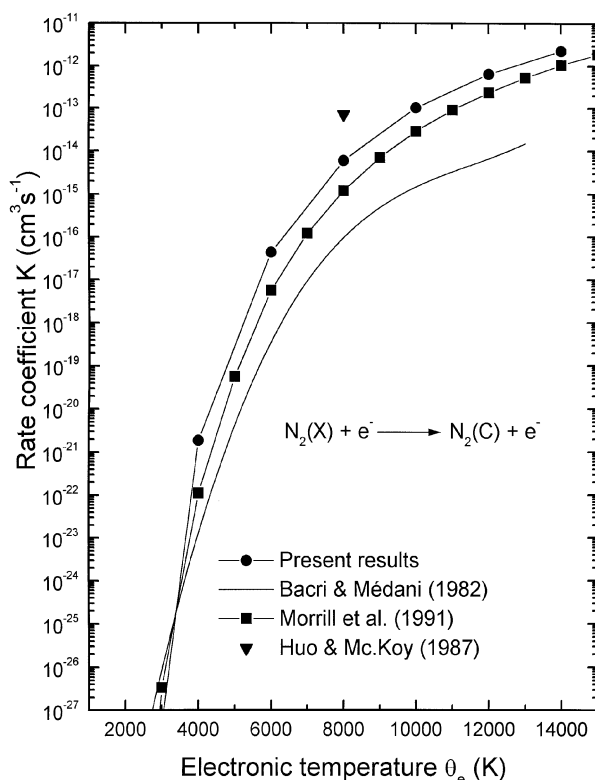


Fig. 6. Comparison between our rate coefficient and the literature values for electron impact excitation of  $N_2(X)$  to  $N_2(C)$ .

To our knowledge, multitemperature reaction rate coefficients have only been calculated by Huo and Mc Koy [6] for transitions in  $N_2$ : ( $X \rightarrow B$ ) and ( $X \rightarrow C$ ). These authors present reaction rate coefficients depending on  $\theta_e$ ,  $\theta_v$  and  $\theta_r$ .

In the case where  $\theta_g = \theta_e = \theta_v = \theta_r = 8000$  K (cf. Table 17), if our rate coefficients are compared with those of the literature, it can be noted that our results are situated between those of Morrill et al. [5] and Slinker and Ali [4], and those of Huo and Mc Koy [6] for the two processes considered:  $N_2$  ( $X \rightarrow B$ ) and ( $X \rightarrow C$ ).

Let us also consider the case  $\theta_g = \theta_r = 8000$  K. Our two-temperature rate coefficients can be compared with those of Huo and Mc Koy for  $\theta_e = \theta_v = 5000, 10000$  and  $15000$  K (cf. Table 18). Our results are approximately one order of magnitude lower than those of Huo and Mc Koy for the two transitions  $N_2$  ( $X \rightarrow B$ ) and ( $X \rightarrow C$ ).

Concerning electron impact dissociation processes, a comparison of our dissociation rate coefficients of the electronic ground states of  $N_2$ ,  $O_2$  and  $NO$  with those of Park [19] and Losev [20] has already been made in a previous publication [13].

Table 17  
Comparison between the literature values and our excitation rate coefficients for the processes N<sub>2</sub> (X → B) and (X → C) at 8000 K

Transition	Slinker and Ali [4]	Morrill et al. [5]	Huo et al. [6]	This work
N <sub>2</sub> (X → B)	$1.07 \times 10^{-13}$	$1.16 \times 10^{-13}$	$2.2 \times 10^{-11}$	$1.42 \times 10^{-12}$
N <sub>2</sub> (X → C)	$1.52 \times 10^{-15}$	$1.20 \times 10^{-15}$	$7.16 \times 10^{-14}$	$6.01 \times 10^{-15}$

Note: Rate coefficients are given in cm<sup>3</sup> s<sup>-1</sup>.

Table 18  
Comparison between Huo and Mc Koy's and this work upon the excitation rate coefficients (in cm<sup>3</sup> s<sup>-1</sup>) of N<sub>2</sub> (X → B) and (X → C) for  $\theta_g = \theta_r = 8000$  K

N <sub>2</sub> (X) + e <sup>-</sup> → N <sub>2</sub> (B) + e <sup>-</sup>			N <sub>2</sub> (X) + e <sup>-</sup> → N <sub>2</sub> (C) + e <sup>-</sup>		
$\theta_e = \theta_v$ (K)	Huo et al. [4]	This work	$\theta_e = \theta_v$ (K)	Huo et al. [4]	This work
5000	$3.8 \times 10^{-14}$	$3.8 \times 10^{-15}$	5000	$5.3 \times 10^{-18}$	$7.4 \times 10^{-19}$
10000	$1.7 \times 10^{-10}$	$1.1 \times 10^{-11}$	10000	$1.65 \times 10^{-12}$	$1.15 \times 10^{-13}$
15000	$2.6 \times 10^{-9}$	$1.6 \times 10^{-10}$	15000	$9.8 \times 10^{-11}$	$5.3 \times 10^{-12}$

5. Conclusion

Electron impact excitation, ionization and dissociation cross sections and rate coefficients were calculated for the main electronic states of diatomic air molecules (N<sub>2</sub>, O<sub>2</sub>, NO and their positive ions).

This method for cross section calculation based upon WTCS theory is relatively simple and easy to extend to any diatomic molecule provided that the spectroscopic constants are sufficiently well known for the considered electronic state.

The results obtained and the new assumptions made in the semi-empirical method of WTCS determination were validated by comparison (when possible) with the published data of Slinker and Ali [4], Morrill et al. [5] and Huo and Mc Koy [6].

Concerning processes for which no experimental results have been published as yet, the validity of the assumed normalization coefficients  $\alpha_{g_1g_2}$  is relatively dubious. So, it would be advisable to recalculate these normalization coefficients if new experimental cross section measurements become available in the future.

Another way to check our reaction rate coefficients is to use them in collisional radiative modeling of nitrogen, oxygen or air plasmas [11]. Then, the theoretical spectra can be calculated and compared with experimental ones. This work is in progress in our laboratory [73].

## Appendix: Elementary cross section

- Excitation without change in spin multiplicity  $\Delta S = 0$  [24]

$$q_{T_1 v_1 J_1}^{T_2 v_2 J_2}(r, \varepsilon) = 4\pi a_0^2 \alpha_{g_1 g_2} \xi \left( \frac{U_{12} - 1}{U_{12}^2} \right)$$

where

$$U_{12} = \varepsilon / \Delta U \quad \text{with} \quad \Delta U = U(T_2, v_2, J_2, r) - U(T_1, v_1, J_1, r).$$

$a_0$  is the Bohr radius and  $\xi$  is the number of optical electrons in state  $T_1$ . Drawin formalism only gives the shape of the cross section (position of threshold and maximum). Thus, the cross section is determined with a normalization factor  $\alpha_{g_1 g_2}$  (this coefficient is nondimensional and depends on the spin multiplicities  $g_i = 2S_i + 1$  of initial state  $T_1$  and final state  $T_2$ ). These coefficients are calculated from experimental cross sections from 300 K upwards and are discussed in Section 2.4. Knowing the normalization factors allows the cross section and rate coefficient calculations to be extended to temperatures higher than 300 K.

- Excitation with change in spin multiplicity  $\Delta S \neq 0$  [24]

$$q_{T_1 v_1 J_1}^{T_2 v_2 J_2}(r, \varepsilon) = 4\pi a_0^2 \alpha_{g_1 g_2} \xi \left( \frac{U_{12}^2 - 1}{U_{12}^5} \right)$$

- Ionization [24]

$$q_{T_1 v_1 J_1}^{T_2 v_2 J_2}(r, \varepsilon) = 2.66\pi a_0^2 \left( \frac{E_1^H}{\Delta U} \right)^2 \alpha_{g_1 g_2} \xi \left( \frac{U_{12} - 1}{U_{12}^2} \right) \ln(1.25 U_{12})$$

$E_1^H$  is the ionization energy of the hydrogen atom.

- Dissociation [25]

$$q_{T_1 v_1 J_1}^D(r, \varepsilon) = 4\pi a_0^2 \left( \frac{E_1^H}{\Delta E} \right)^2 \xi g(u, v)$$

with

$$g(u, v) = \frac{1}{u} \left( 1 - \frac{1}{u} \right)^{1 + (v/(1+v))} \left( \frac{u}{u+v} \right)^{1.5} \left[ 1 + \frac{2v}{3} \left( 1 - \frac{1}{2u} \right) \ln \left( e + \left( \frac{u-1}{v} \right)^{0.5} \right) \right]$$

$$u = \varepsilon / \Delta E, \quad v = E_L / \Delta E, \quad \Delta E = U(T_1, v_1 = 0, J_L(v_1 = 0), r) - U(T_1, v_1, J_1, r).$$

$E_L = I(r) - U(T_1, v_1, J_1, r)$ ,  $e = 2.718$  is the natural logarithm base,  $U(T_1, v_1 = 0, J_L(v_1 = 0), r)$  is the ultimate stable potential energy curve of electronic state  $T_1$ . For the dissociation of neutral species,  $I(r)$  is the potential energy curve  $U(X, v = 0, J = 0, r)$  of the molecular ion in its fundamental state  $X$ ; for the dissociation of singly-ionized molecules,  $I(r)$  is the second level ionization energy of the neutral molecule.  $E_L$  is therefore the energy binding the optical electron to the molecule.

This formalism does not have a normalization coefficient. It does not allow the calculated cross sections to be adapted to available experimental results at 300 K.

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