

General Physical Chemistry III

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Session Overview: General Physical Chemistry contributed oral presentations.

543. Infrared Spectroscopy of Size-Selected Protonated CO₂ Clusters

Brian W. Ticknor, Gary E. Douberly, Allen M. Ricks and Michael A. Duncan, University of Georgia, Athens, GA

Protonated molecular clusters such as (CO₂)_nH⁺ are formed in a pulsed electric discharge in a supersonic expansion. The ions are mass selected and fragmented upon resonant vibrational excitation with the output of a tunable infrared OPO. The infrared spectra in the range 700 to 4000 cm⁻¹ provide information on the dynamics of the proton within the cluster.

544. INFRARED LASER SPECTROSCOPY of [C₂H₂]_NH⁺ N=1,2

Allen M. Ricks, Gary E. Douberly, Brian W. Ticknor and Michael A. Duncan, University of Georgia, Athens, GA

The monomer and dimer of protonated acetylene are formed in a pulsed electric discharge in a supersonic expansion. The mass selected ions are fragmented upon resonant vibrational excitation with the output of a tunable infrared OPO. For the monomer, the infrared spectra from 3 to 10 μm is consistent with the non-classical bridged proton structure. The (C₂H₂)H⁺ bridged proton stretch is shifted 1000 cm⁻¹ to the red upon the addition of the second acetylene, suggesting a bridged dimer in which the proton is equally shared between the two acetylene species.

545. Photothermal Studies of CO Binding to Horseradish Peroxidase and Soybean Peroxidase

Audrey Mokdad and Randy W. Larsen, University of South Florida, Tampa, FL

In this report, the results of photoacoustic calorimetry (PAC) studies involving CO photodissociation from Horseradish Peroxidase (HRP) and Soybean Peroxidase (SBP) are discussed. HRP and SBP, contain a heme active site which can oxidize a large diversity of organic and inorganic compounds. The heme group of both HRP and SBP is 5 coordinate, high spin, where His 170 and His 169 are the HRP and SBP proximal ligands, respectively. It also has been demonstrated that HRP has a direct exit channel from the heme active site to the solvent. In addition, SBP can bind a Tris molecule in the distal pocket near the heme group that could potentially regulate ligand binding. Results of PAC indicate a monophasic relaxation for both HRP and SBP subsequent to CO photolysis in phosphate and Tris buffers and with varying concentrations of Tris. The molar volume/enthalpy changes associated with the monophasic decay are similar for both HRP and SBP: ~7mL/15kcal/mol. The results suggest that for both HRP and SBP, the volume change was due to the displacement of CO to the bulk solvent and the enthalpy change was due to the breaking Fe-CO bond. The results also suggest that the binding of a Tris molecule to SBP doesn't affect the energetics of diffusional CO exit from the SBP active site.

546. Photodissociation of Yttrium and Lanthanum Oxide Cluster Cations

Zachary D. Reed and Michael A. Duncan, University of Georgia, Athens, GA

Transition metal oxide cations of the form M_nO_m (M=Y, La) are produced by laser vaporization in a pulsed nozzle cluster source and detected with time-of-flight mass spectrometry. Clusters oxides for each value of n form only a limited number of stoichiometries; MO(M₂O₃)_x clusters are particularly intense. Cluster cations are mass selected and photodissociated using the third harmonic (355 nm) of an Nd:YAG

laser. Multiphoton excitation is required to dissociate these clusters, due to their strong bonding. Yttrium and lanthanum oxides show different dissociation channels, but some common trends can be identified. Larger clusters undergo fission to create certain particularly stable cation clusters, especially $\text{MO}(\text{M}_2\text{O}_3)_x^+$ fragments. Specific cations are identified to be particularly stable due to their repeated production in the decomposition of larger clusters. These include M_3O_4^+ , M_5O_7^+ , $\text{M}_7\text{O}_{10}^+$, and $\text{M}_9\text{O}_{13}^+$, along with Y_6O_8^+ . Theoretical calculations were performed to investigate the relative stabilities and structures of experimentally interesting clusters.

547. Orientation of Dye Molecules on TiO_2 Films as Determined by Second Harmonic Generation

Baohua Wu, **Chantelle Anfuso-Cleary** and Tim Lian, Emory University, Atlanta, GA

Knowledge of dye orientation on a semiconductor surface is imperative to the full understanding of the mechanism of interfacial electron transfer, dye-sensitized solar cells, and molecular electronics. Second harmonic generation (SHG) spectroscopy has been recognized as an important tool for determining the average orientation of a molecular monolayer at an interface due to its interface specificity and monolayer sensitivity. We have used this method to investigate the average orientation of dye molecules on a semiconductor film. Specifically, three dyes were adsorbed onto thin TiO_2 films prepared on fused silica windows: coumarin 343 (C343), rhodamine 6G (Rh6G), and $\text{Re}(\text{Lp})(\text{CO})_3\text{Cl}$ (ReC1P) [Lp= 2,2'-bipyridine-4,4'-bis- $\text{CH}_2\text{-PO}_3\text{H}_2$]. The polarization dependence of the SHG signal was recorded at select resonant wavelengths for each dye. A global fitting procedure can be applied to this polarization dependence data to determine the average dye orientation on the TiO_2 film. We will present our results of this ongoing study of the orientation of C343, Rh6G, and ReC1P on TiO_2 films.

548. Infrared Spectroscopy of Size-Selected Carbocations Isolated in the Gas Phase

Gary E. Douberly, Allen M. Ricks, Brian W. Ticknor and Michael A. Duncan, University of Georgia, Athens, GA

Infrared argon vibrational predissociation spectroscopy is used to probe the structures of carbocations $(\text{C}_n\text{H}_m)^+$, formed in a pulsed electric discharge through a dilute hydrocarbon supersonic expansion. Size specific infrared spectra are obtained by mass selection in a reflectron time of flight mass spectrometer followed by the resonant photo-fragmentation of the ion with tunable (2-16 μm) output from a pulsed infrared OPO. Spectra are presented for the gas phase t-butyl, protonated benzene, and propargyl cations. A family of cations based on the allyl cation core $(\text{C}_3\text{H}_5)^+$ is formed from several hydrocarbon precursors and appears to be intrinsically stable. Two isomers of $(\text{C}_3\text{H}_5)^+$ (the allyl and propenyl cations) are observed and assigned based on distinct spectral features in the fingerprint region of the infrared spectrum, corresponding to the C-C-C asymmetric stretches.

549. Infrared Photodissociation Spectroscopy of Noble Metal Cation Water Complexes

Prosser D. Carnegie II, Biswajit Bandyopadhyay and Michael A. Duncan, University of Georgia, Athens, GA

The complexes $\text{NM}^+(\text{H}_2\text{O})_{1,2}\text{Ar}_{2,1}$ (NM = Cu, Ag, and Au) are formed via laser vaporization in a pulsed molecular beam configuration and analyzed by infrared photodissociation spectroscopy. $\text{NM}^+(\text{H}_2\text{O})\text{Ar}_2$ complexes exhibit red shifts in the OH stretching frequency as a result of the metal binding to the water molecule. The dihydrated complexes show more complicated spectra with multiple peaks resulting from the formation of various isomers. Some of these isomers contain hydrogen bonded structures, which can be determined from the appearance of a hydrogen bond stretching frequency in the spectra. The experimental results are compared to predicted frequencies from density functional calculations to determine the isomers present in each complex.