

Microwave-laser-field modification of molecular collisions at low temperatures

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We present a rigorous study of low-temperature collisions of polar molecules and atoms in a microwave laser field. Our calculations show that inelastic relaxation of molecules in a microwave cavity may occur through collision-induced absorption of photons stimulated by the anisotropy of the atom-molecule interaction potential. Our results indicate that molecular collisions at temperatures below 1 K can be efficiently manipulated with microwave laser fields of moderate strength.

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Controlling molecular interactions with laser radiation has been an important goal in chemical dynamics research for the past five decades [1–3]. This goal stimulated the development of the research fields of coherent and optimal control of molecular processes [1], attosecond spectroscopy [2], and stereodynamics [3]. Many experiments demonstrated that laser fields can be used to selectively induce or suppress unimolecular dynamical processes such as photodissociation [1,2,4]. Controlling molecular collisions has, however, proven to be much more difficult. The effects of external laser fields are usually negated by thermal motion of molecules and perturbative molecule-field interactions do not affect molecular collisions in a thermal gas [5]. In order to achieve external field control over molecular collision processes, it is necessary to create molecular ensembles with the temperature smaller than the energy of molecule-field interactions. Recent technological advances in cooling molecules allow for the production of dense molecular gases at temperatures below 1 K [6–8]. Are molecular collisions at sub-Kelvin temperatures sensitive to external laser fields? In this Rapid Communication, we study collisions of polar molecules in a microwave laser cavity using the dressed-state formalism [9] to describe molecule-field interactions. We present rigorous calculations of cross sections for low-temperature elastic scattering and inelastic collisions of diatomic molecules with He atoms. Several authors have previously studied collisions of ultracold atoms in rf and microwave fields [10]. Interactions between molecules and atoms are characterized by strong interaction anisotropy, which makes the dynamics of molecular collisions more complicated and interesting than the dynamics of atomic collisions. Our results identify a mechanism for inelastic collisions of molecules in a microwave cavity due to couplings between different photon manifolds induced by the anisotropy of the atom-molecule interaction potential. Our calculations demonstrate that atom-molecule collisions at low temperatures can be efficiently manipulated by microwave laser fields.

We present rigorous calculations for collisions of CaH molecules with He atoms. Our choice of the CaH-He system is motivated by the availability of an accurate interaction potential for this collision complex [11]. We emphasize, however, that the results presented in this Rapid Communication are largely determined by the molecule-field interac-

tions and are therefore qualitatively general and should apply to any diatomic molecule in the $^2\Sigma$ state. The Hamiltonian of an atom-molecule collision complex in a microwave field can be written as

$$\hat{H} = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\hat{\ell}^2}{2\mu R^2} + \hat{V}(R, r, \theta) + \hat{H}_{\text{mol}}, \quad (1)$$

where R is the atom-molecule separation, r is the internuclear distance of the diatomic molecule, θ is the angle between the vectors \mathbf{R} and \mathbf{r} , μ is the reduced mass of the collision complex, \hat{V} is the atom-molecule interaction potential, and $\hat{\ell}$ is the orbital angular momentum for the collision. The last term in Eq. (1) can be represented as

$$\hat{H}_{\text{mol}} = B_e \hat{N}^2 + \hat{H}_{\text{mol},f} + \hbar\omega(\hat{a}\hat{a}^\dagger - \bar{N}), \quad (2)$$

where B_e is the rotational constant and \hat{N} is the rotational angular momentum of the molecule. The interaction of the molecule with a linearly polarized microwave laser field $\hat{\epsilon}(t) = \hat{\epsilon}_0 \cos \omega t$ is

$$\hat{H}_{\text{mol},f} = -\frac{\Omega}{2\sqrt{N}}(\hat{a} + \hat{a}^\dagger)\cos\chi. \quad (3)$$

Here, χ is the angle between the molecular axis and the polarization vector of the radiation field, the operators \hat{a}^\dagger and \hat{a} create and annihilate microwave photons, \bar{N} is the average number of photons in the cavity, $\Omega = \epsilon_0 d$, and d is the permanent electric dipole moment of the molecule. Changing the polarization of the microwave field modifies the molecule-field interaction [12], which leads to additional couplings between the rotational states of different M_N , where M_N is the projection of \hat{N} on the space-fixed quantization axis. This may lead to interesting new mechanisms of laser-field control of molecular dynamics, which will be explored in future work.

The energy levels of the molecule in a microwave cavity can be obtained by diagonalizing Hamiltonian (2) in the field-dressed basis $|NM_N\rangle|\bar{N}+n\rangle$, where $|\bar{N}+n\rangle$ are the photon number states. In a microwave laser cavity [12], $n \ll \bar{N}$ and

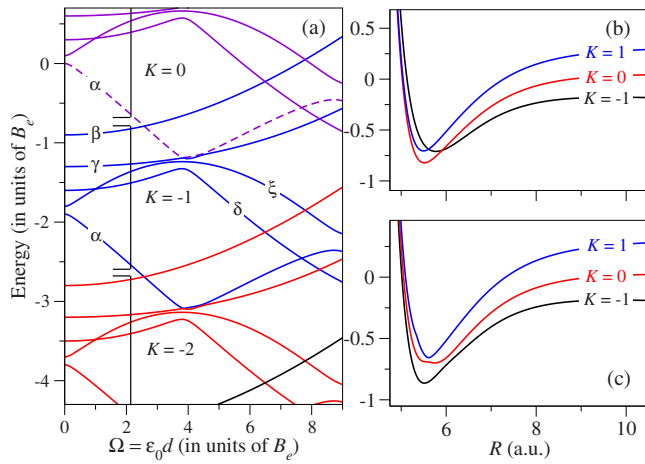


FIG. 1. (Color online) (a) Energy levels of a polar molecule in a microwave cavity as functions of the field-induced coupling strength Ω at $\hbar\omega/B_e=1.9$. The initial state for scattering calculations is shown by the dashed line. At $\Omega \rightarrow 0$, the field-dressed states for $K=-1$ are $|N=0, n=-1\rangle$ (α), $|N=4, n=-11\rangle$ (β), $|N=3, n=-7\rangle$ (γ), $|N=1, n=-2\rangle$ (ξ), and $|N=2, n=-4\rangle$ (δ). (Right panels) The eigenvalues of the atom-molecule Hamiltonian (c) with and (b) without the term $\hat{H}_{\text{mol},f}$. The results in panel (c) are for $\hbar\omega/B_e=0.3$ and $\Omega/B_e=0.5$.

the matrix elements of Eq. (3) are independent of \bar{N} . Diagonalization of molecule-field Hamiltonian (2) yields

$$|\nu K\rangle = \sum_{N, M_N} \sum_{n=-n_{\max}}^{n_{\max}} C_{NM_N n, \nu K} |NM_N\rangle |\bar{N} + n\rangle, \quad (4)$$

where the indices ν and K label the field-dressed states and the coefficients $C_{NM_N n, \nu K}$ depend on Ω and ω . Figure 1(a) shows the energy levels of CaH (or any other polar diatomic molecule) in a microwave field as functions of the field-induced coupling strength Ω at $\hbar\omega/B_e=1.9$. The field-dressed levels are arranged in manifolds separated by multiples of the photon energy $\hbar\omega$. The quantum number ν denotes the state of the molecule within a photon manifold, and K labels the photon manifold. We consider collisions of CaH molecules in the state $|\nu=\alpha, K=0\rangle$, which correlates with the ground rotational state $N=0$ of CaH at zero field. In the absence of molecule-field coupling, the products $|NM_N\rangle |\bar{N} + n\rangle$ form an infinite series of states representing the energy of the quantized field with different numbers of photons and the molecule in a particular rotational state. The field-dressed states at nonzero Ω are coherent superpositions of these product states. If the field is switched off adiabatically, molecules must populate a single rotational state given by the $\Omega \rightarrow 0$ limit. If the field is switched off rapidly, molecules will remain in coherent superpositions of rotational states. Our results show that collisions may induce inelastic transitions between the field-dressed states due to the anisotropy of the atom-molecule interaction potential.

The total wave function of the collision complex is expanded in the products of field-dressed wave functions [Eq. (4)] and spherical harmonics $|\ell m_\ell\rangle$. The probabilities for collision-induced transitions between the microwave field-

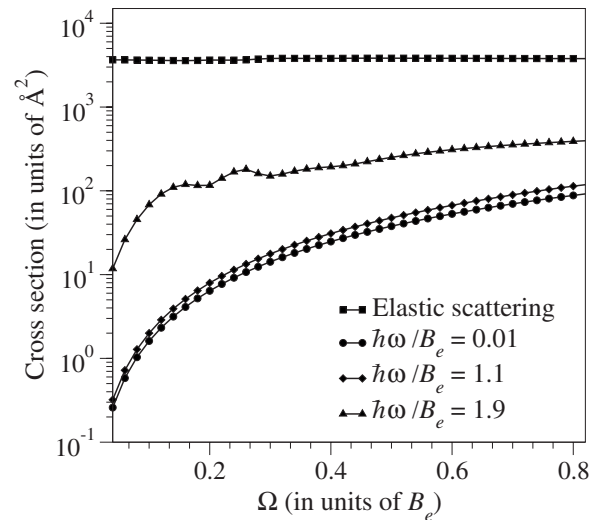


FIG. 2. Cross sections for elastic scattering (squares) and inelastic relaxation of CaH molecules induced by collisions with He in a microwave field with $\hbar\omega/B_e=1.9$ (triangles), 1.1 (diamonds), and 0.01 (circles) as functions of Ω . The elastic cross section is for the microwave field energy $\hbar\omega/B_e=1.9$. The inelastic cross sections are summed over all energetically accessible field-dressed states except the elastic channel. The collision energy is 0.3 cm^{-1} .

dressed states [Eq. (4)] are obtained from the solution of the multichannel Schrödinger equation [13].

Figure 2 shows the cross sections for elastic scattering and inelastic relaxation in CaH-He collisions as functions of Ω at a collision energy of 0.3 cm^{-1} . In order to obtain converged results, we included in the total wave-function expansion five rotational states of the molecule, 14 photon number states, and four angular momenta ℓ , which yields a system of 1744 differential equations for zero total angular momentum projection. The probabilities for inelastic collisions increase with decreasing the detuning from resonance $\Delta=2B_e-\hbar\omega$. For the off-resonant microwave photon energies of $0.01B_e$ and $1.1B_e$, the inelastic cross sections increase monotonically with increasing Ω . At a near-resonant photon energy of $1.9B_e$, the cross sections increase by a factor of ~ 50 and show broad oscillations. The difference between the cross sections corresponding to different microwave frequencies becomes smaller with increasing the field strength.

In order to elucidate the propensities for collision-induced transitions in a microwave field, we present in Fig. 3 the state-resolved cross sections for inelastic transitions to various final field-dressed states. As our initial state is the ground state in the $K=0$ manifold, inelastic relaxation involves transitions between different photon manifolds. Figure 3 shows that the total relaxation probability is determined by two transitions, $|\alpha, K=0\rangle \rightarrow |\alpha, K'=-1\rangle$ and $|\alpha, K=0\rangle \rightarrow |\xi, K'=-1\rangle$. The field-dressed states $|\alpha, K=0\rangle$ and $|\alpha, K'=-1\rangle$ differ exactly by one quantum of microwave field energy. Therefore, the transition $|\alpha, K=0\rangle \rightarrow |\alpha, K'=-1\rangle$ should be interpreted as a collision process accompanied by absorption of a microwave photon. The molecule-field interaction [Eq. (2)] couples the product states with $\Delta N = \pm 1$ and $\Delta n = \mp 1$ so the strongest couplings occur between the field-dressed states in the adjacent photon manifolds ($\Delta K = \pm 1$). Figure 3 shows

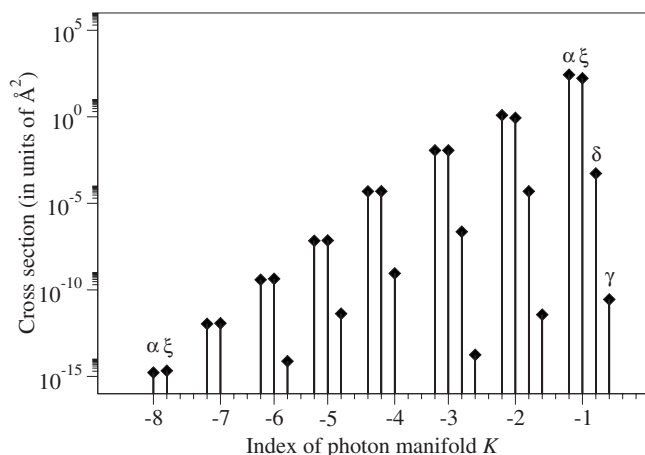


FIG. 3. State-resolved cross sections for inelastic relaxation of CaH in a microwave field with $\hbar\omega/B_e=1.9$ and $\Omega/B_e=0.5$. The collision energy is 0.3 cm^{-1} . The inelastic channels are labeled according to Fig. 1.

that the transitions with the minimal change in K are the most probable and that the transition probabilities decrease rapidly with increasing ΔK .

The transitions between states with different K are induced by the matrix elements of the atom-molecule interaction potential in the field-dressed basis. The anisotropic part of the interaction potential couples different $|NM_N\rangle$ states causing rotationally inelastic transitions. Although the interaction potential only couples the $|NM_N\rangle|\bar{N}+n\rangle$ states with the same n , molecule-field Hamiltonian (3) has the selection rules $\Delta N = \pm 1$ and $\Delta n = \mp 1$ [9]. A combination of the molecule-field and atom-molecule interactions thus leads to couplings between different K , inducing collisional absorption or emission of microwave photons. We have verified that if either the molecule-field interaction or the anisotropy of the interaction potential is omitted, the different photon manifolds are uncoupled and the transitions $|\nu K\rangle \rightarrow |\nu' K'\rangle$ cannot occur unless $K' = K$. In order to examine in detail the effects of the microwave field on molecular collisions, we diagonalized atom-molecule Hamiltonian (1) in the field-dressed basis as a function of R . Figure 1(b) shows the eigenvalues of the Hamiltonian (the adiabatic curves) correlating with the field-dressed states $|\alpha K\rangle$ with $K = -1, 0, \text{ and } 1$ in the limit of large R . In the absence of field-induced couplings, the adiabatic curves corresponding to different K do not interact, which illustrates that transitions between different photon manifolds are strictly forbidden. Figure 1(c) shows that the molecule-field interaction transforms crossings between the adiabatic curves into avoided crossings. From Fig. 1(c), we see that the microwave-field-induced transitions occur in the region of strong atom-molecule interaction ($R \sim 6a_0$). This mechanism is similar to that described by Agosta *et al.* [10] in their study of dipolar relaxation of spin-polarized atomic hydrogen in a microwave trap.

Microwave fields may also modify the probability of elastic collisions near scattering resonances. Figure 4 presents the energy dependence of CaH-He elastic scattering. In the absence of a microwave field, the cross section increases by 2 orders of magnitude near a shape resonance at a collision

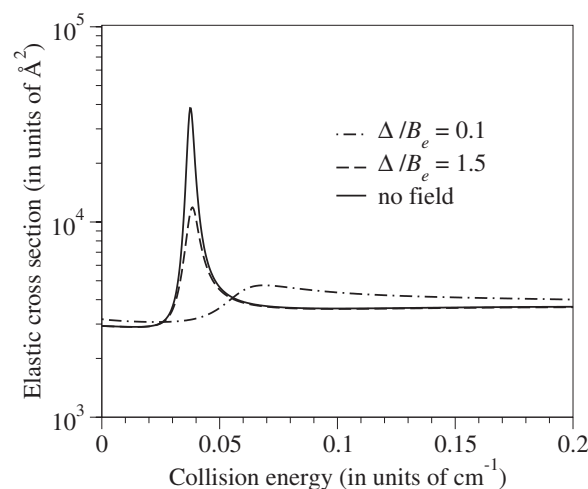


FIG. 4. Modification of a shape resonance by microwave laser fields. The elastic cross section is plotted as a function of the collision energy for zero microwave field (full line), $\Delta/B_e=1.5$ (dashed line), and $\Delta/B_e=0.1$ (dotted line). $\Omega/B_e=0.5$.

energy of 0.04 cm^{-1} . The microwave field of $\Omega/B_e=0.5$ suppresses the shape resonance. As the microwave detuning decreases from $1.5B_e$ to $0.1B_e$, the cross-section maximum becomes smaller and shifts to higher collision energies. The interaction of the molecule with a microwave field [Eq. (2)] leads to indirect couplings between different partial waves, which alter the shape of the centrifugal barrier and suppress shape resonances [14].

Cold molecules with unpaired electrons (e.g., $^2\Sigma$ radicals) can be confined in a magnetic trap and used for a variety of applications ranging from quantum computing [15] to quantum simulation of condensed-matter systems [16]. The spin-dependent interactions in open-shell molecules give rise to nonadiabatic processes and the geometric phase effects in chemical reactions [5]. It would therefore be extremely useful to design a scheme for controlling the spin-dependent dynamics in molecular collisions. In order to explore the effect of microwave fields on spin-dependent interactions in collisions of cold molecules, we extended our calculations of CaH-He scattering to include the spin degrees of freedom and an external magnetic field. Figure 5 presents the cross sections for spin relaxation in the $K=0$ field-dressed state of CaH at a magnetic field of 0.1 T. This calculation was carried out with five rotational states of the molecule, six photon number states, and six angular momenta ℓ in the basis set, yielding a system of 4233 differential equations for zero angular momentum projection. The results show that the spin-relaxation process can be altered by a factor of $\sim 10^3$ by varying the detuning from resonance. The enhancement of spin relaxation at small Δ might be used to stimulate spin-forbidden chemical reactions in magnetic traps [5,13].

In summary, we have presented a rigorous quantum-mechanical study of low-temperature collisions of polar molecules in a microwave laser field. Our results show that both elastic and inelastic collisions of molecules at temperatures below 1 K may be very sensitive to an external laser field. In particular, we find that inelastic relaxation may occur through transitions between different photon manifolds even

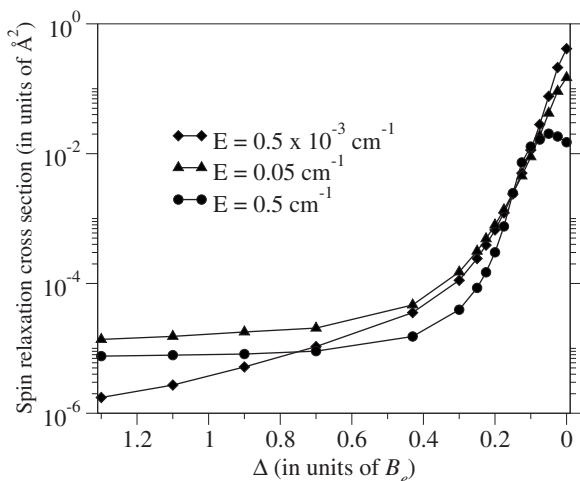


FIG. 5. The cross section for spin relaxation in CaH-He collisions as a function of the detuning at a magnetic field of 0.1 T and $\Omega=0.5B_e$. The collision energies are (in units of 10^{-3} cm^{-1}) 500 (circles), 50 (triangles), and 0.5 (diamonds).

when the colliding molecules are in the absolute ground state. This process, driven by the anisotropy of the atom-molecule interaction potential, should be interpreted as collision-induced absorption of microwave photons followed

by rotational de-excitation. It is sensitive to both the intensity and frequency of the microwave laser field.

DeMille *et al.* [12] recently proposed a scheme to trap polar molecules in a microwave cavity. Microwave traps may potentially confine molecules in the absolute ground state at temperatures as high as 0.5–1 K. The molecules in the trap are immune to spontaneous decay [12] but further cooling may be required to reach the interesting regime of ultracold dynamics [17]. This can be achieved by evaporative cooling, which relies on the relative efficiency of elastic and inelastic collisions. The results shown in Figs. 2 and 3 have important implications for microwave trapping. The inelastic processes described by the figures lead to trap loss and heating. The microwave trap depth varies as Ω^2/Δ [12], and the collisional loss rate scales as $(\Omega/\Delta)^2$. Therefore, collisional cooling in a microwave trap should be most efficient at large microwave detunings. Recent experimental demonstration of neutral molecule trapping on a chip [18] provides opportunities for controlling collisions and chemical reactions of cold molecules with microwave laser fields.

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