

From combustion radicals to state-resolved dynamics at the gas-liquid interface: Insights from high-resolution laser spectroscopy

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The synergistic combination of high resolution laser spectroscopy with supersonic molecular beams provides a uniquely powerful tool for probing important chemical phenomena. This talk will address recent work in our group involving two quite different classes of quantum state resolved investigations. The first is based on high resolution infrared absorption spectroscopy in a slit supersonic discharge, which provides a remarkably versatile and yet highly sensitive technique for study of jet cooled radicals. Specifically, we will present results on highly reactive combustion transients ranging from large amplitude H atom tunneling dynamics in vinyl radical (H_2CCH), to state-resolved vibronic interactions in ethynyl radical (C_2H), to first gas phase IR studies of aromatic open shell species such as phenyl radical (C_6H_5). Secondly, we will discuss recent efforts toward developing new spectroscopic capabilities for studies of quantum state resolved rovibrational collision dynamics of CO_2 , HCl , and NO at the gas-liquid, gas-solid and gas-molten metal interface.

HIGH RESOLUTION QUANTUM CASCADE LASER STUDIES OF THE ν_3 BAND OF METHYL FLUORIDE IN SOLID PARA-HYDROGEN

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Spectra of solid *para*-H₂ doped with CH₃F (~ 0.4 ppm) are studied at 1.8 K in the ν_3 region (~ 1040 cm⁻¹) using a quantum cascade laser source. As shown previously, residual *ortho*-H₂ in the sample (~ 100 ppm) gives rise to distinct spectral features due to clusters of the form CH₃F-(*ortho*-H₂)_N, with $N = 0, 1, 2, 3$, etc.^a Brief “super-annealing” at 7 K is found to give narrower spectral lines (as sharp as 0.006 cm⁻¹) than conventional (5 K) annealing, and it also causes the $N = 3$ and 4 lines to fragment into multiple components. The $N = 0$ line (no *ortho*-H₂ neighbors) is resolved into two closely-spaced components which may be assigned to the $K = 0$ and 1 states of CH₃F rotating around its C_{3v} symmetry axis (*ortho*- and *para*-CH₃F, respectively).^b Similar K -structure is also evident for $N = 1, 2$, and 3. Weak features (“ $N = 1/2$ lines”) are observed almost half way between $N = 0$ and 1. The laser power was sufficient to significantly affect the sample, enabling novel spectral bleaching and hole-burning experiments to be performed on a solid *para*-H₂ matrix-isolated sample.

^aK. Yoshioka and D.T. Anderson, *J. Chem. Phys.* **119**, 4731 (2003).

^bY.-P. Lee, Y.-J. Wu, and J.T. Hougen, *J. Chem. Phys.* **129**, 104502 (2008).

Presentation mode: lecture

Time required: 15 min

Comment: *lecture is preferred, but poster is okay if necessary*

DOPANT-INDUCED INFRARED ABSORPTION FEATURES IN Cl-DOPED SOLID HYDROGEN

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Solid parahydrogen (pH₂) matrices containing open-shell (²P) Cl and Br atoms as substitutional impurities exhibit several infrared (IR) absorption features associated with intermolecular interactions between the halogen atom and nearby pH₂ molecules [1, 2]. These dopant-induced IR absorption features are associated with (i) spin-orbit (SO) excitation of the halogen atom, and (ii) cooperative excitations in which a single IR photon both triggers SO excitation of the halogen atom and excites the H–H stretching coordinate of a nearby pH₂ molecule. The IR spectral features thus contain detailed information about the interaction between the open-shell halogen atom and the surrounding pH₂ molecules, and in particular tell us about the coupling between the atom’s electronic degrees of freedom and the nuclear motion of its H₂ neighbors.

Here we present initial steps towards decoding the Cl-induced features in the IR absorption spectrum of Cl-doped solid pH₂. This system represents a prototypical arena for testing theoretical approaches for combining multiple low-lying Cl–H₂ pair potential energy surfaces [3] to generate non-pairwise-additive many-body interactions that describe the open-shell Cl atom’s interaction with many nearby pH₂ molecules.

Our analysis must account for the fact that the individual pH₂ molecules in the doped solid undergo large amplitude zero-point motions, even at $T = 0$ K [4]. We therefore use quantum Monte Carlo simulations to sample the ground state probability density function for the nuclear degrees of freedom of the Cl-doped solid. By coupling these simulations to accurate quantum chemical Cl–H₂ potential energy [3] and transition dipole moment functions, we generate fully first-principles theoretical IR spectra for comparison with experimental results. We use a reduced dimensionality model to understand how the electronic degrees of freedom of the Cl dopant are coupled to the rotational degrees of freedom of neighboring H₂ molecules; this model points out the need to include the H₂ rotational coordinates in the quantum Monte Carlo simulations.

[1] P.L. Raston and D.T. Anderson, *J. Chem. Phys.* **126**, 021106 (2007).

[2] S.C. Kettwich, L.O. Paulson, P.L. Raston, and D.T. Anderson, *J. Phys. Chem. A* **112**, 11153 (2008).

[3] G. Capecchi and H.-J. Werner, *Phys. Chem. Chem. Phys.* **6**, 4975 (2004).

[4] I.F. Silvera, *Rev. Mod. Phys.* **52**, 393 (1980).

Presentation mode: lecture

Time required: 15 min

ELECTRONIC SPECTROSCOPY OF $\text{Li}(\text{NH}_3)_4$

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The dissolution of lithium in liquid ammonia has been a source of scientific interest for many years due to the predisposition of the solution to form solvated electrons. $\text{Li}(\text{NH}_3)_4$ clusters have been proposed as key components in lithium-ammonia solutions, but their spectral signature has so far proved impossible to distinguish from other species found in these solutions. Here, in an effort to understand the electronic structure of this important cluster, we present the first electronic spectrum of $\text{Li}(\text{NH}_3)_4$ in the gas phase recorded using mass-selective depletion spectroscopy. Strong absorption is observed in the near-infrared region and the band system is assigned to the $\tilde{A}^2T_2 - \tilde{X}^2A_1$ transition in a nominally tetrahedral complex. However, an extensive vibrational progression in a low frequency bending mode is indicative of a substantial Jahn-Teller effect in the excited electronic state. Our observations confirm a recent theoretical prediction that the electronic spectrum of $\text{Li}(\text{NH}_3)_4$ will strongly overlap with the spectrum of the solvated electron in liquid ammonia.

Presentation mode: lecture

Time required: 15 min

Comment: *Two back to back talks are requested, for this talk and the talk titled "NEAR INFRARED SPECTROSCOPY OF LiNH_3 "*