

Why is understanding vibronic interactions important to the production and utilization of laser-cooled molecules?

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The fast advance of laser-cooling of molecules [1] and their broad applications in physical sciences [2] require more detailed investigation and quantitative understanding of the spin-rovibronic (spin-rotational-vibrational-electronic) energy level structure and transition intensities, both by laser-spectroscopy measurements and by first-principles calculations. Recently, our group and collaborators accomplished the first quantitative spin-vibronic analysis of the lowest electronic states of nonlinear alkaline earth monoalkoxide (MOR) free radicals, including calcium methoxide (CaOCH_3), [3] calcium ethoxide (CaOC_2H_5), [4] and calcium isopropoxide ($\text{CaOCH}(\text{CH}_3)_2$), [5] which have been proposed as candidates for laser-cooling. Experimentally, laser-induced fluorescence/dispersed fluorescence (LIF/DF) and cavity ring-down (CRD) spectra of the $\tilde{A}-\tilde{X}$ electronic transition of these three free radicals were recorded under jet-cooled conditions. An essentially constant $\tilde{A}_2-\tilde{A}_1$ energy separation for different vibronic levels is observed in the LIF spectra of all three radicals, which is attributed to the spin-orbit (SO) interaction and, in the case of CaOC_2H_5 and $\text{CaOCH}(\text{CH}_3)_2$, the non-relativistic effects as well. Electronic transition energies, vibrational frequencies, and spin-vibrational eigenfunctions calculated using the complete active space self-consistent field (CASSCF) and the coupled-cluster (CC) methods have been used to predict the vibronic energy level structure and simulate the recorded LIF/DF spectra. Although the vibrational frequencies and Franck-Condon (FC) factors calculated under the Born-Oppenheimer approximation and the harmonic oscillator approximation reproduce the dominant spectral features well, the inclusion of the Jahn-Teller (JT), the pseudo-Jahn-Teller (pJT), and the SO interactions, especially those between the \tilde{A}_1/\tilde{A}_2 and the \tilde{B} states, induces a number of off-diagonal FC matrix elements leading to additional vibronic transitions, which significantly improve the accuracy of the spectral simulations. A spin-vibronic Hamiltonian has been developed in a quasi-diabatic basis for the spectral simulation. (See talk by Ketan Sharma.) CRD and DF spectra were used for the accurate determination of the FC constants and vibrational branching ratios (VBRs), which have been used to predict the efficiency of laser cooling. A second spectroscopic model for the rotational and fine structure of open-shell molecules in quasi-degenerate electronic states has been developed to predict the rotational branching ratios (RBRs), [6] which is closely related to Hönl-London factors and also crucial to laser cooling of molecules. Finally, I will present the ongoing efforts in our lab toward accurate measurement of VBRs and RBRs.

[1] Science, 369, 1366 (2020).

[2] Phys. Rev.X 10, 031022 (2020).

[3] J. Chem. Phys. 151, 134303 (2019).

[4] J. Chem. Phys. 155, 024301 (2021).

[5] Phys. Chem. Chem. Phys. 24, 8749 (2022).

[6] J. Chem. Phys. 148, 124112 (2018).