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Translational Energy Relaxation of Hot O(^1D) Atoms

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Quantum mechanical calculations of the thermalization of initially energetic O(^1D) atoms in bath gas of N_2 molecules are carried out. The results are in excellent agreement with measurements of the translational energy relaxation of O(^1D) atoms produced in the 157 nm photodissociation of O_2 and the 193 nm photodissociation of N_2O in an N_2 atmosphere.

I. Introduction

The role of energetic atoms in the heat and energy balance of the upper atmosphere is an important aspect of atmospheric chemistry. Energetic atoms in ground or excited electronic states are produced in the upper atmosphere by dissociative recombination, collisional quenching, photodissociation, and photoelectron impact dissociation. Their energy is redistributed to the surrounding atmospheric bath gases through elastic and inelastic collisions. If molecules are present in the bath gas, their rovibrational levels may be excited in collisions with the atoms or they may undergo chemical reaction. Many exothermic chemical reactions result in the formation of products with high internal excitation. An example is collisions of nitrogen atoms with O_2. Observations aboard the space shuttle[1] detected infrared emissions from highly rovibrationally excited NO, and it was suggested[2] that reactions of energetic nitrogen atoms with O_2 are responsible. Considerable theoretical effort[3−9] has been made to understand the thermalization of energetic nitrogen atoms in the thermosphere and to calculate their energy distribution function.

The thermalization of hot atoms is determined by the cross sections for elastic and inelastic collisions of the hot atoms with the bath gas. Not only the energy but also the angular dependence of the cross section is important in the thermalization process. The majority of studies in the past used the hard-sphere model. The hard-sphere approximation facilitates the evaluation of the kernel of the Boltzmann equation, but it ignores the energy and angular dependence of the cross sections.[11,12] We have constructed a procedure[8−10] for calculating the parameters needed to describe the thermalization or translational relaxation of energetic atoms in a bath gas. An analytical expression was developed[8] for the kernel for arbitrary elastic or inelastic collision cross sections that takes explicit account of their variation with energy and with angle.

Sophisticated laboratory experiments[13−16] have been carried out in which the Doppler profiles of initially energetic metastable atoms moving in different bath gases are measured as a function of time, and effective hard-sphere cross sections were derived for energy and angular relaxation. Of particular relevance to atmospheric chemistry[17] are the measurements on the collisions of energetic O(^1D) atoms produced in the photolysis of O_2 and N_2O in an atmosphere of N_2.[15,16] The cross sections for energy and angular relaxation were taken as separate parameters in the interpretation of the data, but they are not independent. We present here quantum mechanical calculations of the energy and angular dependence of the collision cross sections and use them to predict the energy relaxation as a function of time. We obtain close agreement with the experimental data.

The metastable O(^1D) atoms are quenched at low energies in collisions with N_2 but from the calculations of Tully,[18] Zahr et al.,[19] and Tachikawa et al.[20,21] it appears that the quenching does not effect the thermalization above 0.2 eV.

II. Boltzmann Kernel

The rate of energy relaxation of an initially energetic atom with energy E in the laboratory frame (LF) to a final energy E' in the LF in collision with a bath gas atom or molecule is given by the kernel of the Boltzmann equation, which we denote by $B(E'|E)$. In an isotropic bath gas whose density is much higher than the density of the projectile atom, the energy distribution $f(E,t)$ of the projectile is related to the kernel of the Boltzmann equation according to the linear kinetic equation[8]

$$\frac{\partial}{\partial t} f(E,t) = \int B(E|E')\, f(E',t)\, \mathrm{d}E' - f(E,t)\int B(E'|E)\, \mathrm{d}E' - \xi(E)\, f(E,t) + S(E,t) \quad (1)$$

where $S(E,t)$ is the rate of production of fast atoms with an energy E and $\xi(E)$ is the rate of the sink reactions that remove them. An analytic expression for $B(E'|E)$ may be derived by considering the rate of binary collisions $W(\mathbf{p}',\mathbf{p}'_b|\mathbf{p},\mathbf{p}_b)$ that change the momenta of the colliding particles from $\{\mathbf{p}, \mathbf{p}_b\}$ to $\{\mathbf{p}', \mathbf{p}'_b\}$ in the LF where the subscript b refers to the bath gas. The rate of binary collisions is obtained from the doubly differential cross section $\mathrm{d}^2\sigma/\mathrm{d}\Omega\, \mathrm{d}\epsilon$ according to[8]

$$W(\mathbf{p}',\mathbf{p}'_b|\mathbf{p},\mathbf{p}_b) = \frac{\left|\mathbf{p} - \frac{M}{M_b}\mathbf{p}_b\right|}{\left|\mathbf{p}' - \frac{M}{M_b}\mathbf{p}'_b\right|} \frac{1}{\mu^2} \frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\, \mathrm{d}\epsilon}\, \delta(\mathbf{p}' + \mathbf{p}'_b - \mathbf{p} - \mathbf{p}_b) \quad (2)$$

where the LF momenta $\{\mathbf{p}, \mathbf{p}_b\}$ and $\{\mathbf{p}', \mathbf{p}'_b\}$ are related to the initial and final relative collision energies ϵ and ϵ', Ω is the center-of-mass scattering angle, M and M_b are the masses of the projectile and the bath gas atom or molecule, and μ is their reduced mass. The energy relaxation kernel is given by the integral of the rate of binary collisions with the bath gas, which

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transforms the projectile particle momentum $|\mathbf{p}| = \sqrt{2ME}$ to $|\mathbf{p}'| = \sqrt{2ME'}$:

$$B(E'|E) = \frac{N_b M^{3/2}}{2\sqrt{2}\pi\mu^2}\sqrt{E'}\int\sqrt{\frac{\epsilon}{\epsilon'}}\,\frac{d^2\sigma(\epsilon, \epsilon', \cos\chi)}{d\Omega\, d\epsilon'} \times \rho(\mathbf{p}_b)\, d\mathbf{p}_b\, d\Omega_{\mathbf{p}}\, d\Omega_{\mathbf{p}'} \quad (3)$$

where $\Omega_{\mathbf{p}}$ and $\Omega_{\mathbf{p}'}$ are the solid angles of initial and final momenta in the LF for fixed values of $|\mathbf{p}|$ and $|\mathbf{p}'|$ and N_b is the density of the bath gas. The distribution function $\rho(\mathbf{p}_b)$ of the bath gas is the Maxwell–Boltzmann distribution at the bath temperature. Characteristic parameters of the thermalization process are readily extracted from the kernel.[8] For example, the mean thermalization time of the fast atoms may be evaluated from

$$t(E) = \int_E^{E_0} \frac{dE'}{\gamma(E')} \quad (4)$$

where

$$\gamma(E) = \int_0^\infty B(E'|E)(E - E')\, dE' \quad (5)$$

is the average rate of energy loss. We have included only the first moment of energy transfer in the above expression for γ, which is a good approximation at energies sufficiently higher than kT. At longer times, when the energy approaches the thermal energy of the bath gas, it may be necessary to consider higher moments of energy transfer with the actual energy distribution function.[10,11]

III. Results

The translational energy relaxation of O(^1D) atoms in an N_2 bath gas involves both elastic and inelastic collisions with the molecule. Here we explore the influence of elastic collisions. Explicit calculations of energy loss of energetic nitrogen and oxygen atoms in their ground electronic states through rotational and vibrational excitations of N_2 show it to be much less efficient than energy loss through elastic collisions.[9,10] The quantum mechanical approach we used to calculate the elastic differential cross sections employs a sudden approximation for the rotational motion and a close-coupled expansion for the vibrational motion of the molecule. The details of the calculation are given in a previous publication.[9] We adopted the ab initio potential energy surface of Tachikawa et al.,[20] who performed[21] classical trajectory surface hopping calculations to determine the efficiency of translational relaxation versus electronic quenching.

In Figure 1 we show the total elastic cross section and the momentum transfer (transport) cross section as functions of the O(^1D) atom energy. The momentum transfer cross section is defined as

$$\sigma_{tr}(\epsilon) = \int \frac{d\sigma(\epsilon,\chi)}{d\Omega}(1 - \cos\chi)\, d\Omega \quad (6)$$

where $d\sigma(\epsilon,\chi)/d\Omega$ is the differential cross section for scattering into the solid angle $d\Omega = 2\pi \sin\chi\, d\chi$. The calculated cross sections vary rapidly with the energy, with the total cross section decreasing from 3.7×10^{-14} cm^2 at 0.1 eV to 8.5×10^{-15} cm^2 at 2.0 eV and the momentum transfer cross section decreasing from 4.0×10^{-15} cm^2 at 0.1 eV to 1.2×10^{-15} cm^2 at 2.0 eV. In a study of O(^1D) atoms in the atmosphere, Shematovich et

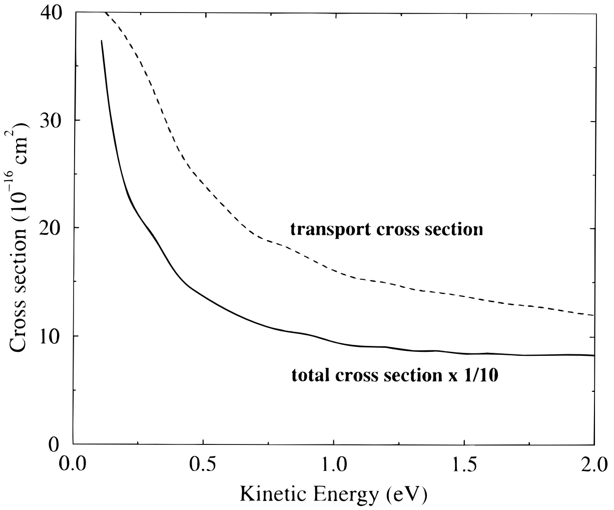

Figure 1. Total elastic cross section (×1/10) and momentum transfer cross section for O(^1D) + N_2 collisions as functions of center-of-mass kinetic energy.

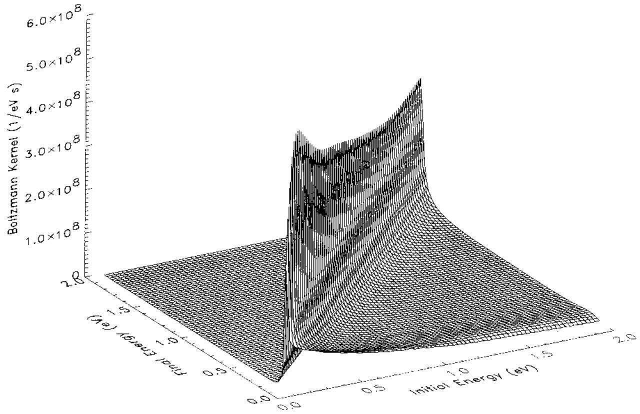

Figure 2. Boltzmann kernel in units of eV^{-1} s^{-1} for elastic O(^1D) + N_2 collisions for a bath temperature of 298 K and an N_2 bath gas density of 3.6×10^{16} cm^{-3}.

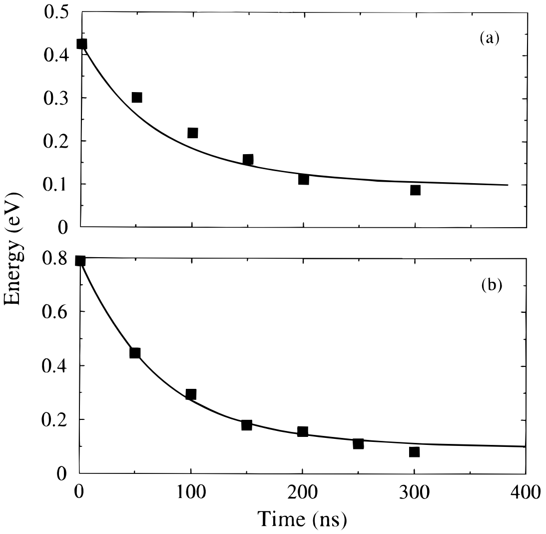

Figure 3. Mean energy of O(^1D) atoms in an N_2 atmosphere of 1 Torr pressure and a temperature of 298 K as a function of time. The solid curve is the present result, and the filled squares are the experimental results: (a) comparison with the experimental data of Matsumi et al.,[15] in which the O(^1D) atoms are produced with an initial energy of 0.425 eV in the 157 nm photodissociation of O_2; (b) comparison with the experimental data of Matsumi and Chowdhury,[16] in which the O(^1D) atoms are produced with an initial energy of 0.789 eV in the 193 nm photodissociation of N_2O.

al.[17] adopted a hard-sphere cross section of 3.0×10^{-15} cm^2 independent of energy.

In Figure 2 we present the Boltzmann kernel for the energy relaxation for a bath gas density of 3.6×10^{16} cm^{-3} and bath temperature of 298 K. It is highly anisotropic as the elastic cross section is dominated by small angle scattering involving small energy losses.

In Figure 3a we compare our results on the translational energy degradation of O(^1D) atoms with an initial energy of 0.425 eV with the experimental results of Matsumi et al.,[15] in which the O(^1D) atoms were produced in the photodissocation of O_2 at 157 nm. The agreement with the experimental results is quite satisfactory. In Figure 3b we provide a similar comparison with the experimental results of Matsumi and Chowdhury,[16] in which O(^1D) atoms were produced with an initial energy of 0.789 eV from the photodissociation of N_2O at 193 nm. The excellent agreement with the experimental results indicates that the energy losses arise predominantly from elastic scattering with a small contribution from inelastic rotational and vibrational excitation. The small discrepancies at low energies, if real, may be due to our neglect of electronic quenching, which modifies the energy distribution function. When the energy of the O(^1D) atoms approaches the thermal energy of the bath gas, the influence of the actual energy distribution function and higher moments of energy transfer should be included in the calculation of the energy relaxation. Such calculations will be undertaken when more experimental data become available.

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