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Cooling and trapping of molecules in highly excited rotational states

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Collisional relaxation of highly rotating hydrogen molecules is investigated as a function of energy. Calculations demonstrate that inelastic collisions are dramatically suppressed for specific rotational levels of the molecule as the energy is lowered due to the closing of quasiresonant rotation-vibration channels. It is predicted that a ^{3}He buffer gas may be used to load these highly excited molecules into a trap without a significant loss of population. It is further predicted that evaporative cooling may be used to cool the ''super rotors'' to even lower temperatures.

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Recent experimental schemes [1,2] have been reported that produce diatomic molecules in very highly excited rotational levels. These so-called ''super rotors'' may be produced over a distribution of rotational levels [1] or in a single selected rotational level [2]. The collisional properties of such molecules are expected to be very interesting at low temperatures [2–4]. In the case of H_2, the ultracold collisional dynamics of such highly rotating molecules produces remarkable structure in the distribution of the total quenching rate coefficient versus the rotational level. For example, there is a five order of magnitude decrease in the rate coefficient for the 22nd rotational level compared to the surrounding levels [3]. This striking effect is due to the closing of a classically quasiresonant channel. The effect is believed to be general to any atom-diatom system [3], however, it will be most pronounced for light diatoms whose moment of inertia is small. The behavior may allow an experimental scheme to be developed for translationally cooling and trapping molecular super rotors.

Buffer gas cooling has become a standard technique for loading paramagnetic atoms and molecules into a magnetic trap [5]. The same cooling mechanism, namely the elastic collisions with a cryogenically cooled ^{3}He buffer gas, could also be used to cool molecules such as H_2 that do not possess a permanent magnetic dipole moment. Collisional experiments could be performed by passing a beam of hot H_2 molecules through a buffer gas cell [6]. Trapping the molecules would be more difficult. One possibility would be to use a nonresonant electric field as the trap. If the intensity of the field can be made large enough to compensate for the small polarizability, then the highly rotating molecules would correlate with high-field seeking pendular states [7] and be confined by an electric-field maximum in free space. The feasibility of any cooling or trapping scheme will ultimately depend on the collisional relaxation rates of the highly rotating molecules.

The term ''super rotor'' was previously introduced [2] to describe diatomic molecules in highly excited rotational states. At ordinary temperatures, these molecules relax with great efficiency and may provide competition for the spinning up process that created them [4]. In the present work, we investigate the possibility for producing super rotors that do not relax as a result of collisions. The idea is to use a highly rotating diatomic molecule whose rotational level is characteristic of a quasiresonant transition, but whose temperature is cold enough that the classically quasiresonant channel is closed. The efficiency of collisional relaxation is then reduced by many orders of magnitude compared to ''ordinary'' highly rotating molecules. If the decrease in relaxation efficiency occurs sharply at a high enough temperature (e.g., above 240 mK for ^{3}He), then it should be possible to use a buffer gas to cool the super rotors and load them into a trap without a significant loss in population.

The collisions that are considered in this work are atom-diatom and diatom-diatom, where the atom is ^{3}He and the diatom is H_2 in a highly excited rotational level. The calculations of atom-diatom collisions are needed to determine whether a ^{3}He buffer gas can be used to cool the super rotors to the point where they become stable against collisions. The calculations of diatom-diatom collisions are needed to determine whether evaporative cooling could be used to further cool the molecules assuming they have been trapped. All results described in this work were obtained from fully quantum mechanical calculations using the general purpose scattering program MOLSCAT [8].

Figure 1 shows the product of the cross section and the relative velocity for $^3\mathrm{He}+\mathrm{H}_2$ collisions as a function of the initial kinetic energy. The upper set of curves is for elastic collisions and the lower set is for the sum of all possible inelastic collisions. The molecule is initially in the state $v=2$, $j=22$, where v and j are the respective vibrational and rotational quantum numbers. Convergence tests were performed by using a sufficiently large rovibrational basis set and varying the total angular-momentum quantum number J. Good convergence is obtained for all of the energies shown when J is summed from 20 to 24. Similar convergence patterns were found for other initial states of the molecule. Although the results have not been thermally averaged, it is clear that the rate coefficients for elastic and inelastic scattering of the $v=2$, $j=22$ state will be in the vicinity of 10^{-10} cm^3 s^{-1} and 10^{-16} cm^3 s^{-1}, respectively.

Figure 2 shows the ratio of inelastic to elastic cross sections for $^3\mathrm{He}+\mathrm{H}_2$ collisions as a function of the initial kinetic energy. Compared to surrounding rotational levels, the ratios for the $j=22$ level are dramatically reduced at energies below 10 cm^{-1}. This is due to the closing of classically quasiresonant $\Delta j=-2\Delta v$ channels as the energy is lowered. The relaxation efficiency drops by 5–6 orders of magnitude

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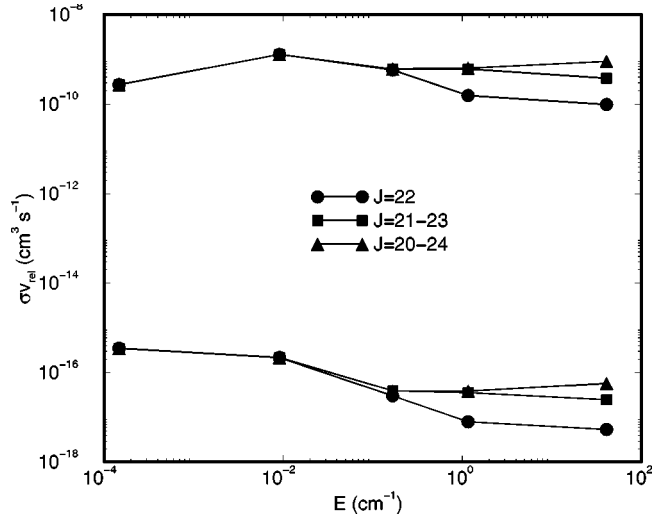

FIG. 1. Convergence tests for $^3He+H_2$ collisions as a function of kinetic energy. The upper set of curves is for elastic collisions and the lower set is for the sum of all possible inelastic collisions. The molecule is initially in the state of $v=2$, $j=22$. Good convergence is obtained when the total angular momentum J is summed from 20 to 24.

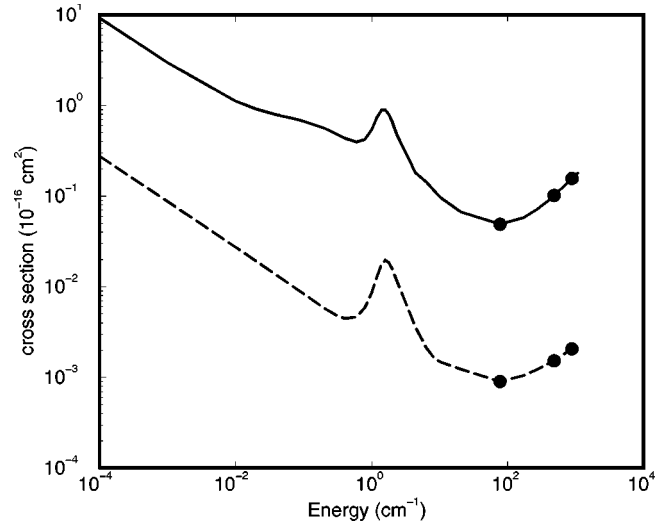

FIG. 3. Energy dependence of the rotational relaxation cross section for $H_2(j=2)+H_2(j=2)$. The solid curve is for one diatom making a $\Delta j=-2$ transition, and the dashed curve is for both diatoms making a $\Delta j=-2$ transition. The circles are obtained from the calculations of Green [9] using detailed balance.

for a molecule in the $j=22$ state. At this point the super rotor become stable against collision. The effect occurs sharply in an energy range (10–200 cm^{-1}) that is larger than the 240 mK temperature limit achievable using a ^{3}He buffer gas. Therefore, it should be possible to use the buffer gas collisions to cool the $j=22$ super rotors and load them into a trap without a significant loss in population.

Because cold $j=22$ super rotors cannot efficiently exchange vibrational energy, it is sufficient to approximate them as rigid rotors when considering diatom-diatom collisions. Even within the rigid rotor approximation, it becomes impractical to perform full quantum mechanical calculations

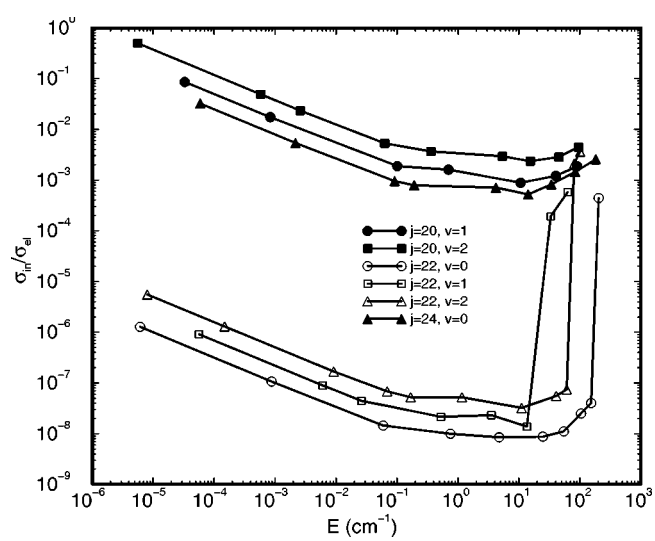

FIG. 2. Ratio of inelastic cross section for $^3He+H_2$ collisions as a function of kinetic energy. The ratios for $j=22$ are dramatically reduced when the classically quasiresonant rotation-vibration channels are closed. This occurs at energies between 10 and 200 cm^{-1}.

for large values of j. Figure 3 shows the relaxation cross section for $H_2(j=2)+H_2(j=2)$ as a function of translational kinetic energy. The solid curve is for one diatom making a $\Delta j=-2$ transition, and the dashed curve is for both diatoms making a $\Delta j=-2$ transition. The circles are obtained from calculations of Green [9] using detailed balance. The hump that occurs in both curves just above 1 cm^{-1} is due to the presence of the van der Waals well, which accelerates the molecules into the interaction region when the kinetic energy is less than the depth of the well [10]. Below 10^{-2} cm^{-1} the s-wave contributions dominate the cross section as the Wigner threshold region is approached.

Figure 4 shows the real and imaginary components of the complex scattering length for $H_2(j_1)+H_2(j_2)$ collisions as a function of $j=j_1=j_2$. The real part of the scattering length (shown by the triangles for $j=2,4,6,8$) is a measure of the zero temperature elastic scattering cross section. The imaginary part of the scattering length is a measure of the total inelastic rate coefficient at zero temperature. In these calculations, it was assumed that the diatoms were polarized such that the total angular-momentum quantum number is equal to j_1+j_2. Figure 4 shows that the imaginary component is dominated by the $\Delta j_1=-2$, $\Delta j_2=0$ transition. Because the computational effort scales as the 12th power of the highest rotational level included in the basis set [9], it is impractical to perform calculations for high values of j. However, reasonable estimates may be obtained using an exponential energy gap fit [11]. Figure 4 shows that the imaginary part of the scattering length is completely negligible for large values of j. This suggests that it should be possible to evaporatively cool a sample of trapped super rotors without significant loss due to relaxation.

Adiabatic invariance provides a theoretical justification for the predictions described here. If the phase space of the atom-diatom system contains large isolated nonlinear reso-

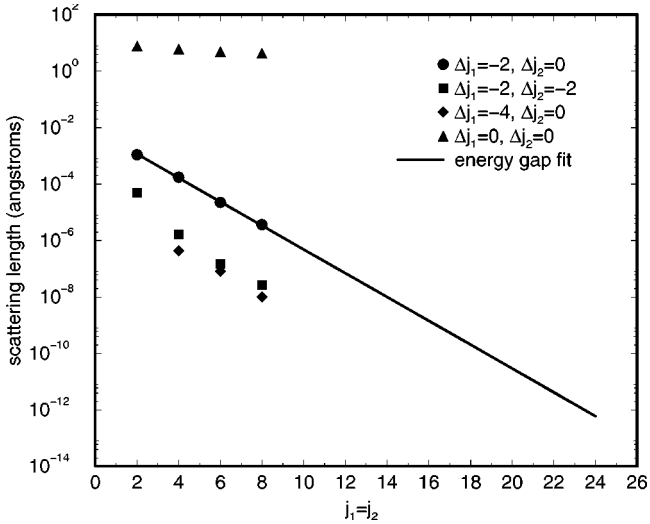

FIG. 4. Real and imaginary components of the complex scattering length for $H_2(j_1)+H_2(j_2)$ collisions as a function of initial rotational quantum number. The imaginary part is dominated by the $\Delta j_1=-2$, $\Delta j_2=0$ transition and may be extrapolated using an exponential energy gap fit. The real part (triangles) decreases very slowly with increasing rotation.

nances, then the classical trajectories will be governed by very strong propensity rules [12,13] (e.g., $\Delta j=-2\Delta v$ discussed above). These propensity rules typically hold well beyond the point of resonant rotation-vibration energy transfer, producing cross sections that are very large and specific [13]. If the dominant quasiresonant channel is energetically closed for a particular rotation level, then there will be a strong suppression of the total quenching cross section for this level compared to neighboring levels.

The correlation between Δj and Δv that is found in quasiresonant classical trajectories at ordinary temperatures [13] is also found at ultracold temperatures [3]. However, in the ultracold case, the magnitudes of Δj and Δv are small fractions that can never be achieved with quantized values of v and j. Nevertheless, the quantum-mechanical cross sections are extremely specific and efficient when the quasiresonant channels are open, and the total quenching cross section is strongly suppressed when the quasiresonant channels are closed. This is consistent with the idea that classical trajectories provide a coarse-graining mechanism that may be used together with energy and angular-momentum constraints to describe the atom-diatom collisions [14].

It should be noted that potential energy surfaces are not generally designed for ultracold interactions. However, calculations that employ approximate surfaces will still be reliable when the collision preserves the adiabaticity of the total classical action. This means that the interaction cannot be too strongly impulsive. Most atomic and molecular interactions satisfy this criterion. Furthermore, the ratio of real to imaginary part of the complex scattering length provides a dimensionless parameter that is less sensitive to the details of the potential energy surface than the individual state-to-state cross sections. It is this parameter that ultimately determines whether evaporative cooling is possible, and in the case of H_2 super rotors, it is favorable.

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