On the Quenching of Rovibrationally Excited Molecular Oxygen at Ultracold Temperatures†

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We report quantum mechanical scattering calculations of zero temperature quenching rate coefficients for vibrationally and rotationally excited O_2 in collisions with ^{3}He. It is found that vibrational energy is channeled into more specific rotational levels in the ultracold regime than at thermal energies where a broad range of rotational levels are populated. The influence of the van der Waals interaction on the low-temperature quenching rate coefficients and the possibility of trapping vibrationally excited O_2 by the buffer gas cooling technique are also discussed.

I. Introduction

The conventional method of creating translationally cold molecules by seeded supersonic expansion has met with significant challenges in achieving temperatures lower than 1 K. The scenario has changed in the past few years with the advent of new methods for cooling and trapping atoms which led to the realization of Bose−Einstein condensation in dilute atomic gases. The associated progress in developing methods for cooling and trapping molecules to sub Kelvin temperatures also increased the prospects of creating ultracold molecules and the possibility of studying ultracold molecular collisions.[1−4] Indeed, Doyle and co-workers[5,6] have successfully trapped CaH molecules in a magnetic trap in which the molecules were cooled to ∼240 mK by collisions with cold ^{3}He buffer gas. Meijer and co-workers[8,9] devised a promising scheme based on time-varying electric fields to cool and trap polar molecules. They illustrated this approach[9] by cooling metastable CO molecules to temperatures of about 4 mK and ammonia molecules to about 350 mK.[10] Translationally cold molecules with temperatures of the order of μK can be produced by photoassociating ultracold atoms[11−15] but this leads to preferential population of high-lying vibrational levels of the ground electronic state. The efficiency of quenching of the vibrationally excited molecules thus produced is an issue in the experiment because it can limit the density of molecules that can be trapped. Thus important questions such as how efficiently vibrational or rotational degrees of freedom of a molecule are quenched by collisions at ultracold temperatures have arisen. This is especially relevant for systems which possess a van der Waals attractive potential because at temperatures lower than the well depth of the potential the relaxation rate coefficients will be modified by the attractive van der Waals interaction. Moreover, as a consequence of Wigner's threshold law,[16] at sufficiently low temperatures where the s-wave scattering dominates, the rate coefficients will be further modified by the requirement that the cross sections vary inversely as the velocity.

In an effort to address these issues and understand molecular relaxation processes and possibly chemical reactions at ultracold temperatures, we have been exploring atom−diatom collision phenomena over a wide range of temperatures extending into the Wigner regime.[17−23] By taking H−H_2[17,18] and He−H_2[19−22] as illustrative examples, we have explicitly shown that the rate coefficients for the quenching of excited vibrational levels become finite in the limit of zero temperature and the limiting values increase with increase in vibrational excitation. For these systems, the magnitudes of the limiting values of the quenching rate coefficients are comparable to their counterparts at room temperature. More recently, for the He−CO system,[23] we have shown that in addition to the shape resonances supported by the van der Waals attractive well there occur Feshbach resonances which may drastically modify the zero temperature quenching rate coefficients.

In this paper, we focus on the He−O_2 system. The He−O_2 system has been the topic of considerable interest, especially in connection with studying molecular alignment in seeded supersonic expansion.[24−29] Unlike the van der Waals complexes of O_2 with Ne and Ar, no spectroscopic data are available for the He−O_2 system. Empirical estimates of the anisotropies of the interaction have been obtained by Keil et al.,[24] Faubel et al.,[25] and Beneventi et al.[26] from molecular beam scattering data. Ab initio determinations of the interaction potential between He and O_2 are complicated by the fact that O_2 is an open shell molecule.[30−32] As a result, all ab initio calculations of the interaction potentials reported in the literature[30−32] resorted to a rigid rotor model with the O_2 bond distance fixed at its equilibrium value. Motivated by the current interest in the He−O_2 system, a full three-dimensional He−O_2 interaction potential with explicit dependence on the O_2 stretch has been calculated by Groenenboom and Struniewicz.[33] This potential agrees nearly quantitatively with the best estimates for a few important points presented in the rigid rotor potential study of Cybulski et al.[32] and it is used in the present work.

The He−O_2 system has also been of interest in the buffer gas cooling method of Doyle et al. though experimental studies are yet to be carried out. In the buffer gas cooling method, a solid sample of the molecule is laser-ablated inside a chamber containing cold ^{3}He buffer gas. Elastic collisions with the buffer gas slows down the molecule while inelastic spin-exchange collisions and rovibrational transition collisions may lead to trap loss. The role of spin-exchange collisions has been recently explored by Bohn[34] using the rigid rotor potential energy surface

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of Cybulski et al.[32] Here we focus on rovibrational transitions using the full three-dimensional potential energy surface of Groenenboom and Struniewicz.[33]

The paper is organized as follows: In Section II we briefly describe the quantum scattering calculations. Section III describes the results, and a summary of our findings is given in Section IV.

II. Method

We used the MOLSCAT[35] program suitably adapted to the present system to carry out the scattering calculations. It makes use of a close-coupled expansion of the wave function in terms of the rovibrational eigenfunctions of the diatom together with an expansion of the angular dependence of the interaction potential in Legendre polynomials. In the Legendre expansion we retained terms of orders up to 12. Due to symmetry, only the even terms contribute. For O_2 we adopted the potential constructed by Friedman[36] and modified by Babb and Dalgarno.[37] The vibrational wave functions of O_2 were obtained in a basis set of Hermite polynomials, and a Gauss Hermite quadrature rule was used to compute the matrix elements of the interaction potential between the vibrational wave functions. The coupled-channel Schrödinger equations were solved using the R-matrix method.[38]

O_2 is an open-shell molecule with electronic spin angular momentum **s** and nuclear rotational angular momentum **j** to give a total angular momentum **I**. As in previous studies,[28,29] we assume that **j** and **s** are effectively decoupled during the collision process.

In the total angular momentum representation used in the close-coupled formalism cross sections for transitions from an initial vibrational-rotational level labeled by quantum numbers vj to a final level labeled by quantum numbers $v'j'$ can be expressed in terms of the corresponding S-matrix elements:[39,40]

$$\sigma_{vj\to v'j'}(E_{vj}) = \frac{\pi}{(2j+1)k_{vj}^2}\sum_{J=0}^{\infty}(2J+1)\sum_{l=|J-j|}^{|J+j|}\sum_{l'=|J-j'|}^{|J+j'|}|\delta_{jj'}\delta_{ll'}\delta_{vv'} - S^J_{jj'll'vv'}|^2 \tag{1}$$

where J and l are respectively the total and the orbital angular momentum quantum numbers of the atom-molecule collisional system. The primed quantities denote their unprimed counterparts after the collision. For a given total energy, the wave vector k_{vj} is defined as $k_{vj} = \sqrt{2\mu(E-\epsilon_{vj})}/\hbar$ where ϵ_{vj} is the eigen energy of the initial rovibrational state and μ is the three-body reduced mass. The kinetic energy in the initial channel is given by $E_{vj} = \hbar^2 k_{vj}^2/(2\mu)$.

It is useful to define the total de-excitation (quenching) cross section from a given initial state

$$\sigma_{vj}^{in}(E_{vj}) = \sum_{v'j'}\sigma_{vj\to v'j'}(E_{vj}) \tag{2}$$

where the summation includes both vibrationally inelastic and pure rotationally inelastic transitions but excludes purely elastic $v'j' = vj$ transitions.

In the limit of zero kinetic energy, it is convenient to express the scattering cross section in terms of the scattering length. The scattering length is real for single-channel scattering where purely elastic scattering occurs but it has an imaginary part when two or more channels are open due to the presence of inelastic scattering. The complex scattering length may be written $a_{vj} = \alpha_{vj} - i\beta_{vj} = -\lim_{k_{vj}\to 0}(S_{vj,vj} - 1)/2ik_{vj}$ where α_{vj} and β_{vj} are the real and imaginary parts of the scattering length and $S_{vj,vj}$ is an element of the S-matrix corresponding to the initial channel. The imaginary part β_{vj} of the scattering length is related to the total inelastic quenching cross section σ_{vj}^{in} in the limit of zero velocity:[18]

$$\beta_{vj} = \lim_{k_{vj}\to 0}\frac{k_{vj}\sigma_{vj}^{in}}{4\pi} \tag{3}$$

and the zero temperature quenching rate coefficient is given by[18,19]

$$r_{vj}(T\to 0) = 4\pi\beta_{vj}\hbar/\mu \tag{4}$$

The zero temperature limit of the quenching rate coefficient is finite because according to Wigner's law[16] the quenching cross section σ_{vj}^{in} varies inversely as the velocity as the kinetic energy approaches zero. The quenching rate coefficients at other temperatures are obtained by averaging the cross sections over a Boltzmann distribution of velocities of the incoming atom at a specified temperature T:

$$r_{vj}(T) = (8k_BT/\pi\mu)^{1/2}\frac{1}{(k_BT)^2}\int_0^\infty \sigma_{vj}^{in}(E_{vj})\exp(-E_{vj}/k_BT)E_{vj}\,dE_{vj} \tag{5}$$

where k_B is the Boltzmann constant.

III. Results and Discussion

We have restricted the vibrational quenching cross section calculations to the $v = 1, j = 1$ level of O_2. Only odd rotational levels exist for the ground electronic state of O_2 and allowed levels from $j = 1$ to 25 were included in both $v = 0$ and $v = 1$ vibrational levels. Cross section are computed for kinetic energies in the range 10^{-6} cm^{-1} to 1500 cm^{-1}. At each value of the energy a sufficient number of total angular momentum partial waves has been included in the sum in eq (1) to ensure convergence of the cross sections. The maximum value of J employed in the calculation is 60.

The He$-O_2$ interaction potential employed here[33] has a global minimum at the T-shaped geometry for $R = 6.0$ au arising from the van der Waals interaction where R is the separation between He and the center of mass of O_2. The depth of the potential well for this geometry is 27.9 cm^{-1}. A local minimum exists for the collinear geometry at $R = 6.9$ au with a well depth of 25.6 cm^{-1}. At thermal energies, the shallow van der Waals interaction has little effect on the collision dynamics but at kinetic energies comparable to the well depth, the dynamics is significantly influenced by the potential well. This is illustrated in Figure 1 where we show the quenching cross section for the $v = 1, j = 1$ level of O_2 as a function of kinetic energy in the range $10^{-6}-1500$ cm^{-1}. For energies less than 0.05 cm^{-1} only s-wave scattering contributes and the cross sections vary inversely as the velocity in accordance with Wigner's law. For energies higher than 50 cm^{-1}, the cross section increases with energy as is normally expected for vibration−translation/rotation energy transfer process. In the intermediate energy regime the cross sections exhibit an oscillatory behavior. The oscillations are due to shape resonances supported by the van der Waals interaction potential.

Rate coefficients were obtained by averaging the cross sections over a Boltzmann distribution of velocities of the He atom as a function of the temperature. They are shown in Figure

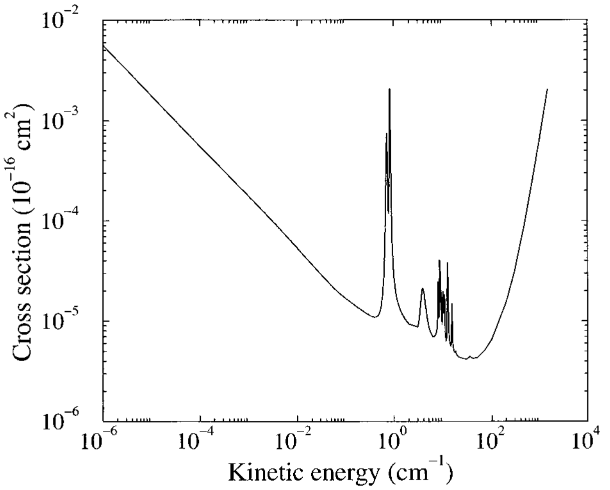

Figure 1. Cross section for quenching of the $v = 1, j = 1$ level of O_2 in collisions with ^{3}He as a function of the incident kinetic energy.

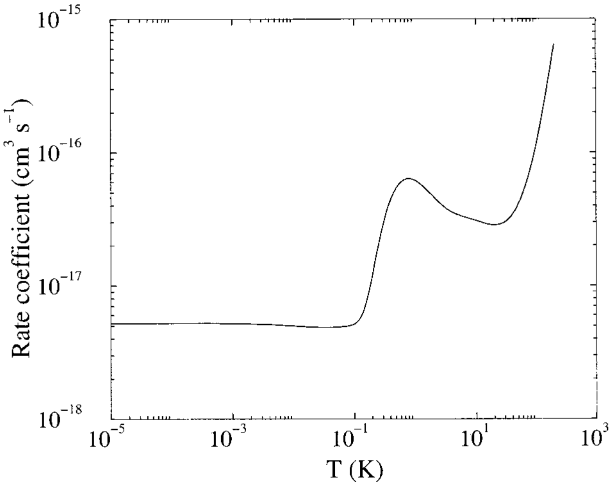

Figure 2. Rate coefficient for quenching of the $v = 1, j = 1$ level of O_2 in collisions with ^{3}He as a function of the temperature.

2 for temperatures ranging from 10^{-5} K to 200 K. Figure 2 shows three distinct regimes: the Wigner regime below a temperature of about 10^{-2} K where the rate coefficient become constant, the van der Waals interaction-dominated regime between 10^{-1} K and 30 K where the rate coefficient exhibits an unusual temperature dependence, and the normal temperature regime above 30 K where the rate coefficient increases with increase in temperature. The upturn of the rate coefficient below a temperature of 30 K is due to the presence of shape resonances shown in Figure 1. The local maximum that occurs at about 0.8 K is due to the sharp resonance at that energy in Figure 1. The subsequent rapid decrease in the magnitude of the rate coefficient before attaining the zero temperature limiting value is due to the decay of all higher partial waves. From the zero temperature quenching rate coefficient the imaginary part of the scattering length is estimated to be $\beta_{11} = 1.8 \times 10^{-7}$ Å (cf. eq 4).

The final rotational distributions in $v = 0$ resulting from the quenching of the $v = 1, j = 1$ level at kinetic energy values of 10^{-5}, 10, and 500 cm^{-1} are shown, respectively, in Figure 3, parts (a)−(c). The lowest energy corresponds to the Wigner threshold regime, the intermediate energy value corresponds to the van der Waals regime, and the highest energy corresponds to the normal high-temperature regime. The distribution is narrow and it is peaked at $j' = 3$ in the ultracold regime in accordance with the $|\Delta j| = 2$ selection rule for homonuclear molecules but it becomes broader as the energy is increased. The broadening occurs because more partial waves contribute at higher energies leading to a larger number of partial waves in the outgoing channel.

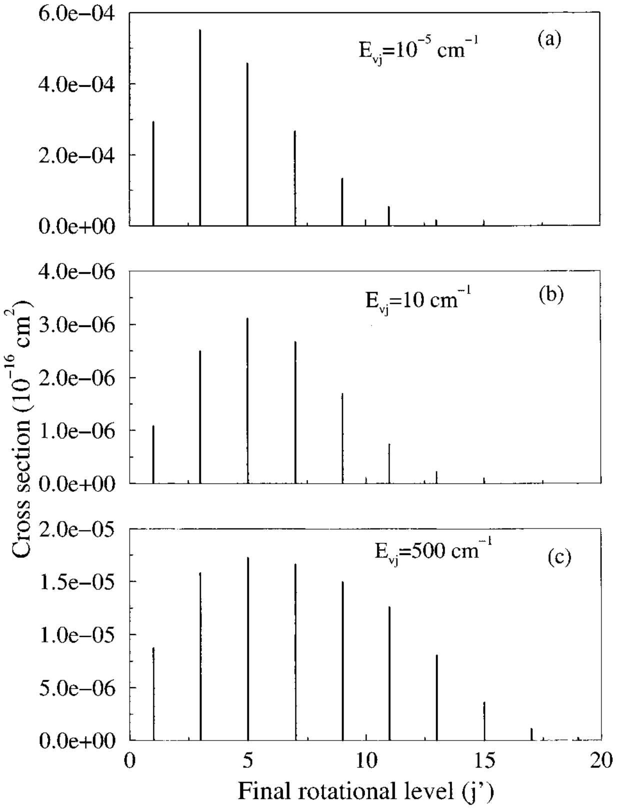

Figure 3. Distribution of final rotational level in $v = 0$ following quenching of the $v = 1, j = 1$ levels of O_2 in collisions with ^{3}He. The upper panel (a) is for an incident kinetic energy of 10^{-5} cm^{-1}, the middle panel (b) is for an incident kinetic energy of 10 cm^{-1}, and the lower panel (c) is for an incident kinetic energy of 500 cm^{-1}.

In scattering the final state angular distribution is usually represented by the square of a sum of amplitudes but for an incident s-wave it is determined by the sum of squares of amplitudes, each of which is directly proportional to the cross section for transition into a particular final rotational angular momentum state with a specific final kinetic energy. Measurements of the angular distribution would provide a sensitive test of the anisotropy of the intermolecular potential surface on which the rotational cross sections depend.

In Figure 4 we show the elastic scattering cross section for the ground rovibrational level of O_2. The zero energy limiting value of the cross section is found to be 6.4 Å^2. However, the corresponding scattering length is found to be negative with a value $a_{01} = -0.71$ Å. Using the potential of Cybulski et al.,[32] Bohn[34] estimated the scattering length for ^{3}He−O_2 collisions to be in the range $-0.64 \leq a_{01} \leq 2.3$ Å. The potential of Cybulski et al.[32] underestimates the van der Waals well depth by as much as 20% and the lower bound of the scattering length reported by Bohn[34] is obtained from a calculation in which the entire potential is multiplied by 1.2 to account for the uncertainty. Thus our value of −0.71 Å for the scattering length is close to the lower bound of −0.64 Å estimated by Bohn.

The rotational quenching rate coefficient also becomes finite in the limit of zero temperature and is several orders of magnitude larger than the vibrational quenching rate coefficient. For $j = 3$, it is characterized by $\beta_{03} = 0.394$ Å corresponding to a value of 1.15×10^{-11} cm^3 s^{-1} for the rate coefficient. The

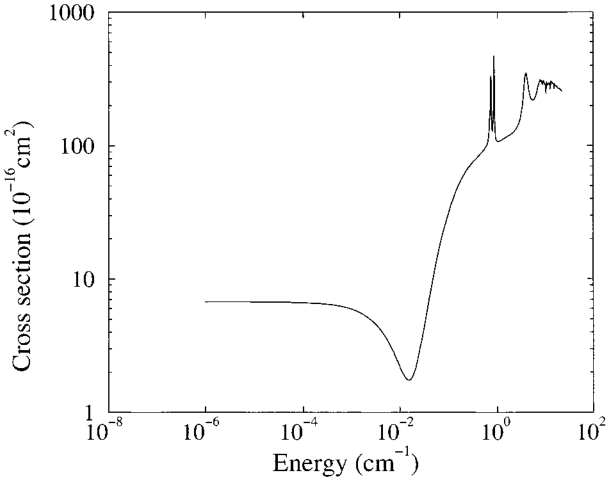

Figure 4. Cross section for elastic scattering between ^{3}He and O_2 in its ground rovibrational level as a function of the incident kinetic energy.

large value of the rotational quenching rate coefficient compared to vibrational quenching is due to the large angular anisotropy of the interaction potential compared to the small change in the potential from the stretching of the O_2 bond. On the other hand, the relatively low efficiency of vibrational quenching shows that it is possible to cool and trap rotationally cold O_2 in a vibrationally excited level. This could lead to interesting experiments involving collisions of translationally cold but vibrationally hot molecules.

IV. Summary and Conclusions

Quantum mechanical scattering calculations of vibrational and rotational relaxation of O_2 by ^{3}He atoms show that the relaxation rate coefficients for rotational and vibrational degrees of freedom differ by several orders of magnitude. The vibrational motion is quenched less efficiently than rotational motion, owing to the large angular anisotropy of the interaction potential compared to the stretching of the molecule. Similar results were obtained for the He−CO system.[23] The present study together with our previous investigations of H−H_2,[17,18] He−H_2,[19−22] and He−CO[23] have clearly demonstrated that long-range van der Waals interaction and quantum mechanical threshold phenomena can have dramatic effects on the low-temperature scattering process and that the current interest in low-temperature collisions offers promising opportunities for ultracold chemical dynamics.

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