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Letter

Vibrationally resolved NO dissociative excitation cross sections by electron impact

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Abstract

A theoretical investigation of the dissociative excitation by electron impact on the NO molecule is presented, aiming to make up for the lack of data for this process in the literature. A full set of vibrationally-resolved cross sections and corresponding rate coefficients are calculated using the local-complex-potential approach and five resonant states of NO^-.

Keywords: plasma physics, molecular dynamics, NO pollution, NO dissociation

S Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

The nitric oxide (NO) molecule is one of the minor components of terrestrial atmosphere. Generated in atmospheric plasma from chemical reactions of nitrogen with oxygen, NO and its radicals are very important in many industrial technologies [1–5] and play a key role in the combustion of fossil fuels [6, 7]. Of the nitrogen oxide compounds, the so-called NOx gases, the NO molecule has the greater impact on environment and on pollution caused by human activities [8, 9].

In order to make kinetic plasma models involving nitric oxide, many sets of molecular data [10–12], spectroscopic properties [13–15] and reaction rate coefficients [16–19] are available in the literature but, in spite of its importance, none of them provide complete data on electron impact dissociation. More specifically, rate constants for electron-NO reactions, both theoretical [14, 20–22] and experimental [23–27], exist only for vibrational excitation and dissociative electron attachment processes at low-energy. A recent compilation of all the known electron collision cross sections is given by Song *et al* [16].

To fill this gap, we present calculations—based on the formalism used previously [20]—of vibrational state resolved cross sections and the corresponding rate coefficients for dissociative excitation (DE) of NO by electron impact, *i.e.*:

$$\begin{aligned} e + NO(X\,^2\Pi; v) \rightarrow NO^- \rightarrow e + NO(X\,^2\Pi; \epsilon_c) \rightarrow e \\ + N\left(^4S\right) + O\left(^3P\right). \end{aligned} \qquad (1)$$

We consider electron collision energies where numerous NO^- resonances exist, direct dissociation is negligible and the DE reaction is dominated by resonant processes [28, 29]. Our aim is to cover a large range of incident electron energies, so we take into account five resonance states of NO^-: the three low-lying states of $^3\Sigma^-$, $^1\Sigma^+$ and $^1\Delta$ symmetries and two higher ones, with $^3\Pi$ and $^1\Pi$ symmetry, which lie close to the NO dissociation threshold. In the following, we number these resonances by $r = 1, \ldots, 5$, respectively. The vibrational excited states of which converge on the $N\left(^4S\right) + O\left(^3P\right)$ dissociation

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Table 1. Summary of the parameters used in the theoretical model: reduced mass μ; Morse parameters for NO and NO$^-$ potential energies; the coefficients c_r entering in equation (4) and the spin-statistical factors $\frac{2S_r+1}{(2S+1)\,2}\frac{g_r}{g\,2}$.

	$\mathrm{NO}\left(\mathrm{X}\,^2\Pi\right)$	$\mathrm{NO}^-(^3\Sigma^-)$	$\mathrm{NO}^-(^1\Delta)$	$\mathrm{NO}^-\left(^1\Sigma^+\right)$	$\mathrm{NO}^-(^3\Pi)$	$\mathrm{NO}^-(^1\Pi)$
μ (a.u.)			13 614.1			
D_e (eV)	6.610	5.161	5.90	5.60	1.85	0.729
R_e (a.u.)	2.175	2.393	2.38	2.37	3.18	3.14
α (a.u.)	1.48	1.20	1.18	1.20	0.75	1.049
W (eV)	0	−0.015	0.775	1.08	5.70	6.80
c_r (eV$^{0.5-l_r}$)	—	0.81	0.60	0.50	0.023	0.013
spin-stat	—	$\frac{3}{8}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{3}{4}$	$\frac{1}{4}$

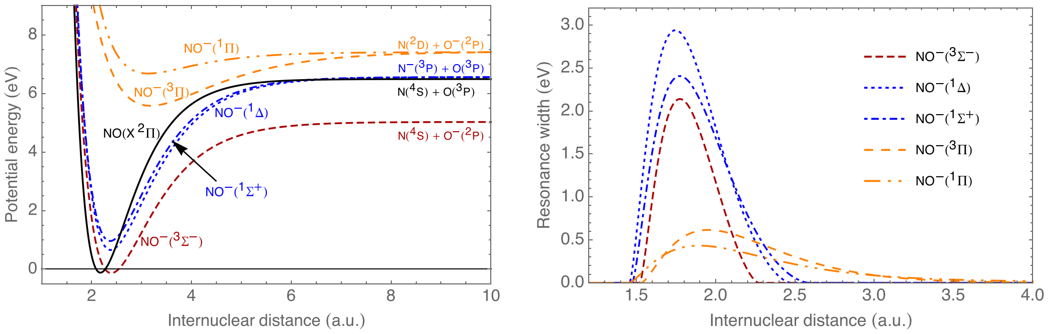

Figure 1. (Plot on the left) Potential energy curves for the ground electronic state of NO molecule (solid line) and for the five NO$^-$ resonances (broken lines) included in the calculations; (plot on the right) the corresponding widths of the resonances.

limit of equation (1), due to their symmetry, have small oscillator strengths and short lifetimes [10, 30, 31] so their influence on the DE process can be neglected.

NO is a stable, open-shell molecule with a $^2\Pi$ ground electronic state, and a very accurate theoretical treatment of the electron-NO scattering therefore needs to take into account the spin-dependence of the process. However, the spin–orbit coupling effects are only important at very low energies [23] and, consequently, in the following we will neglect them.

We start by briefly describing the theoretical model used to calculate the cross sections for the process (1), restricting ourselves to the major equations of the local-complex-potential (LCP) model. For a comprehensive treatment of the resonant collisions, we refer to the seminal articles [28, 29, 32]. The LCP approach was used to calculate the low-energy vibrational excitation of NO [20] and CO [33] by electron impact and the DE of oxygen molecule [34, 35], which gave results in good agreement with experiment.

Table 2. Energies of the vibrational levels of the electronic ground state of the NO molecule. $D_0 = 6.490$ eV.

v	ϵ_v(eV)	v	ϵ_v(eV)	v	ϵ_v(eV)
0	0.000	18	3.581	36	5.745
1	0.236	19	3.739	37	5.823
2	0.468	20	3.892	38	5.897
3	0.695	21	4.040	39	5.967
4	0.918	22	4.185	40	6.033
5	1.137	23	4.324	41	6.094
6	1.351	24	4.460	42	6.150
7	1.561	25	4.591	43	6.203
8	1.767	26	4.718	44	6.251
9	1.968	27	4.840	45	6.294
10	2.164	28	4.958	46	6.333
11	2.357	29	5.072	47	6.368
12	2.545	30	5.181	48	6.399
13	2.729	31	5.286	49	6.425
14	2.908	32	5.386	50	6.446
15	3.083	33	5.483	51	6.464
16	3.253	34	5.574	52	6.477
17	3.419	35	5.662	53	6.485

In the LCP model, the DE cross section for an NO molecule initially in vibrational level v by an incident electron of energy ϵ is given by [32]:

$$\sigma_v(\epsilon) = \sum_{r=1}^{5} \frac{2S_r+1}{(2S+1)\,2}\,\frac{g_r}{g\,2}\,\frac{64\,\pi^5\,m^2}{\hbar^4}\int_{\epsilon_v^{\mathrm{th}}}^{\epsilon_v^{\mathrm{max}}} \mathrm{d}\epsilon_{\mathrm{c}}\,\frac{k'}{k}\,|\langle\chi_{\mathrm{c}}|\mathcal{V}_r|\xi_v^r\rangle|^2, \qquad (2)$$

where $2S_r + 1$ and $2S + 1$ are the spin-multiplicities of the resonant anion state and of the neutral target state, respectively, g_r and g represent the corresponding degeneracy factors, $k(k')$ are the incoming (outgoing) electron momenta, m is the electron mass, χ_{c} stands for the continuum wave function of NO asymptotically converging to $\mathrm{N}\left(^4\mathrm{S}\right) + \mathrm{O}\left(^3\mathrm{P}\right)$, and ξ_v^r is the resonance nuclear-motion wave function which is obtained for

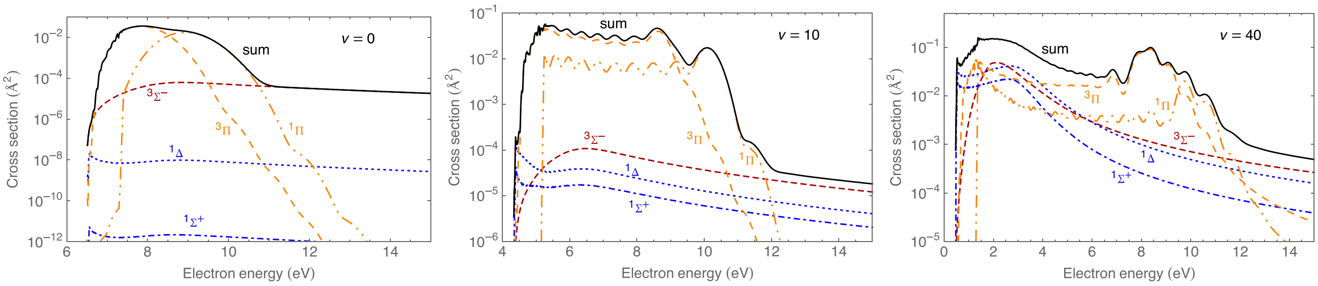

Figure 2. Contributions coming from the five resonant states (broken lines, same colors as in figure 1) to the total dissociative excitation cross section (solid line) for $v = 0$ (plot on the left), $v = 10$ (plot on the middle) and $v = 40$ (plot on the right).

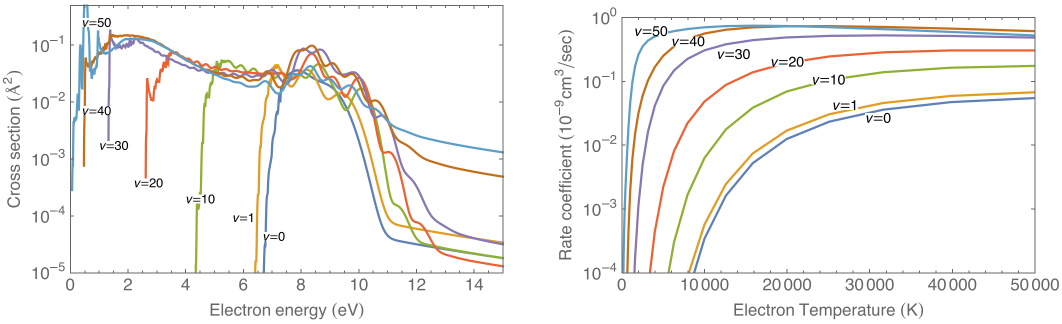

Figure 3. Vibrational state-resolved cross sections and the corresponding rate coefficients for NO dissociative excitation by electron impact.

each resonance as the solution of the equation:

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}R^2}+V_r^-(R)-\frac{i}{2}\Gamma_r(R)-E\right]\xi_v^r(R)=-\mathcal{V}_r(R)\,\chi_v(R),$$
$$r=1,\ldots,5. \tag{3}$$

where μ is the NO reduced mass, V_r^- and Γ_r represent the potential energies and the autoionization widths, respectively, for the five resonant NO$^-$ states included in the calculation, χ_v is the wave function of the initial vibrational state of NO with energy ϵ_v, and $E = \epsilon + \epsilon_v$ is the total energy of the system. Following reference [32], the widths Γ_r were expressed as:

$$\Gamma_r = c_r\left(V_r^- - V_0\right)^{l_r+\frac{1}{2}} H\left(V_r^- - V_0\right), \qquad r=1,\ldots,5, \tag{4}$$

where V_0 is the NO potential energy, H is a Heaviside step-function and l_r is the angular momentum of the lowest contributing partial wave associated with the incident electron. Experimental results show that the dominant contribution come from the p-wave [22] so l_r was set to one. In order to reproduce the positions and widths of the peaks in the low-energy region of the experimental cross sections, the constants c_r in equation (4) were introduced as phenomenological external parameters as reported in the paper [20]. Their values are given in table 1. In equations (2) and (3), $\mathcal{V}_r$ is the discrete-to-continuum coupling given by [21]:

$$\mathcal{V}_r^2 = f_r^{2l_r+1}\frac{\hbar}{2\pi}\frac{\Gamma_r}{\sqrt{2\,m\left(V_r^- - V_0\right)}}, \qquad r=1,\ldots,5, \tag{5}$$

where f_r is the so-called penetration factor introduced to reproduce the correct dependence of the cross sections on the energy near the excitation threshold, namely,

$$f_r^2(\epsilon) = \begin{cases} \epsilon/\left(V_r^- - V_0\right) & \text{if } \epsilon < \left(V_r^- - V_0\right) \\ 1 & \text{otherwise} \end{cases},$$
$$r=1,\ldots,5. \tag{6}$$

The sum in the cross section formula (2) runs over all the five resonance states of the NO$^-$ anion involved in the dissociation process. The integral extends to the continuum part of the NO potential from the dissociation threshold energy ϵ_v^{th} corresponding to the vibrational level v up to $\epsilon_v^{\max} = \epsilon_v^{\mathrm{th}} + 10$ eV. The spin-statistical factors are listed in table 1.

In the model shown above, the potentials $V_0(R)$ and $V_r^-(R)$ are expressed as a standard Morse function $U(R) = D_\mathrm{e}\left[1-\mathrm{e}^{-\alpha(R-R_\mathrm{e})}\right]^2 + W$ whose parameters, for the NO molecule and for the three low-lying resonances $^3\Sigma^-$, $^1\Sigma^+$ and $^1\Delta$, were determined by a fit procedure explained in [20]. In order to take into account the recent results presented in [12], the asymptotes for the singlet states $^1\Sigma^+$ and $^1\Delta$ have been shifted to the correct threshold N$^-$(^{3}P) + O(^{3}P). We have checked, and the results in [20] are not affected by these changes. Analogously, the $^3\Pi$ and $^1\Pi$ symmetry parameters were obtained by a fit to the data presented in [11] and the *ab initio* R-Matrix results in the reference [12]. All Morse parameters are summarized in table 1. The NO ground state potential energy curve, as well as those for the five NO$^-$ resonances and their corresponding autoionization widths are reported in figure 1. Table 2 contains the list of the vibrational levels supported by the NO molecule.

Figures 2 and 3 summarize the results of the present letter. The cross sections were computed up to 15 eV, at which point they drop off and become negligible, to cover temperatures up to 50 000 K for the reaction rates, relevant for the applications mentioned above.

Figure 2 contains the results of cross sections for the process of dissociation in (1) for three specific vibrational levels of NO molecule. Partial contributions coming from the five resonances as well as the sum are shown. Some features can be noticed: (i) basically, as expected, for all cases, the major contribution to the total cross section comes from the $^3\Pi$ and $^1\Pi$ resonances due to their closeness to the dissociation threshold, whereas the $^1\Sigma^+$ and $^1\Delta$ resonances, in general, make a minor contribution, in particular for low and middle vibrational levels ($v = 0$ and $v = 10$). (ii) As a consequence of the Franck–Condon overlap, the $^3\Pi$ and $^1\Pi$ contributions to the cross section for $v = 0$ extends up to 11.5 eV, with a maximum around 9 eV. (iii) Beyond 11.5 eV, the asymptotic behavior is driven by the $^3\Sigma^-$ resonance. (iv) Since high vibrational levels ($v = 40$) approach the NO dissociation limit, the contributions from $^3\Sigma^-$ and, in particular, from the $^1\Sigma^+$ and $^1\Delta$ states, become comparable to those from the $^3\Pi$ and $^1\Pi$ resonances at threshold.

Finally, figure 3 reports the full set of DE cross section results resolved over the vibrational ladder. By assuming a Maxwellian distribution for the electrons, the corresponding rate coefficient K_v is given, as a function of the electron temperature T_e, by:

$$K_v(T_e) = \left(\frac{1}{m\,\pi}\right)^{1/2} \left(\frac{2}{k_B T_e}\right)^{3/2} \int \epsilon\,\sigma_v(\epsilon)\,\mathrm{e}^{-\epsilon/k_B T_e}\,\mathrm{d}\epsilon, \quad (7)$$

where k_B is the Maxwell–Boltzmann constant.

In conclusion, vibrational state-resolved cross sections for dissociation of nitric oxide by electron-impact are computed for the first time using a phenomenological local-complex-potential approach. Among the five resonances we considered in the calculations, the $^3\Pi$ symmetry is the one which makes the largest contribution. The full set of data obtained in the present work is available as supplementary material to this letter, which can be found online at [http://stacks.iop.org/JPhysPSST/29/05LT02/mmedia].

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