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as of 20-Dec-2018

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STEM Degrees: **STEM Participants:**

Major Goals: 1. Determine the reactivity and catalytic behavior of metal oxide and sulfide clusters (eg, Co, Fe, Ni, V)
2. Determine the decomposition and reaction mechanisms for energetic materials.
3. Construct a new state of the art photoelectron apparatus for the above studies.

Accomplishments: Reports for ARO/AFOSR and DURIP
1. Hydrogenation Reactions of Ethylene on Neutral Vanadium Sulfide Clusters: Experimental and Theoretical Studies
The reactions of C2H4 with H2 on neutral vanadium sulfide clusters in a fast flow reactor are investigated by time of flight mass spectrometry employing 118 nm (10.5 eV) single photon ionization. The experimental products of these reactions are VmSnC2Hx (m = 1, n = 1-3; m = 2, n = 1-5 and x = 4-6). Observation of these products indicates that these VmSn clusters have high catalytic activity for hydrogenation reactions of C2H4. Density functional theory calculations at the BPW91/TZVP level are carried out to explore the geometric and electronic structures of the VmSn clusters, and to determine reaction intermediates, transition states, as well as reaction mechanisms. All reactions are estimated as overall barrierless or with only a small barrier (0.1 eV), and are thermodynamically favorable processes at room temperature.
We find that the hydrogenation reactions of C2H4 are thermodynamically available on VmSn (m = 1, n = 1-3; m = 2, n = 1-5) clusters. The V atoms are the active sites for these VmSn clusters to attach a C2H4 molecule. Two types of association products for ethylene on active V sites of catalytic VmSn clusters are determined by DFT calculations. The C2H4 can connect with the active V atom through its π orbital or form a σ bond with active V atoms. Both π and σ associated ethylene can be hydrogenated with H2 on catalytic VmSn clusters. PESs are calculated for hydrogenation reactions of C2H4 on the VS1-3, V2S2 clusters. The H2 molecule is predicted to be adsorbed on the V sites of VS1,2C2H4 and V2S2C2H4 clusters, and dissociate to form -VH and/or -SH groups. On the VS3C2H4 cluster, the H-H bond of the H2 molecule ruptures directly on two adjacent S sites and forms -SH groups. Theoretical calculations suggest that the reaction of the H2 molecule on the VmSnC2H4 cluster is associated with electron density localized on different active sites. Sufficient electron spin density on V or S atoms is responsible for the adsorption or dissociation of H2. The H atoms of -VH and -SH groups transfer to C2H4 step by step. The ethane molecule can be formed through an ethyl intermediate species which bonds to an active V site, and desorbs to the gas phase with the catalytic VmSn cluster unchanged. Additionally, all reactions are estimated as overall barrierless or with a small barrier (~0.1 eV), in thermodynamically favorable processes. A catalytic cycle for the hydrogenation reaction of C2H4 on a condensed phase vanadium sulfide catalyst surface is proposed based on the present gas phase cluster experimental and theoretical studies. The exposed V sites on a vanadium

sulfide catalyst surface are suggested to be important for holding the C2H4 and H2 molecules; S sites near an active V site are responsible for breaking the H-H bond of the adsorbed H2 molecule.

2. Gas Phase Neutral Binary Oxide Clusters: Distribution, Structure, and Reactivity toward CO

Neutral binary (vanadium−cobalt) oxide clusters are generated and detected in the gas phase for the first time. Their reactivities toward carbon monoxide (CO) are studied both experimentally and theoretically. Experimental results suggest that neutral VCoO4 can react with CO to generate VCoO3 and CO2. DFT calculations illustrate that the approaching of CO to the Co site, and the subsequent interaction of CO with one Ot atom of the ObObVOtOt moiety of the VCoO4 cluster is crucial to complete the CO oxidation process. Our studies and results illuminate the mechanism for catalytic processes occurring on the surfaces of real supported catalysts, and suggest new types of multicomponent catalysts.

3. Experimental and Theoretical Studies of Ammonia Generation: Reactions of H2 with Neutral Cobalt Nitride Clusters

Ammonia generation through reaction of H2 with neutral cobalt nitride clusters in a fast flow reactor is investigated both experimentally and theoretically. Single photon ionization at 193 nm is used to detect neutral cluster distributions through time of flight mass spectrometry. ComNn clusters are generated through laser ablation of Co foil into N2/He expansion gas. Mass peaks ComNH2 (m = 6, 10) and ComNH3 (m = 7, 8, 9) are observed for reactions of H2 with the ComNn clusters. Observation of these products indicates that clusters ComN (m = 7, 8, 9) have high reactivity with H2 for ammonia generation. Density functional theory (DFT) calculations are performed to explore the potential energy surface for the reaction Co7N + 3/2H2 → Co7NH3, and a barrierless, thermodynamically favorable pathway is obtained. An odd number of hydrogen atoms in ComNH3 (m = 7, 8, 9) probably come from the hydrogen molecule dissociation on two active cobalt nitride clusters based on the DFT calculations.

Both experimental observations and theoretical calculations suggest that the reaction of ammonia generation requires two active clusters, and hydrogen dissociation on these two active clusters is the key step to form NH3 in the gas phase reaction. Clusters ComN (m = 7, 8, 9) have high reactivity with H2 for ammonia generation. A catalytic cycle for ammonia generation from N2 and H2 on a cobalt catalyst surface is proposed based on the present gas phase cluster experimental and theoretical studies.

4. Double C-H Bond Activation of Hydrocarbons by a Gas Phase Neutral Oxide Cluster: The Importance of Spin State

The neutral cluster V2O5 is generated and detected in the gas phase. Its reactivity toward butane is studied both experimentally and theoretically. Experimental results show clearly that neutral V2O5 can react with n-butane (C4H10) to generate V2O5H2, indicating double hydrogen atom transfer from C4H10 to V2O5 to produce C4H8. Further experimental evidence indicates that V2O5 is only partially reacted even at very high concentrations of C4H10. Density functional theory (DFT) studies show that the lowest energy triplet state of V2O5 is reactive toward C4H10, whereas the ground state singlet V2O5 is inert.

A hydrogen atom transfer (HAT) from C4H10 to the spin located Ot site of excited state 3V2O5 is overall barrierless, whereas a hydrogen atom transfer from C4H10 to singlet ground state 1V2O5 shows a significant barrier. The HAT reaction of C2H6 with V2O5 displays similar behavior to that of C4H10 and DFT results parallel the experimental data, as well. The reactions of V2O5H2 with several oxidants are exothermic and the reaction mechanisms are studied in detail to regenerate 3V2O5.A catalytic cycle for the reaction is presented and a catalytic mechanism on the surface of a condensed phase VxOy catalyst is proposed. Our studies not only provide new insights into gas phase reactions but also shed light on catalytic processes on the surfaces of condensed phase supported catalysts.

5. Catalytic Oxidation of CO by N2O Conducted by a Neutral Oxide Cluster Couple VO2/VO3

Neutral vanadium and cobalt oxide clusters are generated at the same time employing a V–Co mixed target. Experimental results indicate that the reaction VO2 +N2O → VO3 +N2 occurs in a fast flow reactor. This result is further supported by a CO and N2O gas mixture sample as the regeneration of VO2 is observed via the reaction VO3 + CO → VO2 + CO2. A full catalytic cycle for the reaction N2O + CO → N2 + CO2 is thus complete, conducted by the VO2/VO3 cluster couple. DFT calculations show that the whole catalytic process is overall barrierless and parallels the experimental results quite well. Our results provide new insight for the catalytic oxidation of CO by N2O in the gas phase by neutral oxide clusters. This study sheds light not only on the catalytic mechanism for a real solid material surface, but also can suggest an approach to global motor vehicle gas pollution problems.

6. Formaldehyde and Methanol Formation from Reaction of Carbon Monoxide and Hydrogen on Neutral Fe2S2 Clusters in the Gas Phase

Training Opportunities: Five post docs and one student

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as of 20-Dec-2018

Results Dissemination:

2018

278. J. Ghosh, H. Gajapathy, E. R. Bernstein and Atanu Bhattacharya, "Molecular Finger-print of Explosive Property of Energetic Molecules: Unified Role of Dissociative (pi-sigma*) States", J. Phys. Chem. A, (2018) submitted.

277. M. R. D. Sylvinson, A. Bera, P. Mishra, A. Bhattacharya, and E. R. Bernstein, "Unimolecular Decomposition of Novel High Nitrogen Content Energetic Molecules Following Electronic State Excitation: BTATz and DATz," in preparation.

276. Zhen Zeng and Elliot R. Bernstein, "RDX and HMX Related Anionic Species Explored by Photoelectron Spectroscopy and Density Functional Theory", J. Phys. Chem. C, 2018, DOI: 10.1021/acs.jpcc.8b07728. PDF

275. S. Yin and E. R. Bernstein, "Fe-V Sulfide Clusters Studied through Photoelectron Spectroscopy and Density Functional Theory", Phys. Chem. Chem. Phys. 20, 22610 (2018). PDF

274. Zhen Zeng and Elliot R. Bernstein, "Isomeric Structures of Isolated Ammonium Nitrate and Its Hydrogenated Species Identified Through PES Experiments and DFT Calculations", Phys. Chem. Chem. Phys. 20, 11224 (2018). PDF

273. Shi Yin and Elliot R. Bernstein, "Photoelectron Spectroscopy and Density Functional Theory Studies of (FeS)mH- (m = 2 - 4) Cluster Anions: Effects of the Single Hydrogen", Phys. Chem. Chem. Phys. 20, 367 (2018). PDF

2017

272. Zhen Zeng and Elliot R. Bernstein, "Photoelectron Spectroscopy and Density Functional Theory Studies of (fructose+(H2O)n)- (n = 1-5) Anionic Clusters," Phys. Chem. Chem. Phys. 19, 31121 (2017). PDF

271. J. -W. Shin and E. R. Bernstein, "IR + VUV double resonance spectroscopy and extended density functional theory studies of ketone solvation by alcohol: 2-butanone (methanol)n, n = 1 - 4 clusters," J. Chem. Phys. 147, 124311 (2017). PDF

270. Zhen Zeng and Elliot R. Bernstein, "Anionic Ribose Related Species Explored Through PES Experiments, DFT Calculations, and Through Comparison with Anionic Fructose Species," Phys. Chem. Chem. Phys. 19, 28950 (2017). PDF

269. S. Yin and E. R. Bernstein, "Photoelectron Spectroscopy and Density Functional Theory Studies of Iron Sulfur FemSm- (m = 2 - 8) Cluster Anions: Co-existing Multiple Spin States ," J. Phys. Chem. A 121, 7362 (2017) PDF

268. Zhen Zeng and Elliot R. Bernstein, "Anionic Fructose-Related Conformational and Positional Isomers Assigned Through PES Experiments and DFT Calculations," Phys. Chem. Chem. Phys. 19, 23325 (2017). PDF

267. B. Yuan and E. R. Bernstein, "Initial Mechanisms for the Unimolecular Decomposition of Electronically Excited Bisfuroxan based Energetic Materials," J. Chem. Phys. 146, 014301 (2017). PDF

2016

266. Zhen Zeng and Elliot R. Bernstein, "Photoelectron Spectroscopy and Density Functional Theory Studies of N-rich Energetic Material," J. Chem. Phys. 145, 164302 (2016). PDF

265. S. Yin and E. R. Bernstein, "Properties of Iron Sulfide, Hydrosulfide, and Mixed Sulfide/Hydrosulfide Cluster Anions Through Photoelectron Spectroscopy and Density Functional Theory Calculations," J. Chem. Phys. 145, 154302 (2016). PDF

264. B. Yuan and E. R. Bernstein, "Initial Mechanisms for the Unimolecular Decomposition of Electronically Excited Nitrogen-rich Energetic Salts with Tetrazole Rings: (NH4)2BT and TAGZT," J. Chem. Phys. 145, 064306 (2016). PDF

263. B. Yuan and E. R. Bernstein, "Initial Mechanisms for the Decomposition of Electronically Excited Nitrogen-rich Energetic Materials with Tetrazole Rings: 1-DTE, 5-DTE, BTA, and BTH," J. Chem. Phys. 144, 234302 (2016). PDF

262. B. Yuan, J. -W. Shin and E. R. Bernstein, "Dynamics and Fragmentation of van der Waals and Hydrogen Bonded Cluster cations: (NH3)n and (NH3BH3)n Ionized at 10.51 eV," J. Chem. Phys. 144, 144315 (2016). PDF

261. S. Yin and E. R. Bernstein, "Ethylene C-H Bond Activation by Neutral Mn2O5 Cluster Under Visible Light Irradiation," J. Phys. Chem. Lett. 7, 1709 (2016). PDF

2015

260. B. Yuan, Z. Yu and E. R. Bernstein, "Initial Mechanisms for the Decomposition of Electronically Excited Energetic Materials: 1,5'-BT, 5,5'-BT and AzTT" J. Chem. Phys. 142, 124315 (2015). PDF

259. B. Yuan, Z. Yu and E. R. Bernstein, "Initial Mechanisms for the Decomposition of Electronically Excited Energetic Salts: TKX-50 and MAD-X1" J. Phys. Chem. A, 119, 2965 (2015). PDF

258. E. R. Bernstein, "Neutral Cluster Mass Spectrometry," Int. J. Mass Spectrom., 377, 248 (2015). PDF

2014

257. E. R. Bernstein, "On the Release of Stored Energy from Energetic Materials," Adv. Quant. Chem. 69, 31 (2014).

256. S. Yin and E. R. Bernstein, "Experimental and Theoretical Studies of H2O Oxidation by Neutral Ti2O4,5 Clusters Under Visible Light Irradiation," Phys. Chem. Chem. Phys. 16, 13900 (2014). PDF

255. B. Yuan, Z. Yu and E. R. Bernstein, "Initial Decomposition Mechanism for the Energy Release from Electronically Excited Energetic Materials: FOX-7 (1,1-diamino-2,2-dinitroethene, C2H4N4O4)," J. Chem. Phys. 140, 074708 (2014). PDF
254. J-W. Shin and E. R. Bernstein, "Vacuum Ultraviolet Photoionization of Carbohydrates and Nucleotides," J. Chem. Phys. 140, 044330 (2014). PDF
253. B. Yuan, Z. Yu and E. R. Bernstein, "Azole Energetic Materials: Initial Mechanisms for the Energy Release from Electronical Excited Nitropyrazoles," J. Chem. Phys. 140, 034320 (2014). PDF
2013
252. Z. C. Wang, S. Yin and E. R. Bernstein, "Generation and Reactivity of Putative Support Systems, Ce-Al Neutral Binary Oxide Nanoclusters: CO Oxidation and C-H Bond Activation," J. Chem. Phys. 139, 194313 (2013). PDF
251. Y. Hu, J Guan and E. R. Bernstein, "Mass-selected IR-VUV (118?nm) spectroscopic studies of radicals, aliphatic molecules, and their clusters," Mass Spectrom. Rev. 32, 484 (2013). PDF
250. Z. Yu and E. R. Bernstein, "Sensitivity and Performance of Azole Based Energetic Materials," J. Phys. Chem. A, 117, 10889 (2013). PDF
249. S. Yin, Z. C. Wang and E. R. Bernstein, "O-Atom Transport Catalysis by Neutral Manganese Oxide Clusters in the Gas Phase: Reactions with CO, C2H4, NO2, and O2," J. Chem. Phys. 139, 084307 (2013). PDF
248. S. Yin, Z. C. Wang and E. R. Bernstein, "Formaldehyde and Methanol Formation from Reaction of Carbon Monoxide and Hydrogen on Neutral Fe2S2 Clusters in the Gas Phase," Phys. Chem. Chem. Phys. 15, 4699 (2013). PDF
247. Z. C. Wang, S. Yin and E. R. Bernstein, "Catalytic Oxidation of CO by N2O Conducted by a Neutral Oxide Cluster Couple VO2/VO3," Phys Chem Chem Phys. 15, 10429 (2013). PDF
246. Z. C. Wang, S. Yin and E. R. Bernstein, "Double C-H Bond Activation of Hydrocarbons by a Gas Phase Neutral Oxide Cluster: The Importance of Spin State," J. Phys. Chem. A 117, 2294 (2013). PDF
245. Z. Yu and E. R. Bernstein, "On the Decomposition Mechanisms of new Imidazole-Based Energetic Materials," J. Phys. Chem. A, 117, 1756 (2013). PDF
2012
244. S. Yin, Y. Xie and E. R. Bernstein. "Experimental and Theoretical Studies of Ammonia Generation: Reactions of H2 with Neutral Cobalt Nitride Clusters," J. Chem. Phys. 137, 124304 (2012). PDF
243. Z. Yu and E. R. Bernstein, "Experimental and Theoretical Studies of the Decomposition of New Imidazole Based Energetic Materials: Model Systems," J. Chem. Phys. 137, 114303 (2012). PDF
242. Z. C. Wang, S. Yin and E. R. Bernstein, "Gas Phase Neutral Binary Oxide Clusters: Distribution, Structure, and Reactivity toward CO," J. Phys. Chem. Lett. 3, 2415 (2012). PDF
241. S. Yin, and E. R. Bernstein, "Gas Phase Chemistry of Neutral Metal Clusters: Distribution, Reactivity and Catalysis," Int. J. Mass Spectrom., 321-322, 49 (2012). PDF
240. A. Bhattacharya, Y. Q. Guo, and E. R. Bernstein, "A Comparison of the Decomposition of Electronically Excited Nitro-Containing Molecules with Energetic Moieties C-NO2, N-NO2, and O-NO2," J. Chem. Phys. 136, 024321 (2012). PDF

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CAS invited scholar – 2017
Colorado Section ACS Research Chemist award 2016

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Abstract: Carbohydrates (2-deoxyribose, ribose, and xylose) and nucleotides (adenosine-, cytidine-, guanosine-, and uridine-5?-monophosphate) are generated in the gas phase, and ionized with vacuum ultraviolet photons (VUV, 118.2 nm). The observed time of flight mass spectra of the carbohydrate fragmentation are similar to those observed [J.-W. Shin, F. Dong, M. Grisham, J. J. Rocca, and E. R. Bernstein, Chem. Phys. Lett. 506, 161 (2011)] for 46.9 nm photon ionization, but with more intensity in higher mass fragment ions. The tendency of carbohydrate ions to fragment extensively following ionization seemingly suggests that nucleic acids might undergo radiation damage as a result of carbohydrate, rather than nucleobase fragmentation. VUV photoionization of nucleotides (monophosphate-carbohydrate-nucleobase), however, shows that the carbohydrate-nucleobase bond is the primary fragmentation site for these species. Density functional theory (DFT) calculations indicate that the removed carbohydrate e
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PHOTOELECTRON SPECTROSCOPY (PES) OF ENERGETIC MATERIALS (EMs), SACCHARIDES, AMMONIUM NITRATE, AND THEIR COMPOUNTS

(6/18/2017-6/17/2018)

We performed reflectron time of flight mass spectrometer (rTOFMS) and magnetic bottle photoelectron spectrometer (mbPES) experiments with state-of-the-art sensitivity and resolution, as well as ab initio calculations on gas phase, isolated energetic materials, saccharides and ammonium salts. For nitrogen rich energetic materials, their geometric and electronic structures, intramolecular interaction, and decomposition mechanism of anionic energetic materials were studied, for emphasizing the importance of ionic states for the stored energy release processes from these molecules. The energetic materials include DAAF, FOX-7, 5,5'-BT, 1,5'-BT, LLM-172, DNTF, RDX, HMX, and TATB. Saccharides, also as energetic materials, were taken into consideration for understanding their geometric and electronic structures as well as dissociations mechanism in order to investigate if they can improve the energetic materials performance by adding or bonding them to high-N content energetics. These new composite EMs may have the special properties of both the high N-content EMs and the proper C, H, N, O balance afforded by the covalently bonded saccharide moiety, enabling complete release of stored energy (e.g., products CO_2, N_2, and H_2O) calculated for the bonded EM/saccharide such systems. Also, a further outreaching goal for studying and comparing different sugar molecules is to shed light on the ribose selected nature as the sugar constituent of RNA. Saccharides include fructose, ribose, mannose, arabinose, fructose+$(H_2O)_n$, saccharides phosphate. For ammonium nitrate and other ammonium salts, as important energy storage materials, it is necessary to study species involved in their decomposition/energy release chemistry in order to understand their behaviors.

N-rich energetic materials

Anionic photoelectron spectroscopy (PES) and density functional theory (DFT) studies of isolated, N-rich energetic materials, as well as DCM dye, are reported. The electron binding energies for $DAAF^-$, $DAAF^-$-H, FOX-7^--H, 5,5′-BT^--H-N2, 1,5′-BT^--H, and DCM^- are determined and assigned by comparing the calculated and experimental corresponding VDEs (Vertical Detachment Energy), respectively.

The anionic structures of $DAAF^-$, $DAAF^{--}H$, FOX-7^--H, 5,5′-BT^--H-N_2, 1,5′-BT^--H, and DCM^- are predicted by the DFT calculations: the electronic and geometric structures of these species are reliable based on agreement between their respective calculated and observed electron binding energies. The electron binding energies and structures of FOX-7^-, 5,5′-BT^-, and 1,5′-BT^- can be confidently assigned based on the accurate VDE calculated results, even though these species are not directly detected in the TOFMS or PES spectra. The theoretical results enable one to understand the geometric and electronic structures, and intramolecular interactions of these EMs with an excess electron. The anionic electronic structures of these EMs have a significant and important effect for their decomposition reactions mechanisms. Reactivity based on the anionic initial fragments of these EM species further reinforces their respective highly reactive and explosive nature. The energetic molecules minus H are additionally good candidates for intermediates in the EM stored energy release reactions and mechanisms. Parent and fragment ions are components of energy release mechanisms. This further illustrates energetic materials can release their stored energy in different molecular forms, and the anionic electronic structures has a significant and important effect for their initial decomposition reactions, further reinforces their highly reactive nature.

Energetic materials nitramine RDX and HMX generated by matrix assisted laser desorption ionization (MALDI) method are also studies through PES and DFT approaches. Their anionic parent species are not observed but instead accessible fragmentations ions are observed. The VDEs of these anionic dissociation ions are experimentally determined, and the corresponding structures are identified with aid of theoretical calculations by comparing calculated VDEs to the experimental ones. RDX^- and HMX^- can fragmentate through loss of HNO_2, NO_2, NCH_2 groups. RDX^- evidences losing with up to two NO_2 groups and one NCH_2 moiety, and HMX^- can fragmentate by loss of up to three NO_2 groups and two NCH_2 moieties. The mass units of $(RDX - H - NO_2)^-$, $(RDX - H - (NO_2)_2)^-$, and $(RDX - NCH_2 - (NO_2)_2)^-$ are the same as those of $(HMX - H - (NO_2)_2 - NCH_2)^-$, $(HMX - H - (NO_2)_3 - NCH_2)^-$, and $(HMX - (NO_2)_3 - (NCH_2)_2)^-$, respectively. These dissociation anions with the same mass units share nearly identical photoelectron spectra and geometrical structures, which suggests the structural and dissociation routine similarities between RDX and HMX anions. Another energetic material TATB (2,4,6-triamino-1,3,5- trinitrobenzene) has also been taken into consideration: its parent anion generated from MALDI can be observed in the mass spectrum. The presence of

$TATB^-$ but not RDX^- and HMX^- further demonstrates TATB's higher thermal stability than that of RDX and HMX.

Saccharides

Saccharides themselves can be considered as EMs, as they have an excellent C, H, O balance which is absent in the new, high N-content EMs that are currently being synthesized and explored as the next generation replacement, environmentally friendly EMs. We have posited and are exploring saccharides as substituents on these latter EMs to improve the C, H, N, O balance for complete stored energy release. This suggestion can be augmented with nitrated saccharides for perhaps still better performance of high N-content EMs. The conformational, positional, and electronic structure studies of saccharide related species, especially saccharides with one or more water molecules, help to understand the intermolecular interactions between saccharides and other molecules. Such cluster studies can provide further information to support the suggestion that saccharide substituted high N-content EMs may be a new direction for synthetic efforts. Saccharides and their Ions are also biologically important for secondary low energy radiation damage control and stability, as well as the preservation consideration of RNA/DNA.

Gas phase, isolated fructose anionic species, $fructose^-$, $(fructose\text{-}H)^-$, $(fructose\text{-}OH)^-$, and $(fructose\text{-}H_2O)^-$, are investigated employing anionic PES combined with DFT calculations. The PES vertical detachment energies (VDEs) for these anions are determined and, based on these experimental values, their calculated anionic structures are assigned. Generation of these four species through the matrix assisted laser desorption ionization (MALDI) process is sample desorption substrate dependent. The parent anion $fructose^-$ exists as a single, dominant open chain structure in the gas phase, with substrate dependent specific conformational isomers. $(Fructose\text{-}H)^-$ and $(fructose\text{-}OH)^-$ are mainly produced from the laser ablation process rather than from fragmentation reaction pathways associated with the parent anion species. Both conformational and positional isomers are identified in the gas phase for these latter anions. $(Fructose\text{-}H_2O)^-$ has two types of positional isomers, both of which contribute to two different components of the observed PES feature. The fixed positions for losing an OH group and an H atom, in addition to thermodynamic calculations, provide reaction pathways for generating a dehydration product (open chain structures) from the parent anion (open chain and

furanose structures), further demonstrating the active nature of fructose upon capturing an extra electron.

Ribose, a subunit of the RNA (ribonucleic acid) backbone, is an essentially important monosaccharide: ribose also appears as the substrate in ATP/ADP/AMP (adenosine tri/di/mono-phosphate). It plays key roles in energy storage of biochemical system. Investigation of the conformations of ribose related anionic species helps to understand fragmentation mechanisms, as well as the stability and activity of ribose with regard to its natural selection for biopolymer backbone supports. Ribose related species, $(ribose\text{-}H)^-$ and $(ribose\text{-}H_2O)^-$, are investigated through anionic PES combined with DFT calculations. Their vertical detachment energies (VDEs) are experimentally determined and their anionic structures with positional and conformational isomers are definitively assigned. $Ribose^-$ parent anion is not detected in the present experiments. $(ribose\text{-}H)^-$ and $(ribose\text{-}H_2O)^-$ anions can be accessed as the characteristic fragmentation ions of the parent species. Generation of $(ribose\text{-}H)^-$ through the MALDI process is sample desorption substrate dependent, while generation of $(ribose\text{-}H_2O)^-$ is independent of a wide range desorption substrates. Both conformational and positional isomers of $(ribose\text{-}H)^-$ are identified in the gas phase. Two types of positional isomers of $(ribose\text{-}H_2O)^-$ (both from open chain structures) are assigned to contribute to two different components of the observed PES feature. The dehydration process can be thermodynamically accessed through both the parent anion and the neutral.

Arabinose and mannose are also taken into consideration for comparison the behavior of different saccharides. Isolated $arabinose^-$ parent anion is observed in the mass spectrum and is identified to exist as open chain structures. $Mannose^-$ parent anion is not accessible in the experiments. $(SAC\text{-}H)^-$ and $(SAC\text{-}H_2O)^-$ are both available for arabinose and mannose. Many different conformational and positional isomers are predicted and observed for $(arabinose\text{-}H)^-$ and $(mannose\text{-}H)^-$. Two types of positional isomers are assigned to contribute to PES of $(arabinose\text{-}H_2O)^-$ and $(mannose\text{-}H_2O)^-$ with conformational differences, respectively. Based on the ions observed and assigned by our system (RTOFMS PES/DFT) for all four sugar molecular related species, cyclic structures are only accessed in the minus H species. Therefore, $(Sac - H)^-$ must be considered for RNA stability since the sugar moiety presents a furanose cyclic structure for DNA/RNA backbone supports. The relative energies of $(ribose\text{-}H)^-$ and $(mannose\text{-}H)^-$ with regard to the corresponding lowest energy isomer as well as the lowest energy furanose structures are lower than $(arabinose\text{-}H)^-$ and $(fructose\text{-}H)^-$. Therefore, by assuming that the

ablation/supersonic expansion process gives lower lying states, all SAC should have similar cooling conditions, arabinose and fructose can be eliminated for energy considerations. By considering the protection of ribose from $(ribose\text{-}H)^-$ back to neutral parent species, since furanose $(ribose\text{-}H)^-$ can lose electron more easily than furanose $(mannose\text{-}H)^-$ does, and can also bind H more easily than furanose $(mannose\text{-}H)^-$ does, furanose $(ribose\text{-}H)^-$ anion can go back to furanose ribose neutral easier than $(mannose\text{-}H)^-$ can return to mannose neutral. Thus, ribose is better than mannose with regard to the protection of RNA. Moreover, the dynamics and kinetics favor ribose rather than mannose and the other saccharides.

Saccharides+H_2O

The $(fructose+(H_2O)_n)$ (n = 1-5) clusters are also explored employing the same techniques, which helps to understand the intermolecular interaction between saccharides with other molecules. This can further elucidate how to join EMs and saccharides to form composite molecular species. From our experimental and theoretical results of $(fructose+(H_2O)_n)^{-/0}$ (n = 1-5), it is found that gas phase, isolated $(fructose+(H_2O)_n)^-$ (n = 1-5) cluster anions mainly exist as open chain structures in the present experiments. Many conformational and positional open chain isomers are identified to coexist and contribute to the broad PES features determined for $(fructose+(H_2O)_n)^-$ (n = 1-5) anionic clusters. Some cyclic structures of $(fructose+(H_2O)_n)^-$ (n = 3, 4) are apparently present in the experiments and their VDEs can contribute to the lower energy shoulders of PES features observed for $(fructose+(H_2O)_n)^-$ (n = 3, 4). Cyclic $(fructose+(H_2O)_n)^-$ (n = 1-5) clusters have the added electron as dipole bound, whereas open chain structures have the added electron in a valence orbital. Water molecules in open chain anions predominantly interact with the (1)C side (including (1)OH, (2)O, and (3)OH) of $fructose^-$: they finally form a quasi-cubic structure with OH groups and carbonyl O in the most stable structures for $(fructose+(H_2O)_4)^-$ and $(fructose+(H_2O)_5)^-$ cluster anions. Water molecules solvating cyclic anions form water-water hydrogen bond networks that preferentially interact with OH groups at (1), (2), and (3) positions of fructose pyranose anions, and (3), (4), and (6) positions of fructose furanose anions. Structures of neutral $(fructose+(H_2O)_n)$ (n = 1-5) are pyranose related as the lower energy isomers rather than open chain structures: this observation is consistent with the fructose solution tautomeric equilibrium with neutral fructose pyranose being the preponderant species. Water molecules also tend to form water-water hydrogen bond networks, interacting with OH groups at (1), (2), and (3) positions for neutral pyranose conformations.

In order to draw comparisons between the behavior of different monosaccharides with regard to cluster formation with, and solvation by water, microscopic hydration studies of sugar are also explored in our laboratory employing the same techniques reported herein. Ribose+$H_2O_{1,2...}^-$ cluster anions are, however, not observed in the TOFM spectrum. Such absence can possibly be understood from the point of view of the solubility of the different monosaccharides in water. Fructose (a ketohexose) has a very high solubility in water (> 3×10^3 g/L @ 25 °C), while the solubility of ribose (an aldopentose) in water is comparatively relatively quite low (~ 100 g/L @ 25 °C) for any monosaccharide. The absence of ribose+$H_2O_{1,2...}^-$ cluster anions, but the presence of fructose+$H_2O_{1,2...}^-$ cluster anions, implies a stronger interaction between fructose and water than between ribose and water. Such behavior is consistent with both the present reported cluster and solubility data. Additionally, the ribose parent anion is not observed in the present experiments, but the fructose parent anion is, implying that the ribose parent anion is not as a stable species as the fructose parent anion. Thus, ribose+$H_2O_{1,2...}^-$ clusters might not be expected to exist in the present experiments, based on the low concentration of its parent anion.

Saccharide phosphates

Ribose phosphate and fructose phosphate are studied employing the same techniques, and no parent anionic species are observed in the mass spectra but some fragmentation ions PO_2^-, PO_3^- and $C_5O_5H_8^-$ for both saccharide phosphates are observed. For both saccharide phosphate anionic parent species, the NBO/HSOMOS analysis shows that the open chain structures exhibit excess electron valence bound character, but furanose phosphates display excess electron as dipole bound. The dipole bound electron mainly diffuses on sugar moiety in ribose phosphate but on phosphate group in fructose phosphate. $C_5O_5H_8^-$ can be formed from ribose phosphate through loss of one phosphate group (PO_3H_2) and one H atom of sugar OH group. $C_5O_5H_8^-$ is formed from fructose phosphate with loss of one phosphate group and one CH_2OH unit, which damages the sugar moiety. Thus, we suggest that fructose is not protective, but that ribose is.

Ammonium nitrate

From PES experiments in conjunction with DFT calculations, the electronic and geometric structures of gas phase, isolated ammonium nitrate related anionic species, as well as their hydrogenated species with up to five added hydrogens are investigated. These species are directly generated by laser ablation and cooled in a

supersonic expansion. Their vertical detachment energies (VDE: $E_{neutral} - E_{anion}$, both at the anionic geometry) are experimentally determined and the corresponding anionic structures are characterized and assigned through calculations. Based on the experimentally evaluated calculation algorithm, the corresponding neutral structures are also determined. The parent anionic species exists as $(NH_2OH●HONO)^-$ in the gas phase with the extra electron valence bound. Crystal structure anion $NH_4NO_3^-$ is not present in our experiments, as within this structure the extra electron is dipole bound (electron affinity ~ 0 eV). The isomerization must therefore occur for ammonium nitrate upon capturing an extra electron or during the laser ablation process itself. The ammonium nitrate anion is apparently a very reactive species. The calculated global minimum for the isolated parent neutral species has an $HNO_3●NH_3$ structure, different from the crystal structure in the bulk phase. The hydrogenated cluster anions can evolve from the parent $(NH_2OH●HONO)^-$ species and exhibit moieties, which bind together as a single unit through interactions between noncovalently bonded species and are stable on the experimental timescale. The hydrogenation process forms stable moieties in the cluster anions, including water (H_2O), nitroxyl (HNO), ammonia (NH_3), or (HNOH). The calculated global minimum structures for hydrogenated cluster neutrals (NH_4NO_3 + nH, n = 1,…,5) contain ammonia and water, along with stable moieties (HONO, NO, and HNO). These stable moieties, along with intermediate species NO_2H_2 and ONH_2, offer new insights into the behavior of ammonium nitrate energetic materials.

Ammonium perchlorate and ammonium dihydrogen phosphate

No parent related species exit in the experiments, but fragmentation ions with loss of H_2O and further loss of an NH_2 group to form ClO_3 anion from ammonium perchlorate. Similarly, only dissociation ions are present in the mass spectrum of ammonium dihydrogen phosphate by losing H_2O and further losing NH_4 to form PO_3 anion. The parent anions are calculated to be dipole bound. All the calculated VDEs of fragmentations ions exceed the 266 nm photon energy. The dissociation pattern characteristics of ammonium perchlorate and ammonium dihydrogen phosphate anions can occur through loss of an H_2O unit first.

Overall, reflectron TOF mass spectrum combined with anion photoelectron spectroscopy, supported by DFT calculations, is an excellent, forefront set of techniques for the elucidation of properties of selected ions, neutrals, their kinetic/dynamic interchanges, and chemistry through obtaining and comparing

VDE/EA. Structural details can be accessible with regard to intermolecular hydrogen bonding, cyclic furanose and pyranose as well as open chain structures for saccharides. Further structural and chemical information can be obtained for isomeric and newly detected, reactive and reacted species for organic and inorganic ions and neutrals.