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Inelastic collisions of cold polar molecules in nonparallel electric and magnetic fields

E. Abrahamsson, T. V. Tscherbul,[a] and R. V. Krems
Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada

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The authors present a detailed study of low-temperature collisions between CaD molecules and He atoms in superimposed electric and magnetic fields with arbitrary orientations. Electric fields do not interact with the electron spin of the molecules directly but modify their rotational structure and, consequently, the spin-rotation interactions. The authors examine molecular Stark and Zeeman energy levels as functions of the angle between the fields and show that rotating fields may induce and shift avoided crossings between the Zeeman levels of the rotationally ground and rotationally excited states of the molecule. The dynamics of molecular collisions are extremely sensitive to external fields near these avoided crossings and it is shown that molecular collisions may be controlled by varying both the strength and the relative orientation of the fields. The effects observed in this study are due to interactions of the isolated molecules with external fields so the conclusions should be relevant for collisions of molecules with other atoms or collisions of molecules with each other. This study demonstrates that electric fields may be used to enhance or suppress spin-rotation interactions in molecules. The spin-rotation interactions induce nonadiabatic couplings between states of different total spins in systems of two open-shell species and it is suggested that electric fields might be used for controlling nonadiabatic spin transitions and spin-forbidden chemical reactions of cold molecules in a magnetic trap. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2748770]

I. INTRODUCTION

The dynamics of molecules in external electromagnetic fields has recently been a subject of many experimental and theoretical studies.[1–9] Electric fields may be used to orient and align molecules in the space-fixed coordinate frame.[7] Orienting and aligning molecules allow for direct measurements of the anisotropy of intermolecular interactions.[10–12] Interactions of molecules with dc and laser fields have been exploited in the experiments on selective bond breaking and rearrangement,[13] molecular tomography,[14,15] and the design of a molecular synchrotron.[16,17] Precise spectroscopic measurements of molecular energy levels in superimposed electric and magnetic fields may provide sensitive tests of fundamental symmetries of nature.[18,19] A major thrust of recent research in molecular physics has been to produce dense ensembles of cold and ultracold molecules.[20] Electric and magnetic traps have been designed to confine and isolate cold molecules prepared in particular Zeeman or Stark energy levels.[21–24] Experiments with cold molecules may yield detailed information on intermolecular interactions and allow for unprecedented control of inelastic collisions and chemical reactions.[18,19] For example, it was demonstrated by McCarthy *et al.*[3] that even extremely weak molecule-field interactions such as the interaction of the nuclear spin with magnetic fields can be used to distort molecular trajectories in a slow molecular beam. Staanum *et al.*[25] and Zahzam *et al.*[26] have recently reported the first experiments on ultracold chemical reactions of alkali metal atoms with alkali metal diatomic molecules in an optical trap. Jung *et al.*[27] proposed to tune the threshold fragmentation of cold SO_2 molecules with electric fields. Gilijamse *et al.*[28] carried out a crossed-beam collision experiment with slow OH molecules produced in a Stark decelerator. All these studies are generating an increasing demand for the development of rigorous theories for accurate simulations of molecular collisions in the presence of external fields.

Electromagnetic fields modify molecular energy levels and may induce inelastic transitions in collisions of molecules.[19] In particular, spin-flipping transitions between molecular Zeeman levels —spin relaxation— may occur in a magnetic field.[19,29–32] The spin relaxation of cold $^2\Sigma$ molecules was first observed in 1998 by Weinstein *et al.*[33] who cooled CaH($^2\Sigma$) molecules in a cryogenic cell filled with ^{3}He buffer gas and loaded them into a magnetic trap. Collision-induced Zeeman transitions have later been studied for a variety of molecules in several experiments.[34,35] Spin relaxation produces molecules in high-field-seeking Zeeman states, which leads to trap loss and heating.[23] It is therefore important to find mechanisms for suppressing spin relaxation in collisions of cold molecules in order to increase the number of trapped molecules in buffer-gas loading[23,33] and evaporative cooling experiments.[36]

An adequate theoretical description of molecular alignment and cold collisions should be based on quantum mechanical calculations of dynamics in the presence of external electric and magnetic fields. The methodology for quantum scattering calculations in magnetic fields was developed by

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[a] Electronic mail: timur@chem.ubc.ca

Volpi and Bohn[29] and by Krems and Dalgarno.[32] Bohn and co-workers calculated cross sections for collisions of two diatomic molecules in an electric field[37,38] and suggested the possibility of creating novel field-linked, long-range molecular states.[39] González-Martínez and Hutson[40] and Lara *et al.*[41,42] reported extensive calculations of nonreactive atom-molecule collisions in a magnetic field. We have recently examined the influence of combined electric and magnetic fields on spin relaxation[43] and the rotationally inelastic scattering[44] of polar molecules at low temperatures. In particular, we demonstrated that dc electric fields can be used to suppress the spin relaxation of cold molecules and that the dynamics of molecules may be extremely sensitive to external fields when the Zeeman levels of rotationally excited and rotationally ground manifolds intersect.[43]

Here, we extend the work in Ref. 43 to present in detail the theory of atom-molecule collisions in nonparallel electric and magnetic fields. We examine the Zeeman and Stark energy levels of $^2\Sigma$ molecules as functions of the angle between the fields and show that the positions and number of the avoided crossings between rotationally ground and rotationally excited states depend on the relative orientation of the fields. The cross sections for spin relaxation near the crossings are therefore very sensitive to the angle between the fields. We calculate the rates for both cold and ultracold collisions and discuss the possibility of external field control of cold molecules. Finally, we suggest that spin-forbidden chemical reactions of open-shell atoms in the ^2S state with $^2\Sigma$ molecules in a magnetic trap may be stimulated or suppressed by electric fields.

II. THEORY

The Hamiltonian for a $^2\Sigma$ polar molecule in superimposed electric and magnetic fields can be written as

$$H_{\mathrm{mol}} = -\frac{1}{2\mu_m r}\frac{d^2}{dr^2}r + \frac{\boldsymbol{N}^2(\hat{r})}{2\mu_m r^2} + V(r) + \gamma \boldsymbol{S}\cdot\boldsymbol{N} - \boldsymbol{E}\cdot\boldsymbol{d} + 2\mu_B \boldsymbol{B}\cdot\boldsymbol{S}, \tag{1}$$

where μ_m is the reduced mass and $V(r)$ is the potential energy function of the diatomic molecule. The coupling between the rotational ($\boldsymbol{N}$) and spin ($\boldsymbol{S}$) angular momenta is determined by the spin-rotation interaction constant γ. The hat over the symbol denotes the unit vector. The interaction with electric fields can be written as $-\boldsymbol{E}\cdot\boldsymbol{d} = -Ed\cos\chi$, where χ is the angle between the electric field direction $\hat{E}$ and the molecular axis $\hat{r}$, E is the electric field strength, and d is the electric dipole moment of the molecule. Using the spherical harmonic addition theorem,[46] this term can be rewritten as a sum over products of spherical harmonics,

$$-Ed\cos\chi = -Ed\frac{4\pi}{3}\sum_q Y^*_{1q}(\hat{r})Y_{1q}(\hat{E}). \tag{2}$$

The interaction of the electron spin with the magnetic field $\boldsymbol{B}$ is given by $2\mu_B\boldsymbol{B}\cdot\boldsymbol{S}$, where μ_B is the Bohr magneton. We orient the space fixed quantization axis Z along the magnetic field direction so that only the Z component of the vector $\boldsymbol{B}$ is nonzero and the last term in Eq. (1) reduces to $2\mu_B BS_Z$. The spin-rotation interaction constant γ for CaD is $0.021\ \mathrm{cm}^{-1}$,[47] and the dipole moment d is 2.94 D.[48]

The Hamiltonian for the atom-molecule complex has the following form[29,32]

$$H = -\frac{1}{2\mu R}\frac{d^2}{dR^2}R + \frac{\ell^2(\hat{R})}{2\mu R^2} + V(R,r,\theta) + H_{\mathrm{mol}}, \tag{3}$$

where μ is the reduced mass of the CaD–He system, R is the distance between the center of mass of the diatomic molecule and the atom, and ℓ is the orbital angular momentum for the collision. The interaction potential $V(R,r,\theta)$ vanishes as $R\to\infty$. We used a recent *ab initio* potential energy surface of Balakrishnan *et al.*[49] and fixed the interatomic distance r at its equilibrium distance of 2.008 Å, which is a good approximation for collisions at low energies.[50]

Following the work of Krems and Dalgarno,[32] we expand the total wave function of the collision system in a set of uncoupled space-fixed basis functions,

$$|NM_N\rangle|SM_S\rangle|\ell M_\ell\rangle, \tag{4}$$

where M_N, M_S, and M_ℓ denote the projections of $\boldsymbol{N}$, $\boldsymbol{S}$, and $\boldsymbol{\ell}$ on the magnetic field axis.[32] When the electric and magnetic fields are parallel or antiparallel, the projection of the total angular momentum $M = M_N + M_S + M_\ell$ is conserved, and the scattering calculations can be carried out in a cycle over M.[32,44] If the electric and magnetic fields are rotated, the electric field couples states with different M_N, and the projection of the total angular momentum M is no longer a good quantum number. The R-dependent expansion coefficients $F_{NM_NSM_S\ell M_\ell}(R)$ of the total wave function in basis set (4) are obtained by solving a set of close-coupled equations,[32,44]

$$\left[\frac{d^2}{dR^2} + 2\mu E_{\mathrm{tot}} - \frac{\ell(\ell+1)}{R^2}\right]F_{NM_NSM_S\ell M_\ell}(R) = 2\mu \sum_{N',M'_N,M'_S,\ell',M'_\ell} \langle NM_NSM_S\ell M_\ell|V(R,r,\theta) + H_{\mathrm{mol}}|N'M'_NSM'_S\ell' M'_\ell\rangle F_{N'M'_NSM'_S\ell' M'_\ell}(R), \tag{5}$$

where E_{tot} is the total energy of the system. The expressions for the matrix elements of the operators $V(R,r,\theta)$ and $2\mu BS_Z$ can be found in Ref. 32. The matrix of the interaction with electric fields (2)

$$\langle NM_N|-Ed\cos\chi|N'M'_N\rangle = -Ed\frac{4\pi}{3}\sum_q Y_{1q}(\hat{E})\langle NM_N|Y^*_{1q}(\hat{r})|N'M'_N\rangle \tag{6}$$

is diagonal in S, M_S, ℓ, and M_ℓ quantum numbers. The evaluation of the integrals in Eq. (6) provides a general expression for the matrix elements of the interaction with electric fields of arbitrary orientation,

$$\langle N M_N S M_S \ell M_\ell | -Ed\cos\chi | N' M'_N S M'_S \ell' M'_\ell\rangle = -\delta_{\ell'\ell}\delta_{M'_\ell M_\ell}\delta_{M'_S M_S} Ed(-1)^{M_N} Y_{1,M'_N-M_N}(\hat{E})[(2N+1) \times(2N'+1)]^{1/2}\begin{pmatrix} N' & 1 & N \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} N' & 1 & N \\ M'_N & M_N-M'_N & -M_N\end{pmatrix}, \tag{7}$$

where the symbols in parentheses are $3-j$ symbols.

When the magnetic and electric fields are both oriented along the Z axis, the spherical harmonics $Y_{1q}(\hat{E})$ in Eq. (6) reduce to

$$Y_{1q} = \left(\frac{3}{4\pi}\right)^{1/2}\delta_{q0}, \tag{8}$$

which, when inserted in Eq. (2), gives

$$-Ed\cos\chi = -Ed\left(\frac{4\pi}{3}\right)^{1/2} Y_{10}(\hat{r}). \tag{9}$$

For parallel fields, $q=M'_N-M_N=0$, and Eq. (7) reduces to the previously used expression as follows:[44]

$$\langle N M_N S M_S \ell M_\ell | -Ed\cos\chi | N' M'_N S M'_S \ell' M'_\ell\rangle = -\delta_{\ell'\ell}\delta_{M'_\ell M_\ell}\delta_{M'_S M_S}\delta_{M'_N M_N} Ed(-1)^{M_N}[(2N+1) \times(2N'+1)]^{1/2}\begin{pmatrix} N' & 1 & N \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} N' & 1 & N \\ -M_N & 0 & M_N\end{pmatrix}. \tag{10}$$

Energy levels of the diatomic molecule in an electric field were computed by diagonalizing Hamiltonian (1). In order to verify our program, we have compared our Stark energies with the data of Ref. 45. In the calculations with parallel fields we included the molecular states with $N \leqslant 7$ and $\ell \leqslant 8$ to ensure the convergence of inelastic cross sections at collision energies below 20 K. This resulted in 808 collision channels for $M=1/2$. At higher collision energies, the basis was extended to $N \leqslant 8$ and $\ell \leqslant 9$. If the magnetic and electric fields are rotated, the states with different M become coupled, and the total angular momentum projection M is no longer conserved. This dramatically increases the complexity of the problem, and the same calculation at the lowest collision energy would involve the integration of 10 368 coupled equations. This is beyond our computational resources, so we reduced the basis set to $N \leqslant 5$ and $\ell \leqslant 6$ and integrated 3528 coupled equations in order to study the effects of rotated fields.

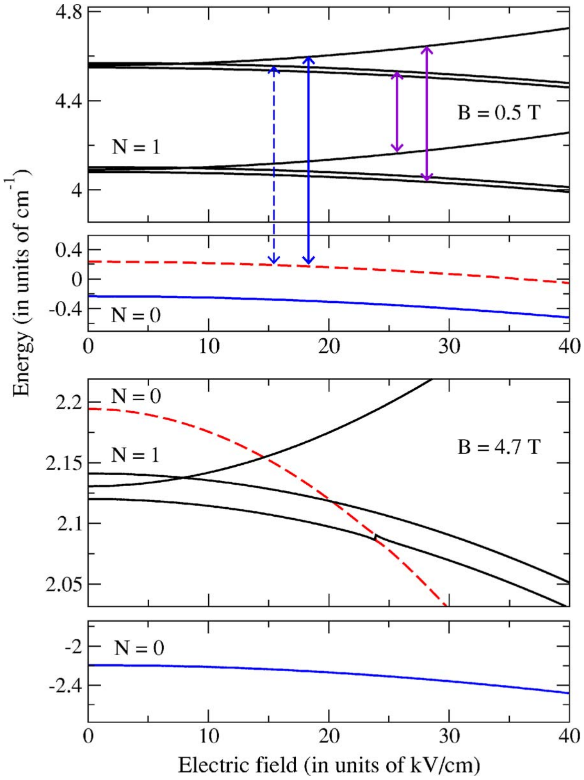

FIG. 1. (Color online) Stark levels of the CaD molecule in magnetic fields of 0.5 T (upper panels) and 4.7 T (lower panels) as functions of the electric field strength. The curves are labeled by the rotational quantum number of the molecule at zero electric field. The initial magnetic low-field-seeking state $|00\frac{1}{2}\rangle$ is shown by the dashed lines. Two arrows on the left denote couplings induced by electric fields; two straight arrows on the right connect the levels coupled by the spin-rotation interaction. The dashed arrow on the left joins the levels coupled by nonparallel electric and magnetic fields.

III. RESULTS

A. CaD($^2\Sigma$) molecules in electric and magnetic fields

1. Parallel fields

If the vectors $\boldsymbol{E}$ and $\boldsymbol{B}$ in Eq. (1) are parallel, the electric field couples the rotational states with the same projection M_N. As we showed previously, the dynamics of molecular collisions is sensitive to external fields near the avoided crossings between the ground and rotationally exited states at high magnetic fields.[43] Figure 1 shows the molecular energy levels coupled by the interaction with electric fields as well as by the spin-rotation interaction. The initial state for our calculations is the magnetic low-field-seeking state $|N=0,M_N=0,M_S=\frac{1}{2}\rangle$. This is the lowest state of magnetically trapped molecules in the buffer gas cooling experiments.[33] This state is coupled by electric fields to the $|10\frac{1}{2}\rangle$ level which, in turn, is coupled to the $|11-\frac{1}{2}\rangle$ state by the spin-rotation interaction. The matrix representation of Hamiltonian (1) in the basis of these three states is

$$\mathsf{H} = \begin{array}{c} \\ \\ \\ \end{array}\left(\begin{array}{ccc} |0\,0\,\frac{1}{2}\rangle & |1\,1\,-\frac{1}{2}\rangle & |1\,0\,\frac{1}{2}\rangle \\ \hline \mu_0 B/2 & 0 & -Ed/\sqrt{3} \\ 0 & 2B_e-\mu_0 B/2-\gamma/2 & \gamma/\sqrt{2} \\ -Ed/\sqrt{3} & \gamma/\sqrt{2} & 2B_e+\mu_0 B/2 \end{array}\right)\begin{array}{l} \\ |0\,0\,\frac{1}{2}\rangle \\ |1\,1\,-\frac{1}{2}\rangle \\ |1\,0\,\frac{1}{2}\rangle \end{array}, \tag{11}$$

where the diagonal matrix elements are the unperturbed energies of the molecule with the rotational constant B_e in a magnetic field of strength B. The spin-rotation interaction induces the coupling $\gamma/\sqrt{2}$, and the coupling due to the electric field is given by

$$-Ed\sqrt{3}\begin{pmatrix} 0 & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 = -Ed/\sqrt{3}.$$

The unperturbed Zeeman levels cross at the magnetic field value B_c defined by the equation $\mu_0 B_c = 2B_e - \gamma/2$ ($B_c \sim 4.7$ T for CaD). The diagonalization of Hamiltonian (11) gives the energies ϵ_i of the molecule in the presence of superimposed electric and magnetic fields,

$$\epsilon_1 = \frac{\mu_0 B}{2}, \quad \epsilon_{2,3} = B_e + \frac{\mu_0 B}{2} \pm B_e\left(1 + \frac{\gamma^2}{2B_e^2} + \frac{E^2 d^2}{3B_e^2}\right)^{1/2}. \tag{12}$$

Equation (12) shows that electric fields induce an avoided crossing between the degenerate Zeeman levels, lifting their degeneracy by $\Delta = \epsilon_1 - \epsilon_3 = B_e(\sqrt{1+\gamma^2/2B_e^2 + E^2d^2/3B_e^2} - 1)$.

If the electric field is small compared to the rotational constant of the molecule, the expansion of the square root suggests a quadratic dependence of the splitting on the electric field strength: $\Delta \sim B_e(\gamma^2/2B_e^2 + E^2d^2/3B_e^2)$. Note that in the absence of electric fields, the crossing is real and occurs at a slightly different value of the magnetic field because the off-diagonal matrix elements of the spin-rotation interaction shift the energy of the rotationally excited levels. The crossing is also real if the spin-rotation interaction is omitted; the quasidegenerate states $|00\tfrac{1}{2}\rangle$ and $|11-\tfrac{1}{2}\rangle$ would then again remain uncoupled. It is thus a *combination* of the spin-rotation interaction and the electric field that leads to the avoided crossing of the ground and the first excited rotational levels.

2. Perpendicular fields

When the electric field is perpendicular to the magnetic field, $\chi = \pi/2$ and the initial $|00\tfrac{1}{2}\rangle$ state is coupled to two rotationally excited states $|11\tfrac{1}{2}\rangle$ and $|1-1\tfrac{1}{2}\rangle$ [cf. Eq. (7)]. The spin-rotation interaction couples the second of the two $N=1$ states with the spin-down state $|10-\tfrac{1}{2}\rangle$. We therefore include the states $|00\tfrac{1}{2}\rangle$, $|1-1\tfrac{1}{2}\rangle$, and $|10-\tfrac{1}{2}\rangle$ in our model basis set. The matrix of the Hamiltonian in this basis is

$$\mathsf{H} = \left(\begin{array}{ccc|l} |0\,0\,\tfrac{1}{2}\rangle & |1\,0\,-\tfrac{1}{2}\rangle & |1\,1\,\tfrac{1}{2}\rangle & \\ \hline \mu_0 B/2 & 0 & Ed/\sqrt{3} & |0\,0\,\tfrac{1}{2}\rangle \\ 0 & 2B_e - \mu_0 B/2 & \gamma/\sqrt{2} & |1\,0\,-\tfrac{1}{2}\rangle \\ Ed/\sqrt{3} & \gamma/\sqrt{2} & 2B_e + \mu_0 B/2 + \gamma/2 & |1\,1\,\tfrac{1}{2}\rangle \end{array}\right). \tag{13}$$

The eigenvalues of the matrix are again given by Eq. (12). However, the avoided crossing now occurs between the ground rotational state $|00\tfrac{1}{2}\rangle$ and the *different* Zeeman state $|10-\tfrac{1}{2}\rangle$. As a result, the position of the crossing in perpendicular fields is shifted with respect to that for parallel fields (see Fig. 1). As illustrated in the following section, this leads to the possibility of controlling molecular collision dynamics by rotating the electric field.

3. Fields at an arbitrary angle

In this more general case, the initial $N=0$ state is directly coupled to three rotationally excited states. The spin-rotation interaction couples in two other states resulting in the following model Hamiltonian matrix:

$$\left(\begin{array}{ccccc|l} |0\,0\,\tfrac{1}{2}\rangle & |1\,1\,-\tfrac{1}{2}\rangle & |1\,0\,\tfrac{1}{2}\rangle & |1\,-1\,\tfrac{1}{2}\rangle & |1\,0\,-\tfrac{1}{2}\rangle & \\ \hline \mu_0 B/2 & 0 & -Ed\cos\chi/\sqrt{3} & Ed\sin\chi/\sqrt{3} & 0 & |0\,0\,\tfrac{1}{2}\rangle \\ 0 & 2B_e - \mu_0 B/2 - \gamma/2 & \gamma/\sqrt{2} & 0 & 0 & |1\,1\,-\tfrac{1}{2}\rangle \\ -Ed\cos\chi\sqrt{3} & \gamma/\sqrt{2} & 2B_e + \mu_0 B/2 & 0 & & |1\,0\,\tfrac{1}{2}\rangle \\ Ed\sin\chi/\sqrt{3} & 0 & 0 & 2B_e + \mu_0 B/2 - \gamma/2 & \gamma/\sqrt{2} & |1\,-1\,\tfrac{1}{2}\rangle \\ 0 & 0 & 0 & \gamma/\sqrt{2} & 2B_e - \mu_0 B/2 & |1\,0\,-\tfrac{1}{2}\rangle \end{array}\right), \tag{14}$$

If the angle χ is small, matrix (14) is nearly block diagonal, with the eigenvalues given by Eq. (12) perturbed by the off-diagonal couplings $Ed\sin\chi/\sqrt{3}$. The perturbation of the levels at small χ is then proportional to $E^2\sin^2\chi$. At larger values of χ, the matrix has to be diagonalized numerically. We present below converged results of the numerical diagonalization using the complete basis as defined in Sec. II.

Figure 2 shows the angular dependence of the three eigenvalues exhibiting an avoided crossing (one of which corresponds to our initial state $|00\tfrac{1}{2}\rangle$) at different magnetic fields near the crossing. In the upper panel, the initial state is only weakly coupled to the $|11-\tfrac{1}{2}\rangle$ state so it depends weakly on

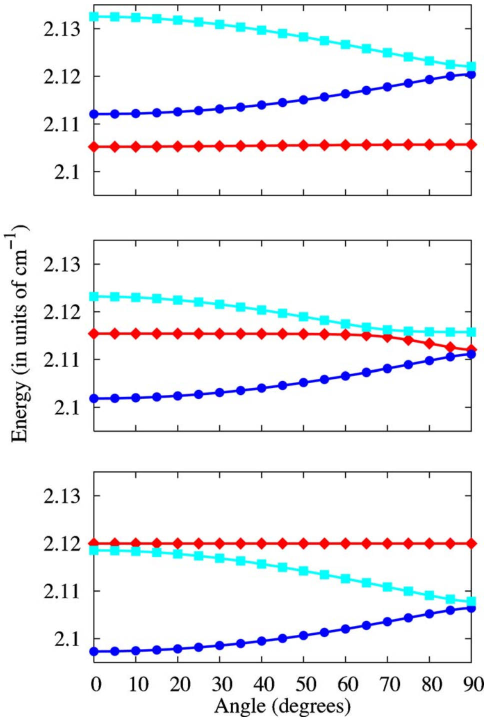

FIG. 2. (Color online) Stark shifts of the CaD molecule at an electric field of 20 kV/cm and magnetic fields of 4.67 T (upper panel), 4.690 T (center), and 4.70 T (lower panel) as functions of the angle between the directions of the magnetic and electric fields. The eigenvectors corresponding to these energies are dominated by the basis states $|00\frac{1}{2}\rangle$ (diamonds), $|11-\frac{1}{2}\rangle$ (circles), and $|1-1-\frac{1}{2}\rangle$ (squares). The energy is referred to the ground rovibrational state of the molecule at zero fields.

the angle between the fields. Increasing the magnetic field induces the crossing of the initial state with the lower of the two $N=1$ states. In the middle panel of Fig. 2, the initial state is above the lower of the $N=1$ states. It undergoes an avoided crossing with the upper of the two $N=1$ levels, dominated by the $|1-1-\frac{1}{2}\rangle$ state, at large angles. At even higher magnetic fields (lower panel), the initial level is above both of the other two levels, so its energy is independent of the angle between the fields.

Figure 3 shows the dependence of the three eigenvalues on the electric field at selected values of the angle between the fields. For parallel fields, there is only one avoided crossing between the $|00\frac{1}{2}\rangle$ and $|11-\frac{1}{2}\rangle$ levels, as discussed in Sec. III A 1. Another crossing can be included by rotating the fields, as illustrated in the middle panel of Fig. 3 for $\chi=\pi/4$. As the angle χ increases, the two avoided crossings approach each other and merge at $\chi=\pi/2$ (Sec. III A 2). The results shown in Figs. 2 and 3 suggest that the positions of the crossings can be controlled not only by varying the strength of the magnetic and electric fields but also by changing the relative orientation of the fields. By rotating the fields it is also possible to transform real crossings into avoided crossings which alters the collision dynamics, as illustrated in the following section.

B. CaD–He collisions in crossed fields

The electric field dependence of the cross sections for spin relaxation at ultralow energies is shown in Fig. 4. It has

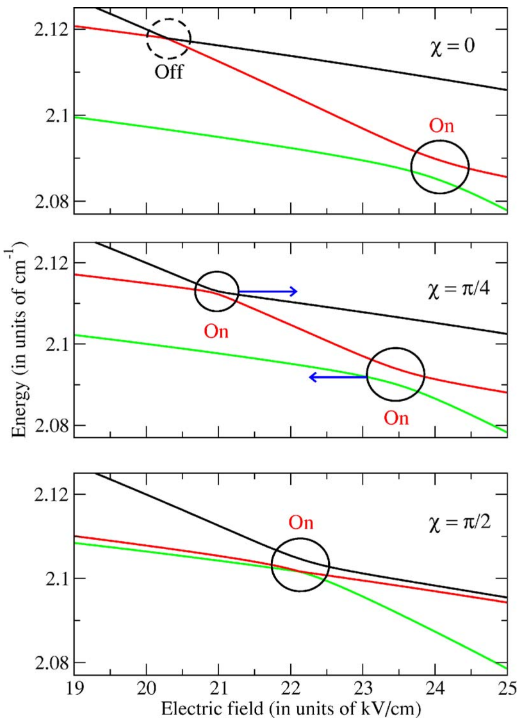

FIG. 3. (Color online) Manipulating avoided crossings by rotating the fields. The graph shows the electric field dependence of molecular adiabatic energy levels at $B=4.7$ T and $E=20$ kV/cm (see also lower panel of Fig. 1). The angle between the fields is 0 (upper panel), $\pi/4$ (middle panel) and $\pi/2$ (lower panel).

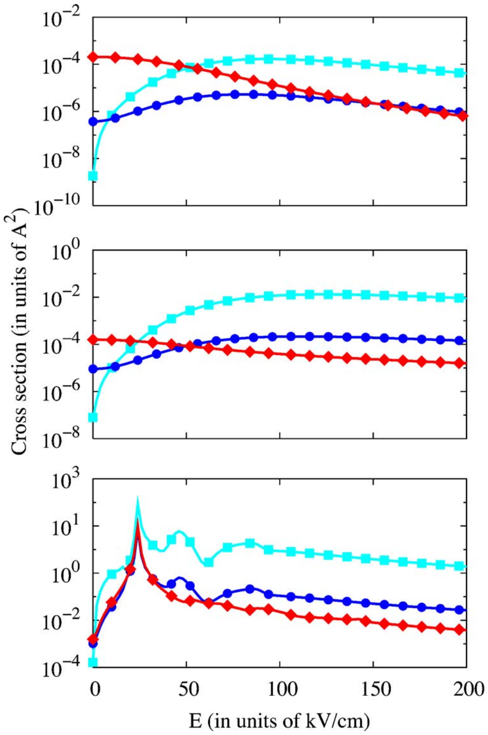

FIG. 4. (Color online) Electric field dependence of the cross sections for spin relaxation in CaD–He collisions at magnetic fields of 0.01 T (upper panel), 0.5 T (center), and 4.7 T (lower panel). The collision energies are 10^{-6} K (squares), 10^{-2} K (circles), and 10^{-0} K (diamonds). The magnetic and electric fields are parallel.

previously been demonstrated[30] that the spin relaxation of $^2\Sigma$ molecules in the rotationally ground state $N=0$ proceeds through coupling to the rotationally exited $N=1$ state, followed by spin flip in the $N=1$ state. The probability of spin relaxation therefore increases with (i) the coupling between the $N=0$ and $N=1$ states and (ii) the strength of the spin-rotation interaction γ determining the spin-changing transitions in rotationally excited states [cf. Eq. (1)]. Electric fields induce couplings between the $N=0$ and $N=1$ levels. At the same time, they *decrease* the effective spin-rotation interaction by splitting the $N=1$ level into a manifold of states with different M_N (see Fig. 1). The net result depends on the balance between these two effects. At low collision energies and small electric fields, the splitting between the different M_N levels varies quadratically with the electric field E (see Sec. III A) and the spin-rotation interaction is significant. The coupling between the $N=0$ and $N=1$ levels, on the other hand, varies linearly with the electric field. As a result, the cross sections for the spin relaxation increase with increasing electric fields at low fields, as shown in Fig. 4 for the lowest two collision energies.

At higher electric fields (~50 kV/cm), the energy gaps between $N=0$ and $N=1$ states and between different $|M_N|$ levels of the $N=1$ state increase linearly with the field strength. The effective spin-rotation interaction in the $N=1$ state and the potential couplings between the $N=0$ and $N=1$ states decrease, which result in the suppression of spin relaxation. Figure 4 shows that this effect is pronounced both at ultracold temperatures and in the multiple partial wave regimes. We conclude that high electric fields suppress spin relaxation. A similar effect was observed by Friedrich *et al.*[5] for the rotationally inelastic scattering of ICl–Ar. The suppression should be more effective in molecules with smaller rotational constants.[43]

Molecular Zeeman levels corresponding to different rotational states cross at high magnetic fields (Fig. 1). The intersecting states do not interact in the absence of an electric field, due to the conservation of parity.[51,52] Electric fields induce couplings between the states of different parities and these crossings become avoided crossings. The orientation and alignment of molecules are very sensitive to external fields near the crossings.[51] The lower panel in Fig. 4 shows the cross sections for spin relaxation at a magnetic field of 4.7 T. The cross sections increase by four to five orders of magnitude near the avoided crossing of the $|00\frac{1}{2}\rangle$ and $|11-\frac{1}{2}\rangle$ levels at $\chi=0$ (see Fig. 3, upper panel). The shape of this electric-field-induced "resonance" does not vary much with the collision energy, although more structure is observed at lower energies.

The location of the avoided crossings depends on both the magnetic and the electric fields (see Sec. III A). Figure 5 is a two-dimensional plot of the cross section for the spin relaxation as a function of electric and magnetic fields. According to Eq. (11), the levels $N=0$ and $N=1$ cross at the magnetic field $B_c=(2B_e-\gamma/2)/\mu_0$. The electric field increases the effective rotational constant B_e and shifts the crossing to the right. The avoided crossing becomes significant at the magnetic field of ~4.6 T and the electric field of ~9 kV/cm, and the position of the avoided crossing evolves toward higher magnetic fields, first quadratically and then linearly, with increasing electric fields (the first-order Stark effect sets in at ~50 kV/cm). The spin relaxation cross section increases exponentially as the fields approach the avoided crossing region and decreases quickly away from this region (see Fig. 6). The peak value of the cross section for spin relaxation can be as high as 100 Å^2, which corresponds to a rate constant of about 10^{-10} cm^3/s, comparable with that for elastic scattering. Under such conditions, electric fields can dramatically change the properties of an ultracold molecular gas, and perhaps lead to phenomena similar to the collapse of quantum degenerate gases after the magnetic field sweep through a Feshbach resonance.[53]

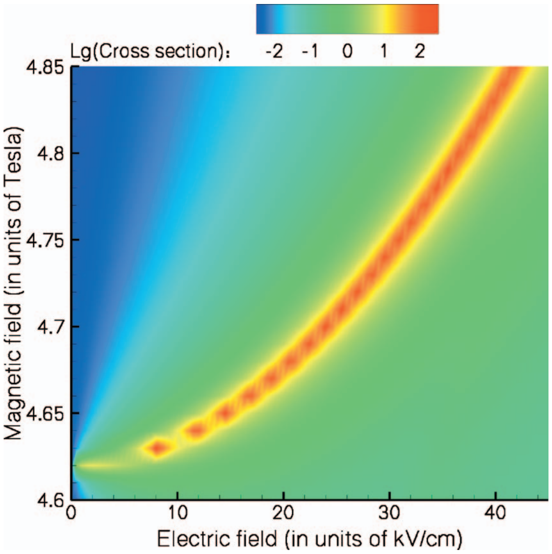

FIG. 5. (Color) Decimal logarithm of the cross sections for spin relaxation as a function of electric and magnetic fields. The fields are parallel. The collision energy is 0.5 K. The cross section increases exponentially near the avoided crossing.

The spin-changing transitions in collisions of $^2\Sigma$ molecules with atoms are nearly forbidden at zero temperature in weak magnetic fields.[32] Electric fields induce couplings between the Zeeman states and strongly enhance the cross section for the spin transitions at ultracold temperatures (Fig. 7). The cross sections for inelastic transitions follow the Wigner law, i.e., the cross sections are inversely proportional to the

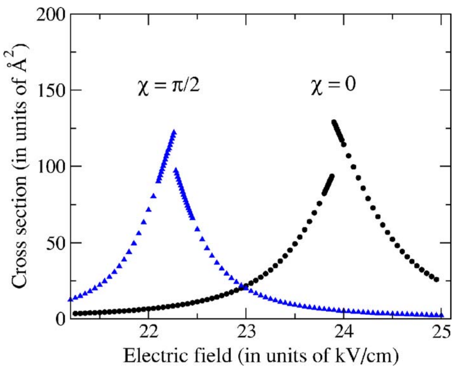

FIG. 6. (Color online) Cross sections for the spin relaxation as functions of the electric field at the angles $\chi=0$ and $\chi=\pi/2$ between the electric and magnetic fields. The magnetic field is 4.7 T. The positions of the maxima correspond to the avoided crossings in Fig. 3.

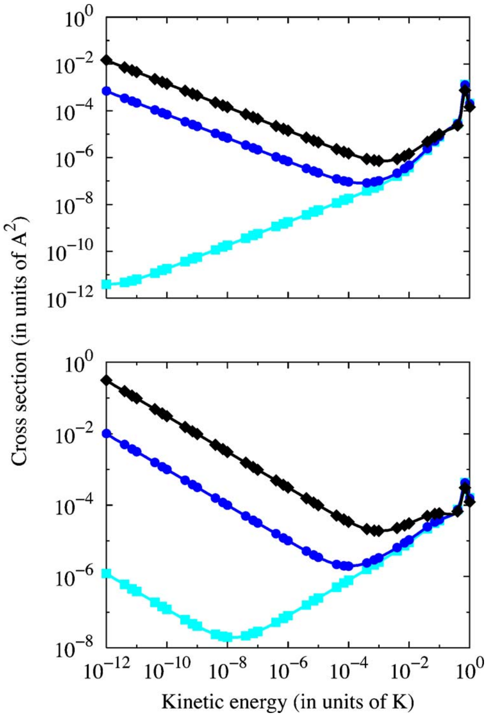

FIG. 7. (Color online) Collision energy dependence of the cross sections for spin relaxation in CaD–He collisions at magnetic fields of 0.01 T (upper panel) and 0.50 T (lower panel) and zero electric field (squares), $E=10$ kV/cm (circles), and $E=30$ kV/cm (diamonds). The magnetic and electric fields are parallel.

collision velocity $\sigma \sim 1/v$. As seen in Fig. 7, the onset of the $1/v$ dependence of the cross sections is shifted to higher collision energies by electric fields. The upper panel of Fig. 7 shows the effect at a low magnetic field of 0.01 T. The upturn of the cross section at zero electric field occurs at 10^{-12} K, which is outside the scale of the graph. The application of an electric field of 10 kV/cm leads to the enhancement of the cross section for spin relaxation at the upturn energy ($\sim 10^{-12}$ K) by eight orders of magnitude. When the magnetic field is much higher (lower panel), the upturn occurs at 10^{-8} K, and the cross sections increase by a factor of 10^4 at an electic field strength of 10 kV/cm.

Figure 8 presents cross sections for spin relaxation in a magnetic field of 0.5 T at collision energies up to 80 K. The energy dependence of the cross sections is dominated by scattering resonances. The positions of these resonances are sensitive to the magnitude of an external electric field, and Fig. 8 thus demonstrates that inelastic collisions of molecules can be significantly modified by electric fields even at high collision energies. For a quantitative prediction, we present in Fig. 9 and Table I rate constants for collisional spin relaxation in a magnetic field of 0.5 T as functions of temperature up to 60 K at three values of the electric field.

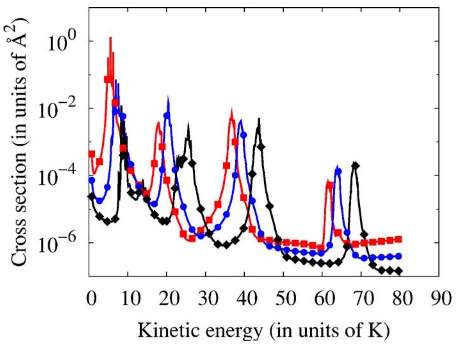

FIG. 8. (Color online) Collision energy dependence of the cross sections for spin relaxation in CaD–He collisions at a magnetic field of 0.50 T and zero electric field (squares), $E=100$ kV/cm (circles), and $E=200$ kV/cm (diamonds). The magnetic and electric fields are parallel.

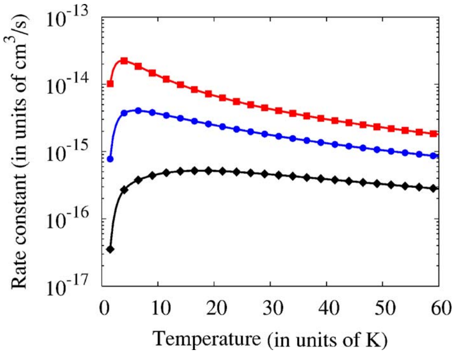

FIG. 9. (Color online) Rate constants for spin relaxation in CaD–He collisions at a magnetic field $B=0.50$ T and zero electric field (squares), $E=100$ kV/cm (circles), and $E=200$ kV/cm (diamonds). The rate constants are converged to within 30%.

Figure 10 shows the dependence of cross sections for spin relaxation on the magnetic field and the angle χ between the fields. The electric field $E=20$ kV/cm is chosen for the avoided crossing to occur at $B=4.7$ T. We see that the cross sections vary significantly with the angle χ near the avoided crossing. The detailed form of the χ dependence of the spin relaxation probabilities can be inferred from the analysis of the Stark levels plotted in Fig. 2. At the values of the magnetic fields far to the left from the crossing point (upper panel), the initial Stark state $|00\frac{1}{2}\rangle$ is not mixed with any of the $N=1$ states, and the cross sections do not depend on χ. As the magnetic field increases, the initial state crosses and interacts with one of the excited $N=1$ states [see Eq. (14)]. The strongest mixing at $B=4.69$ T occurs at $\chi \sim 70°$, where the cross sections for the spin relaxation are maximal. The crossing due to the rotation of the fields moves to smaller χ angles with increasing magnetic fields. For example, as follows from the lower panel of Fig. 2, the cross sections should *decrease* with increasing χ because the interaction between the $N=0$ and $N=1$ levels is most significant at $\chi=0°$. Figure 10 confirms this.

C. Electric field control of chemical reactions via nonadiabatic transitions

In this section we consider the spin relaxation of $^2\Sigma$ molecules in collisions with ^2S atoms. Such collisions are of particular interest for experiments on ultracold chemistry since both the atoms and the molecules can be confined in a magnetic trap and chemical reactions can be directly observed by monitoring the trap loss.[25,26] The sympathetic cooling of open-shell molecules by elastic collisions with ultracold alkali metal atoms is effective only if collisional

TABLE I. Rate constants (in units of cm^3/s) for spin-changing and spin-conserving transitions from the $|N=0, M_N=0, M_S=\frac{1}{2}\rangle$ magnetic low-field-seeking state of $\mathrm{CaD}(^2\Sigma)$ in collisions with He atoms at different electric fields and temperatures T. The magnetic field is 0.5 T. The rate constants are converged to within 30%. The magnetic and electric fields are parallel.

Electric field (kV/cm)	Final state	$T=1.5$ K	$T=10$ K	$T=30$ K
0	$\lvert 00-\frac{1}{2}\rangle$	1.02×10^{-14}	1.35×10^{-14}	4.28×10^{-15}
	$\lvert 00\frac{1}{2}\rangle$	8.73×10^{-10}	7.32×10^{-10}	3.92×10^{-10}
	$\lvert 1-1-\frac{1}{2}\rangle$		8.31×10^{-16}	4.83×10^{-16}
	$\lvert 1-1\frac{1}{2}\rangle$		4.78×10^{-11}	3.94×10^{-11}
100	$\lvert 00-\frac{1}{2}\rangle$	7.75×10^{-16}	3.66×10^{-15}	1.76×10^{-15}
	$\lvert 00\frac{1}{2}\rangle$	7.98×10^{-10}	7.51×10^{-10}	4.20×10^{-10}
	$\lvert 1-1-\frac{1}{2}\rangle$		1.95×10^{-15}	1.30×10^{-15}
	$\lvert 1-1\frac{1}{2}\rangle$		3.60×10^{-11}	3.28×10^{-11}
200	$\lvert 00-\frac{1}{2}\rangle$	3.53×10^{-17}	4.60×10^{-16}	4.58×10^{-16}
	$\lvert 00\frac{1}{2}\rangle$	7.55×10^{-10}	7.56×10^{-10}	4.37×10^{-10}
	$\lvert 1-1-\frac{1}{2}\rangle$		2.34×10^{-16}	3.09×10^{-16}
	$\lvert 1-1\frac{1}{2}\rangle$			2.82×10^{-11}

spin relaxation and chemical reactions are slow enough to allow for a significant number of elastic collisions to occur before the molecules leave the trap or react.

The Hamiltonian of the $\mathrm{A}(^2S)+\mathrm{BC}(^2\Sigma)$ system is obtained from Eqs. (1) and (3) by adding the term $2\mu_{\mathrm{B}}\boldsymbol{B}\cdot\boldsymbol{S}_{\mathrm{A}}$ where $\boldsymbol{S}_{\mathrm{A}}$ denotes the electron spin of atom A. The basis set for the expansion of the wave function (4) is augmented by spin functions describing atom A,

$$|S_{\mathrm{A}}M_{S_{\mathrm{A}}}\rangle|S_{\mathrm{BC}}M_{S_{\mathrm{BC}}}\rangle|N_{\mathrm{BC}}M_{N_{\mathrm{BC}}}\rangle|\ell M_\ell\rangle, \tag{15}$$

where the quantum numbers labeled by the index "BC" refer to the diatomic molecule. The eigenfunctions of the total spin $|SM_S\rangle$ of the triatomic system are obtained by the vector coupling of $|S_{\mathrm{A}}M_{S_{\mathrm{A}}}\rangle$ and $|S_{\mathrm{BC}}M_{S_{\mathrm{BC}}}\rangle$,

$$|(S_{\mathrm{A}}S_{\mathrm{BC}})SM_S\rangle = \sum_{M_{S_{\mathrm{A}}}}\sum_{M_{S_{\mathrm{BC}}}}(-1)^{S_{\mathrm{A}}-S_B+M_S}(2S+1)^{1/2} \times\begin{pmatrix} S_{\mathrm{A}} & S_{\mathrm{BC}} & S \\ M_{S_{\mathrm{A}}} & M_{S_{\mathrm{BC}}} & M_S \end{pmatrix}|S_{\mathrm{A}}M_{S_{\mathrm{A}}}\rangle|S_{\mathrm{BC}}M_{S_{\mathrm{BC}}}\rangle. \tag{16}$$

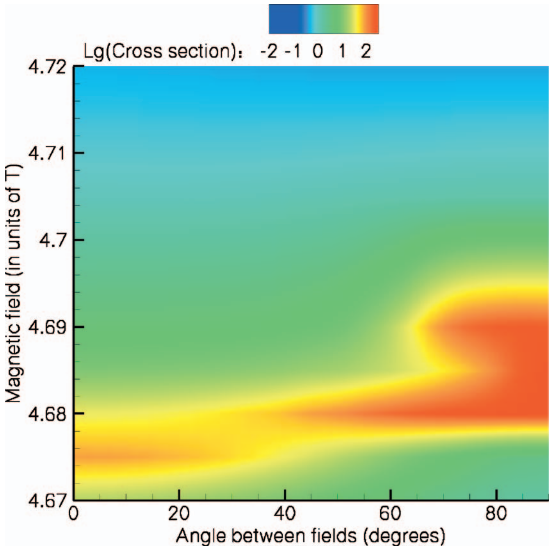

FIG. 10. (Color) Cross sections for spin relaxation in CaD–He collisions as functions of the magnetic field strength and the angle between the magnetic and electric fields. The electric field is 20 kV/cm, and the collision energy is 0.5 K.

The total spin of the $\mathrm{A}(^2S)+\mathrm{BC}(^2\Sigma)$ system can be 0 or 1 and there are two potential energy surfaces $V^S(R,r,\theta)$ corresponding to the different values of the total spin. The matrix elements of the atom-molecule interaction $\langle SM_S|V^S(R,r,\theta)|S'M'_S\rangle$ are diagonal in S and M_S quantum numbers. The interaction with magnetic and electric fields is also diagonal in S and M_S due to the conservation of the total angular momentum projection in parallel fields. The only interaction that couples different spin angular momenta is the spin-rotation interaction. To show this, we derive the explicit expression for the matrix elements of the spin-rotation interaction,

$$\begin{aligned}\gamma\boldsymbol{N}_{\mathrm{BC}}\cdot\boldsymbol{S}_{\mathrm{BC}} &= -\gamma\sqrt{3}[Y^{(1)}(\hat{r})\otimes S^{(1)}_{\mathrm{BC}}]^{(0)}_0 \\ &= \gamma\sum_{q=-1}^{1}(-1)^q Y^{(1)}_{-q}(\hat{r})S^{(1)}_{\mathrm{BC},q},\end{aligned} \tag{17}$$

in the $|SM_S\rangle$ basis. The matrix elements of the operator $S^{(1)}_{\mathrm{BC}}$ can be obtained using the Wigner-Eckart theorem:

$$\begin{aligned}&\langle(S_{\mathrm{A}}S_{\mathrm{BC}})SM_S|S^{(1)}_{\mathrm{BC},q}|(S'_{\mathrm{A}}S'_{\mathrm{BC}})S'M'_S\rangle \\ &\quad=(-1)^{S-M_S}\begin{pmatrix} S & 1 & S' \\ -M_S & q & M'_S \end{pmatrix} \\ &\qquad\times\langle(S_{\mathrm{A}}S_{\mathrm{BC}})S\|S^{(1)}_{\mathrm{BC}}\|(S'_{\mathrm{A}}S'_{\mathrm{BC}})S'\rangle.\end{aligned} \tag{18}$$

The reduced matrix element can be expressed as[46]

$$\begin{aligned}&\langle(S_{\mathrm{A}}S_{\mathrm{BC}})S\|S^{(1)}_{\mathrm{BC}}\|(S'_{\mathrm{A}}S'_{\mathrm{BC}})S'\rangle \\ &\quad=\delta_{S_{\mathrm{A}}S'_{\mathrm{A}}}(-1)^{S_{\mathrm{BC}}+S_{\mathrm{A}}+S'+1}[(2S+1)(2S'+1)]^{1/2} \\ &\qquad\times\begin{Bmatrix} S_{\mathrm{BC}} & S & S_{\mathrm{A}} \\ S' & S'_{\mathrm{BC}} & 1 \end{Bmatrix}\langle S_{\mathrm{BC}}\|S^{(1)}_{\mathrm{BC}}\|S_{\mathrm{BC}}\rangle.\end{aligned} \tag{19}$$

The substituton of this expression into Eq. (17) yields the matrix elements of the spin-rotation interaction in spin-coupled basis (16),

$$
\begin{aligned}
&\langle (S_{\mathrm{A}}S_{\mathrm{BC}})SM_S|\gamma \boldsymbol{N}_{\mathrm{BC}}\cdot \boldsymbol{S}_{\mathrm{BC}}|(S'_{\mathrm{A}}S'_{\mathrm{BC}})S'M'_S\rangle \\
&\quad = -\delta_{S_{\mathrm{A}}S'_{\mathrm{A}}}(-1)^{S-M_S+S_{\mathrm{BC}}+S_A+S'+1}[(2S+1)(2S'+1)]^{1/2} \\
&\quad \times \begin{Bmatrix} S_{\mathrm{BC}} & S & S_{\mathrm{A}} \\ S' & S'_{\mathrm{BC}} & 1 \end{Bmatrix} \langle S_{\mathrm{BC}}\|S^{(1)}_{\mathrm{BC}}\|S_{\mathrm{BC}}\rangle \gamma \sum_{q=-1}^{1}(-1)^q Y^{(1)}_{-q}(\hat{r}) \\
&\quad \times \begin{pmatrix} S & 1 & S' \\ -M_S & q & M'_S \end{pmatrix}. \qquad (20)
\end{aligned}
$$

The reduced matrix element in Eq. (20) is equal to $[(2S_{\mathrm{BC}}+1)S_{\mathrm{BC}}(S_{\mathrm{BC}}+1)]^{1/2}=\sqrt{3/2}$ for $S_{\mathrm{BC}}=1/2$. Equation (20) shows that different total spin states are directly coupled by the spin-rotation interaction.

Interaction potentials of the $\mathrm{A}(^2S)-\mathrm{BC}(^2\Sigma)$ system in the maximally stretched spin state are usually characterized by significant exchange interactions, leading to strong repulsive forces at short atom-molecule separations.[54] If the atom and the molecule are both confined in a magnetic trap, they are initially in the state with the total spin $S=1$. Chemical reactions of $\mathrm{A}(^2S)$ atoms with $\mathrm{BC}(^2\Sigma)$ molecules on the triplet-spin potentials will therefore occur through an activation barrier, so they will be determined by tunneling at low temperatures. The tunneling rates are suppressed at low temperatures and the reactions of magnetically trapped $\mathrm{A}(^2S)$ atoms with $\mathrm{BC}(^2\Sigma)$ molecules in the triplet-spin state should be slow. The interactions in the singlet spin state are usually strongly attractive, leading to short-range minima and insertion reactions.[54] Chemical reactions determined by such interactions are often barrierless and occur very rapidly at low temperatures.[25,26,55,56] In the absence of electric fields, the spin-rotation interaction is ineffective and may not induce significant spin conversion. We have shown in this paper that external electric fields may enhance the spin interactions by inducing avoided crossings between different spin states. Electric fields can thus be used for inducing the triplet↔singlet transition in $\mathrm{A}(^2S)-\mathrm{BC}(^2\Sigma)$ reactive complexes, which should lead to the significant enhancement of chemical reaction rates at low temperatures.

IV. SUMMARY

We have presented a detailed study of low-temperature collisions between $\mathrm{CaD}(^2\Sigma)$ molecules and He atoms in superimposed electric and magnetic fields with arbitrary orientations. Our study shows that the dynamics of molecular collisions may be sensitive not only to the strength but also to the relative orientation of the fields. Electric fields do not interact with the electron spin of the molecules directly but modify their rotational states and, consequently, the spin-rotation interactions. The structure of the molecules subjected to superimposed electric and magnetic fields, therefore, changes with the angle between the fields (see Fig. 2). Rotating fields may induce and shift avoided crossings between the Zeeman levels of the rotationally ground and rotationally excited states of the molecules (see Fig. 3). Different spin states are strongly mixed and the dynamics of magnetic spin relaxation is extremely sensitive to external fields near the avoided crossings. Inelastic Zeeman transitions in collisions of molecules may therefore be effectively controlled by varying the strength and the relative orientation of the applied fields near the avoided crossings (see Figs. 5, 6, and 10). We used He as the collision target for the simplicity of the numerical calculations. The effects observed in this study are due to interactions of the isolated molecules with external fields. Changing the collision partner will change the interaction potential and intensities of the inelastic transitions but not the qualitative dependence on external fields. These conclusions should therefore apply to collisions of molecules with other atoms or collisions of molecules with each other. The rotational constant of the CaD molecule is 2.2 cm^{-1}. The crossings between the rotationally ground and rotationally excited molecular levels will occur at lower magnetic and electric fields in molecules with larger rotational constants.

We have reported calculations of rate constants for rotationally inelastic collisions of CaD molecules at temperatures up to 60 K. Most previous studies of molecular collisions in external fields focused on ultracold *s*-wave scattering. Our results show that molecular collisions can be sensitive to electric fields even at high temperatures (∼10 K), where the collision dynamics are determined by multiple partial waves. We demonstrated that external fields modify the resonance structure of the cross sections at collision energies up to 60 K (see Fig. 8) and showed that electric fields may induce forbidden transitions in atom-molecule scattering at ultracold temperatures (see Fig. 7). The wide range of temperatures we considered in this work is experimentally accessible and our results can be tested in a variety of experiments with cold molecules. One limitation of our control scheme is that it cannot be applied to molecules without permanent dipole moments. However, such molecules may interact with alternating electric fields. Friedrich and Hershbach[6] proposed to use the interaction between the molecular polarizability and an oscillating laser field to induce ac Stark shifts[57] in nonpolar molecules. We are currently studying collisions of homonuclear molecules in the presence of nonresonant laser fields.

Our study demonstrates that the orientation of the molecular electron spin may be effectively manipulated by electric fields. As the interactions between two $^2\Sigma$ molecules or between $^2\Sigma$ molecules and atoms with nonzero electron spin depend significantly on the total spin of the system, we proposed that chemical reactions of open-shell molecules might be controlled at low temperatures by electric fields. If the reacting species are confined in a magnetic trap, their electron spins are coaligned and their interaction is determined by the interaction potential of the maximum spin state. The maximum spin state is coupled to a lower spin state by the spin-rotation interaction, which is responsible for the reorientation of the electron spin of the molecules. Electric fields may suppress or enhance the spin-rotation interaction, which should affect the nonadiabatic spin transitions in prereactive complexes involving $^2\Sigma$ polar molecules. We hope that our analysis will stimulate rigorous theoretical and experimental studies of chemical reactions of $^2\Sigma$ polar molecules in electric fields.

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