Cold collisions of highly rotationally excited CO_2 with He: The prospects for cold chemistry with super-rotors

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Building on recent advances in ultrafast lasers and methods to slow molecules, an experiment is proposed to produce translationally cold CO_2 super-rotors ($j \sim 200$) by combining an optical centrifuge with helium-buffer-gas cooling. Quantum mechanical calculations of the complex scattering length for He-CO_2 collisions demonstrate that the efficiency of rotational quenching decreases rapidly with increasing rotational excitation j in the ultracold regime. Extrapolating to helium cryogenic temperatures, rotational quenching is predicted to remain inefficient up to ~1 K, allowing for the possible creation of a beam of translationally cold, rotationally hot molecules.

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I. INTRODUCTION

The cooling and trapping of molecules produces unique environments that can be used to study molecular interactions at very low and even ultracold temperatures. The availability of such cold molecular systems can be used to investigate a variety of phenomena, including the variation of fundamental constants, quantum computing algorithms, strongly correlated systems [1,2], inelastic collisions, cold chemistry [3,4], and a host of other areas in the forefront of contemporary physics [5]. A variety of approaches have been developed to produce translationally cold molecules [6], but a major workhorse is the helium-buffer-gas method in which the molecules are slowed down through elastic collisions with cryogenically cold He atoms [7].

Over the past decade, there has been an increasing interest in generating molecules in high rotational levels, so-called super-rotors [8–10]. An interesting aspect of super-rotors is their prospect to possess unique properties at very low temperatures. Forrey [11,12] proposed that super-rotors could be translationally cooled and trapped as ultracold molecular rotational quenching rates generally decrease with increasing rotational excitation. If rovibrational quenching is also small, as is often the case for specific rotational levels at temperatures accessible to helium-buffer-gas methods, then the super-rotors would be stable against collision. Here, we demonstrate the feasibility of producing cold super-rotors by exploring the dependence on scattering properties with rotational excitation for inelastic He-CO_2 interactions.

II. THE COMPLEX SCATTERING LENGTH

In the Wigner-threshold regime [13], multichannel scattering can be described conveniently by the complex scattering length $a = \alpha - i\beta$ [14,15]. β is derived from the inelastic cross section and gives a measure of the total decay probability of an internal excited state [14]. For an initial state with vibrational and rotational quantum numbers v and j, the imaginary part of the scattering length β_{vj} in the limit of zero initial kinetic energy is given by

$$\beta_{vj} = k\sigma_{vj}^{\text{in}}/4\pi, \tag{1}$$

where k is the initial wave vector and σ_{vj}^{in} the sum of the inelastic cross sections of all open channels [14]. In the limit $k \to 0$, the relation between the elastic cross section σ_{vj}^{el} and the complex scattering length a_{vj} is given by [14]

$$\sigma_{vj}^{\text{el}} = 4\pi\left(\alpha_{vj}^2 + \beta_{vj}^2\right) = 4\pi|a_{vj}|^2, \tag{2}$$

from which the magnitude of the real part of the scattering length is given by

$$|\alpha_{vj}| = \sqrt{\sigma_{vj}^{\text{el}}/4\pi - \beta_{vj}^2}, \tag{3}$$

while the sign of α_{vj} is determined from the sign of the phase shift. An application of the complex-scattering-length formalism to low lying rotational levels of the He-CO_2 system, and other linear and nonlinear molecules, was given in Ref. [16].

III. COMPUTATIONAL METHOD

To study the scattering properties of the ^{4}He-CO_2 collision system, cross sections were obtained with the nonreactive scattering code MOLSCAT [17], assuming a rigid-rotor approximation in the vibrational ground state. The potential energy surface of Ran and Xie [18] for the He-CO_2 interaction was adopted. The scattering calculations were performed using the

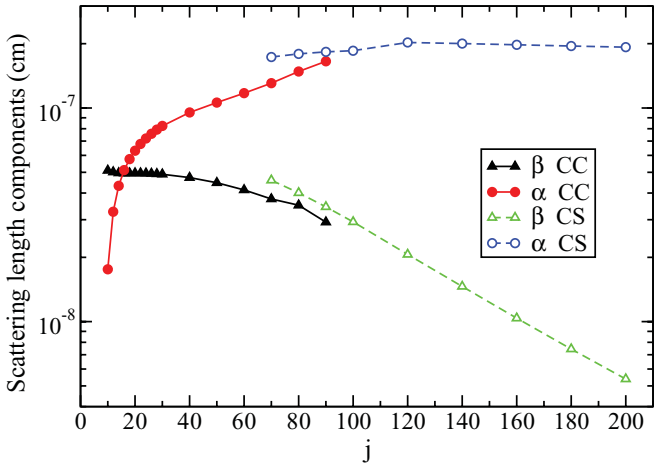

FIG. 1. (Color online) Real and imaginary parts, α and β, respectively, of the scattering length as a function of the rotational level j. All calculations were performed at 10^{-6} cm^{-1}.

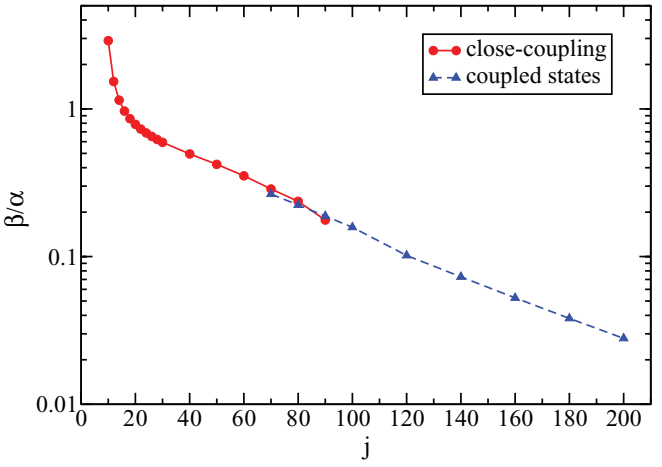

FIG. 2. (Color online) Ratio of the imaginary part β to the real part α of the scattering length for ^{4}He collisions with CO_2 as a function of the rotational level j. All calculations were performed at 10^{-6} cm^{-1}.

full close-coupling (CC) method with appropriate convergence tests performed for the basis set size, asymptotic matching distance, and number of quadrature points to evaluate the matrix elements of the interaction potential. For large j, the coupled-states (CS) approximation was used. Further details regarding the scattering calculations for He-CO_2 can be found in Ref. [19].

IV. RESULTS AND DISCUSSION

Figure 1 presents the real part α and the imaginary part β of the scattering lengths for the ultracold collision energy of 10^{-6} cm^{-1}. Results are shown for both the CC and CS methods as the CS approximation is more computationally efficient for larger j. As β depends only on the inelastic cross sections, it is a measure of the quenching of j. Similarly, an increase in α indicates an increase in the elastic scattering. For $j \leqslant 16$, β is larger than α, indicating that rotational quenching will be very efficient. As j increases, α increases rapidly, plateauing at $j \gtrsim 120$. On the other hand, β decreases slowly with j but then drops relatively rapidly at $j \gtrsim 80$. This trend is alternatively shown in Fig. 2 for the ratio β/α where it is noted that the differences between results obtained with the CC and CS methods are largely removed.

In cooling and trapping experiments, inelastic or quenching cross sections need to be small compared to the elastic cross sections to avoid trap loss. A figure of merit for the ability to trap a species is given by the ratio of the elastic to inelastic cross sections $\sigma^{\rm el}/\sigma^{\rm in}$, which is related to the components of the complex scattering length by

$$\frac{\sigma^{\rm el}}{\sigma^{\rm in}} = \frac{k(\alpha^2+\beta^2)}{\beta}. \tag{4}$$

In the limit of $\alpha \gg \beta$, as shown for large j in Figs. 1 and 2,

$$\frac{\sigma^{\rm el}}{\sigma^{\rm in}} \approx \frac{\alpha}{\beta} k\alpha. \tag{5}$$

In the zero-temperature limit, α and β are constant for a given j, hence their utility. As the energy (or k) increases, while remaining within the Wigner regime, the figure of merit improves as it is approximately proportional to k. As an illustration, we show in Fig. 3 the elastic- and inelastic-quenching cross sections for the slightly higher energy of 10^{-4} cm^{-1}. Trends similar to that of the scattering lengths are evident. The ratio β/α (not shown) is nearly identical to that given in Fig. 2. For large j, rotational quenching is dominated by the $\Delta j = -2$ transition. However, its efficiency decreases with j and for $j = 200$ its cross section is about a factor of 5 smaller than that of elastic scattering.

The gas temperatures for He-buffer-gas cooling are typically beyond the range of the Wigner regime so that Eqs. (4) and (5) are no longer valid. As the collision energy increases to the He-buffer-gas region, the number of required partial waves also increases. The computational time for scattering calculations within the CS approximation scales as $\propto j_{\rm max}^4/2$ per partial wave, where $j_{\rm max}$ is the largest rotational state included in the basis. At present, computations of elastic and inelastic cross sections up to 1000 cm^{-1} have only been

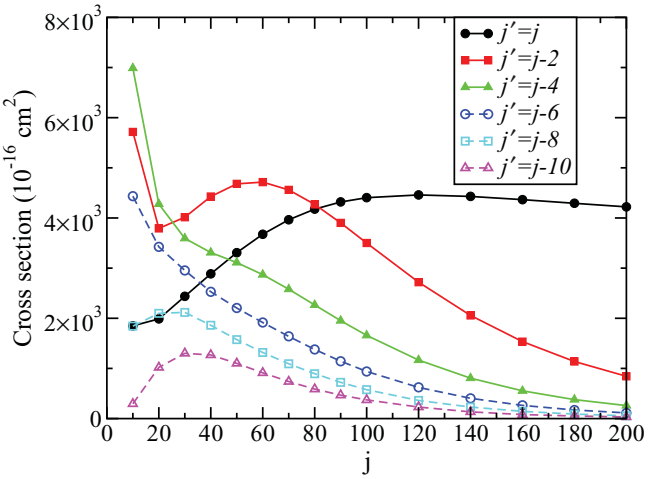

FIG. 3. (Color online) Elastic and final-state j'-resolved cross sections as a function of initial rotational level j for a collision energy of 10^{-4} cm^{-1} obtained with the CS approximation for ^{4}He-CO_2.

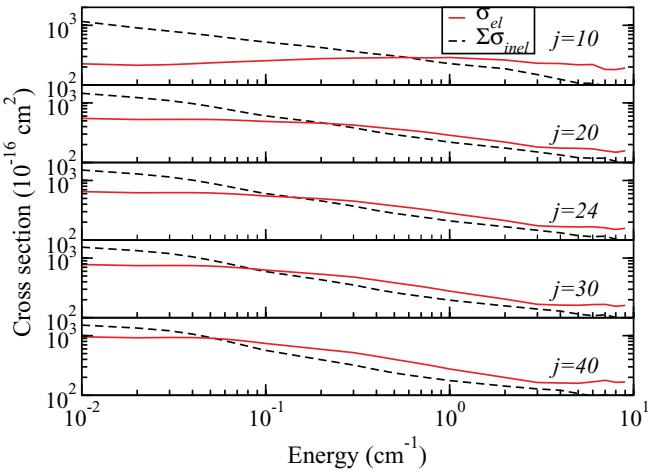

FIG. 4. (Color online) Elastic cross section and total inelastic cross section as a function of energy for He collisions with CO_2 and various j's.

completed for $j = 40$ (higher-j computations are in progress). For example, the total number of partial waves needed to secure convergence for $j = 40$ at a collision energy of 1000 cm^{-1} was 50. We therefore estimate by extrapolation that the figure of merit will be large for He-CO_2 ($j = 200$) at 0.5 K.

To illustrate this, the elastic and total inelastic cross sections for $j = 10$, 20, 24, 30, and 40 are shown in Fig. 4 from 10^{-2} to 10 cm^{-1}. The typical Wigner-threshold behavior of the cross sections is clearly evident at low energies. The cross sections typically depart from the Wigner regime near the collision energy where the total inelastic cross section is equal to that of the elastic cross section. Figure 5 shows that the crossing energy is a monotonically decreasing function of j. At $j = 70$, the crossing energy is significantly smaller than the He cryogenic temperature. A simple extrapolation of Fig. 5 suggests that the crossing energy will be less than 10^{-3} cm^{-1} for $j \sim 200$.

The ratio of the elastic to total inelastic cross section, or figure of merit, is displayed in Fig. 6 for various collision temperatures in the cold regime as a function of j. The ratio

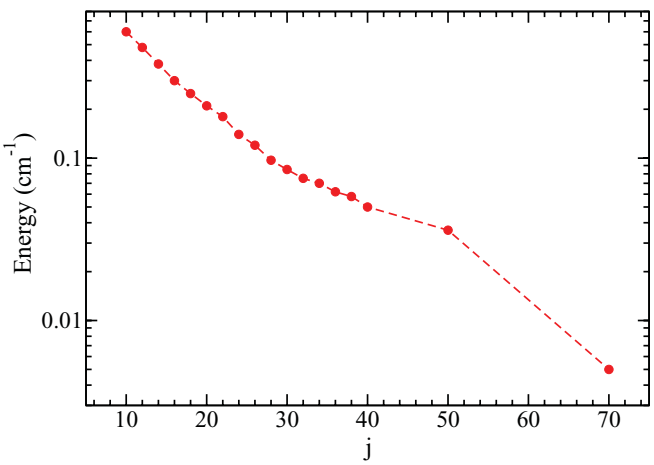

FIG. 5. (Color online) The energy at which the elastic cross section is equal to the total inelastic cross section as a function of the rotational level j.

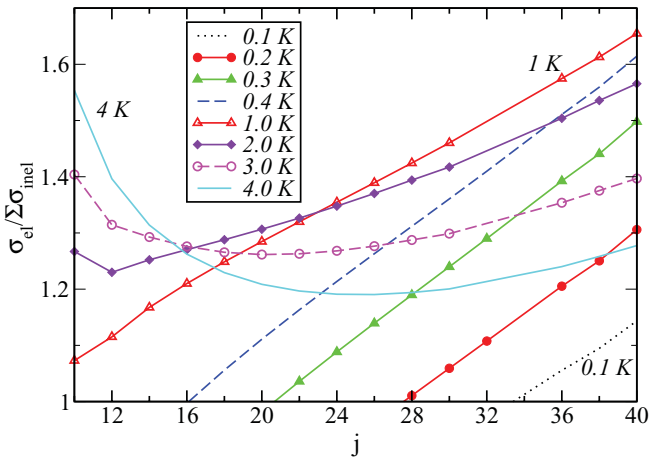

FIG. 6. (Color online) The ratio of the elastic cross section to the total inelastic cross section at different temperatures as a function of j.

is seen to increase with j and with temperature up to 1 K. Simple extrapolation to $j \sim 200$ suggests a figure of merit of ~10, which is encouraging for possible cooling and trapping experiments, if such highly excited states could be created.

To create super-rotors, Karczmarek *et al.* [8] proposed that two circularly polarized laser fields could be used to spin diatoms up to very high rotational levels. This so-called optical-centrifuge approach was experimentally demonstrated for Cl_2 by Villeneuve *et al.* [9], reaching a maximum rotational angular momentum of $j \sim 420$. Preliminary experiments on O_2 and CS_2 gave similar results [9]. The original experiments were done in a supersonic molecular beam containing the molecules to be spun up. If a surface was inserted into the beam just downstream from the laser, the super-rotors would hit the surface with the jet's velocity, which would be about 700 m/s [20].

A related proposal was made by Li *et al.* [10], but unlike the work of Refs. [8,9], which results in a distribution of rotational levels, their scheme would produce molecules in a single, selected j level. Numerical simulations found that Li_2 could be excited to $j > 115$ [10]. Following on earlier studies of CO_2 collisions with highly vibrationally excited azulene [21], Mullin *et al.* [22] applied the optical-centrifuge approach to room-temperature CO_2, obtaining excitations to $j \sim 200$.

The experiments described above produce molecular super-rotors that are also translationally hot. These molecules are generally extremely fragile against collisions due to efficient quasiresonant vibration-rotation (QRVR) energy transfer. If the super-rotors are produced from a translationally cold gas, however, the QRVR transitions are energetically closed, and the molecules are stable against collision [11,12]. Merging these two concepts, we propose a scheme to produce rotationally hot but translationally cold molecules which could be readily realized for the explicit case of carbon dioxide by combining an optical centrifuge in a helium-buffer-gas cell. A possible scheme would be as follows. (i) Introduce room-temperature CO_2 into the gas cell with cryogenic ^{4}He or ^{3}He. CO_2 would be rapidly translationally cooled through elastic collisions and rotationally cooled to $j = 0$ via inelastic collisions (see Fig. 4, for example). (ii) With ultrafast laser

pulses, spin up the molecules to high rotational levels. Elastic collisions with He would maintain low translational energies for the high j levels while a limited fraction would be lost due to inefficient inelastic collisions. (iii) Both He and CO_2 would then be allowed to exit the cell via a small hole [23], creating a beam of CO_2 super-rotors that would be considerably slower than what would be produced by a supersonic jet. These super-rotors would be much less fragile against collision due to the closed QRVR transitions. The rotational-level distribution of the beam would be highly stable as CO_2 lacks a dipole moment. An optical centrifuge generally produces a range of j and m_j levels in accordance with Raman selection rules. If the molecules are initially in the $j = 0$ state, then the distribution of super-rotors would include only even j and m_j levels. Further selection of m_j levels could be obtained through magnetic Feshbach tuning of β before ejection of the beam. A variety of low-temperature experiments could then be envisioned, including collisions with electrons, photons, atoms, molecules, and surfaces, which may reveal unique properties (see also [9]). While Li *et al.* did mention the possibility of using cold molecules in their super-rotor scheme, we demonstrate with accurate scattering calculations the feasibility of our approach here with current available technology.

Finally, the scheme could be extended to highly vibrationally excited states for specific rotational levels that allow QRVR transitions at normal temperatures but are energetically closed as the temperature is lowered to that in the He-buffer-gas cell. The availability of downward vibrational transitions generally increases the rotational-state selectivity of collisionally stable super-rotors [12].

V. CONCLUSIONS

Complex scattering lengths and elastic- and inelastic-rotational-quenching cross sections have been computed for carbon dioxide, with rotational excitation j as high as 200, due to ultracold ^{4}He collisions. It is predicted that the ratio of the elastic to inelastic cross section, or figure of merit, is sufficiently large that highly rotationally excited CO_2 could be a viable candidate for cooling and trapping. An experiment combining a He-buffer-gas cell with an optical centrifuge is proposed as a means of producing rotationally hot but translationally cold CO_2. A high-flux beam of cold CO_2 super-rotors could be created and used for a variety of scattering experiments.

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