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Supporting Information

A Combined Experimental and Computational Study on the $\widetilde{A_1}\,^2A'/\widetilde{A_2}\,^2A'' - \tilde{X}\,^2A'$ Transition of the Calcium Isopropoxide Radical as a Candidate for Direct Laser Cooling

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S.1. Experimental

The LIF/DF and CRD apparatuses were described in our previous publication on the $CaOCH_3$ and $CaOC_2H_5$ radicals[1, 2] and are only briefly described here. In the present work, calcium isopropoxide [$pCaOCH(CH_3)_2$] radicals were produced by 1064 nm laser ablation of a calcium metal rod with a Nd:YAG laser (Continuum, Powerlite Precision II 8000) in the throat of a supersonic jet of helium seeded with isopropanol. The alcohol precursor was contained in a stainless steel reservoir at room temperature and entrained in the flow by passing high-pressure helium (backing pressure = 180 psi above 1 atm) through the reservoir. The supersonic jet molecular beam was produced by expanding the seeded flow through a pinhole valve (0.3 mm diameter) into the vacuum chamber (stagnation pressure = 20 mTorr). A 12 mm thick Teflon extension with a 1.5 mm diameter orifice at its center was attached to the supersonic nozzle for additional vibrational cooling.

The excitation laser used in the LIF/DF experiment is a pulsed dye laser (Spectra-Physics, Cobra Stretch) pumped by the second harmonic of an Nd:YAG laser (Spectra-Physics, GCR-4). The laser-induced fluorescence was collected by a lens system perpendicular to both the excitation laser beam and the jet expansion. A photomultiplier tube (PMT, Hamamatsu, H10721-01) was used to detect the focused fluorescence in the LIF measurement. The spectral linewidth of the LIF spectrum is $\approx$0.1 cm^{-1}, limited mainly by the linewidth of the pulsed dye laser ($\approx$0.06 cm^{-}) and the residual Doppler width. The frequency of the pulsed dye laser was calibrated by a wavemeter (HighFinesse, W7). The accuracy of the vibronic transition frequencies in the LIF spectrum is limited to $\approx$1 cm-1, mainly by the width of the rotational contour. For the DF experiment, the fluorescence is dispersed by a monochromator (Acton Research, SpectraPro 300i) equipped with an intensified CCD camera (Princeton Instruments, PI-MAX 512). The width of the entrance slit

of the monochromator was adjusted to balance the spectral linewidth and the signal-to-noise ratio (S/N). The typical spectral resolution of DF spectra recorded in the present work is $\approx$20 cm^{-1}. The wavelength of the DF spectra was calibrated using a mercury arc lamp, and the frequency uncertainty is $\approx$5 cm^{-1}, limited mainly by the linewidth.

Intensities of the recorded LIF transitions were calibrated by the wavelength-dependent sensitivity of the PMT. Intensities of the DF spectra were calibrated by the grating efficiency of the spectrograph and the quantum efficiency of the iCCD camera, both of which are wavelength-dependent. Further details of intensity calibration can be found in our previous work on $CaOCH_3$ and $CaOC_2H_5$.[1, 2] The origin-band transitions in the LIF experiment are significantly saturated so that an accurate measurement of their transition intensities is impractical. Therefore, pulsed-laser CRD spectra were also recorded to obtain accurate transition intensities. The CRD mirrors (Los Gatos Research, R $\geqslant$ 99.995%, center wavelength = 620 nm) were mounted on the two arms of the vacuum chamber to form a ring-down cavity with a length of L = 76 cm. The ring-down mirrors were purged by a nitrogen flow continuously to prevent contamination (mainly by the metal vapor). Transmission of the ring-down beam from a pulse dye laser (Sirah, PrecisionScan) through the cavity was focused onto a PMT (Hamamatsu, H10721-01). The empty-cavity ring-down time (τ_0) was about 250 μs. Ring-down signals were recorded at each wavelength with the ablation laser on and off. The "ablation laser off" CRD spectrum is subtracted from the "ablation laser on" spectrum to obtain the absorption spectrum of radicals.

Figure S.1. The υ_{10} mode with the in-plane CaOC bending character.

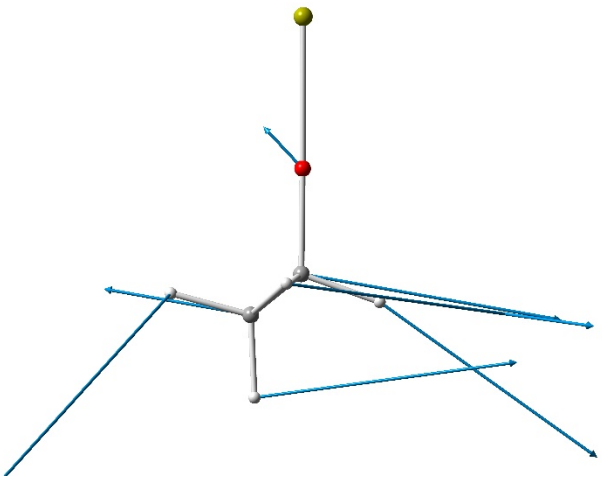
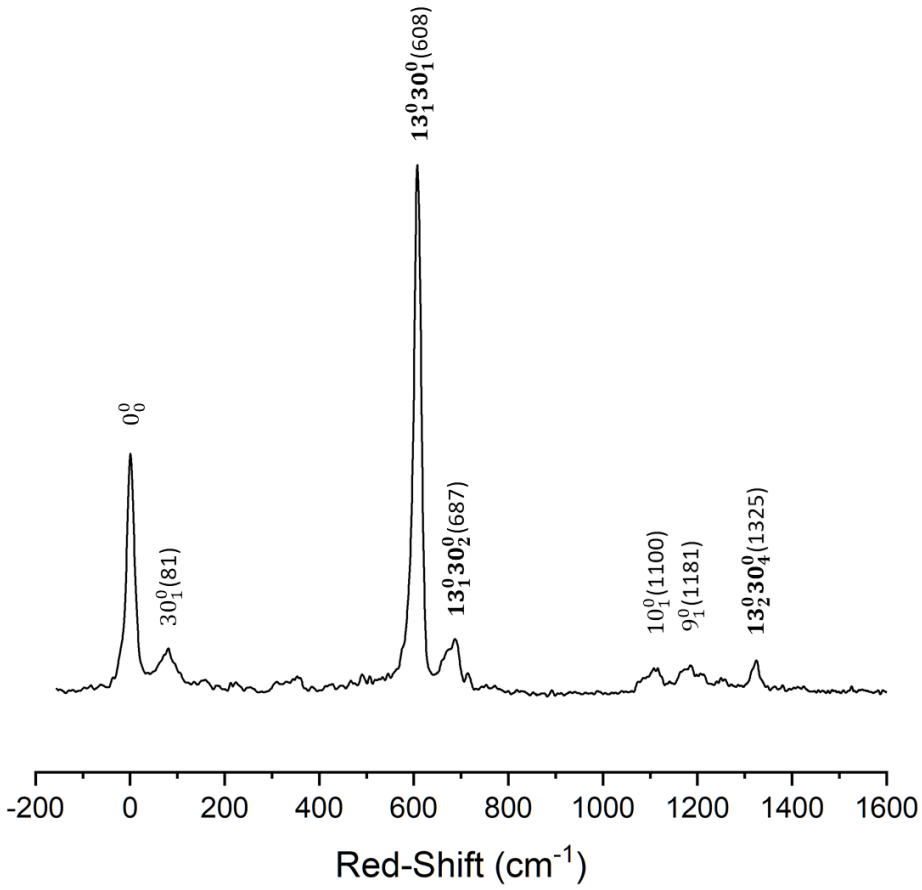


Figure S.2. DF spectrum obtained by pump the vibronic band at 188 cm^{-1} in the $\widetilde{A_1}\,^2A'/\widetilde{A_2}\,^2A'' \leftarrow \widetilde{X}\,^2A'$ LIF spectrum.



References:

1. A. C. Paul, K. Sharma, M. A. Reza, H. Telfah, T. A. Miller and J. Liu, *J. Chem. Phys.*, 2019, **151**, 134303.
2. A. C. Paul, K. Sharma, H. Telfah, T. A. Miller and J. Liu, *J. Chem. Phys.*, 2021, **155**, 024301.