Controlling collisional spin relaxation of cold molecules with microwave laser fields

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(Received 14 July 2009; published 29 September 2009)

We explore the effects of microwave laser fields on spin-changing transitions in collisions of polar molecules in a \( ^2\Sigma \) electronic state with atoms in the presence of a static magnetic field. We use the dressed-state formalism of quantum optics to describe the interaction of the radiation field with the collision complex and perform rigorous scattering calculations to study spin-changing transitions in collisions of CaH molecules with He atoms at temperatures below 1 K. Our calculations demonstrate that collision-induced spin relaxation of \( ^2\Sigma \) molecules is enhanced near avoided crossings between different Zeeman levels. We show that the positions of the avoided crossings can be modified by varying the frequency and the intensity of the microwave laser field and discuss the mechanisms of microwave field control of spin-dependent interactions in cold open-shell molecules.

DOI: 10.1103/PhysRevA.80.033419

PACS number(s): 37.10.−x, 33.20.−t, 34.50.−s

I. INTRODUCTION

The development of experimental techniques for cooling molecules to low and ultralow temperatures has opened up a manifold of exciting research opportunities [1, 2]. Experiments with cold and ultracold molecules may yield new insights into fundamental problems in several areas of physics [1–8]. These experiments have stimulated new studies of external field effects on molecular dynamics at low collision energies. Electric and magnetic fields are used to confine the translational motion of molecules in specific Stark or Zeeman states, resulting in external field traps [9–12]. The trapping fields modify molecular energy levels and may affect collisional properties of molecules. Collision-induced Zeeman and Stark relaxation processes lead to loss of molecules from static magnetic and electric traps. Atoms and molecules can generally be cooled to very low temperatures using buffer gas [9, 13, 14], sympathetic [15], and evaporative [16–18] cooling techniques, all of which rely on the relative efficiency of elastic and inelastic collisions in electromagnetic traps. The effective interactions between molecules can be manipulated using scattering resonances induced by dc magnetic [19], electric [20], or laser fields [21], allowing for realization and simulation of strongly correlated quantum systems with ultracold atoms and molecules [22]. Electromagnetic fields can also be used to orient and align polar molecules [23] and induce molecular predissociation [24]. The orientation of molecules with external fields allows for the study of the anisotropy of intermolecular interactions. It is therefore very important to understand the effects of static and laser electromagnetic fields on collision dynamics of molecules at sub-Kelvin temperatures and develop mechanisms for external field control of elastic and inelastic collisions of cold molecules.

DeMille et al. recently proposed to trap polar molecules in a microwave laser cavity [25]. This approach has several advantages over optical, dc Stark, and magnetic traps. The trapping potential of the microwave cavity can be made deeper and the size of the trap is much larger than those of the magnetic and optical [1, 12] traps, which makes the trap loading easier. Molecules in microwave cavities can potentially be confined in their absolute ground state, which eliminates the possibility of inelastic collisions leading to trap loss. Microwave traps can potentially hold a large number of molecules at temperatures as high as 0.5–1 K. However, further cooling may be required to reach the ultracold temperature regime. This can be achieved by evaporative or sympathetic cooling inside the trapping area. It is therefore particularly important to analyze the collision dynamics of polar molecules in the presence of microwave fields.

Low-temperature collisions of polar molecules in external fields have been studied by several authors. The theory of molecular scattering in the presence of external fields was developed by Volpi and Bohn [26] and Krems and Dalgarno [27]. Volpi and Bohn [26] found that angular-momentum transfer such as collision-induced Stark or Zeeman relaxation in weak external electric or magnetic fields is suppressed at low collision energies due to the presence of long-range centrifugal barriers in outgoing collision channels. Recently, we showed that the suppression mechanism discovered by Volpi and Bohn can be exploited to explore the effects of the external space symmetry on inelastic collisions of ultracold molecules confined in two dimensions [28]. Bohn and co-workers [29, 30] calculated the cross sections for molecule-molecule collisions in electric fields and analyzed the possibility of the creation of long-range molecular states. Tscherbul and Krems [31] explored the effects of dc electric fields on chemical reactions of diatomic molecules with atoms. Nonreactive atom-molecule collisions in a magnetic field were also examined in the work of González-Martínez and Hutson [32] and Lara et al. [33, 34]. Tscherbul and Krems studied the effects of superimposed dc electric and magnetic fields on radial and rotational inelastic scattering [35, 36] and rotationally inelastic scattering [37] of open-shell polar molecules at low temperatures. In particular, they demonstrated that electric fields can be used to suppress spin relaxation of cold molecules and that the scattering dynamics may be very sensitive to external fields near avoided crossings between Zeeman levels corresponding to the rotationally ground and rotationally excited states. Molecule-molecule collisions in a magnetic field were examined by Tscherbul et al. [38]. Kajita and Avdeenkov used the Born approximation to analyze elastic and inelastic collisions of polar molecules in circularly polarized microwave field [39]. Avdeenkov performed a coupled-channel analysis of scattering cross sections for cold collisions of polar molecules in a microwave field based on a...
model interaction potential [40]. He found that ground-state molecules undergo inelastic collisions in a microwave cavity, which do not reduce the number of molecules in the trap. We have recently shown [41] that both elastic and inelastic collisions of polar molecules at temperatures below 1 K may be very sensitive to an external microwave laser field. In particular, we found that inelastic relaxation in atom-molecule collisions in a microwave cavity is driven by the anisotropy of the atom-molecule interaction potential and occurs predominantly through collision-induced absorption of microwave photons followed by rotational de-excitation.

In this paper we extend the work of Ref. [41] to discuss in detail the theory of atom-molecule collisions in combined dc magnetic and microwave laser fields. We present accurate calculations of cross sections for spin-changing transitions in collisions of CaH($^3\Sigma$) molecules with He atoms. We show that microwave fields enhance collision-induced spin relaxation. Our results demonstrate that collision dynamics of polar $^3\Sigma$ molecules are very sensitive to the field magnitude near avoided crossings between different field-dressed states. We use helium as a weak perturber to explore general features of the scattering dynamics of $^3\Sigma$ molecules in a microwave field. We note that most of the effects described in this paper are determined by the molecule-field interactions and should be observable in collisions of $^3\Sigma$ molecules with other atoms and molecules.

II. THEORY

A. $^1\Sigma$ molecules in a microwave cavity

The molecule-field interaction for a molecule in a microwave laser-field cavity can be described using the field-dressed formalism [42]. The dressed-state picture is particularly convenient in the strong-field regime. The idea to use the dressed-state formalism for quantum-scattering calculations of atom-atom collisions in an intense near-resonant laser field was proposed by Julienne [43]. The rotational energy levels of a $^3\Sigma$ molecule in the absence of external fields are described by the Hamiltonian $B_N\hat{N}^2$ with the rotational angular momentum $\hat{N}$ and the rotational constant $B_N$. The eigenstates of this Hamiltonian are spherical harmonics of rank $N$,

$$B_N\hat{N}^2|NM_N\rangle = B_NN(N+1)|NM_N\rangle,$$

where $M_N$ is the projection of $\hat{N}$ on a space-fixed quantization axis.

The microwave field is described by the number of photons $\bar{n}+n$ in a given laser mode, where $\bar{n}$ is a mean number of photons in the cavity and $n$ is a small integer number. Here, we consider a single-mode laser field. The Hamiltonian of the single-mode laser field can be written as $\hbar\omega(\hat{a}\hat{\gamma}^\dagger - \bar{n})$, where $\hat{a}$ and $\hat{\gamma}$ are the photon creation and annihilation operators,

$$\hat{a}|\bar{n}+n\rangle = \sqrt{\bar{n}+n+1}|\bar{n}+n+1\rangle,$$

$$\hat{\gamma}|\bar{n}+n\rangle = \sqrt{\bar{n}+n}|\bar{n}+n-1\rangle.$$  

The energy of the field is given by:

$$\hbar\omega(\hat{a}\hat{\gamma}^\dagger - \bar{n})|\bar{n}+n\rangle = n\hbar\omega|\bar{n}+n\rangle.$$  \hfill (3)

The wave function of the rigid rotor in a microwave field can be expanded in the basis of direct products

$$|NM_N\rangle|\bar{n}+n\rangle.$$  \hfill (4)

The energy levels of the molecule in the laser field can then be found by diagonalizing the following Hamiltonian in the basis set (4):

$$\hat{H}_{m,f} = B_N\hat{N}^2 + \hbar\omega(\hat{a}\hat{\gamma}^\dagger - \bar{n}) + \hat{H}_{mf},$$  \hfill (5)

where the operator $\hat{H}_{mf}$ describes the molecule-field interaction. We consider linearly polarized light with the polarization along the space-fixed quantization $z$ axis. For such a field orientation, the projection of the total angular momentum of the system on $z$ axis is conserved. The interaction of the dipole moment of the molecule with a linearly polarized laser field is described by

$$\hat{H}_{mf} = -\frac{\Omega}{2\sqrt{n}}(\hat{a} + \hat{a}^\dagger)\cos \phi,$$  \hfill (6)

where $\phi$ is the angle between the laser polarization axis and the molecular axis, $\Omega = ed$ is the strength of the field-induced coupling, $d$ is the permanent dipole moment of the molecule, and $e$ is the electric field component of the laser light. We assume that $\bar{n} \gg n$. Under this condition $\sqrt{\bar{n}+n} \approx \sqrt{\bar{n}+n-1} \approx \sqrt{\bar{n}}$. Therefore, the matrix elements of the operator $H_{mf}$ in the basis (4) have the following form:

$$\langle N'M'_{M'}|\bar{n}+n'|\hat{H}_{mf}|NM_N\rangle|\bar{n}+n\rangle$$

$$= -\frac{\Omega}{2}(\delta_{N',N} - \delta_{N',N+1})b_{N'M'_{M'}|NM_N\rangle},$$  \hfill (7)

where $b_{N'M'_{M'}|NM_N\rangle}$ is the matrix elements of $\cos \phi |NM_N\rangle$. The matrix elements of $\cos \phi$ can be evaluated using the spherical harmonics addition theorem and the Wigner-Eckart theorem, leading to the following expression:

$$b_{N'M'_{M'}|NM_N\rangle} = \delta_{M,M'}(-1)^{N'}(2N'+1)(2N+1)$$

$$\times \left( \begin{array}{ccc} N' & N & 0 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} N & N & -M_N \\ 0 & 0 & M_N \end{array} \right).$$  \hfill (8)

where the parentheses denote $3j$ symbols. The first $3j$ symbol in Eq. (8) vanishes unless $N' = N + 1$. Therefore, $\hat{H}_{mf}$ has no diagonal matrix elements and it couples states with different photon numbers $n' = n + 1$ and rotational angular-momentum quantum numbers $N' = N + 1$.

The eigenspectrum of operator (5) can be divided into manifolds separated by multiplets of the photon frequency, as illustrated in Fig. 1. Each state can be labeled by two quantum numbers: index $K$ for the photon manifold and index $\nu$ for the field-dressed states within the manifold. An alternative way to label the quantum states could be to assign them the quantum numbers of the molecular state and the photon number state $(N,M_N,n)$, which adiabatically correlate with a state of interest at zero $\Omega$.

The field-dressed states can be generally represented as
absence of the molecule-field interaction, the states are described by the Zeeman operator 
\[ \hat{H}_{\text{Zeeman}} = -1 \hat{S}_{\text{Zeeman}} / H \]

The transitions \( |vK\rangle \rightarrow |v'K'\rangle \) decrease (increase) for \( K' = K - 1 \) (\( K' = K + 1 \)) the number of microwave photons in the cavity by one. Therefore, these transitions should be interpreted as accompanied by absorption (emission) of a photon. In the absence of the molecule-field interaction, the states (9) are direct products \( |NM_NS_M S_n\rangle = |\bar{n} + n\rangle \), representing the molecule in a particular rotational state and the quantized electromagnetic field with a given number of photons. When \( \Omega > 0 \), the field-dressed states are coherent superpositions of these product states. If the field is switched off adiabatically, the field-dressed states become the rotational states of the molecule in the \( \Omega = 0 \) limit. If the field is switched off rapidly, the molecule must remain in a coherent superposition of rotational states. The field-dressed states in a laser cavity can be observed spectroscopically [44].

### B. \(^2\Sigma\) molecules in combined dc magnetic and microwave fields

The dressed-state formalism can be generalized to more complex molecules. For example, the effects of combined dc magnetic and microwave laser fields on dynamics of \(^2\Sigma\) molecules can be analyzed by including spin functions and spin-dependent interactions in the rigid-rotor model described in the previous section.

The Hamiltonian \( \hat{H}_{\text{ad}} \) for a \(^2\Sigma\) molecule in the presence of dc magnetic and microwave laser fields takes on the following form:

\[ \hat{H}_{\text{ad}} = B_0 \hat{S}^2 + \alpha \hat{S} \cdot \hat{S} + 2 \mu_B B \cdot \hat{S} + h \omega \hat{a}^\dagger \hat{a} - \bar{n} + \hat{H}_{\text{mic}}. \]

where the interaction of the molecule with the magnetic field \( B \) is described by the Zeeman operator \( 2 \mu_B B \cdot \hat{S} \), \( \mu_B \) is a Bohr magneton, \( \alpha \hat{S} \cdot \hat{S} \) describes the spin-rotation interaction, and \( \gamma \) is a phenomenological constant [45]. In the present work, we use the value \( \gamma = 0.0415 \text{ cm}^{-1} \), which describes the fine-structure interaction in the CaH molecule. We note that the cross sections for inelastic collisions induced by the spin-rotation interaction are quadratic functions of \( \gamma \) [27]. We assume that the magnetic field is oriented along the \( z \)-axis of the space-fixed coordinate frame. The energy levels and the field-dressed states of the molecule inside the cavity can be obtained by diagonalizing \( \hat{H}_{\text{ad}} \) in the basis of direct products of the molecular states and the photon number states \( |NM_N S_M S_n\rangle = |\bar{n} + n\rangle \), where we have added the spin functions \( |SM_S\rangle \) defined in the space-fixed coordinate frame. In the presence of a magnetic field, each state of a \(^2\Sigma\) molecule splits into two Zeeman components (see Fig. 2). The spin-independent part of the Hamiltonian (5) and the interaction with magnetic fields do not couple molecular states with different spin projections. The matrix elements of the spin-rotation interaction can be obtained using the identity [47]

\[ \gamma \hat{N} \cdot \hat{S} = \gamma \left[ \hat{N}_+ \hat{S}_+ + \frac{1}{2} (\hat{N}_- \hat{S}_- + \hat{N}_0 \hat{S}_0) \right], \]

where \( \hat{N}_+ \) and \( \hat{S}_+ \) are the ladder operators. The spin-rotation interaction is diagonal in \( N \) and the photon number states, and couples molecular states with different \( M_N \) and \( M_S \),

\[ \langle N'M_{N}'S'M_{S}'\bar{n}' | \gamma \hat{N}' \cdot \hat{S}' | N'M_NS_Sn \rangle = \delta_{n',\bar{n}} \delta_{N',N} \gamma \delta_{M_{N}',M_N} \delta_{M_{S}',M_S} \left( M_{N} + 1 \right)^{1/2} \left( M_{S} + 1 \right)^{1/2}. \]

The upper panel of Fig. 3 shows the field-dressed energy levels of the CaH molecule as a function of the field-induced coupling strength \( \Omega \) of the microwave field at a magnetic field of 0.1 T and a laser frequency value of \( h \omega / B_z = 0.8 \). At nonzero fields, the rotational ground \( N=0 \) and first-excited \( N=1 \) states split into two and six components, respectively. The interaction with the magnetic field at \( B=0.1 \text{ T} \) is stron-
The avoided crossings occur at lower magnetic fields as the frequency of the laser field is increased. Increasing \( \Omega \) shifts the positions of the avoided crossings to higher magnetic fields. The Zeeman levels \(|a\rangle=|N=0\ M_N=0\ M_S=\frac{1}{2}\ n=0\rangle\) and \(|b\rangle=|N=1\ M_N=1\ M_S=\frac{1}{2}\ n=-1\rangle\) cross at the magnetic field value \( B_c \), which can be defined to zeroth order by the equation \( 2\mu_B B_c=\Delta \), where \( \Delta=2B_c-\hbar\omega \) is the detuning from resonance.

The energy levels near the avoided crossings can be described by an effective Hamiltonian [42],

\[
\hat{H}_{\text{eff}} = \begin{pmatrix}
\mu_B B + \hat{R}_{ao}(\Delta/2) & \hat{R}_{ao}(\Delta/2) \\
\hat{R}_{bo}(\Delta/2) & -\mu_B B + \hat{R}_{bo}(\Delta/2)
\end{pmatrix},
\]

(13)

where \( \hat{R}(\Delta/2) \) is a level-shift operator evaluated at the energy of the crossing \( \Delta/2 \). The level-shift operator \( \hat{R}(z) \) can be represented by the following perturbative expansion [42]:

\[
\hat{R}(z)=\hat{\nu}+\hat{\nu}\frac{\hat{O}}{z-H_0}+\hat{\nu}\frac{\hat{O}}{z-H_0}+\hat{\nu}\frac{\hat{O}}{z-H_0}+\cdots,
\]

(14)

where \( \hat{H}_0 \) and \( \hat{\nu} \) are parts of the Hamiltonian (5) \( (\hat{H}_{\text{as}}=\hat{H}_0+\hat{\nu}) \) and \( \hat{O} \) is a projector on the subspace spanned by non-crossing states. We include in \( \hat{\nu} \) the spin-rotation and the

![Figure 3](image3.png)  
![Figure 4](image4.png)
like in the case of dc electric fields where crossings are

Note that no crossings occur in the absence of the laser field

The minimum-energy difference between the adiabatic states is

\[ \Delta E = \frac{\Omega^3 \gamma}{72 \sqrt{\pi} \hbar \omega (2B_\varepsilon - \hbar \omega)(2B_\varepsilon - 3\hbar \omega)}. \]  

Note that no crossings occur in the absence of the laser field unlike in the case of dc electric fields where crossings are real in the absence of the electric field and become avoided in the presence of the electric field [35]. The crossings of the Zeeman states in the absence of the laser field occur at high magnetic fields \((B_\varepsilon \sim 9.1 \text{ T for CaH})\). The dc electric field cannot shift these crossings significantly. As our analysis shows, microwave laser fields induce avoided crossings in a much wider range of magnetic field values, which suggests new mechanisms for controlling the dynamics of spin-dependent interactions in polar molecules.

The interaction of the molecule with the circularly \(\sigma_\pm\) polarized laser field defined by \( \epsilon = (\hat{x} \pm i\hat{y})/\sqrt{2} \) can be described by the Hamiltonian

\[ \hat{H}_{m_z}^{\sigma_\pm} = -\frac{\Omega}{2 \sqrt{n}} (4\pi/3)^{1/2} \left[ \hat{\alpha} Y_{1 \pm 1}(r) \pm \hat{\beta} Y_{1 \pm 1}(r) \right]. \]  

The matrix elements of \( \hat{H}_{m_z}^{\sigma_\pm} \) have the following form:

\[ \langle N' M_{S}' M_{J}' | \hat{H}_{m_z}^{\sigma_\pm} | N M_{S} M_{J} \rangle \]

\[ = -\left( \frac{\Omega}{2} \delta_{M_{S}' M_{S}} \right) \]

\[ \times \left[ \pm \delta_{n', n} \delta_{n_{1}'}^{1} b_{N' M_{S}' N M_{J}}^{1} \pm \delta_{n', n+1} \delta_{n_{1}'}^{1} b_{N' M_{S}' N M_{J}}^{1} \right], \]  

where \( b_{N' M_{S}' N M_{J}}^{n} \) are given by

\[ b_{N' M_{S}' N M_{J}}^{n} = (-1)^{M_{S}' \left(2N' + 1\right)} \left( \begin{array}{ccc} N' & 1 & N \\ 0 & 0 & 0 \end{array} \right) \]

\[ \times \left( \begin{array}{ccc} N' & 1 & N \\ -M_{S}' & n & M_{J} \end{array} \right). \]  

In the case of circularly polarized field, absorption and emission of photons are accompanied by a change in the rotational angular-momentum projection of the molecule. For example, the \( \sigma_- \) \((\sigma_+)\) polarized laser field couples the state \(|N = 0 \ M_S = 1/2 \ n = 0\) with the states \(|N = |m\rangle \ M_N = m \ M_S = 1/2 n = -m\rangle \) \((|N = |m\rangle \ M_N = m \ n = m\rangle\), where \(m\) is an integer number. The \( \sigma_- \) light couples the same state to the rotationally excited state \(|N = 1 \ M_N = -1 \ M_S = 1/2 \ n = -1\), which in turn is coupled by the spin-rotation interaction with the magnetic high-field-seeking states. The avoided crossings of the \(|N = 0 \ M_S = 1/2 \ n = 0\rangle \) and \(|N = 1 \ M_N = -1 \ M_S = 1/2 \ n = -1\rangle \) levels in the presence of \( \sigma_- \) polarized laser field occur at different values of the magnetic fields (see Fig. 6). The \( \sigma_- \) laser field couples the rotationally ground spin-up state to the maximally stretched state \(|N = 1 \ M_N = 1 \ M_S = 1/2 \ n = -1\). Therefore there is no avoided crossings of the initial spin-up state with spin-down states (see Fig. 6) for the laser frequencies below resonance. Figure 7 shows the field-dressed energy levels as functions of the field-induced coupling for the \( \sigma_- \) laser polarization. The spin-up and spin-down states do not exhibit avoided crossings at moderate field strengths.

C. Scattering formalism

The interaction of a diatomic molecule with a structureless atom in the presence of external fields can be described by the following Hamiltonian [26,27]:

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The total wave function of the collision complex is expanded in products of the field-dressed states (9) and the rotational functions of the collision complex $|lm_i\rangle$ as follows:

$$
\Psi = \sum_{\nu Km_i} F_{\nu Km_i}^{M}(R)|\nu K|lm_i\rangle.
$$

The substitution of expansion (23) into the Schrödinger equation with Hamiltonian (22) leads to a system of coupled differential equations for the expansion coefficients $F_{\nu Km_i}^{M}(R)$ parametrized by fixed values of the total angular-momentum projection $M=M_\lambda+M_\nu+m_i$ (for the case of parallel fields) and the total energy $E_{tot}$,

$$
\left[\frac{d^2}{dR^2} + 2\mu(E_{tot} - E_{\nu K}) - \frac{l(l+1)}{R^2}\right] F_{\nu Km_i}^{M}(R) = 2\mu \sum_{\nu'K'l'm'_i} \langle \nu Klm_i | \hat{V}(R,r,\theta) | \nu'K'l'm'_i \rangle F_{\nu'K'l'm'_i}^{M}(R).
$$

Here, $E_{\nu K}$ is an eigenvalue of $\hat{H}_\nu$, [given by Eq. (5) for $^{1}\Sigma$ molecules or Eq. (10) for $^{3}\Sigma$ molecules], i.e., the energy of a given $|\nu K\rangle$ field-dressed state. The matrix elements of the interaction potential $V(R,r,\theta)$ in the basis (23) can be written as follows:

$$
\langle \nu Klm_i | \hat{V} | \nu'K'l'm'_i \rangle = \sum_{nM_NnM_{N'}M_{l'}} C_{NM_NnM_{N'}M_{l'}} \times C_{N'M_NnM_{N'}nM_{l'}} \times \langle NM_Nlm_i | \hat{V} | N'M_{N'}lm_i' \rangle,
$$

where the integrals $\langle NM_Nlm_i | \hat{V} | N'M_{N'}lm_i' \rangle$ can be evaluated by expanding the interaction potential in spherical harmonics,

$$
V(R,r) = \sum_{\lambda} \left(\frac{4\pi}{2\lambda+1}\right) \frac{Y_\lambda(r)}{Y_\lambda(\hat{R})} \sum_{m_\lambda} (-1)^m_\lambda Y_{\lambda,-m_\lambda}(\hat{R}) \times Y_{\lambda m_\lambda}(\hat{\theta}),
$$

and applying the Wigner-Eckart theorem [27]. They have the form

$$
\langle NM_Nlm_i | \hat{V} | N'M_{N'}lm_i' \rangle = \sum_{\lambda} \frac{V_\lambda(R,r)}{Y_\lambda(\hat{R})} \left(\begin{array}{ccc} 1 & \lambda & \lambda' \\ 0 & 0 & 0 \end{array}\right) \left(\begin{array}{ccc} N & \lambda & N'' \\ 0 & 0 & 0 \end{array}\right) \\
	imes [(2l+1)(2l'+1)]^{1/2} \left[ (2N+1)(2N'+1) \right]^{1/2} \\
\times \sum_{m_\lambda} (-1)^{m_\lambda-m_{l'}} Y_{\lambda,-m_\lambda}(\hat{R}) Y_{\lambda m_{l'}}(\hat{\theta}) \times Y_{N,-N'} \left(\begin{array}{ccc} \lambda & \lambda' & \lambda' \\ -m_l & m_{l'} & m_{l'} \end{array}\right) \left(\begin{array}{ccc} N & \lambda & N'' \\ -M_N & m_\lambda & M_{N'} \end{array}\right).
$$

The coupled-channel Eqs. (24) are integrated using the log-derivative method [49]. The numerical solutions subject to the scattering boundary conditions yield the scattering matrix $S_{\nu Km_i;\nu'K'l'm'_i}$ or the probability amplitudes for transi-
tions between different scattering channels labeled by \( \nu, K, l, m_l \).

The state-resolved cross sections for elastic and inelastic collision processes in a microwave cavity are computed from the \( S \) matrix as [27]

\[
\alpha_{\nu,K-\nu',K'} = \left( \frac{\pi}{k^2_{\nu K}} \right) \sum_{l m_l} \sum_{l' m'_l} \sum_{l'' m''_l} \left| \delta_{l m_l l' m'_l} \delta_{l' m'_l l'' m''_l} - S^M_{\nu K \nu' K'} \right|^2,
\]

where \( k^2_{\nu K} = 2\mu(E_{\text{microwave}} - E_{\nu K}) \).

In this paper, we consider collisions of \( \text{CaH} \) molecules with \( ^3\text{He} \) atoms. The interaction potential for the \( \text{CaH-He} \) system was calculated by Groenenboom and Balakrishnan [50]. The photon number basis is generated by fixing \( \bar{n} \) and varying \( n \) from \( n_{\text{max}} \) to \( n_{\text{max}} \). We use \( n_{\text{max}} = 5 \), a total number of six rotational states (\( N = 5 \)) and seven partial waves (\( l \leq 6 \)) in the scattering basis set, which for \( M = 0 \) leads to the system of 3938 coupled differential equations.

### III. SCATTERING CALCULATIONS

#### A. Microwave field dependence

The interaction of \(^2\Sigma\) molecules with a magnetic field separates different \( M_S \) sublevels and the ac electric field lifts the degeneracy of the rotational states with different \( |M_N| \). Our initial and final states correlate with the magnetic low-field-seeking \( \{|N = 0, M_S = 1/2, n = 0\} \) and high-field-seeking \( \{|N = 0, M_S = -1/2, n = 0\} \) states of the \( \text{CaH} \) molecule at zero laser field. In terms of \( \nu \) and \( K \) they are labeled as \( |10\rangle \) and \( |00\rangle \) correspondingly. The energy levels of the \( \text{CaH}(^2\Sigma) \) molecule in a microwave field are shown in Fig. 3. A linearly polarized microwave field couples states with \( N' = N \pm 1 \) and \( n' = n \pm 1 \) and conserves the angular-momentum projection of the molecule, i.e., \( M'_N = M_N \). The dependence of the cross sections for collision-induced spin relaxation \( |N = 0, M_S = 1/2, n = 0\rangle \rightarrow |N = 0, M_S = -1/2, n = 0\rangle \) and \( |N = 0, M_S = 1/2, n = 0\rangle \rightarrow |N = 0, M_S = -1/2, n = -1\rangle \) on the field-induced coupling strength \( \Omega \) is shown in the lower panel of Fig. 3. For moderate \( \Omega \approx B_z \), the cross section for transitions between different photon manifolds increases with increasing coupling strength. The cross section for processes conserving the number of photons has a weak dependence on \( \Omega \). The cross sections increase by three orders of magnitude near \( \Omega / B_z = 0.81, 1.15, \) and 1.45, the values corresponding to the avoided crossings between the field-dressed states.

#### B. Resonances near avoided crossings

The lower panel of Fig. 4 shows the cross sections for spin relaxation as a function of the magnetic field magnitude near the avoided crossing of the initial \( |N = 0, M_S = 1/2, n = 0\rangle \) and excited \( |N = 1, M_N = 1, M_S = -1/2, n = -1\rangle \) states at laser-field parameters \( \Omega = 0.1 \) \( B_z \) and \( \hbar \omega = 1.9 \) \( B_z \). The crossing occurs at the magnetic field \( B_z \sim 0.47 \) \( T \). The cross section for spin relaxation accompanied by absorption of the microwave photon is 100 times larger than for scattering within the same photon manifold. The cross sections increase by the factor of about 100 near the avoided crossing.

Figure 8 shows the cross sections for spin relaxation near the avoided crossing as functions of the magnetic field for different laser frequencies. The position of the crossing shifts to lower magnetic field values \( B_z \) with increasing laser frequency. The cross sections increase by four orders of magnitude near the avoided crossings between the \( |N = 0, M_S = 1/2, n = 0\rangle \) and \( |N = 1, M_N = 1, M_S = -1/2, n = 1\rangle \) levels.

Figure 9 shows the cross sections for spin relaxation near the avoided crossing as functions of the magnetic field for different coupling strength \( \Omega \). The position of the crossing shifts to higher magnetic fields as the coupling strength increases. The magnitude of the cross sections increases by the factor of 10^3 near the avoided crossings.

#### C. Collision energy dependence

The collision energy dependence of the spin-relaxation cross sections at a magnetic field of \( B = 0.1 \) \( T \) is shown in Fig. 10. The cross sections for the spin-flipping transition follow the Wigner threshold law [51]. For small collision energies they are inversely proportional to the collision velocity \( \sigma \sim 1/\nu \). For a weak magnetic field in the absence of the microwave field the spin-changing transition is nearly
Forbidden [52]. Microwave fields induce couplings between different Zeeman states and enhance the cross sections. The onset of the $1/t$ behavior is shifted to higher collision energies in the presence of the laser field.

**IV. SUMMARY**

We have presented a detailed study of inelastic spin-relaxation in collisions of CaH($^2\Sigma$) molecules with He atoms in superimposed magnetic and microwave laser fields. Our study demonstrates that the dynamics of molecular collisions may be sensitive to both the frequency and the intensity of the laser field. External fields modify the rotational structure of molecules and affect the spin-rotation interaction. Our study shows that microwave fields enhance collision-induced spin relaxation. Spin-changing transitions are dominated by the process accompanied with photon absorption. The structure of the molecules changes with varying magnetic field or laser-field parameters. Variation in the laser fields may induce and shift avoiding crossings between molecular Zeeman levels of different symmetry. Different spin states are strongly mixed and the dynamics of magnetic spin-relaxation is extremely sensitive to external fields near the avoided crossings. Changing the laser polarization can significantly influence the dynamics of the spin-changing processes. The number of avoided crossings is reduced in the circularly polarized light. Circularly polarized light couples selectively the initial state of the molecule to the maximally stretched states that are not directly coupled by the spin-rotation interaction, which suppresses collisional spin-relaxation. For example, the use of $\sigma_+$ polarization reduces collisional spin relaxation of molecules in the rotationally ground low-field-seeking state. Inelastic Zeeman transitions in collisions of molecules with atoms may thus be effectively controlled by varying the strength, the frequency, and the polarization of the microwave laser field. The effects predicted in this work can be observed in the experiments with magnetically trapped molecules [9,16], as well as in the experiments with molecular samples in a cold He gas in a static magnetic field [53]. It might be particularly interesting to explore the effect of microwave laser fields on spin-forbidden chemical reactions of nitrogen atoms with NH radicals in a magnetic trap, a system recently realized in Ref. [54].

**ACKNOWLEDGMENT**

We thank Timur Tscherbul for interesting and useful discussions. This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada.
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The value of $\gamma$ used is 0.0415 cm$^{-1}$ [46].


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