OPTICAL AND MICROWAVE SPECTROSCOPY OF TRANSIENT METAL-CONTAINING MOLECULES

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Small metal containing molecules are ideal venues for testing Fundamental Physics, investigating relativistic effects, and modelling spin-orbit induced unimolecular dynamics. Electronic spectroscopy is an effective method for probing these phenomena because such spectra are readily recorded at the natural linewidth limited resolution and accuracy of 0.0001 cm^{-1}. The information garnered includes fine and hyperfine interactions, magnetic and electric dipoles, and dynamics. With this in mind, three examples from our recent (unpublished) studies will be highlighted.

SiHD: Long ago Duxbury et al.[a] developed a semi-quantitative model invoking Renner-Teller and spin-orbit coupling of the $\tilde{a}^3B_1$, $\tilde{X}^1A_1$, and $\tilde{A}^1B_1$, states to explain the observed local perturbations and anomalous radiative lifetimes in the visible spectrum. More recently, the $\tilde{a}^3B_1$ to $\tilde{A}^1B_1$ intersystem crossing has been modeled using both semi-classical transition state theory and quantum trajectory surface hopping dynamics [b]. Here we investigate the effects of the reduced symmetry of SiHD on the spectroscopy and dynamics using 2D spectroscopy [c]. Rotationally resolved lines in the origin $\tilde{X}^1A' \rightarrow \tilde{A}^1A''$ band are assigned to both *c*-type transitions and additional axis-switching [d] induced transitions.

AuO and AuS: The observed markedly different bonding of thiols and alcohols to gold clusters should be traceable to the difference in Au-O and Au-S bonding. To investigate this difference we have used optical Stark and Zeeman spectroscopy to determine the permanent electric dipole moments and magnetic g-factors. The results are rationalized using simple m.o. correlation diagrams and compared to ab initio predictions.

TaN: TaN is the best candidate to search for a T,P- violating nuclear magnetic quadrupole moment[e]. Here we report on the optical 2D, Stark, and Zeeman spectra, and our efforts to record the pure rotational spectrum using the separated field pump/probe microwave-optical double resonance.Implications for T,P- violating experiments will be presented.

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