CaF+CaF interactions in the ground and excited electronic states: implications for collisional losses

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The rich internal structure of ultracold paramagnetic polar molecules, arising from their rotational and vibrational degrees of freedom, makes them promising candidates for applications in quantum simulation [1], precision measurement [2], and ultracold chemistry [3].

Recently, ultracold two-body collisional losses between two ground-state CaF molecules have been studied in optical tweezer traps [4]. The interaction between two ground-state CaF molecules can form a singlet channel (1) $^1A'$, and a triplet channel (1) $^3A'$. Notably, we observe that the spin-singlet surface is reactive, undergoing an exothermic chemical reaction [5] that contributes to collisional losses. In contrast, the triplet surface of the CaF + CaF system is nonreactive but may still experience losses either due to spin-orbit transitions to the reactive singlet surface or due to the photoexcitation process by absorbing photons from the 1064 nm light of the optical dipole trap (ODT). The primary objective of this study is to investigate the interaction between two CaF molecules in their excited states and analyze the mechanisms responsible for collisional losses in the nonreactive triplet surface.

Using quantum chemical methods, we compute and analyze one-dimensional (1D) cuts of potential energy surfaces (PESs), and two-dimensional (2D) PESs under the rigid rotor approximation. We calculate 1D-PES for the twelve lowest electronic states corresponding to the three lowest dissociation channels of CaF + CaF, considering excitation energies up to approximately 20,000 cm^{-1} for Ca_2F_2. Additionally, we evaluate first-order and second-order spin-orbit couplings (SOC) between the lowest two pairs of states, $^1A'$ and $^3A'$. Notably, we find no real curve crossings between the $^1A'$ and $^3A'$ states, and the SOC between these states is weak, suggesting that spin-orbit transitions from the initial triplet to singlet surfaces may be inefficient. Alternatively, we identify that the incident colliding triplet channel, under the influence of 1064 nm light, undergoes curve crossings with excited states from higher dissociation channels, which may potentially contribute to the observed collisional losses of the triplet surface.

References

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