

TUNNELING-SYMMETRY-RESOLVED VIBRATIONAL SPECTROSCOPY AND DYNAMICS OF THE C<sub>2</sub>H<sub>4</sub>-H<sub>2</sub>S COMPLEX MEASURED USING COHERENCE-DETECTED FOURIER TRANSFORM MICROWAVE (FTMW)-INFRARED SPECTROSCOPY

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The pure rotational spectrum of the C<sub>2</sub>H<sub>4</sub>-H<sub>2</sub>S weakly bound complex displays a four-line pattern from the tunneling motions of the hydrogens in both the H<sub>2</sub>S and C<sub>2</sub>H<sub>4</sub> subunits.<sup>a</sup> The rotational spectra of isotopic species show that the larger tunneling splitting (1.67 MHz) is attributed to motion of the H<sub>2</sub>S subunit and the smaller (0.14 MHz) to tunneling of the ethylene unit. We extend the study of this complex through measurements of its hydride stretching fundamentals using coherence-detected FTMW-infrared spectroscopy. This technique permits background-free detection of the infrared spectrum through a three-pulse sequence (MW-IR-MW) that converts the laser-induced population difference to a detectable microwave coherence. By measuring the infrared spectrum through its resonance with the pure rotational transitions, we obtain vibrational spectra with rotational level and tunneling symmetry assignments. The observed changes in the tunneling splitting upon vibrational excitation are consistent with the assignments from the isotopic pure rotational measurements. At the experimental IR resolution (0.02 cm<sup>-1</sup>) we are able to detect vibrational predissociation in the “bound” S-H stretching fundamental through Lorentzian broadening of the lineshape. The other vibrational bands (the “free” S-H stretch and the two infrared-active ethylenic C-H stretch fundamentals) have instrument-limited lineshapes indicating slower vibrational predissociation rates. The different selection rules for the two ethylenic C-H stretch fundamentals make it possible to estimate the energy difference between tunneling levels associated with the ethylene unit. We also observe some local perturbations in the vibrational spectrum and a vibrational band that is tentatively assigned as a combination band of the S-H stretch and a low-frequency van der Waals mode of the complex.

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<sup>a</sup>M. Goswami, P.K. Mandal, D.J. Ramdass, and E. Arunan, *Chem. Phys. Lett.* 393 (2004) 22.