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## Spin-flipping transitions in ${}^2\Sigma$ molecules induced by collisions with structureless atoms

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It is shown that spin-flipping transitions in low energy collisions of  ${}^2\Sigma$  diatomic molecules in the lowest rotational  $N=0$  level with structureless atoms proceed through coupling to the rotationally excited  $N>0$  levels, and are determined by the spin-rotation interaction in the rotationally excited molecule. We carry out calculations for collisions of CaH and  ${}^3\text{He}$ . For the spin-flip rate coefficient corresponding to an interaction potential that does not generate a shape resonance, we obtain  $1.20 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$  at a temperature of 0.4 K consistent with the measured value of  $10^{-17 \pm 1} \text{ cm}^3 \text{ s}^{-1}$ . We make predictions as to which molecules should have the least probability of spin-flipping in collisions with atoms.

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The recent success of experiments with atomic Bose-Einstein condensate (BEC) has stimulated research aiming at the creation of a molecular BEC. Several techniques have been proposed for the generation of cold and ultracold molecules [1–7], among which the buffer-gas loading method is applicable to a wide variety of paramagnetic molecules. Buffer-gas loading is a cryogenic technique based on energy equilibration of molecules in elastic collisions with cold buffer-gas atoms and subsequent trapping of the cooled molecules in a magnetic field. This method was recently used for trapping CaH ( ${}^2\Sigma$ ) molecules in a buffer gas of  ${}^3\text{He}$  at temperatures around 0.4 K [7]. The CaH molecules were trapped in the ground weak-field-seeking state with rotational angular momentum  $N=0$  and the space-fixed projection  $m = +1/2$  of the electronic spin angular momentum  $s$ . The strong-field-seeking state ( $m = -1/2$ ) of  ${}^2\Sigma$  molecules is not trappable in a magnetic field, and the  $m = +1/2 \rightarrow m = -1/2$  transition leads to trap loss. If the extremely small interaction between the nuclear spin of helium and the electronic spin of CaH is neglected, there is no direct mechanism by which the interaction with the buffer-gas atoms may induce the spin-flipping transition. The experimental data, however, show that the spin-flipping transitions do occur in cold He-CaH ( $N=0$ ) collisions at a rate much larger than those mediated by nuclear-spin–electronic-spin interaction in atom-atom collisions [7]. We consider here the collisions of structureless atoms with  ${}^2\Sigma$  diatomic molecules in the absence of magnetic fields.

In this work, we identify a mechanism involving an interaction of spin with rotation, and investigate its efficiency for the spin-flipping  $m = +1/2 \rightarrow m = -1/2$  transition in collisions of rotationally ground-state  ${}^2\Sigma$  molecules with structureless atoms at cold and ultracold temperatures. We present calculations for a test CaH ( ${}^2\Sigma$ )- ${}^3\text{He}$  system.

The probabilities of spin-flipping transitions in CaH-He collisions may be computed by the numerical integration of

the following system of close-coupled equations:

$$\left[ \frac{d^2}{dR^2} + k_{j(Ns)}^2 - \frac{l(l+1)}{R^2} \right] F_{j(Ns)l}^J(R) = 2\mu \sum_{j'(N's')l'} \langle Jj(Ns)l | \hat{V} + \hat{V}_{\text{SR}} | Jj'(N's')l' \rangle F_{j'(N's')l'}^J(R), \quad (1)$$

where  $R$  is the center-of-mass separation between He and CaH;  $k_{j(Ns)}^2 = 2\mu(E - \epsilon_N)$ , where  $\mu$  is the reduced mass of the colliding particles,  $E$  is the total energy for the collision, and  $\epsilon_N$  is the energy of the diatomic molecule in the rotational state  $N$ ;  $\hat{j} = \hat{N} + \hat{s}$ ;  $l$  is the orbital angular momentum for the collision, and  $J$  is the total angular momentum of the system. The spin-rotation interaction is represented by

$$\hat{V}_{\text{SR}} = \gamma \hat{s} \cdot \hat{N}, \quad (2)$$

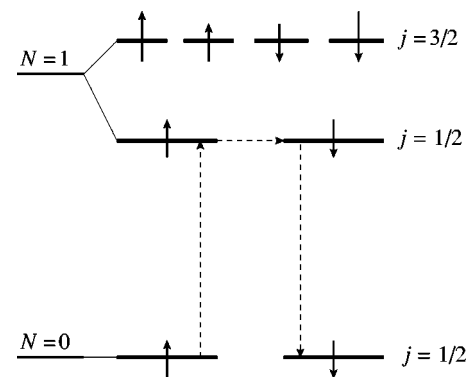


FIG. 1. Energy levels of a  ${}^2\Sigma$  diatomic molecule with positive  $\gamma$ . The dashed line shows a possible mechanism of the spin-flipping transition. The arrows indicate the projection of  $\hat{j}$ .

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where  $\gamma$  is the spin-rotation interaction constant equal to  $0.0415 \text{ cm}^{-1}$  for CaH ( $^2\Sigma$ ) [8,9]. A schematic diagram of several lowest-energy levels of a  $^2\Sigma$  molecule with a positive  $\gamma$  constant is shown in Fig. 1. The potential for the He-CaH interaction computed using a high-level

*ab initio* method [10] is expanded in a Legendre series. We use the space-fixed representation of Arthurs and Dalgarno [11] for the scattering wave function, in which the elements of the interaction potential coupling matrix are given by

$$\begin{aligned} \langle j(Ns)l|\hat{V}|j'(N's')l'\rangle = & \sum_{\lambda} V_{\lambda}(-1)^{2j'+J+s+\lambda} [(2l+1)(2l'+1)(2j+1)(2j'+1)(2N+1)(2N'+1)]^{1/2} \\ & \times \begin{Bmatrix} N & j & s \\ j' & N' & \lambda \end{Bmatrix} \begin{Bmatrix} j & l & J \\ l' & j' & \lambda \end{Bmatrix} \begin{pmatrix} l & \lambda & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} N & \lambda & N' \\ 0 & 0 & 0 \end{pmatrix}, \end{aligned} \quad (3)$$

where  $\lambda$  labels the Legendre expansion terms of the potential and the symbols in the curly brackets and parentheses are  $6j$  and  $3j$  symbols. The vibrational motion of the diatomic molecule is neglected, and the bond length of the diatomic molecule is fixed at the equilibrium distance of CaH. The numerical integration of Eqs. (1) for a set of total angular-momentum values  $J$  yields the scattering  $T$  matrix, and the cross sections for projection-flipping cross sections can be evaluated from the  $T$  matrix as follows [11,12]:

$$\begin{aligned} \sigma_{jm \rightarrow j'm'} = & \frac{\pi}{k_j^2} \sum_{J_1} \sum_{J_2} \sum_l \sum_{m_l} \sum_{l'} \sum_{m_{l'}} T_{jl \rightarrow j'l'}^{J_1*} T_{j'l \rightarrow j'l'}^{J_2} (2J_1+1)(2J_2+1)(-1)^{2j+2j'} \sum_{M_1} \sum_{M_2} (-1)^{2M_1+2M_2} \\ & \times \begin{pmatrix} j & l & J_1 \\ m & m_l & -M_1 \end{pmatrix} \begin{pmatrix} j & l & J_2 \\ m & m_l & -M_2 \end{pmatrix} \begin{pmatrix} j' & l' & J_1 \\ m' & m_{l'} & -M_1 \end{pmatrix} \begin{pmatrix} j' & l' & J_2 \\ m' & m_{l'} & -M_2 \end{pmatrix}, \end{aligned} \quad (4)$$

where  $m$ ,  $m_l$ , and  $M$  denote the space-fixed projections of  $j$ ,  $l$ , and  $J$ , respectively. When the  $^2\Sigma$  molecule is in the ground rotational state,  $j=s$ .

Figure 2 shows the cross sections for the spin-flipping  $m = +1/2 \rightarrow m = -1/2$  transition and for elastic scattering which conserves the value of  $m$  in collisions of CaH ( $N=0$ ) with  $^3\text{He}$  at cold and ultracold collision energies. The cross section for the spin-flipping transition is much smaller than the elastic cross section, and it decreases as  $E_{\text{col}}^2$  with decreasing collision energy  $E_{\text{col}}$  in the ultracold limit. Both cross sections show a substantial peak arising from an  $l=2$  shape resonance at a collision energy of  $0.023 \text{ cm}^{-1}$ . The magnitudes of the resonance peak are very different for the two cross sections. The elastic cross section varies by one order of magnitude through the resonance, while the probability of the spin-flipping transition increases by seven to eight orders of magnitude. When the system is in a long-lived resonance, the population of  $m$  states apparently tends to a statistical distribution and the spin-flipping cross section is comparable to the elastic cross section. Thus, even narrow shape and Feshbach resonances may enhance substantially the rates for the spin-flipping transitions.

We have shown [10] that a slight modification of the He-CaH interaction potential removed the  $l=2$  shape resonance in the elastic cross sections. The dot-dashed line of Fig. 2 is

the spin-flip cross section computed with this potential (the  $f=0.15$  potential of Ref. [10]). In the absence of the shape resonance, the peak of the cross section for spin flip is reduced by seven orders of magnitude and the rate coefficient at 0.4 K is reduced by three orders of magnitude from  $1.65 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$  to  $1.20 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ , which is consistent with the measured value of  $10^{-17 \pm 1} \text{ cm}^3 \text{ s}^{-1}$ .

It follows from the previous analyses [13,14] of the rotational and fine-structure energy transfer in collisions of  $^2\Sigma$  molecules with atoms that the spin-flipping transitions are determined by the spin-rotation interaction in the diatomic molecule. When the molecule is in the ground rotational  $N=0$  state, however, the spin-rotation interaction vanishes. In order to understand how the spin-rotation coupling in CaH drives the spin-flipping transition in  $N=0$  molecules, we performed a set of calculations with varying spin-rotation constant  $\gamma$ . Figure 2 shows that an increase of  $\gamma$  by a factor of 3 enhances the probability of the  $m = +1/2 \rightarrow m = -1/2$  transition by almost one order of magnitude, independent of the collision energy, and Fig. 3 demonstrates that the spin-flipping cross section at a given energy increases as  $\gamma^2$ . In the Born or distorted-wave approximation, the cross section is given by the square of the coupling matrix element, and the quadratic dependence of the spin-flipping cross section on  $\gamma$  establishes that the spin-flipping transition in the  $N$

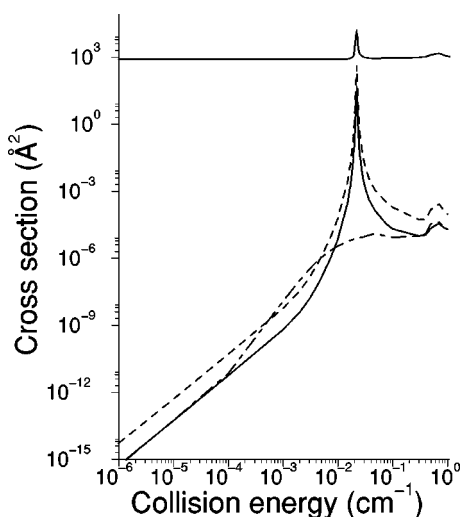


FIG. 2. Cross sections for the spin-flipping transition (lower full curve) and elastic scattering (upper full curve) in collisions of CaH ( $N=0$ ) with  $^3\text{He}$ . The broken curve is the cross section for the spin-flipping transition computed with the value of the spin-rotation constant  $3\gamma$ . The dot-dashed curve—calculations with the potential that does not support the  $l=2$  resonance.

$=0$  level of CaH is controlled by the spin-rotation interaction. This suggests that the  $m = +1/2 \rightarrow m = -1/2$  transition in the  $N=0$  state occurs through an intermediate step involving transitions to the asymptotically closed  $N>0$  channels in which the spin-rotation interaction couples states with different projections of  $j$ .

In order to verify that the coupling to the  $N>0$  channels is important for the spin-flipping transition in  $N=0$ , we changed the rotational constant of the diatomic molecule so

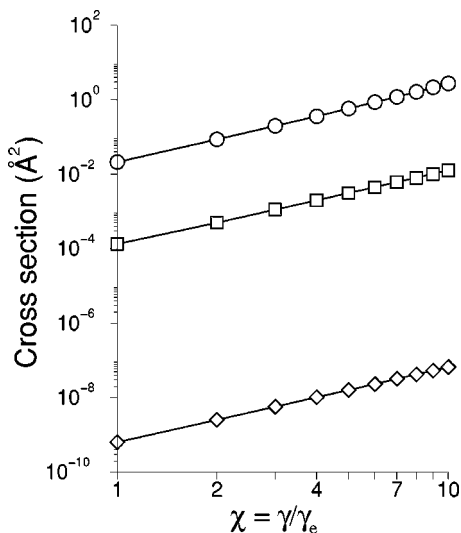


FIG. 3. Cross sections for the spin-flipping transition in CaH ( $N=0$ )- $^3\text{He}$  collisions as functions of the spin-rotation constant  $\gamma$  at different collision energies:  $0.019\text{ cm}^{-1}$  (circles);  $0.477\text{ cm}^{-1}$  (squares);  $10^{-3}\text{ cm}^{-1}$  (diamonds). The value of the spin-rotation constant in the CaH molecule is denoted by  $\gamma_c$ . The slopes of the curves are 2.12 (circles), 1.98, (squares) and 2.02 (diamonds).

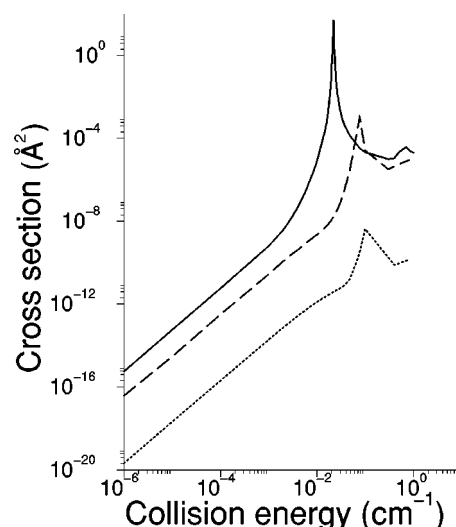


FIG. 4. Cross sections for the spin-flipping transition in CaH ( $N=0$ )-He collisions computed with the rotational constants of CaH corresponding to the different energy separation between the  $N=0$  and  $N=1$  levels:  $\Delta\epsilon = 8.4\text{ cm}^{-1}$  (full curve);  $\Delta\epsilon = 16.8\text{ cm}^{-1}$  (broken curve);  $\Delta\epsilon = 82.0\text{ cm}^{-1}$  (dotted curve).

as to increase the energy separation between the rotational levels. Figure 4 shows that increasing the energy gap between  $N=0$  and  $N=1$  by a factor of 2 suppresses the spin-flipping transition in  $N=0$  by more than one order of magnitude. A further increase of the energy separation between the  $N=0$  and  $N=1$  levels leads to even smaller probabilities of the spin-flipping transition.

In summary, we have provided evidence that the spin-flipping transitions in the rotational  $N=0$  level of CaH ( $^2\Sigma$ ) molecules are induced by collisions with He through the coupling to the rotationally excited levels and the action of the spin-rotation interaction in the  $N>0$  states. A possible mechanism of the transition is indicated by the dashed line in Fig. 1. This mechanism should be common to all  $^2\Sigma$  diatomic molecules. We conclude that the collision-induced spin-flip transitions will be least efficient for the diatomic molecules with large rotational constants and small spin-rotation constants  $\gamma$ , interacting with a collision partner through a weakly anisotropic potential. They may be enhanced if the atom-molecule interaction is strongly attractive with a deep potential well.

Because the efficiency of the spin-flipping transitions affects directly the possibility of the buffer-gas loading of ultracold molecules, these predictions should assist in the choice of molecules for experiments at cold and ultracold temperatures. The mechanism of the spin-flipping transitions in  $\Sigma$  molecules with higher multiplicity may also be different from that in the  $^2\Sigma$  molecules due to the strong spin-spin interaction.

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