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An approximate quantum mechanical study of the $N + O \rightarrow NO^+ + e^-$ associative ionisation

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ABSTRACT

The time-dependent wavepacket method is used to study the associative ionization process $N + O \rightarrow NO^+ + e^-$. We make use of the sudden approximation, effectively assuming that the ionization process itself is fast with respect to the timescale of the motion of the wavepacket and we calculate probabilities and cross-sections for transition to various rovibrational levels of the NO^+ ion. The dependence of these quantities on the initial collision energy and the initial partial wave singles out interesting three-dimensional effects which we interpret here.

1. Introduction

The NO^+ species is an important component of many planetary atmospheres. Its dissociative recombination (collision with an electron to yield a N and a O atom) has been studied in the past through multichannel quantum defect theory (MQDT)) [1] and other methods [2,3]. The reverse process, associative ionization to yield the NO^+ species, between the ions $N^+ + O^-$ has also been the subject of a study in the literature [4], where the relevant cross sections have been found to be quite high (of the order of 10^{-14} cm^2. Moreover, the associative ionisation process between excited N (^{2}P) and O (^{3}P) atoms has been utilised to explain the decay dynamics of nitrogen plasmas [5]. Detailed balance calculations have been utilised to determine partial near-threshold cross sections for this process [6].

In general, we can say that associative ionization is a way to induce ionization by high energy collisions (another kind of collisional ionization is so-called Penning ionization (see, for example, [7,8]) in high energy regions. In particular, the N + O associative ionization, involving the third and fifth most abundant species in the universe, could be a way to form a chemical bond. The presence of ions has been documented in different interstellar regions and their origin explained by various mechanisms [9]. Associative ionization also plays a role in combustion physics. The title process has been acknowledged as the primary source of the NO^+ cation in ammonia and hydrogen–oxygen–nitrogen burning flames [10,11]. Finally, the title process has also been included in models of interpretation of the ionization rate behind shock waves in air [12].

Here, we have used a time-dependent wavepacket algorithm written by us to study more in detail the dynamics of the associative ionisation $N + O \rightarrow NO^+ + e^-$. The method, given the reduced number of degrees of freedom of the system (three, one of which is degenerate by symmetry), represents a particular case of our algorithm used in the past [13–15] in which the three-dimensional calculation is decomposed into several 1-dimensional propagations of the wavepacket along the radial coordinate representing the distance between the N and O atoms. The sudden approximation is used in order to calculate probabilities (from which cross sections can be derived) for the transition to specific NO^+ bound levels.

The specific motivation of the present work lies therefore in the relevance of the above-mentioned process not only in plasma chemistry [5], but also in its important role in the modelling of phenomena in planetary atmospheres (which is also the objective of our Phys4entry [16] project). To our knowledge there are no previous experimental data on the microscopic dynamics of this process at high collision energies. Because of its importance, it is crucial to include it in models of plasmas or planetary atmospheres with reliable values of its energy-dependent cross section and/or temperature-dependent rate constant. Moreover, the fraction of energy released as translational, rotational or vibrational energy of the product NO^+ ion constitutes valuable input for the modeling of subsequent processes.

2. Theoretical and computational procedure

2.1. Potential energy surfaces

The electronic potential energy surfaces used in the calculation are:

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Table 1
Values of parameters of the interaction potential.

Molecule	D_e/eV	r_e/Å	ω_e/cm^{-1}	β/Å^{-1}
NO	6.615	1.151	1904	2.743
NO$^+$	10.851	1.063	2377	2.673

(1) The surface of the neutral NO species, where the N and O atoms propagate. It is assumed that the N atom finds itself in the ground ^{4}S state, whereas the O atom is in the ground ^{3}P state and that the two atoms are on the adiabat leading to the neutral NO diatomic molecule. Within the manifold of electronic states which asymptotically correlate with N (^4S) + O (^3P) we have selected the $X^2\Pi$ ground state of NO. This state is actually composed of a multiplet of four sublevels (taking into account the possibility of spin–orbit coupling and Λ-doubling). We use here the average of the four. To this state, we have assigned a dissociation energy D_e referred to the minimum of the potential well, an equilibrium distance r_e and a vibrational frequency ω_e, whose values, taken from the literature [17], are given in Table 1.

(2) The surface of the NO$^+$ ion. This system also exhibits a manifold of molecular states, some of them bound and others repulsive, which are asymptotically shifted with respect to NO by its ionization potential (9.26 eV). Among them, we have selected again the ground electronic state, of $^1\Sigma^+$ symmetry. The interaction involved is characterized by a binding energy D_e higher than that of NO in the neutral state, since the NO$^+$ species has one antibonding electron less. The D_e, r_e and ω_e values used [17] are also given in Table 1.

In both neutral and ionic states the radial dependence of the interaction potential, $V(r)$, has been described by a Morse function, defined as

$$V(r) = D_e\left(e^{-2\beta(r-r_e)} - 2e^{-\beta(r-r_e)}\right) \tag{1}$$

The shape parameter β depends on the basic features D_e and ω_e defined above through the relation [18]:

$$\beta = \sqrt{\frac{2\pi^2 c\mu}{D_e h}}\omega_e \tag{2}$$

where c is the speed of light, h is Planck's constant and μ is the reduced mass of the diatom. The values of β thus obtained are also in Table 1 [19]. These surfaces, describing correctly vibrational levels and Franck–Condon factors involved in the NO$^+$ + e$^-$ → NO process [20], have already been used by Bartolomei et al. [21] to calculate energy levels and Franck–Condon factors of relevance for the (NO=N$_2$)$^+$ + e$^-$ → NO–N$_2$ process. All such calculations have been performed using the LEVEL 7.4 code by Le Roy [22].

2.2. The energy levels and the sudden approximation

As a preliminary step, all rovibrational energy levels below certain vibrational and rotational quantum numbers are calculated. The procedure is an ordinary diagonalisation of the diatomic Hamiltonian on the given potential energy surface, using a sine-DVR (discrete variable representation) [23–25]. The eigenvectors resulting from the diagonalisation are subsequently stored to be used during the propagation of the wavepacket.

We are using the first-order Born approximation in our calculation, effectively assuming that the coupling between the two surfaces is small. Hence, the first order correction to the wavefunction for a total energy E is given by

$$\Psi^{(1)} = G_0^+(E)H^{(1)}\Psi^{(0)} \tag{3}$$

where $\Psi^{(0)}, \Psi^{(1)}$ are respectively the zero and first order wavefunctions, $H^{(1)}$ the first order coupling and G_0^+ the outgoing Green operator. In the sudden approximation exploited in this calculation we are assuming that the ionisation process is faster than the wavepacket motion and the vibrational period of the NO$^+$ diatom. Thus, the coupling is assumed to be independent of the internuclear distance (and confined within a certain interaction region). Moreover, as far as the electronic degree of freedom is concerned, we assume that the coupling localises the outgoing electron at a distance from the NO$^+$ ion in such a way that all energies in the outgoing electronic wavepacket are equally represented. Within this context, we represent a superposition of $\Psi^{(0)}$ at various energies as a wavepacket. At each time step during the propagation, we project the wavepacket at each rovibrational level of the product individually, thus obtaining a time-dependent overlap function $c_{v'j}(t)$ according to the equation

$$c_{v'j}(t) = \langle \phi_{v'j}|\psi_j(t)\rangle \tag{4}$$

where v' is the product vibrational quantum number, j is the rotational quantum number (as well as the initial orbital quantum number), $\phi_{v'j}$ is the product wavefunction and ψ_j is the nuclear wavepacket. Atomic units are consistently used throughout this Letter and hence $\hbar = 1$ is assumed. Accordingly, our time unit is $1\hbar$/hartree, denoted as $1\hbar/h$. The half-Fourier transform of these overlap functions yields the energy-dependent probabilities according to the equation [26,27]

$$P_{v'j}(E) = \left| \frac{K}{\langle \Phi_j^-(E)|\psi_j(0)\rangle} \int_0^{+\infty} c_{v'j}(t)\; e^{iEt}\; dt \right|^2 \tag{5}$$

where K is a constant depending on the coupling term between the two surfaces (see below). $\Phi_j^-(E)$ is the scattering stationary wavefunction corresponding to the partial wave with orbital quantum number j at energy E and with purely incoming boundary conditions. This half-Fourier transform effectively corresponds to applying the outgoing Green's function to the wavepacket (after having applied to it the perturbation Hamiltonian causing the coupling between the two states). Within the limit of first-order continuum perturbation theory (Born approximation), and assuming that the scattering stationary wavefunctions are normalized with respect to the energy, i.e.

$$\langle \Phi(E_1)|\Phi(E_2)\rangle = \delta(E_1 - E_2) \tag{6}$$

(so that the density of states becomes unity at all energies) the constant K is given by the equation

$$K = \left| \langle \phi_{el,ex}(NO^+)|\hat{H}_1|\phi_{el,gr}(N+O)\rangle \right|^2 \tag{7}$$

and it turns out to be given by the square modulus of the Hamiltonian coupling matrix element between the electronic parts of the N + O and the NO$^+$ wavefunctions divided by the energy spread of the outgoing electronic wavepacket (taken to be 10 eV, the energy between the minimum and the asymptotic region of the excited surface). Following the formalism of previous work on charge transfer processes [28,29] we express the coupling Hamiltonian as

$$H_1 = \frac{A^2}{\Delta E} \tag{8}$$

where ΔE is an average separation of the two electronic states (taken as 0.34 h or 9.2 eV, of the order of magnitude of the NO ionization potential) and A is assumed here to be independent of the interatomic separation, as mentioned before. Judging from similar processes, we have chosen to take a reasonable value of 0.1 eV for the coupling matrix element. Corresponding cross sections can be