Molecular spin relaxation in cold atom-molecule scattering

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Elastic and spin-changing inelastic collision cross sections between oxygen molecules and helium atoms are computed in the energy range 0.1–10 K. This study explores the recently demonstrated buffer-gas cooling process that produces magnetically trapped, translationally cold molecules. Conclusions are drawn about the favorable prospects of cooling oxygen molecules, and about the general feasibility of this cooling technique.

Molecular physics is entering a new regime, with the advent of techniques for producing and trapping translationally cold molecules. Molecular samples have long been prepared in their ground vibrational and rotational states by supersonic expansion from nozzles [1], but reducing their translational temperatures to below 1 K has presented a large technical challenge until recently. Several groups have now achieved this feat, producing cold samples of Cs_2 [2], VO [3], CaH [4], K_2 [5], and Rb_2 [6]. In some cases these samples are also vibrationally and rotationally cold. Translationally ultracold molecules raise a host of possibilities, including extensions of precision spectroscopy (such as possible measurements of the electron's electric-dipole moment [7]), precise determination of intermolecular potential energy surfaces (PES's), and molecular Bose-Einstein condensates possessing internal rotational and vibrational degrees of freedom. We may also expect cold collision dynamics to be even richer than that studied in cold atomic collisions [8]. For example, unusual resonant states can be formed when colliding molecules begin to rotate, leaving them with insufficient translational kinetic energy to overcome their van der Waals attraction.

The theory of molecular collisions in this energy regime is still in its infancy. Such a theory must assess the elastic and inelastic collision cross sections that are vital for interpreting and guiding the first generation of experiments. One set of calculations has studied vibrational quenching in cold He-H_2 collisions [9], since in most experiments the molecules are produced initially in high vibrational levels. This paper by contrast presents a calculation of molecular *spin* relaxation of cold molecules, providing a quantitative understanding of the magnetic trapping process itself.

We focus on molecules produced in the buffer-gas loading technique pioneered by Doyle and collaborators [10]. In this technique, a solid sample of the species of interest is laser ablated inside a chamber containing a cold vapor of helium buffer gas. The molecular sample then cools to the ambient temperature of the buffer, usually <1 K, which is maintained by thermal contact with a dilution refrigerator. Collisions with the buffer gas also serve to relax vibrational and rotational degrees of freedom of the laser-ablated molecules. Cooling is carried out in the presence of a magnetic trapping field that is capable of holding those cold molecules that remain in their ''weak-field-seeking'' spin states, i.e., those whose magnetic moments are aligned antiparallel to the magnetic trapping field.

Molecular oxygen is a natural choice for a theoretical study, as it is a paramagnetic (hence magnetically trappable) species of intense physical and chemical interest. In addition, accurate *ab initio* PES's have been computed for the He-$^{16}O_2$ system [11]. Here we consider the ''stretched'' state of $^{16}O_2$ with total spin $|JM_J\rangle = |22\rangle$ since it is immune to spin-exchange collisions, much as the stretched states of alkali-metal atoms are. However, the $^{16}O_2$ molecule is in some sense a ''worst case'' for spin relaxation, owing to its spin-rotation coupling. To see this, note that nuclear permutation symmetry restricts the ground state of $^{16}O_2$ to having rotational quantum number $N=1$ [12]. Coupling the total spin $S=1$ to this rotation yields total spin states $J=0$, 1, 2 (Fig. 1). Our $|JM_J\rangle = |22\rangle$ state of interest is therefore susceptible to collisions that drive it to the untrapped state $|JM_J\rangle = |00\rangle$. For this reason the mixed-isotope molecule ^{16}O-^{17}O has been suggested as a candidate for buffer-gas cooling [13]. This molecule does have an allowed $N=0$ ground state; hence its lowest total spin state, $J=1$, can be magnetically trapped. In this case the only trap-loss collisions are those that change the magnetic quantum numbers M_J, which are expected to be suppressed at low magnetic fields and low energies by threshold effects.
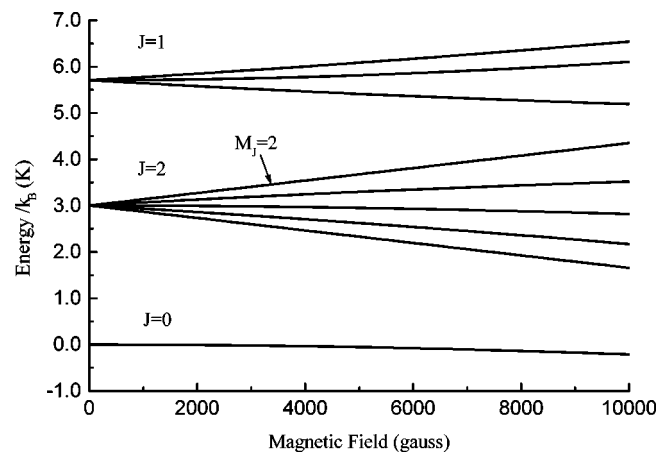

FIG. 1. Zeeman energies vs magnetic field for the total angular momentum J manifolds corresponding to the rotational ground state $N=1$ of $^{16}O_2$. We consider collisions of the He buffer gas with the ''stretched state'' $|JM_J\rangle = |22\rangle$ whose energy is indicated by an arrow.

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However, rather than dismiss the more abundant and widely studied $^{16}O_2$ molecule, we explore in this paper its prospects for buffer-gas cooling. We find that these prospects are generally favorable according to the following criterion: The success of magnetic trapping relies on the ability to reduce the molecules' translational temperature to below the trap depth T_D (typically several kelvin). The time in which this can occur is limited by collisions between the molecules and the He buffer gas that can flip the molecular spins, producing untrapped states. These inelastic collisions are characterized by a trap-loss rate coefficient K_{loss}. Generally speaking, for a cooling strategy to be effective, the ratio of elastic to inelastic collisions, K_{el}/K_{loss}, must be large. In an extreme case, such as evaporative cooling of ultracold atoms, this ratio must be >150 [14]. For buffer-gas cooling, the requirement is less strict. Consider that a fast molecule loses approximately half its kinetic energy in each collision with a cold atom, cooling within several collisions to a kinetic energy comparable to that of the buffer-gas atoms. Once slowed, the molecules thermalize to ambient temperatures within 3–4 additional collisions [15]. We thus expect roughly ten collisions to suffice for cooling a molecule, requiring a ratio of $K_{el}/K_{loss} \sim 10$, although detailed kinetic studies will be required to determine the exact ratio. In this paper we present calculations of ^3He-$^{16}O_2$ scattering that predict a ratio, away from any resonance, of $K_{el}/K_{loss} \approx 100$. This result argues that molecular oxygen should be capable of withstanding buffer-gas cooling. By extension, it implies that molecules with rotationless ground states, such as ^{16}O-^{17}O and CaH, should fare even better. Note that a recent experiment that trapped cold CaH found the extremely favorable ratio $K_{el}/K_{loss} > 10^4$ [4].

The model is based on the PES of Cybulski *et al.*, computed in a rigid rotor approximation using a supermolecular approach [11]. To reduce the scattering problem to a set of coupled channel equations, we first expand the PES into Legendre polynomials,

$$V(R,\theta) = \sum_{l \text{ even}} v_l(R) P_l(\cos \theta), \qquad (1)$$

where R is the distance between the He and O_2 centers of mass, and θ is the molecular orientation angle relative to this axis. We can fit the PES reliably by taking the expansion over $l=0,2,4,6$. Each curve v_l is then extrapolated to large R by matching it smoothly to a lowest-order dispersion potential $-C_6^{(l)}/R^6$. For $l=0$, we find that $C_6^{(0)} = 10.8$ a.u., in good agreement with the value extracted from higher-energy scattering experiments [16]. We then transform $V(R,\theta)$ into the laboratory reference frame and compute its matrix elements in the following basis set:

$$|He(^1S)\rangle |O_2(^3\Sigma_g^-, v=0)\rangle |N,J,M_J,L,M_L\rangle. \qquad (2)$$

Here the first two kets imply that both the helium atom and the oxygen molecule are in their electronic (and vibrational) ground states, while the final ket contains the rotational and total angular momenta of the molecule, as well as the relative orbital angular momentum L of the He-O_2 pair and its lab-

fixed projection M_L. Finally, we add to these potentials the O_2 fine structure, computed as in [17]. Note that the PES (1) is symmetric under the operation $\theta \to \pi - \theta$, whereby only partial waves of the same parity are coupled.

As is customary in cold collision physics, we can characterize the PES to lowest order at low collision energies by its *s*-wave scattering length. This quantity can be determined by a single-channel calculation in the isotropic part of the potential, $v_0(R)$. This potential curve has an extremely shallow well depth of 32 K due to the closed electronic shell of the He atom. This fact, combined with the low reduced mass of the He-O_2 system, leads to *exactly one s*-wave bound state, bound by an energy $E_0/k_B = 5.0$ K. This circumstance lends a certain rigidity to the model: unlike the familiar case of alkali-dimer potentials, we are not free here to vary the potentials to adapt to an empirical threshold scattering length. Rather, the scattering length is narrowly prescribed by the PES. Cybulski *et al.* estimate that their PES may miss the true well depth by perhaps 20% [11]. Accounting for this additional depth gives us *s*-wave scattering lengths in the ranges $-1.2 < a(3) < 4.3$ a.u. and $-68 < a(4) < -5.5$ a.u. for collisions of $^{16}O_2$ with ^3He and ^4He, respectively.

This paper is concerned with collisions of $^{16}O_2$ with ^3He. Experimentally ^3He is preferred over ^4He because of its higher vapor pressure at sub-kelvin temperatures. Moreover, the negative scattering length of the ^4He-$^{16}O_2$ system causes the dominant *s*-wave contribution to the elastic scattering cross section to vanish for small energies (<0.2 K), reducing the efficiency of the cooling. The results below are computed both for the ''nominal'' value $a(3)=4.3$ of the scattering length, and for the value $a(3)=-1.2$ a.u., corresponding to a 20% deeper PES.

The calculations include the partial waves $L=0-10$ and the molecular rotational states $N=1$ and $N=3$. This is sufficient to converge the total cross sections to two or three digits at $E=10$ K, adequate for this pilot study. The computed partial elastic cross sections are presented in Fig. 2, segregated by the parity of the contributing partial waves. These cross sections are computed for a bias magnetic field of $B=0$, appropriate for the center of a quadrupole magnetic trap. The initial spin state is taken to be $|JM_J\rangle = |22\rangle$, but the general features are the same for $|JM_J\rangle = |21\rangle$. Also shown in the Fig. 2 are the *s*- and *p*-wave unitarity limits for these collisions. In the important energy range around 1 K, comparable to the magnetic trap depth T_D, the *s*-wave cross section nearly attains its unitarity value. Similarly, the *p*-wave cross section reaches its unitarity limit at ~ 4 K. Since the other partial waves are suppressed at these energies by the Wigner threshold law, this implies that elastic scattering is, in some sense, as good as can be expected. The total elastic cross section tends to hover near $\sigma_{el} \approx 10^{-14}$ cm^2, somewhat larger than the geometric cross section of these collision partners.

We note in passing that resonant structures appear in the energy range of our calculations. Shape resonance of *g*- and *h*-wave character are apparent at energies of ~ 3 K and ~ 4 K, respectively. For the odd partial waves, there is also a Feshbach resonance near 2.5 K, which spans several partial waves. Such resonances are probably generic: if bound states
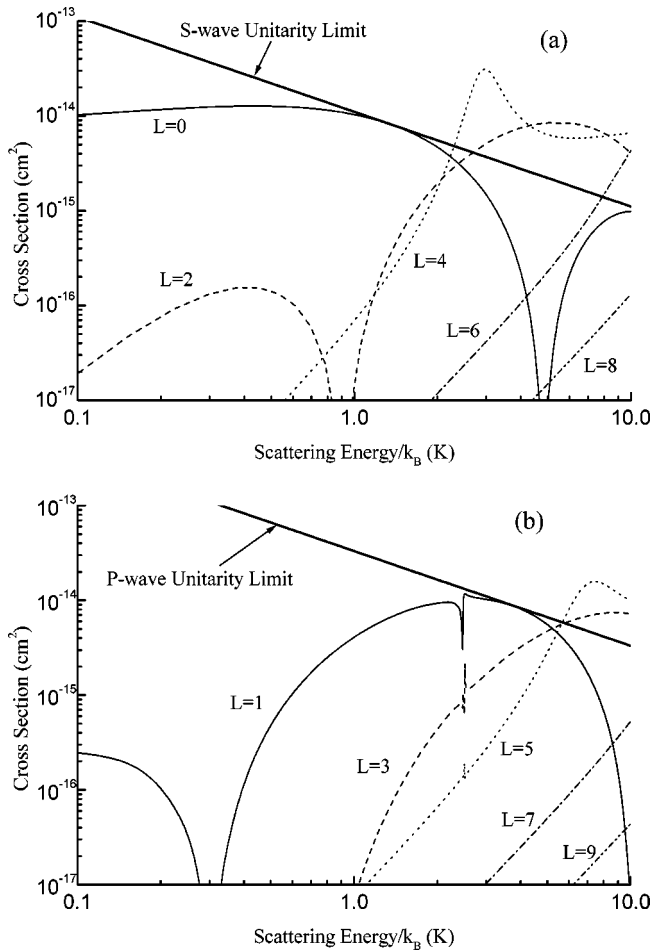
FIG. 2. Partial elastic-scattering cross sections for ^{3}He-^{16}O$_2$ scattering vs scattering energy, for the nominal scattering length $a(3)=4.3$ a.u. The even (a) and odd (b) partial-wave contributions have been separated, since they are not intercoupled by the scattering Hamiltonian. For comparison, the heavy lines show the s-wave [in (a)] and p-wave [in (b)] unitarity limits.

lie several kelvin deep and thresholds are separated by several kelvin, then resonances will appear on a several kelvin energy scale. Details of these resonance features will be reported separately [18].

Figure 3 translates the total elastic-scattering cross section into an elastic rate coefficient K_{el} (solid curve). Also shown (dashed curve) is the total rate constant K_{loss} for inelastic spin-flip collisions that produce untrapped spin states. For the O$_2$ molecule in its rotational ground state, the loss channels consist of those total spin $|JM_J\rangle$ states with $M_J \lesssim 0$. The main contributor to loss is the $|JM_J\rangle = |00\rangle$ channel, with the $|10\rangle$ and $|20\rangle$ channels also contributing significantly at higher energies. For an energy near 1 K, the total loss rate lies near 10^{-12} cm^3/sec, higher than the upper limit of $\approx 10^{-14}$ cm^3/sec estimated for He-CaH collisions in Doyle's experiment [4]. Note also the sharply rising rates at $E/k_B \approx 2.5$ K, where the $J=1$ threshold becomes energetically accessible.

The main result shown in Fig. 3 is the suppression, by two orders of magnitude, of spin-flip rates relative to elastic rates. This suppression is similar to the suppression of dipolar loss
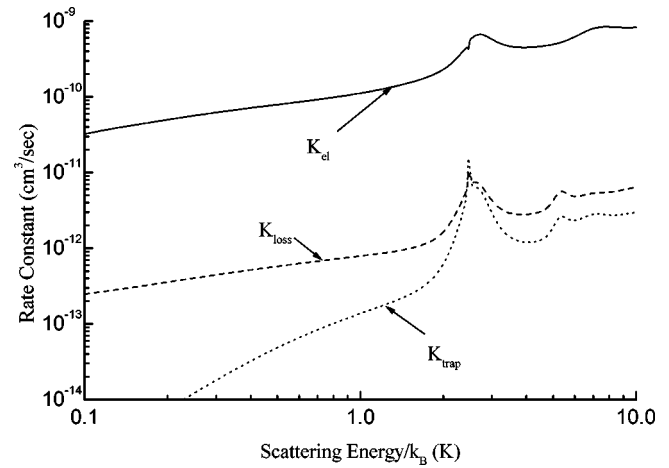

FIG. 3. Rate constants vs scattering energy for ^{3}He-^{16}O$_2$ collisions using the nominal scattering length $a(3)=4.3$ a.u. The solid line shows the total elastic rate K_{el}. Also shown are the inelastic rate constants for collisions that produce untrapped states (K_{loss}, dashed line) and trapped states *other than* $|22\rangle$ (K_{trap}, dotted line). Notice that K_{el} exceeds K_{loss} by over two orders of magnitude at energies of several kelvin.

rates in cold collisions of alkali-metal atoms [19]. Namely, the O$_2$ molecule cannot spin-exchange with the He atom, since He has no electronic angular momentum. For O$_2$ to undergo a spin-changing collision therefore requires that the excess angular momentum go into the mechanical rotation L of the He-O$_2$ system about its center of mass. Thus a collision dominated by an s-wave incident channel can only cause a change in the molecule's spin by exiting in a d-wave channel (or higher). But at these collision energies, d-wave processes are suppressed. We note moreover that not all spin-changing collisions are necessarily bad. The dotted line in Fig. 3 represents the rate of production of trapped states other than $|22\rangle$. Since the mean-free path of O$_2$ at typical buffer-gas densities is of order 0.1 cm, while the trap region is ~ 1 cm across, it may happen that untrapped states can be promoted back into trapped states before leaving the trap.
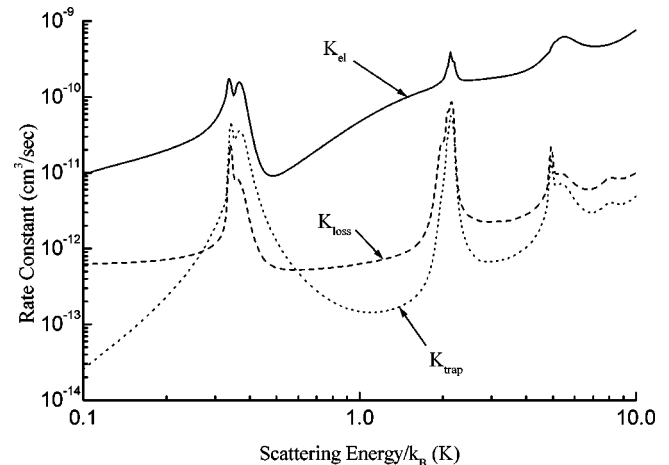

FIG. 4. Same as Fig. 3, but for a scattering length of $a(3) = -1.2$ a.u.

Finally, we return to the question of uncertainty in the PES. Figure 4 shows a set of total rate constants, analogous to the ones in Fig. 3, but for the limiting case where the scattering length is $a(3) = -1.2$ a.u. To perform these calculations we multiply the entire PES by 1.2, to account for the 20% uncertainty in well depth. Doing so naturally changes scattering phase shifts; hence it moves resonance positions. However, away from resonance we see that the ratio K_{el}/K_{loss} is still nearly 100.

Our results thus demonstrate that buffer-gas cooling of $^{16}O_2$ by He should be possible. Note, however, that the typical densities of He buffer gas used in the experiments ($\sim 10^{16}/cm^3$ [4]) would limit the oxygen lifetime in the trap to < 0.1 msec. This will present an experimental challenge, but not necessarily an insurmountable one [20]. A next goal of this study will run realistic rate equation simulations to determine effective cooling strategies for this situation.

In summary, these pilot calculations bode well for the buffer-gas loading process, since even the ''worst-case'' molecule $^{16}O_2$ should be coolable by this technique. Future theoretical work will go beyond the atom-molecule case to investigate molecule-molecule cold collisions. For example, cold O_2 samples could be cooled even further by evaporative cooling techniques. The feasibility of this cooling will hinge on favorable values of K_{el}/K_{loss} for O_2-O_2 scattering, which remain entirely unknown at present. Extensions of the theoretical approach used here will be required to unravel the rich collisions physics that ultracold molecules have to offer.

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