

PHYS 1 [752881]: State- and orbital-dependent functionals leading to a new generation of density-functional methods

Andreas Görling, Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstr. 12, D-53115 Bonn, Germany, Fax: (++49-228) 73-9064, goerling@thch.uni-bonn.de

Abstract

Density-functional methods using state and orbital-dependent functionals are introduced. A new view on the Kohn-Sham formalism is given. It is demonstrated that state- and orbital-dependent functionals solve long-standing shortcomings of Kohn-Sham methods like the presence of unphysical Coulomb self-interactions or the problem of properly treating open-shell systems. By going beyond the traditional formalism based on the Hohenberg-Kohn theorem excited states can be treated self-consistently in a Kohn-Sham like manner. The perspective of orbital-dependent functionals in time-dependent density-functional theory is discussed.

PHYS 2 [755739]: Ab initio DFT: Progress, problems, and potential

Rodney J Bartlett, Victor Lotrich, and Igor Schweigert, Quantum Theory Project, University of Florida, 2301 NPB #92, Box 118435, Museum Ave & B North-South Drive, Gainesville, FL 32601, Fax: 352-392-8722, bartlett@qtp.ufl.edu

Abstract

In our efforts to obtain a correlated (one-particle) orbital theory for chemistry, we have devoted much attention to the interconnections between density functional theory and wavefunction theory. The latter provides us with a converging series of approximations from MP2, thru CCSD(T) and CCSDT, to Full CI. DFT, on the other hand, whether local, gradient corrected, or hybrid; does not provide such a series of converging approximations because its energy functional, E_{xc} is not known. By combining orbital dependent energy expressions from wavefunction theory (WFT), we can bypass this limitation in traditional DFT to provide a series of systematically improving approximations for the energy functional and its associated potential. The cornerstone of this procedure is the optimized effective potential (OEP) method that allows us to solve for the V_{xc} in a gaussian basis set (no numerical quadrature); use ab initio expressions for E_{xc} ; and achieve systematic convergence to the exact answer. These three elements constitute ab initio dft. A series of applications to a wide variety of problems, including potential energy curves, weak interactions, photoelectron spectra, and electronic excited states will be presented to demonstrate the current capabilities and limitations.

PHYS 3 [752798]: Interaction energies from a symmetry-adapted perturbation theory based on density functional theory

Alston J. Misquitta, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, United Kingdom, Fax: 44-1223-336-362, am592@cam.ac.uk

Abstract

We describe a symmetry-adapted perturbation theory based on a density functional description of monomers that is capable of accurately recovering the interaction energy at intermediate and short distances at low computational cost. In this method, termed as SAPT(DFT), the electrostatic and exchange energies are computed using lowest-order symmetry-adapted

perturbation theory with Hartree-Fock orbitals and orbital energies substituted by the Kohn-Sham counterparts [Misquitta and Szalewicz, Chem. Phys. Lett. 357, 301 (2002)]. The dispersion energy is obtained utilizing a generalized Casimir-Polder formula and frequency-dependent density susceptibilities of monomers from time-dependent density functional theory [Misquitta, Szalewicz, and Jeziorski, Phys. Rev. Lett. 91, 33201 (2003)], and the induction energy utilizing static density susceptibilities. We show that SAPT(DFT) provides all interaction energy components at accuracies comparable to or exceeding those obtained using current sophisticated wave function based methods, however, at a small fraction of the computational cost, particularly if density-fitting algorithms are used.

PHYS 4 [753860]: Combination of wavefunction and density functional methods: CAS-DFT - the problem of double counting electron correlation

Dieter Cremer and Jürgen Gräfenstein, Department of Theoretical Chemistry, University of Göteborg, Reutersgatan 2, Göteborg S-41320, Sweden, Fax: +46-31-7735590, Cremer@theoc.gu.se

Abstract

DFT with the approximate functionals in use accounts only for dynamic electron correlation. Non-dynamic effects can be brought in by merging wavefunction theory (WFT) with DFT. Non-dynamic electron correlation is described by the complete active space method using an active space of relative small dimension. Then dynamic correlation is added via the correlation functional thus yielding CAS-DFT. This appears rather simple, however bears a major problem: In CAS-DFT, dynamic correlation is included both by the active space description and by the DFT correlation functional because there is no clear separation between the two types of electron correlation. This leads to a double counting problem of correlation effects. Strategies are discussed to circumvent this and other problems of a CAS-DFT description.

PHYS 5 [747983]: Toward electron-molecule scattering from time-dependent density functional theory

Adam Wasserman¹, Neepa Maitra², and **Kieron Burke**². (1) Department of Chemistry and Chemical Biology, Rutgers, 610 Taylor Rd., Piscataway, NJ 08854, awasser@rutchem.rutgers.edu, (2) Department of Chemistry, Rutgers University, 610 Taylor Road, Piscataway, NJ 08544, Fax: 732-445-5312, kieron@rutchem.rutgers.edu

Abstract

An approach to low-energy electron-molecule scattering based on the linear response formalism of time-dependent density functional theory is given. Exact formulas to extract the transmission amplitude from the susceptibility in one-dimension are tested on a simple model. Scattering from the ground-state Kohn-Sham potential of the neutral atom can be a good approximation at low energies, as shown in electron-He⁺ scattering. The TDDFT corrections are calculated in the limit of zero energy, and yield good results.

PHYS 6 [765070]: A novel current-density functional approach to the electron transport through a molecular electronic device

Sergey N. Maximoff¹, Matthias Ernzerhof², Juan E. Peralta¹, and Gustavo E Scuseria¹. (1) Department of Chemistry, Rice University, 6100 S. Main St., MS-60, Houston, TX 77005, (2) Department of Chemistry, University of Montreal

Abstract

We present a novel physically motivated formalism to model the steady electron transport in a molecular electronic device. In contrast to the techniques routinely utilized in molecular electronics, our method relies on the current-density functional theory rather than on the intricate non-equilibrium Green's functions apparatus. Our approach requires in practice the unknown current-dependent exchange correlation energy functional of a conducting molecule to be approximated. In order to investigate the impact of the current-dependence of the exchange-correlation energy on the conductivity of a few realistic systems, we employ our recent non-empirical current-dependent jPBE functional [Maximoff S.N., Ernzerhof M., Scuseria G. E., J. Chem. Phys. 120, 2105 (2004)] along with several common current-independent approximations.

PHYS 7 [767634]: Non equilibrium catalysis of single enzyme molecules

Rudolf Rigler, Lars Edman, Stefan Wennmalm, Marcel Leutenegger, Tiemo Anhut, and Theo Lasser, Karolinska Institutet, Stockholm SE-17177, Sweden, rudolf.rigler@mbb.ki.se

Abstract

Product formation by single molecule enzyme catalysis (1,2) under non equilibrium condition has been shown to lead to periodic oscillations observed both in experiment (2) as well as in stochastic simulations (3). The situation of catalysis close (Michaelis Menten regime) as well as far from equilibrium will be discussed as well as its implication for the selection of catalytic pathways (memory). New experimental single molecule data obtained in volume elements below the diffraction limit (4) and its implication for single molecule analysis will be presented

PHYS 8 [748428]: New molecule spectroscopy: Photon counting histogram for one-photon excitation

Richard N Zare, Thomas D Perroud, and Bo Huang, Department of Chemistry, Stanford University, S.G. Mudd Building, Stanford, CA 94305-5080, Fax: 650-723-9262, zare@stanford.edu

Abstract

In 1999 Chen, Mueller, So, and Gratton introduced the Photon Counting Histogram (PCH) technique to account for the fluctuations in fluorescence amplitude for molecules diffusing through a confocal laser focus. This method was first applied to two-photon fluorescence excitation. PCH was able to determine two parameters for each fluorescent species present: the average number of particles in the observation volume, N , and the molecular brightness, e . Chen et al. suggested that the same analysis procedure could be applied to one-photon excitation by using a three-dimensional Gaussian profile to describe the observation volume; however, we

have found that this profile is unable to fit the data under many reasonable conditions. We present an alternative model based on the correction to the 3D Gaussian profile. This procedure is able to fit the data, is easy to implement, and appears to be quite robust.

PHYS 9 [755349]: Single molecule spectroscopic investigations of the coil-to-helix transition for model peptide systems

Douglas English¹, Joy A Cunningham², and Kenji Okamoto¹. (1) Department of Chemistry and Biochemistry, University of Maryland, Bldg 091, College Park, MD 20742, denglish@mail.umd.edu, (2) Department of Chemistry and Biochemistry, University of Maryland, College Park

Abstract

We are using single molecule spectroscopy to examine the coil-helix transition in model peptide systems. Specifically, we investigate solvent- and surface-induced folding of helix forming peptides with single-molecule fluorescence resonance energy transfer. These experiments yield peptide conformational distributions which are analyzed to yield properties of the free energy surface for helix formation at an interface relative to formation in solution.

PHYS 10 [744055]: Fluorescence nanoscopy through reversible optically saturable transitions

Stefan W. Hell, Volker Westphal, Marcus Dyba, and Lars Kastrup, NanoBiophotonics, Max-Planck-Institute for Biophysical Chemistry, Am Fassberg 11, 37077 Göttingen, Germany, Fax: +49-551-2011085, hell@4pi.de

Abstract

We discuss the principle of breaking the diffraction barrier through reversible saturable optical transitions. We give first evidence of STED-microscopy displaying a point spread function of <20 nm FWHM, corresponding to a 15-fold enlargement of the optical transfer function (OTF) over Abbe's barrier. The success of STED stems from the fact that the saturation of the single-photon transition of stimulated emission provides strong nonlinearities at comparatively *low* intensities. The reason for that is simple but critical: Unlike in multiphoton events, the nonlinearity produced by saturation does *not* rely on the joint action of multiple photons, but stems from the population kinetics of the fluorophore states. Hence transitions that are easy to saturate. (i.e. with low I_{sat}), allow huge I/I_{sat} at low intensities. In consequence, in 1995 we have proposed as a further option to STED, the saturation of the triplet state, which reduces I_{sat} by $\sim 10^3$, and also the 'switching' between conformational fluorophore states, which gives another factor of 10^3 . We have proposed that such saturable switches are encountered in photochromic compounds and photoswitchable GFP-like proteins such as *asFP*, which should render nanoscale resolution with the ultralow intensities of a lamp. Finally, we show that a slightly modified version of our concept may serve as an alternative to the current X-ray and synchrotron efforts in nanolithography with the potential of providing material (nano)structures of any size and density with visible focused light.

PHYS 11 [751191]: Alfa1-antitrypsin polymerization: A fluorescence correlation spectroscopic study

Pradipta Purkayastha, Jason W. Klemke, Stacey Lavender, Barry Cooperman, and **Feng Gai**, Department of Chemistry, University of Pennsylvania, 231 S. 34th St., Philadelphia, PA 19104, pradiptp@sas.upenn.edu, gai@sas.upenn.edu

Abstract

Alfa1-antitrypsin (AT) is the most abundantly circulating human proteinase inhibitor in the serpin family. The polymerization of AT, leading to a1-antitrypsin deficiency, has been studied extensively in vitro by a variety of ensemble methods. To gain further insight into the understanding of this process, we studied the heterogeneity of AT polymerization by employing fluorescence correlation spectroscopy (FCS). Our measurements of the distribution of diffusion times of polymerizing AT, carried out at 45, 50 and 55 C, clearly show the existence of a kinetic lag phase, during which short oligomers are formed, prior to the formation of longer polymers, and suggest that long polymers, which appear to be metastable, are produced through the condensation of shorter oligomers.

PHYS 12 [755174]: Oriented nanostructures from single molecules of conducting polymers

Michael D Barnes, Department of Chemistry, University of Massachusetts, 710 N. Pleasant St, Amherst, MA 01003-9336, barnesmd1@ornl.gov, Robert M Dickson, Department of Chemistry and Biochemistry, Georgia Institute of Technology, Pradeep Kumar, Department of Chemistry, University of Tennessee, and Adosh Mehta, Life Sciences Division, Oak Ridge National Laboratory

Abstract

Semiconducting polymers and water-soluble variants are beginning to attract attention in biological imaging applications. However, a number of issues related to poor control over inter- and intra-chain organization of these materials limit key aspects of the fluorescence that are important for such applications – namely robust photostability, well defined polarization signature, and narrow bandwidth luminescence. Recent work in our laboratory has explored the effects of 3-dimensional confinement on the self-organization of single chains of conjugated polymers used commonly in polymer LEDs. Isolated in tiny droplets of dilute polymer solution and allowed to dry en route to a glass substrate, these nanoscale species (roughly the size of a protein) adopt structural, spectroscopic, and photophysical properties that are markedly different than those of their (well-studied) thin-film counterparts suggesting practicability in novel imaging applications.

PHYS 13 [742073]: Applications of single molecule fluorescence coincidence spectroscopy

Haitao Li, Liming Ying, Shankar Balasubramanian, and David Klenerman, University Chemical Laboratory, Cambridge University, Lensfield Road, Cambridge, United Kingdom, lh286@cam.ac.uk

Abstract

We have recently developed a new form of single molecule spectroscopy which we have called Single Molecule Fluorescence Coincidence Spectroscopy (SMFCS)[1]. The approach detects

coincident bursts of fluorescence from a single molecule, or complex, labelled with two different fluorophores, when excited by two focused and overlapped lasers. This method significantly extends the sensitivity of the single molecule approach and allowed detection of dual-labelled species at femtomolar concentrations. SMFCS was recently exploited to detect dimerisation of the RNA component of human telomerase [2].

We have extended the method to probe intramolecular dynamics, in solution, on the sub-millisecond time scale. We firstly validated the method using a DNA hairpin and then measured local RNA motion in hTR dimer. We have also applied SMFCS to measure antibody-antigen, protein-DNA and antibody-virus interactions to determine the stoichiometry of the complex formed, the equilibrium constants and dissociation rate. These results demonstrate the wide applicability of the method.

1. Li, H., Ying, L. M., Green, J. J., Balasubramanian, S., Klenerman, D., Ultrasensitive Coincidence Fluorescence Detection of Single DNA Molecules, *Anal. Chem.*, 75, 1664-1670 (2003).

2. Ren, X., Gavory, G., Li, H., Ying, L. M., Klenerman, D., Balasubramanian, S., Identification of a new RNA•RNA interaction site for human telomerase RNA (hTR): structural implications for hTR accumulation and a dyskeratosis congenital point mutation.” *Nucleic Acids Res.*, 31, 6509-6515 (2003).

PHYS 14 [753955]: Collisional energy transfer in atmospheric chemistry

Neil M. Donahue¹, Bao Chuong², Albert Presto², and Jieyuan Zhang². (1) Departments of Chemistry and Chemical Engineering, Carnegie Mellon University, Doherty Hall, Pittsburgh, PA 15213, Fax: 412-268-7139, nmd@andrew.cmu.edu, (2) Department of Chemical Engineering, Carnegie Mellon University

Abstract

Collisional energy transfer can be a critical process governing the behavior of atmospheric chemical mechanisms. This is especially true for substantially exothermic reactions producing highly chemically activated products. Two example systems are ozonolysis and the formation of organic nitrates. In each case, the exact reactive intermediates remain elusive, and in each case yields of important reaction products (OH radicals, organic aerosol, organic nitrates, etc) can vary substantially with pressure, temperature, and the size (carbon number) of the system. We shall explore these issues for each system, combining computational potential energy surfaces, master equation simulations of the statistical reaction dynamics, and experimental measurements of reaction product yields. We shall pay particular attention to the behavior of mechanisms over a wide range of carbon numbers, from small systems, which often have direct global significance (ie, methyl nitrate formation), to large systems, which are very short lived but play a critical role in atmospheric aerosol formation. In some cases, such as nitrate formation, increased carbon number simply forces systems to a predictable high-pressure asymptote. In others, however, such as endocyclic alkenes, increased carbon number can lead to a qualitative change in the reaction mechanism. The broad implications of these findings to problems of atmospheric chemistry will be discussed.

PHYS 15 [755525]: Formation of nitrous acid in the urban nocturnal boundary layer

Jochen Stutz, Shuhui Wang, and Stephen C. Hurlock, Department of Atmospheric Sciences, University California Los Angeles, 7127 Math Sciences, Los Angeles, CA 90095-1565, jochen@atmos.ucla.edu

Abstract

Nitrous acid, HONO, is an important OH radical precursor in the troposphere. Recent studies indicate that HONO photolysis can contribute up to 30% to the diurnally averaged OH formation in polluted areas. While laboratory studies have shown that HONO is formed from the heterogeneous conversion of NO₂ on various surfaces, the behavior of HONO in the atmosphere often differs from laboratory observations. Here we investigate the atmospheric nocturnal NO₂ to HONO conversion based on field experiments from various urban locations in the United States, and modeling studies that consider the mix of surfaces present in urban areas, i.e. building roofs and walls. Observations and model results are compared to test various heterogeneous chemical mechanisms, and to derive new quantitative information on the conversion efficiency. We will also discuss whether the heterogeneous NO₂ to HONO conversion can explain observations of elevated HONO levels during the day in urban areas.

PHYS 16 [755783]: Isomerization of peroxyxynitrites to nitrates: A theoretical approach

John F Stanton, Department of Chemistry, University of Texas, Austin, TX 78712, stanton@jfs1.cm.utexas.edu

Abstract

The focus of this talk will be on a mechanism for the unimolecular isomerization of a peroxyxynitrite (ROONO) to the corresponding nitrate (RONO₂). While the lowest energy pathway for this process is actually via dissociation and recombination, consideration of atmospheric conditions renders the bimolecular approach untenable for the observed formation of nitrates via the reaction of ROO and NO. The mechanism suggested involves a strongly avoided crossing of curves and is described in terms of a diabatic set of states. Molecular geometries and other properties pertinent to spectroscopic characterization and quantification of the ROONO species will also be briefly reviewed.

PHYS 17 [746910]: Spectroscopy and kinetics of large alkoxy radicals

Theodore S. Dibble, Chemistry Department, SUNY-Environmental Science and Forestry, 1 Forestry Drive, Syracuse, NY 13210, Fax: 315-470-6856, tsdibble@mailbox.syr.edu

Abstract

Alkoxy radicals are critical intermediates in atmospheric chemistry. They can react by multiple reaction pathways, both unimolecular and bimolecular, which renders them fascinating targets for experimental and theoretical investigation. Here we focus on our experimental studies of the electronic spectroscopy and kinetics of cyclohexoxy radical (normal and deuterated) and 3- and 4-methylcyclohexoxy radicals. We have obtained the laser-induced fluorescence spectra of

radicals in the near-UV, and obtained rate constants for their reaction with O₂. Arrhenius parameters for this reaction are quite different from those reported previously for smaller (acyclic) alkoxy radicals. We also report preliminary spectra of alkoxy radicals possessing hydroxy substituents, which likely form intramolecular hydrogen bonds to the radical center.

PHYS 18 [753444]: Infrared spectroscopy and unimolecular decay dynamics of HOONO

Marsha I. Lester, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, Fax: 215-573-2112, milester@sas.upenn.edu

Abstract

The atmospheric conversion of OH and NO₂ radicals into stable nitric acid (HONO₂) by a three-body association reaction is of fundamental importance because it terminates several significant catalytic cycles that destroy ozone in the stratosphere as well as chain reactions that produce smog in the troposphere. Several groups have suggested that peroxyxynitrous acid (HOONO), a less stable isomer of HONO₂, may be a significant secondary product of this reaction under atmospheric conditions. We have identified the *trans-perp* (tp) conformer of HOONO by infrared action spectroscopy in the OH overtone region after photolytically generating HOONO a pulsed supersonic expansion. Extensive rotational band structure associated with the OH overtone transition yields structural parameters and transition dipole moment, which are in good accord with *ab initio* values. The internal energy distribution of the OH fragments is consistent with a prior dissociation, and enables an accurate determination of the HOONO binding energy.

PHYS 19 [755029]: *Cis-cis* and *trans-perp* HOONO: Action spectroscopy and isomerization kinetics

Juliane L. Fry¹, Sergey A. Nizkorodov², Mitchio Okumura³, Coleen M. Roehl⁴, Joseph S. Francisco⁵, and Paul O. Wennberg⁴. (1) Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125, Fax: 626-585-1917, fry@caltech.edu, (2) Department of Chemistry, University of California at Irvine, (3) Division of Chemistry and Chemical Engineering, California Institute of Technology, (4) Division of Geology and Planetary Science, California Institute of Technology, (5) Department of Chemistry, Purdue University

Abstract

The weakly-bound HOONO product of the OH + NO₂ + M reaction is studied using the vibrational predissociation that follows excitation of the first OH overtone (2ν₁). We observe formation of both *cis-cis* and *trans-perp* conformers of HOONO. Thermally less stable *trans-perp* HOONO isomerizes rapidly to *cis-cis* HOONO with a temperature dependence in the range 223 – 238 K that yields an isomerization barrier of 33 ± 12 kJ/mol. *Ab initio* calculations at the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ level and RRKM simulations suggest a *perp-perp* HOONO (transition state) energy of ΔE₀ = 42.4 kJ/mol and 40.8 kJ/mol, respectively, above *trans-perp* HOONO. Quantum yield of HOONO dissociation is predicted to vary from 0.1 to 1 over the observed spectrum, leading to highly temperature-dependent band intensities; however, the observed relative band strengths in the *cis-cis* HOONO spectrum do not change substantially over the range 193 - 273 K. Semi-empirical calculations of the oscillator strengths for 2ν₁(*cis-cis* HOONO) and 2ν₁(*trans-perp* HOONO) are performed using a one-dimensional anharmonic

model and *ab initio* dipole moment functions at the B3LYP/AUG-cc-pVTZ, MP2/AUG-cc-pVTZ, and MP3/AUG-cc-pVDZ levels of theory. The calculated ratio of $2\nu_1$ oscillator strengths of *trans-perp* to *cis-cis* HOONO is 3.4:1. Observed band intensities indicate that the concentration of *trans-perp* HOONO early in the OH + NO₂ reaction is significantly greater than predicted by a Boltzmann distribution. In the atmosphere, *trans-perp* HOONO will isomerize nearly instantaneously to *cis-cis* HOONO. Loss of HOONO via photodissociation in the near-IR limits the lifetime of *cis-cis* HOONO during daylight to less than 40h; other loss mechanisms will reduce it further.

PHYS 20 [752782]: AEI: Organonitrate formation in the atmosphere: A unimolecular mechanism for pernitrite isomerization, ROONO → RONO₂

John M. Herbert¹, Anne B. McCoy², Peter G. Szalay³, John F. Stanton³, and G. Barney Ellison⁴. (1) Department of Chemistry, University of California, Berkeley, CA 94720-1460, Fax: 510-643-1255, herbert@bastille.cchem.berkeley.edu, (2) Department of Chemistry, The Ohio State University, (3) Departments of Chemistry and Biochemistry, University of Texas at Austin, (4) Dept. Chem & Biochem, University of Colorado

Abstract

A mechanism is presented that explains the reaction dynamics of ROO + NO, including a unimolecular isomerization pathway ROONO → RONO₂ leading to the formation of organonitrates. When an organoperoxy radical ROO reacts with nitric oxide under atmospheric conditions, the initially-formed pernitrite adduct ROONO may decompose to RO + NO₂ or isomerize to form RONO₂; the latter pathway serves as a sink for radicals in the tropospheric ozone cycle. Our proposed mechanism is based on high-level electronic structure calculations, by means of which we have located for the first time an energetically plausible transition state for the nitrite to nitrate isomerization. The mechanism is represented conveniently in terms of quasi-diabatic states of NO₂ and may be quite general. Classical and quantum dynamics calculations on the model system FO + NO confirm its feasibility and establish estimated rate constants for the two competing product channels.

PHYS 21 [751284]: Water structure and bonding at hydrophobic surfaces

Geraldine L. Richmond, Department of Chemistry, University of Oregon, 1253 University of Oregon, Eugene, OR 97403-1253, Fax: 541-346-5859, richmond@darkwing.uoregon.edu

Abstract

The structure and hydrogen bonding of water molecules provides this unique solvent with properties essential to many physical, chemical and biological processes. At a water surface the intermolecular hydrogen bonding which is so prevalent in the bulk liquid or ice is disrupted in a manner which makes the surface properties of water distinctly different from the properties in the bulk phase. The focus of this presentation is on vibrational sum frequency studies of the structure and hydrogen bonding of water at hydrophobic surfaces including the air/water interface, a variety of organic/water and monolayer/water interfaces. The results, when combined with molecular dynamics simulations, provide a fascinating picture of how water bonds, orients and interacts with the adjacent hydrophobic liquid surface.

PHYS 22 [744627]: X-ray studies of long-chain surfactants at the water-hexane interface

Mark L Schlossman, Department of Physics, University of Illinois at Chicago, 845 W. Taylor St. M/C 273, Chicago, IL 60607, Fax: 312 996 9016, schloss@uic.edu

Abstract

X-ray scattering and interfacial tension measurements are used to study molecular ordering and phase transitions in monolayers of long chain (30 carbon) n-alkanols and n-alkanoic acids at the water-hexane interface. The x-ray measurements provide detailed information about the electron density as a function of interfacial depth. This density can be interpreted in terms of order along the surfactant alkyl chain and water ordering near the surfactant headgroup. Near room temperature triacontanol forms a monolayer with disordered chains and water penetration into the headgroup region. With increasing temperature the alkanols undergo a transition in which they desorb from the interface. In contrast, recent data indicate that triacontanoic acid forms ordered monolayers at room temperature that undergo a transition to disordered liquid-like monolayers at higher temperatures. Since the alkyl chain tailgroups for these two surfactants are the same, the differences must be attributed to the headgroup interactions.

PHYS 23 [755519]: Coherent time-resolved vibrational spectroscopy of surfaces and interfaces

Andrey Bordenyuk and **Alexander V. Benderskii**, Department of Chemistry, Wayne State University, Detroit, MI 48202, Fax: 313-577-8822, anb@chem.wayne.edu, alex@chem.wayne.edu

Abstract

Time- and frequency-domain 3-wave mixing (IR+visible Sum Frequency Generation, SFG) spectroscopies are presented as the lowest-order nonlinear spectroscopic techniques that are both surface-selective and capable of measuring vibrational coherences. Langmuir-Blodgett monolayers of heptadecanoic acid were studied as a model system. In the frequency domain SFG, two distinct bands are observed, the CH₃ symmetric stretch ($\nu_{SS}=2935\text{ cm}^{-1}$) and Fermi resonance of the CH₃-stretch and CH₂-bend overtone ($\nu_{FR}=2875\text{ cm}^{-1}$). In the time-domain, a 70 fs IR pulse excites the vibrational coherence, and a delayed 40 fs visible pulse monitors its Free Induction Decay (FID) by upconverting the oscillating surface polarization into the SFG signal. For the first time, vibrational quantum beats on surfaces are experimentally observed as damped oscillations (540 fs period) at the difference frequency between the two $\nu(\text{CH})$ modes. A model calculation connects the frequency- and time-domain measurements. A mixed time-frequency domain version of this technique, frequency-resolved SFG-FID, is applied to study dynamics of the hydrogen bond network of interfacial water. Along with the vibrational dephasing, we observe ultrafast spectral diffusion of the OD stretch of D₂O at the CaF₂ surface, indicating the H-bond rearrangement on the sub-50 fs time scale. The effect of the interfacial electric field on the H-bonding patterns and dynamics of water will be discussed.

PHYS 24 [751858]: Cluster studies of the local hydration environments of protons, hydroxide ions, and excess electrons

Mark A. Johnson, Sterling Chemistry Laboratory, Yale University, New Haven, CT 06520-8107, mark.johnson@yale.edu

Abstract

We use infrared spectroscopic methods to characterize the intramolecular deformations of water molecules in contact with various ionic species isolated as cluster ions. In this presentation, we will focus on systems where the fabric of a water molecule is compromised in that the hydration involves significant inter-water proton transfer. Particular attention will be given to larger protonated water clusters, which are thought to involve clathrate structures around the pronounced "magic number" at $n=21$. The vibrational spectra obtained for this system are remarkably similar to that obtained for the liquid water-air interface via sum-frequency methods, and we will discuss the implications of this observation.

PHYS 25 [750267]: Simulations of charge transfer processes in nano-confined polar solvents

Ward H. Thompson, Department of Chemistry, University of Kansas, Lawrence, KS 66045, wthompson@ku.edu

Abstract

There has recently been increasing interest in the chemical dynamics of solvents confined in nanostructured materials. Ultimately one would like to design nanostructured materials adapted for specific reactive or spectroscopic purposes, e.g., catalysis or sensing, by controlling the cavity/pore size, geometry, and surface chemistry. However, our understanding of chemistry in solvents is still relatively limited. Simulation studies aimed at addressing this issue will be presented. Specifically, charge transfer processes (e.g., optical spectra and proton transfer) that are strongly coupled to the solvent dynamics (and thus should exhibit pronounced changes upon confinement) will be considered. The effect of cavity size and shape on the spectra, dynamics, and reaction energetics will be discussed.

PHYS 26 [766986]: Probing molecular adsorption and structure at the liquid-solid interface in colloids by optical second harmonic generation

Heather M. Eckenrode¹, Shih Hui Jen¹, Jun Han¹, and Hai Lung Dai². (1) University of Pennsylvania, Philadelphia, PA 99999, schwartz@chem.ucla.edu, (2) Department of Chemistry, University of Pennsylvania

Abstract

Second Harmonic Generation (SHG), a phenomenon highly sensitive to symmetry, can be used to characterize the adsorption of molecules on microparticles in colloidal solutions. Adsorption free energy, density, and geometric configuration of molecules adsorbed at the liquid-solid interface can be determined. The adsorption behavior of two systems will be discussed. The adsorption of poly-l-lysine polymer on polystyrene microspheres was found to be greatly affected by the charge-charge repulsion between the biopolymers. The adsorption of a positively charged dye, malachite green, on three types of polystyrene microsphere surfaces are characterized: sulfate terminated (anionic), amine terminated (cationic) and a neutral surface without any functional group termination. The cationic dye was found to adsorb at all three

surfaces with different density and adsorption configurations, resulting from the interplay between adsorbate-adsorbate and adsorbate-surface interactions.

PHYS 27 [751647]: Forward-backward semiclassical dynamics of quantum fluids

Nancy Makri, Department of Chemistry, University of Illinois, 601 S. Goodwin Avenue, Urbana, IL 61801, Fax: 217-244-3186, nancy@makri.scs.uiuc.edu

Abstract

Recent progress on the development and application of forward-backward semiclassical methods will be presented. Forward-backward semiclassical dynamics (FBSD) provides a practical methodology for including quantum mechanical effects in classical trajectory simulations of polyatomic systems. FBSD expressions for time-dependent expectation values or correlation functions take the form of phase space integrals with respect to trajectory initial conditions, weighted by the coherent state transform of a corrected density operator. It is shown that the initial density in finite temperature expressions can be fully quantized by employing the discretized path integral representation of statistical mechanics, thus ensuring a proper treatment of zero point effects and capturing important imaginary components that are absent from purely classical trajectory methods. Accelerated convergence is achieved through the construction of accurate pair propagators in the coherent state representation of the initial density operator. Optimal sampling is achieved via Monte Carlo or molecular dynamics techniques. The methodology has been extended to systems obeying quantum statistics. Applications to quantum fluids will be presented.

PHYS 28 [750130]: Obtaining thermal rate constants from the zero time flux correlation function

William H. Miller, Cristian Predescu, Sandy Yang, and Michele Ceotto, Department of Chemistry, University of California, Berkeley, CA 94720, Fax: 510-642-6262, miller@cchem.berkeley.edu

Abstract

It is shown that higher order derivatives of the reactive flux correlation function at $t = 0$ can be efficiently computed by Monte Carlo path integral methods, and that these can be used to obtain accurate results for thermal rate constants. This approach can be viewed as an extension and generalization of the 'quantum instanton' model for thermal rates that has recently been developed. Various applications are presented to illustrate the approach.

PHYS 29 [753013]: Nonstationary dynamics: Theory and simulation

Rigoberto Hernandez, Marcus Vogt, Alexander Popov, and Yanping Qin, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, Fax: 404-894-7452

Abstract

A typical approach for simplifying the complex dynamics in chemical and biophysical processes involves the identification of a one- (or reduced) dimensional reaction path or order parameter characteristic of the dynamical event. Unfortunately such simplifications are often not possible

because the projection of the solvent onto the usual stochastic models presumes that the solvent response is linear. In order to begin to correct this limitation, phenomenological nonstationary generalizations of the generalized Langevin equation (GLE) have earlier been developed that satisfy the fluctuation-dissipation relationship in quasi-equilibrium limits while exhibiting somewhat complex behavior away from equilibrium. It has also been shown that such a formalism can approximately arise from the projection of a non-conservative Hamiltonian involving a uniform time-dependent coupling to a harmonic bath. The numerical simulations of the latter are now shown to obey the derived nonstationary statistical relationships. In addition, the nonstationary memory kernel for a hard-sphere system as well as a soft-sphere system are calculated under nonequilibrium conditions. These observations together with the recent theorems describing fluctuations in nonequilibrium systems obtained by Evans provide deeper insight into the deconstruction of systems with multiple time-scale dynamics.

PHYS 30 [752711]: Semiclassical calculation of quantum correlation functions

Peter J. Rossky¹, Jens Aage Poulsen², and Gunnar Nyman². (1) Institute for Theoretical Chemistry, Dept. of Chemistry & Biochemistry, University of Texas at Austin, MC A5300, Austin, TX 78712, Fax: 512-471-1624, rossky@mail.utexas.edu, (2) Department of Chemistry, Goteborg University

Abstract

Considerable progress has been made in developing practical approximate methods for calculating the dynamics of many-body quantum systems. However, the time regime and Hamiltonian models that are accessible at an acceptable level of accuracy and computational effort differ substantially among available methods. In this talk, a recently developed, highly computationally efficient approximation for obtaining quantum correlation functions which implements the so-called "classical Wigner" approximation will be discussed, and results obtained will be presented. The approach combines a Feynman-Kleinert variational effective frequency description with a linearized path integral expression to obtain the Wigner transform Boltzmann operator and correlation functions. Results for the structure, kinetic energy, and Van Hove correlation function of liquid Helium and for the structure and diffusion rate of liquid parahydrogen will be presented. Excellent agreement with available accurate theoretical and experimental results will be demonstrated for these anharmonic, many-body, liquid cases.

PHYS 31 [751111]: New advances in the centroid dynamics method for studying condensed phase quantum dynamics

Gregory A. Voth, Department of Chemistry & Henry Eyring Center for Theoretical Chemistry, University of Utah, 315 South 1400 East, Room 2020, Salt Lake City, UT 84112, Fax: 801-581-4353, voth@chem.utah.edu

Abstract

Recent advances in the Centroid Dynamics (CD) method will be described, including a treatment of electronically nonadiabatic dynamics, a formalism to combine the Semiclassical Initial Value Representation with CD (SC-IVR-CD), and two new and highly efficient algorithms for Centroid Molecular Dynamics (CMD) which make such simulations only somewhat more expensive than classical MD simulations for general problems. Representative applications to several interesting systems will also be described.

PHYS 32 [754105]: Toward a unifying formulation of coherent state theory for quantum molecular dynamics

Jorge A. Morales, Department of Chemistry and Biochemistry, Texas Tech University, PO Box 41061, Lubbock, TX 79409, Fax: 806-742-1289, jorge.morales@ttu.edu

Abstract

Coherent-state (CS) theory is emerging as a cutting-edge methodology for quantum molecular dynamics because it furnishes suitable overcomplete sets to represent functions and operators and permits expressing quantum equations of motion in a quasi-classical format. However, most of the research on CS has exclusively implicated the Glauber CS of the quantum harmonic oscillator to describe nuclear motions. Following pioneering work by Y. Öhrn and E. Deumens, we are systematically developing novel types of CS's for all molecular degrees of freedom (both nuclear and electronic) that are suitable for describing all types of motions (translational, rotational and vibrational; charge transfers). We present three illustrations of our unifying approach to CS theory: (1) An application of the Glauber and Thouless CS to simulate rearrangements and charge-transfer reactions in molecular collisions; (2) An innovative valence-bond/CS formulation of charge-equilibration models based on Sanderson principle; and (3) A CS formulation of the asymmetric rotor.

PHYS 33 [755392]: Quantum chemistry and the density matrix renormalization group

Steven R. White, Department of Physics and Astronomy, UC Irvine, Irvine, CA 92697, Fax: 949-824-2174, srwhite@uci.edu

Abstract

The density matrix renormalization group (DMRG) is a numerical method for finding the ground state of a many-body quantum system. Originally developed for one dimensional systems in solid state physics, DMRG has spread to a variety of other systems, such as two dimensional quantum lattice models, finite temperature classical statistical mechanics, nonequilibrium dynamical systems, nuclear physics, and ab initio quantum chemistry. In addition, its capabilities have grown steadily, most recently to include real-time dynamics. In this talk, I will give a pedagogical introduction to DMRG in the context of 1D models. Then, I will describe the application of DMRG to ab initio quantum chemistry. In the last part of the talk will present the latest developments in real-time dynamics, which have not yet been introduced into quantum chemistry DMRG.

PHYS 34 [748547]: New algorithms for the electronic Schrodinger equation

Garnet K. Chan, Department of Chemistry and Chemical Biology, Cornell University, Baker Lab, Ithaca, NY 148531301, gkc1000@hermes.cam.ac.uk

Abstract

We describe some fast algorithms, based on renormalization group ideas, for approaching the electronic structure problem.

PHYS 35 [762062]: Variational calculation of 2-electron reduced density matrices

David A Mazziotti, Department of Chemistry and the James Franck Institute, University of Chicago, Chicago, IL 60637, damazz@uchicago.edu

Abstract

Variational determination of the 2-electron reduced density matrix (2-RDM) without calculation of the N-particle wavefunction has recently been achieved for atoms and molecules. That the ground-state energy of N-electron systems may be expressed as a linear functional of the 2-RDM was discovered as early as 1940 by Husimi and rediscovered by Lowdin and Mayer, but a 2-RDM approach to N-electronic information eluded significant efforts because not every 2-particle density matrix may be derived from an N-electron wavefunction. Coleman described the required physical constraints on the 2-RDM as N-representability conditions. Advances in theory and computation have made possible the variational 2-RDM optimization of the ground-state energy. We will present a new semidefinite programming algorithm for the energy optimization and illustrate the formalism with chemical applications. Because the N-representability conditions are non-perturbative, the 2-RDM method is able to treat chemical problems with significant multireference correlation as in bond stretching and dissociation.

PHYS 36 [751459]: Structure of the exact wave function and a method of solving the Schroedinger equation

Hiroshi Nakatsuji, Department of Synthetic Chemistry and Biological Chemistry, Kyoto University, Kyoto-Daigaku Katsura, Nishikyo-ku, Kyoto 615-8510, Japan, Fax: -81-75-383-2741, hiroshi@sbchem.kyoto-u.ac.jp

Abstract

Solving the Schroedinger equation and the Dirac equation is a central theme of theoretical chemistry because of its scientific and practical importance. We have investigated the structure of the exact wave function and proposed the methods of calculating the exact wave function. Here, after briefly introducing these studies, I will propose the scaled Schroedinger equation that is equivalent to the original Schroedinger equation. It has the variational principle and the square theorem as the original one. Using the ICI (iterative CI) and ECC (extended (or extreme) coupled cluster) formalisms, we propose general systematic methods for calculating the exact wave functions of atoms and molecules. The nuclear and electron singularity problems no longer occur in these methods. Test applications to helium atom, hydrogen molecule and others are satisfactory, implying high potentiality of the proposed method.

PHYS 37 [753614]: Forum discussion: Alternate takes on the electron correlation problem

Werner Kutzelnigg, Chemistry, Ruhr University Bochum, Universitätsstraße 150, Bochum 44780, Germany

Abstract

A panel chaired by Prof. Werner Kutzelnigg will discuss the prospects of a variety of alternative approaches to the electron correlation problem. Topics of discussion include the direct

calculation of the one- and two-particle reduced density matrices, the density matrix renormalization group, compact exponential representations of the wave function, and mixed wave function - density functional methods.

PHYS 38 [772552]: Dynamic polymorphism of a cellular signal protein Ras studied by single molecule FRET: How does Ras interact with many effectors to regulate signaling pathways?

Y. Arai, M. Sugawa, A.H. Iwane, and **Toshio Yanagida**, Department of Physiology and Biosignaling, Osaka University Graduate School of Medicine, 2-2 Yamadaoka, 565-0871 Suita, Osaka, Japan, Fax: 81-6-6879-3628, yanagida@phys1.med.osaka-u.ac.jp

Abstract

Ras is a key protein in various cellular events such as proliferation, apoptosis and differentiation. Upon binding to GTP, Ras-GTP complex binds to various effector proteins such as Raf, RalGDS and PI3K. This new complex activates signaling pathways corresponding to the cellular events. However, it has not been well understood how Ras can interact with many effector proteins despite having only one effector binding site. Nor is it understood how Ras regulates multiple signaling pathways. In this study, we used a single molecule FRET technique to measure dynamic structures of Ras. H-Ras (1-171) was fluorescently-labeled at the 118th cysteine residue with Cy3 as a donor. Cy5-labeled GTP was used to activate H-Ras. FRET between Cy3-H-Ras and Cy5-GTP bound to Cy3-H-Ras was measured. Cy3-labeled H-Ras was bound to a glass surface. Cy3-H-Ras damage was prevented by the incorporation of antibodies. Single molecule FRET was measured by TIRFM (Funatsu, et al.'95). In order to exclude the blinking of fluorophores effect, Cy5 (acceptor) was excited every one frame (66 msec) and its fluorescence was monitored during the measurement of FRET. The FRET efficiency of Cy3-Ras-Cy5-GTP complexes varied between molecules. For in some cases, FRET efficiency fluctuated for a given molecule before photobleaching. This result strongly suggests that Ras can exist in multiple metastable states and undergoes slow transition between these states. The transition time is probably ten seconds. Interestingly, when H-Ras was mutated to bind to only one effector, Raf (T35S) or RalGDS (E37G), these mutants showed almost single values of FRET efficiency. Furthermore, when Raf bound to wild-type H-Ras, the H-Ras-Raf complex showed a similar value of FRET efficiency to that of the mutant H-Ras (T35S). These results suggest that each conformation corresponds to one effector.

PHYS 39 [753092]: Single molecule study of mechanisms of helicases

Ivan Rasnik, Sua Myong, Sean Mckinney, and Taekjip Ha, Department of Physics, University of Illinois, Urbana-Champaign, 1110 W. Green, Urbana, IL 61801, irasnik@uiuc.edu

Abstract

Single molecule Fluorescence Resonant Energy Transfer (smFRET) has proved to be a powerful technique to study biological systems. Helicases are enzymes that catalyze the unwinding of double stranded DNA into single stranded DNA. As an example of smFRET as a structural tool we show results of experiments on E. Coli Rep helicase. We use eight different Rep mutants site-specifically labeled with a fluorescent dye each, and a partial duplex DNA substrate that is labeled in one of three possible different locations. The dyes in the protein and in the DNA constitute a donor-acceptor FRET pair giving distance constrains for each labeled site in the

protein and each dye location on the DNA in separate experiments. Through a trilateration process and repeating the experiment in presence of ATP analogs it is possible to reconstruct the overall structure of the protein-DNA complex at the different stages of the ATP hydrolysis cycle. To exemplify the use of smFRET for kinetic experiments, we discuss results on the role of T7 helicase in branch migration. It has been shown recently that T7 helicase is able to catalyze branch migration in a 4 way DNA junction (Holliday junction). Labeling two opposite arms of a Holliday junction with a donor-acceptor pair allows us to follow the branch migration process in real time. Using 4 way junctions with different content of homologous and non-homologous regions we were able to show that unidirectional translocation of the hexameric helicase through the duplex region, biases the random walk of the homologous regions favoring the migration in one direction. Because of our few base pair resolution, we can detect single base heterologous regions that appear as stall points in the helicase catalyzed migration reaction.

PHYS 40 [752847]: Fast DNA translocation by FtsK: A force-rectified motor?

Omar A. Saleh¹, Jean François Allemand¹, and François Xavier Barre². (1) Laboratoire de Physique Statistique, Ecole Normale Supérieure, 24 Rue Lhomond, 75005 Paris, France, Fax: 33 1 44 32 34 33, oasaleh@lps.ens.fr, (2) Laboratoire de Microbiologie et de Génétique Moléculaire, CNRS UMR5100

Abstract

Escherichia coli FtsK is an essential cell division protein with a DNA translocase activity involved in chromosome segregation. The pumping action of FtsK must be biased to insure the DNA is moved through the closing septum in the correct direction; however, the underlying mechanism is unknown. We perform single-molecule measurements of translocation by FtsK_{50C}, a derivative shown to translocate on DNA in vitro. FtsK_{50C} translocation follows Michaelis-Menten kinetics, with an impressive maximum speed of ~6.7 kbp/s. We study the effect of applied force on the speed, distance translocated, and the mean times during and between protein activity. Surprisingly, we observe that FtsK_{50C} can spontaneously reverse its translocation direction, indicating that, in contradiction to previous hypotheses, DNA sequence alone does not determine the translocation direction. We conclude that in vivo polarization of FtsK translocation could require cofactors; alternatively, we propose a model in which tension in the DNA directs FtsK translocation.

PHYS 41 [748393]: Single-molecule mechanics and fluorescence polarization for real-time structural dynamics of conventional and unconventional myosins

Yale E. Goldman, Pennsylvania Muscle Institute, School of Medicine, University of Pennsylvania, Richards Bldg. D-700, Philadelphia, PA 19104-6083, Fax: 215-898-2653, goldmany@mail.med.upenn.edu

Abstract

In molecular motors, structural and kinetic parameters are modulated by the mechanical conditions. Single molecule fluorescence polarization techniques, combined with methods to insert fluorescent probes into macromolecules at known local orientation, and mechanical manipulation using optical traps are powerful approaches toward understanding this mechano-chemistry. A novel feedback optical trap allows precise maintenance of actin position when myosin attaches. The effective stiffness of the actin, determined by the characteristics of this

feedback loop, markedly influences the kinetics of actomyosin interactions. Tilting motions of calmodulin (CaM) bound to the neck region of myosin V provide strong support for a hand-over-hand mechanism for processive motility. Some translocating myosin V molecules don't tilt, suggesting that their angles in the leading and trailing positions are the same. The mechanistic implications of these non-tilting CaMs will be discussed. Work of many coworkers and collaborators and support by the NIH, NSF and MRC are gratefully acknowledged.

PHYS 42 [767620]: A local model for the dependence of DNA polymerization rate on mechanical tension, tested by molecular dynamics simulations

Dudley Herschbach, Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford St., Cambridge, MA 02138, Fax: 617-495-4723, herschbach@chemistry.harvard.edu

Abstract

The rate of replication of DNA catalyzed by a single enzyme molecule moving along a stretched template strand has been measured by means of tweezer techniques in the laboratories of Bustamante (Berkeley) and Bensimon (Paris). Theoretical analysis in collaboration with Goel and others [PNAS 98, 845 (2001); 100, 9699 (2003)] developed a "local model" to interpret the dependence of the rate on tension applied to the template. This model considers only enzyme-DNA interactions in the immediate neighborhood of the active site, in contrast to previous models that use stretching curves for the entire DNA strand in the absence of the enzyme. In its original form, the local model was chiefly heuristic, as it required crude assumptions about interactions. The model has now been extensively tested and enhanced by means of a molecular dynamics simulation, in collaboration with Andricioaei and Karplus (in press). The simulation, based on crystal structure data and performed with the CHARMM program, treats explicitly the motion of 5,000 atoms and solvent water. A key aspect of the results is the importance of angular motions of DNA segments at the active site, as restricted by the enzyme. These steric restraints imposed by the enzyme are the major factors determining the dependence on tension of the free energy of activation for the replication rate, in the range below 30 pN. At tensions above about 40 pN, the simulation reveals large conformational changes in the enzyme-bound DNA that may have a role in the experimentally observed tension-induced depolymerization.

PHYS 43 [754582]: Observation of single liposome – bilayer fusion induced by SNARE proteins

Keith R. Weninger¹, Mark E. Bowen², Axel T. Brunger², and Steven Chu³. (1) Department of Physics, North Carolina State University, Raleigh, NC 27695, keith_weninger@ncsu.edu, (2) Molecular and Cellular Physiology, HHMI/Stanford University, (3) Physics Department, Stanford University

Abstract

SNARE (Soluble N-ethylmaleimide Sensitive Factor Attachment Protein Receptor) proteins are essential for membrane fusion during vesicle trafficking in all eukaryotes. The precise molecular mechanism for vesicle-membrane fusion remains unknown. We present a single molecule fluorescence assay to probe the molecular underpinnings of SNARE mediated liposome fusion to supported lipid bilayers. Combinations of protein and content labels were used to detect SNARE complex assembly and the time course of individual liposomes fusing with a bilayer. The role of SNAREs in docking liposomes to bilayers was investigated. The conformation of SNARE

complexes involved in docking was characterized with single molecule inter-protein fluorescence resonance energy transfer (FRET). Spontaneous fusion of docked liposomes with the supported bilayer was observed. Fusion was stimulated by laser illumination and ambient temperature, suggesting a thermally activated process. The neuronal SNAREs alone did not provide the Ca^{2+} dependence of fusion probability associated with neurotransmitter release.

PHYS 44 [750903]: Single-molecule dynamics of calcium signaling

Carey K. Johnson, Brian D. Slaughter, Michael W. Allen, Kenneth D. Osborn, and Jay R. Unruh, Department of Chemistry, University of Kansas, 1251 Wescoe Hall Drive, Lawrence, KS 66045, ckjohnson@ku.edu

Abstract

The calcium signaling protein calmodulin (CaM) binds and activates a diverse array of target enzymes. However, the dynamics of CaM and the mechanisms of target activation remain poorly understood. We used single-pair Förster resonance energy transfer (spFRET) to probe the dynamics and conformations of CaM in solution. Our results show that CaM adopts multiple conformations in solution, of which the dominant population does not match the structure predicted by x-ray crystallography. Dynamics are observed on the 100- μs time scale. We have also investigated CaM bound to an entire enzyme, plasma-membrane calcium ATPase (PMCA), by single-molecule polarization modulation spectroscopy. The results demonstrate that a two-state model cannot adequately describe the function of the calcium pump and a three-state activation model is proposed for PMCA. In each case, the ability of single-molecule spectroscopy to characterize a heterogeneous system allows new insights into the function and dynamics of CaM.

PHYS 45 [754298]: Observation of vinoxy (CH_2CHO) radical in ozonolysis reactions of 2-butenes using cavity ring-down spectroscopy

Liming Wang and **Jingsong Zhang**, Department of Chemistry and Air Pollution Research Center, University of California, Riverside, CA 92521-0403, jingsong.zhang@ucr.edu

Abstract

Ozonolysis reactions of alkenes are important oxidation pathways of alkenes in the atmosphere, and they are also significant sources of tropospheric hydroxyl radicals. In this work, ozone reactions with trans- and cis-2-butene are studied using cavity ring-down spectroscopy (CRDS). Vinoxy (CH_2CHO) radical, a proposed co-product of OH from dissociation of Criegee intermediates following the primary ozonolysis of 2-butenes, is observed. The vinoxy formation is found to decrease with increasing pressure. These results, along with the quantum chemistry studies, suggest that the Criegee intermediate syn- CH_3CHOO , produced from dissociation of the 2-butene primary ozonides, could isomerize to CH_2CHOOH and then dissociate into the $\text{CH}_2\text{CHO} + \text{OH}$ products.

PHYS 46 [788424]: Laboratory studies of the initial steps in VOC oxidation

Paul W. Seakins, School of Chemistry, University of Leeds, Leeds LS2 9JT, England, p.w.seakins@chem.leeds.ac.uk

Abstract

Laboratory studies of elementary reactions are yielding more and more information on mechanisms of VOC oxidation and revealing unexpected subtleties and complexity. Such studies are vitally important; different oxidation routes yield different intermediate products and varying amounts of ozone formation. Unexpected production of radical, especially OH and HO₂, species are particularly important as they can initiate new oxidation.

This talk will describe new experimental studies on crucial elementary steps in VOC oxidation;

- 1) Site selective initiation reactions of chlorine atoms with alkanes as a function of temperature.
- 2) OH yields from R + O₂ chemistry.
- 3) Time resolved studies of alkoxy radical reactions.

Where appropriate, experimental results are complimented by ab initio calculations and the implications of the results on the first generation oxidation products and ozone formation will be discussed.

PHYS 47 [763917]: Direct imaging of atmospheric photodissociation dynamics: Halogen reservoirs and intermediates

Hahkjoon Kim and **Simon W. North**, Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, TX 77842, Fax: 979-845-2971, hahkjoon@mail.chem.tamu.edu, swnorth@tamu.edu

Abstract

The role of anthropogenic and biogenic halogen compounds in stratospheric ozone depletion has been well established. A detailed understanding of the photodissociation of halogen source and reservoir species is critical for modeling atmospheric chemistry. We have carried experiments using a newly constructed molecular beam velocity map ion imaging apparatus to gain insight into photodissociation quantum yields, energy partitioning, and excited dynamics of target compounds. We will present a discussion of the technique, analysis, and recent results.

PHYS 48 [753002]: Photoisomerization dynamics of halooxides and nitrosyl halides

Philip J. Reid and Catherine C. Cooksey, Department of Chemistry, University of Washington, Box 351700, Seattle, WA 98195-1700, preid@chem.washington.edu

Abstract

The solution-phase photoisomerization dynamics of halooxides and nitrosyl halides are presented. Femtosecond pump-probe and time-resolved resonance Raman studies of OClO demonstrate that the photoisomer, ClOO, is produced on the ~10-ps timescale. ClOO then undergoes ground-state thermal decomposition to form Cl and molecular oxygen on the sub-nanosecond timescale. The photoisomerization dynamics of ClOCl are investigated using femtosecond pump-probe spectroscopy. These studies reveal that photoisomerization to form ClClO also occurs on the 10-ps timescale, with this isomer undergoing thermal decomposition to produce Cl and ClO on the 100-ps timescale as well. Finally, femtosecond pump-probe studies of

CINO demonstrate the production CION on the 10-ps timescale. Unlike the behavior observed for halooxides, CION is found to be stable out to the longest delay times investigated (~ 1 ns). In total, these studies suggest that photoisomerization is a general feature of halooxide and nitrosyl halide photochemistry in condensed environments.

PHYS 49 [753713]: Photodetachment studies of the structure and energetics of alkoxy and organo-sulfur radicals

M. Shane Bowen, Zhou Lu, and **Robert E. Continetti**, Department of Chemistry and Biochemistry, University of California, San Diego, 0340, 9500 Gilman Drive, San Diego, CA 92093-0340, Fax: 858-534-7244, msbowen@chem.ucsd.edu, rcontinetti@ucsd.edu

Abstract

Photodetachment of negative ions can provide important insights into the structure and energetics of transient neutral species, and when coupled with photofragment translational spectroscopy can provide further insights into the dissociation pathways and dynamics for short-lived species. In our laboratory, we have studied a number of alkoxy radicals by alkoxide anion photodetachment, and have recently extended these studies into sulfur-containing organic radicals. These radicals are important in a number of chemical processes in the troposphere, and thus represent an interesting confluence of basic and applied experimental chemical physics research. Recent results on the allyl-alkoxy radical (C₃H₅O) and the CH₂SCH₃ radical will be presented. This work was supported by the National Science Foundation under grant CHE-0136195.

PHYS 50 [746505]: Infrared absorption of reaction intermediates probed with matrix isolation or time-resolved FTIR spectroscopy

Yuan Pern Lee, Department of Chemistry, National Tsing Hua University, 101, Sec. 2, Kuang-Fu Rd., Hsinchu 30013, Taiwan, Fax: 886-3-5722892, yplee@mx.nthu.edu.tw

Abstract

Several reaction intermediates important in atmospheric chemistry were produced in matrices and their infrared absorption spectra were recorded with a Fourier-transform infrared (FTIR) spectrometer. New species *t*-HSCO, *t*-OSCS, and *t*-ONCO were produced by irradiation of matrices containing H₂S/CO/Ar, O₃/CS₂/Ar, and CO/NO/Ar, respectively, with laser emission at either 248 or 193 nm. Observed ¹³C-, ¹⁸O-, and ³⁴S-isotopic shifts and B3LYP/aug-cc-pVTZ calculations on vibrational wave numbers, intensities, and isotopic shifts confirm the vibrational assignments. In a second method, a step-scan time-resolved FTIR spectrometer was employed to detect gaseous intermediates upon laser photolysis. Infrared absorption of ClSO at 1163 cm⁻¹ was recorded upon irradiation of Cl₂SO at 248 nm. Similarly, infrared absorption bands of ClSO₂ at 1346 cm⁻¹ and ClCS at 1195 cm⁻¹ were recorded upon photolysis of Cl₂SO₂ and Cl₂CS at 248 nm. The intensities of these absorption bands decrease with reaction time.

PHYS 51 [746823]: Spectroscopic identification and characterization of organic peroxy radicals

Sergey Zalyubovsky, Brent Glover, and **Terry A. Miller**, Department of Chemistry, Ohio State

University, 100 W. 18th Avenue, Columbus, OH 43210, Fax: 614-292-1948,
zalub@chemistry.ohio-state.edu, miller@chemistry.ohio-state.edu

Abstract

Organic molecules are injected in vast quantities from both biogenic and anthropogenic sources into the troposphere. Peroxy radicals, RO_2 , formed from these organic molecules, play key roles in tropospheric chemistry via their reactions with NO_x pollutants and their production of ozone. Historically organic peroxy radicals have been monitored by their UV absorption, which, however is broad and unstructured and therefore ill-suited to distinguishing among peroxy species. The RO_2 radicals have a very weak IR absorption that is sensitive to R. We have exploited near IR cavity ringdown spectroscopy (CRDS) as a species specific diagnostic. Our spectroscopic observations have involved alkyl peroxy radicals with $\text{R}=\text{CH}_3$, C_2H_5 , C_3H_7 , and C_4H_9 . In the latter two cases multiple isomers and conformers exist, and our CRDS spectra are capable of partial distinction among these species. We have also detected the spectra of peroxy radicals with $\text{R}=\text{CF}_3$ and $\text{CH}_3\text{C}(\text{O})$. The former may be of significance in the oxidation of chlorofluorocarbons injected into the atmosphere. The acetyl peroxy radical, $\text{CH}_3\text{C}(\text{O})\text{O}_2$, reacts with NO_2 to form a key pollutant, PAN.

PHYS 52 [754915]: Kinetics of chlorine atom reactions with ethers, aromatics, and PAHs

Scott Hewitt¹, Gabriel Aleman², Michelle Quant¹, Gayathri Nagasundaram¹, Rachel Kelley¹, Xingyu Peng², and Rosa Aguilera¹. (1) Department of Chemistry & Biochemistry, California State University, Fullerton, P.O. Box 6866, Fullerton, CA 92834, Fax: 714-278-5316, shewitt@fullerton.edu, (2) Department of Chemistry and Biochemistry, California State University, Fullerton

Abstract

The Cl atom rate constants for reaction with cyclic ethers, methoxybenzenes, chlorotoluenes, naphthalene, and alkylnaphthalenes have been measured at 298 K and 760 torr using gas chromatography, fourier transform infrared spectroscopy, and the relative rate method. Product studies and kinetic isotope effect measurements were done to determine reaction mechanisms. In addition, ab initio calculations have been performed for Cl + benzene and naphthalene. The implications for fundamental chemistry, atmospheric chemistry, and incineration processes will be presented.

PHYS 53 [752441]: Ionization reactions at liquid interfaces

Ilan Benjamin, Department of Chemistry, University of California, Santa Cruz, 1156 High St., Santa Cruz, CA 95064, Fax: 831-459-2935, benjamin@chemistry.ucsc.edu

Abstract

Understanding the factors that influence the thermodynamics and dynamics of chemical ionization reactions (i.e., at least one of the products is ionic) at liquid interfaces is important for many fields of science and technology, such as electrochemistry, environmental chemistry, catalysis and biophysics. We describe our recent efforts using molecular dynamics computer simulations and simple models to elucidate the role of interface structure and polarity in affecting the free energy profile and dynamics of these reactions. We discuss both equilibrium and non-

equilibrium phenomena and compare the results in bulk liquids with the liquid/vapor and liquid/liquid interfaces.

PHYS 54 [750165]: Mass accommodation of gas phase species on octanol as a function of relative humidity; strange behavior of gas phase hydrogen halides

Paul Davidovits¹, Haizheng Zhang¹, Yongquan Li¹, Leah R. Williams², John T. Jayne², Charles E. Kolb², and Douglas Worsnop². (1) Chemistry Department, Boston College, Chestnut Hill, MA 02467, paul.davidovits@bc.edu, (2) Aerodyne Research, Inc

Abstract

A low pressure droplet train apparatus was used to measure the uptake by 1-octanol of several organic gas phase species and gas phase HCl, HBr and HI. The measurements yielded the mass accommodation coefficient that is the probability that a molecule striking the liquid surface enters the bulk liquid. The measured uptake of the organic gas phase species is in accord with expectations. However, the observed uptake of the gas phase acids is highly surprising. In the absence of water vapor the mass accommodation coefficient for both HBr and HI is unity, for HCl it is much smaller, on the order of 0.015. These values change dramatically as a function of relative humidity. As the relative humidity increases, the mass accommodation coefficient for HBr and HI decreases and for HCl it increases. At a relative humidity of about 50%, the mass accommodation coefficient for all three species reaches values measured earlier on pure water (0.15 to 0.3, depending on temperature). A mechanism is proposed to explain these surprising results

PHYS 55 [755760]: Properties of the liquid/vapor interfaces of water and methanol: A comparison of fixed-charge, polarizable, and ab initio models

I Feng W. Kuo, Chemistry and Material Science, Lawrence Livermore National Laboratory, L-370, PO BOX 808, Livermore, CA 94551-9989, Fax: 925-423-0909, kuo2@llnl.gov, Christopher J. Mundy, Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory, Matthew J. McGrath, Department of Chemistry, University of Minnesota, J. Ilja Siepmann, Departments of Chemistry, Chemical Engineering and Materials Science, University of Minnesota, and Bin Chen, Department of Chemistry, Louisiana State University

Abstract

The structural, dynamical, and electronic properties of the liquid/vapor interfaces of neat water and neat methanol were investigated using a variety of particle-based simulation techniques and a set of different models ranging from empirical fixed-charge force fields, over polarizable (fluctuating-charge) models, to first-principles descriptions. This talk will demonstrate which surface properties are relatively insensitive to the underlying model and for which properties qualitative differences are observed between the different models. The computational results will be compared to recent experimental data.

PHYS 56 [749647]: Molecular dynamics and fluid dynamics analyses of mass accommodation kinetics

Akihiro Morita, Department of Computational Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, Fax: +81-564-55-7025, Masakazu Sugiyama,

Department of Electronics Engineering, School of Engineering, University of Tokyo, Seiichiro Koda, Department of Chemistry, Faculty of Science and Technology, Sophia University, and David R. Hanson, Atmospheric Chemistry Division, National Center for Atmospheric Research

Abstract

Phenomenological mass transfer rate at liquid-vapor interface consists of many kinetic processes in gas, liquid and interface, which could complicate the interpretation of heterogeneous uptake experiments. In order to accurately decompose the uptake coefficient into elemental kinetic steps, the present study employed theoretical analyses of the uptake experiments in two ways, by molecular dynamics and fluid dynamics simulations.

Molecular dynamics simulation of methanol/water system concluded that the mass accommodation coefficient α is almost unity irrespective of the methanol composition, implying that the surface active methyl moieties do not effect on the uptake rate. The value of α appears inconsistent to the droplet train experiments reporting α significantly smaller than 1. Therefore, the computational fluid dynamics calculations for the droplet train flow tube was performed to quantitatively evaluate the gas-phase diffusion resistance, and found that the empirical Fuchs-Sutugin formula may underestimate the gaseous resistance in the flow tube. This is partly attributed to the discrepancy between experimental and theoretical values of α .

PHYS 57 [744352]: Investigation of the molecular structure of liquid surfaces by means of particle spectroscopies

Harald Morgner, Wilhelm-Ostwald Institute of Physical and Theoretical Chemistry, University of Leipzig, Linnestrasse 2, D-04103 Leipzig, Germany, Fax: +49 341 97 36090, hmorgner@rz.uni-leipzig.de

Abstract

During the last decade we have developed several electron spectroscopies and ion spectroscopies for the investigation of liquid surfaces. As the depth resolution of these techniques is of the order of Angstrom it is possible to characterize liquid surfaces by concentration depth profiles to good accuracy. The depth down to which the surface can be probed is about 100 to 200 Angstrom. This is sufficient to have in view not only the surface itself but the bulk composition of the liquid as well. In cases of all surfactant solutions we have studied so far we were able to follow surfactant segregation through the surface until the depth where bulk concentration is taken on. The methods we use depend on the purpose: depth profiling is made possible by ARXPS (=Angular Resolved X-ray Photoelectron Spectroscopy) and NICISS (=Neutral Impact Collision Ion Scattering Spectroscopy). The composition of the top layer is given by the perfectly surface sensitive technique MIES (=Metastable Induced Electron Spectroscopy) while surface sensitive vibrational spectroscopy is performed by HREELS (=High Resolution Electron Spectroscopy). The necessity to provide vacuum for these techniques is not in principal conflict with the vapor pressure of liquids, but requires technical precautions. At present we consent ourselves to studying liquids like formamide or hydroxipropionitrile with vapor pressures lower than water. This allows us to concentrate on physical problems rather than on the technicalities to handle high vapor pressure. Mixtures of liquids, solutions of phase transfer catalysts and solutions of phosphatidylcholines are among the systems studied. Data on the dependence on bulk

concentration as well as the influence of surface age in the range of milliseconds to seconds will be presented.

PHYS 58 [754885]: Adding ions to glycerol to control gas-liquid interfacial reactivity

Annabel H. Muentzer, Jennifer L. DeZwaan, and Gilbert M. Nathanson, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706

Abstract

We use molecular beam scattering experiments to follow collisions and reactions of DCl molecules with different alkali halide, salt glycerol solutions. Our studies indicate that DCl molecules impinging on pure and salty glycerol can undergo rapid D → H exchange within the interfacial region and evaporate as HCl without first dissolving in the bulk. Because this interfacial reaction pathway occurs in the presence of a substantial bulk dissolution pathway, we can investigate what liquid properties control the partitioning of the DCl molecule between bulk and interfacial reaction pathways. By varying both the anion and cation of the salt, we explore how ion size, charge density, and concentration alter DCl's bulk and interfacial reactivity. We observe that an increase in interfacial ion concentration increases the fraction of DCl molecules reacting in the interface and decreases the bulk uptake probability. These opposing trends confirm that the glycerol interface is a distinct reaction medium separate from the bulk.

PHYS 59 [750427]: Ab initio nonadiabatic molecular dynamics simulation of the ultrafast photoinduced electron transfer from molecular donors to the TiO₂ acceptor

Oleg V. Prezhdo, Department of Chemistry, University of Washington, Seattle, WA 98195-1700, Fax: 206-685-8665, prezhdo@u.washington.edu

Abstract

A non-adiabatic molecular dynamics (NAMD) simulation of the photoinduced electron transfer (ET) in the Gratzel solar cell from molecular electron donors to the TiO₂ acceptor will be discussed. The electronic structure and adiabatic dynamics are simulated by ab initio density functional theory, while the NA effects are incorporated by a quantum-classical mean-field approach. The ET occurs on a 30 fs time scale by the NA mechanism at low temperatures and within 5 fs by the adiabatic mechanism at room temperature, in agreement with the recent ultrafast experimental data. The electron acceptor states are localized within the first 3-4 layers of the surface with about 20% of the acceptor state density due to a single Ti atom. The simulations predict a complex non-single-exponential time dependence of the ET process and suggests a mechanism for increasing the solar cell voltage [J. Phys. Chem. B 106 8047 (2002) p.8047; Isr. J. Chem. 42 213 (2003); J. Mol. Struct.-Theochem 630 33 (2003); Adv. Mater. 16 240 (2004)].

PHYS 60 [755317]: Direct photodynamics of green fluorescent protein

Alessandro Toniolo¹, Seth Olsen², Kristina Lamothe², and **Todd J. Martinez**³. (1) Department of Chemistry, University of Illinois, 600 S. Mathews, Urbana, IL 61801, toniolo@spawn.scs.uiuc.edu, (2) Center for Biophysics and Computational Biology, University

of Illinois, (3) Department of Chemistry and the Beckman Institute, University of Illinois at Urbana-Champaign, 600 S. Mathews, Urbana, IL 61801, tjm@spawn.scs.uiuc.edu

Abstract

The chromophore of Green Fluorescent Protein is non-fluorescent in solution, but does fluoresce in the protein environment. The nonradiative decay observed in solution is believed to occur through a conical intersection and to involve isomerization around a double bond. We investigate the photodynamics of the chromophore in three different environments (isolation, solution, and protein) in order to elucidate how the protein environment prevents isomerization. Our simulations use the multiple spawning wavepacket dynamics method to describe the nonadiabatic effects. Potential energy surfaces and couplings are obtained "on the fly" from ab initio methods and/or reparameterized semiempirical methods using QM/MM representations to treat complex environments.

PHYS 61 [764709]: Matching pursuit split operator fourier transform simulations of excited state intramolecular proton transfer reactions

Victor S. Batista, Department of Chemistry, Yale University, 225 Prospect Street, P.O. Box 208107, New Haven, CT 06520-8107, Fax: 203-432-6144, victor.batista@yale.edu

Abstract

The Matching Pursuit Split Operator Fourier Transform (MP/SOFT) method, recently developed by Y. Wu and V.S. Batista [J. Chem. Phys. 118, 6720, 2003, *ibid.* 119, 7606, 2003] is applied in simulations of excited state intramolecular proton transfer reactions as described by full-dimensional reaction surface Hamiltonians. Proton transfer is found to be significantly coupled to internal vibrational modes and substantially affected by both recrossing dynamics and isotopic substitution. The capabilities of the MP/SOFT methodology are also compared to those of the Herman-Kluk Semiclassical Initial Value Representation (HK/SC-IVR) method.

PHYS 62 [753989]: Modeling vibrational and electronic relaxation of photoexcited radical reactions in condensed phases

David F. Coker and Jing Zhang, Department of Chemistry, Boston University, 590 Commonwealth Ave., Boston, MA 02215, Fax: (617) 353-6466, coker@bu.edu

Abstract

The competition between electronic and vibrational relaxation, and radical bond cleavage and formation is explored in photoexcited reactions of polyatomic molecules in condensed phase environments. A combination of semi-empirical excited state electronic structure methods, mixed quantum-classical, and semi-classical molecular dynamics techniques are used to study model excited state reactions of I₂ and ICN in a wide variety of environments from simple rare gas matrices and liquids, to model aluminosilicate zeolites. We explore how environmental factors can be manipulated to control photoexcited radical reaction pathways.

PHYS 63 [753547]: Quantum/classical studies of photoinitiated processes in weakly bound complexes

Anne B. McCoy, Jose G. Lopez, and Feng Chen, Department of Chemistry, The Ohio State

University, 100 W. 18th Ave., Columbus, OH 43210, Fax: 614-292-2516,
mcco@chemistry.ohio-state.edu

Abstract

In this talk, we will focus on two issues. The first is the development of a multiple configuration quantum/classical approach in which several internal degrees of freedom are treated quantum mechanically, while the rest of propagated classically. The challenge in the simplest quantum/classical separation comes in the overcorrelation between the quantum and classical dynamics, particularly when the system has two or more energetically accessible channels. The multiple configuration approach solves many of these issues by propagating separate classical trajectories for each of the channels that are sampled by the quantum wave packet. In this part, we focus on studies of the photodissociation dynamics of argon/water complexes. In the second part, we compare the dynamics predicted by quantum and classical approaches to gain insights into precisely when fully or partially quantum treatments are necessary for these small to moderate sized systems and when we may be able to treat most, if not all, of the degrees of freedom classically. Several systems will be used as examples, including the transition state dynamics of ArnIHI, which were inspired by studies on this system by Neumark and co-workers.

PHYS 64 [755719]: Photodissociation dynamics and spectroscopy of NaI(H₂O)_n clusters

Denise M. Koch, Centre for Research in Molecular Modeling (CERMM) and Department of Chemistry and Biochemistry, Concordia University, Richard J. Renaud Science Complex, 7141 Sherbrooke Street West, Montreal, QC H4B 1R6, Canada, Fax: (514)848-2868, denise@cermm.concordia.ca, Qadir K. Timerghazin, Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University, Gilles Peslherbe, Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University, Branka M. Ladanyi, Department of Chemistry, Colorado State University, and James T. Hynes, Département de Chimie, Ecole Normale Supérieure, UMR 8640 PASTEUR, Department of Chemistry & Biochemistry, Boulder University

Abstract

We present a theoretical study of the photodissociation dynamics of NaI(H₂O)_n [n=1-4] clusters. The NaI system has been a prototype system for the study of photodissociation dynamics involving curve crossing of covalent and ionic states. A semiempirical valence-bond approach is employed to describe the electronic structure of NaI, while classical potentials are used for the water-water and ion-water interactions. The cluster photodissociation dynamics, including possible nonadiabatic transitions between the NaI excited and ground electronic states, are simulated with the “molecular dynamics with quantum transitions” method. We show that the excited state population decays faster with increasing cluster size, because of the dynamical stabilization of the outer, ionic branch of the excited state potential by solvent molecules. As observed previously for NaI(H₂O), the reversed polarity of NaI in the Franck-Condon region of the excited state causes the evaporation of 95% to 100% of the water molecules before NaI reaches the curve crossing region, i.e. within 200 fs of excitation. We discuss possible probe schemes and time-resolved photoelectron spectroscopy in order to monitor the cluster photodissociation in time and make a connection with experiment.

PHYS 65 [754258]: New approaches to fast algorithms for second order Moller-Plesset calculations

Martin Head-Gordon, Department of Chemistry, University of California Berkeley and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, mhg@bastille.cchem.berkeley.edu

Abstract

Electron correlation via wavefunction-based methods has well-known advantages relative to density functional theory, such as systematic improvability, and the correct inclusion of long-range dispersion forces. However computational cost scaling continues to be a significant barrier preventing broad application of these methods to very large systems. In this talk we report new results on the development of fast algorithms designed to overcome this bottleneck, which are implemented and tested at the second order Moller-Plesset (MP2) level of correlation theory. The first part of these studies concern the fraction of correlation energy that can be recovered within particular "local" models, based on pilot calculations. The conclusions from this work guide the second part of the talk, in which we focus on developing and testing new fast algorithms.

PHYS 66 [752861]: Local correlation with density fitting

Martin Schuetz, Department of Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, Stuttgart, Germany, Fax: 711-685-4442, schuetz@theochem.uni-stuttgart.de

Abstract

Local correlation methods with linear scaling of the computational cost as function of molecular size have much extended the applicability of high-level electronic structure methods. The bottleneck in such calculations is the generation of the required 2-electron integrals. By combining local correlation with density fitting (DF) this problem can largely be circumvented, as will be demonstrated for local MP2 (LMP2) and local coupled cluster theory. Furthermore, a new and very efficient LMP2 gradient method will be presented, which uses DF for the MP2 and the Hartree-Fock reference. Any 4-index objects can be avoided this way. This new DF-LMP2 gradient method is applicable for geometry optimizations of molecular systems involving more than 100 atoms in a triple-zeta AO basis. Since the overall cost of the gradient is not dominated by the LMP2 specific parts, it is competitive in efficiency to DF-DFT gradients using Hartree-Fock exchange, as e.g. the popular B3LYP functional.

PHYS 67 [751692]: Atomic orbital based MP2 theory for periodic systems

Gustavo E Scuseria, Department of Chemistry, Rice University, Houston, TX 77005, guscus@rice.edu

Abstract

This presentation will address our current efforts to develop correlated quantum chemistry methods for systems with periodic boundary conditions. Over the last several years we have implemented computational programs for Density Functional [1], Hartree Fock, and Second-Order Perturbation Theory (MP2) [2] calculations of periodic systems. These methods build upon our O(N) efforts for large molecules and clusters [3]. In this talk, we will discuss the methodology and present relevant applications.

[1] Linear Scaling Density Functional Theory with Gaussian Orbitals and Periodic Boundary Conditions: Efficient Evaluation of Energy and Forces via the Fast Multipole Method, K. N. Kudin and G. E. Scuseria, Phys. Rev. B 61, 16440 (2000). [2] Atomic Orbital Laplace transformed MP2 theory for periodic systems, P. Y. Ayala, K. N. Kudin, and G. E. Scuseria, J. Chem. Phys. 115, 9698 (2001). [3] Linear Scaling Density Functional Calculations with Gaussian Orbitals, G. E. Scuseria, J. Phys. Chem. A 103, 4782 (1999).

PHYS 68 [753951]: Dynamical thresholding in local Coupled Cluster methods

Alexander Auer, Institut fuer Chemie, Technische Universitaet Chemnitz, D-09107 Chemnitz, Germany, auer@uwaterloo.ca, and Marcel Nooijen, Department of Chemistry, University of Waterloo

Abstract

We present a refined local CC algorithm in which we formulate the orbital space by using pure atomic orbitals for the virtual space and localized orbitals for the occupied spaces. In order to control the accuracy in the approximation of the CC wavefunction, we suggest a threshold driven procedure which uses amplitudes from perturbation theory to estimate which amplitudes should be treated at the CC level. To obtain an operation and storage minimal local approximation the algorithm includes a dynamical ('on the fly') screening of all formed quantities based on the sparsity of integrals, coefficients and the sparsity of the amplitudes as obtained from an initial MP2 calculation. In our approach we can achieve gradual convergence of the energy as a function of the input thresholds, and no a priori selection of local correlation domains is required. In this contribution we outline the algorithm and discuss results of benchmark calculations focus on the scaling of CPU time, disk and memory usage. Furthermore, a parallel implementation of the new algorithm is discussed. All computer codes used in our approach have been generated automatically using the Tensor Contraction Engine (TCE). This has greatly facilitated the exploratory development of the current algorithm.

PHYS 69 [755140]: Local correlation and molecular response properties

T. Daniel Crawford, Department of Chemistry, Virginia Tech, 107 Davidson Hall, Blacksburg, VA 24061, Fax: 540-231-3255, crawdad@vt.edu

Abstract

For ground-state wave functions and energies, local correlation methods have successfully overcome the polynomial scaling wall of high-accuracy ab initio models such as coupled cluster theory. However, to date the development of local schemes for molecular properties has been limited. This talk will focus on our recent efforts to extend local coupled cluster methods to linear-response properties of large molecules, including excitation energies, dipole polarizabilities (in both the static and dynamic limits), and optical rotation. We will include results using "standard" local-domain schemes, as well as more recently developed methods. The important issue of orbital relaxation will also be considered.

PHYS 70 [742019]: Optical detection of nanometer-sized gold labels

Michel Orrit, MoNOS, University of Leiden, P. O. Box 9504, 2300 RA Leiden, Netherlands, orrit@molphys.leidenuniv.nl

Abstract

Gold colloids as labels for single biomolecules have the advantage that they neither blink nor bleach. However, their photoluminescence is weak, and strongly depends on time and defects. For applications to cell biology, one needs an optical signal easily distinguishable from scattering background. I present two optical contrast mechanisms enabling detection of single gold colloids. One, photothermal interference contrast, is based on heating of the surroundings by the light-absorbing colloid. This method can detect particles less than 5 nm in diameter. Another method is third-harmonic generation under short infra-red pulses. Our current experiments with 1-ps pulses are limited to particles larger than 40 nm. They show a dramatic size-dependence of the nonlinear susceptibility. With 100-fs pulses, 15-nm particles should be detectable. In the rest of the talk, I shall mention and discuss other possible optical signals.

PHYS 71 [741183]: Biological tagging applications for single molecules and cells using semiconductor nanocrystals

A. Paul Alivisatos, Department of Chemistry, Univ. of California, Berkeley, Lawrence Berkeley National Laboratory, Materials Sciences Division, D-43A Hildebrand Hall, Berkeley, CA 94720-1460, Fax: 510-642-6911, alivis@uclink4.berkeley.edu

Abstract

Semiconductor nanocrystals exhibit strongly size dependent emission spectra due to the quantum size effect. Further, the nanocrystals have nearly continuous excitation spectra above the threshold for absorption. As a consequence, the nanocrystals can be used as luminescent probes in biological staining experiments for single molecules and cells. The nanocrystals are in many ways superior to existing organic chromophores. Relevant applications and surface chemistry will be described in this talk.

PHYS 72 [754874]: Highly fluorescent, size-tunable, water-soluble Au and Ag nanodots for single molecule biophysics in living systems

Jie Zheng¹, Lynn A. Capadona¹, Jeffrey T. Petty², Caiwei Zhang¹, Yih Ling Tzeng³, and **Robert M. Dickson**¹. (1) School of Chemistry and Biochemistry, Georgia Institute of Technology, 770 State Street, Atlanta, GA 30332-0400, Fax: 404-894-7452, dickson@chemistry.gatech.edu, (2) Department of Chemistry, Furman University, (3) Division of Infectious Diseases, Emory University School of Medicine

Abstract

Through sub-nm confinement, water soluble gold and silver nanoclusters exhibit discrete, size-tunable absorptions and fluorescence throughout the visible and near IR. The high quantum yield, exceedingly strong absorption cross sections, and fast radiative lifetimes make these size-tunable fluorophores easily observed on the single molecule level with only weak mercury lamp illumination. Surprisingly, upon encapsulation in poly(amidoamine) dendrimers or short peptides, these few-atom nanoclusters even enable the distinctive Raman signal of the scaffold to be observed on the single molecule level – *without a large nanoparticle being present*. Intermediate between discrete atomic transitions and large nanoparticle plasmon absorptions, these several-atom metallic quantum dots act as multi-electron artificial atoms and smoothly link atomic and bulk metallic free electron behavior. These easily prepared, water-soluble and high

quantum yield fluorescent metal nanodots lend insight into the molecular nature of small metal nanoclusters and are poised to become extremely useful single molecule biophysical labels.

PHYS 73 [745566]: Probing single molecules and single cells with quantum dots

Xiaohu Gao, Depts of Biomedical Engineering and Chemistry, Emory University, 1639 Pierce Drive, WMB 2001, Atlanta, GA 30322, Fax: 404-727-9873, xgao2@emory.edu, and Shuming Nie, Biomedical Engineering and Chemistry, Emory University

Abstract

The development of high-sensitivity and high-specificity probes beyond the intrinsic limitations of organic dyes and fluorescent proteins is of considerable interest to many areas of research, ranging from single-molecule biophysics to in-vivo medical imaging. Recent advances have shown that nanometer-sized semiconductor particles can be covalently linked with biorecognition molecules such as peptides, antibodies, nucleic acids, and small-molecule inhibitors for use as fluorescent probes. In comparison with organic fluorophores, quantum dots (QDs) exhibit unique optical and electronic properties such as size- and composition-tunable fluorescence emission, large absorption coefficients, and significantly improved brightness and photostability. Due to their broad excitation profiles and narrow/symmetric emission spectra, high-quality QDs are also well suited for optical multiplexing, in which multiple colors and intensities are combined to encode thousands of genes, proteins, and small-molecule libraries. We present recent developments in bioconjugated QD probes (including far-red and near-infrared-emitting dots) and their applications in ultrasensitive molecular and cellular imaging. Despite their relatively large sizes (2-6 nm), bioconjugated QD probes behave like fluorescent proteins (4-6 nm), and do not suffer from serious kinetics or steric-hindrance problems. In this “mesoscopic” size range, QDs also have more surface areas and functionalities that can be used for linking to multiple diagnostic (e.g., radioisotopic or magnetic) and therapeutic (e.g., anticancer) agents.

PHYS 74 [752716]: Tracking individual proteins in live cells using quantum dots

Maxime Dahan, Department of Physics, Laboratoire Kastler Brossel, Ecole normale supérieure, 24, rue Lhomond, Paris 75005, France, Fax: 33-144323434, maxime.dahan@lkb.ens.fr

Abstract

Quantum dots (QDs) are inorganic probes which hold great promises for advanced biological imaging. Because of their small size, brightness and photostability, they offer a favorable compromise between small dyes and large beads for single-molecule experiments, notably in live cells. We used QDs to track tagged-receptors in the membrane of live neurons for durations of tens of minutes. Using standard optical techniques, single receptors were detected with a high signal to noise ratio (greater than 30) and high spatial resolution (~10 nm). Single molecule experiments revealed: (i) multiple diffusion domains for glycine receptors in dendrites, related to their synaptic, perisynaptic or extrasynaptic localization, (ii) microtubule-dependent directed movements of GABA receptors in growth cones. The fluorescence images were complemented with electron-microscopy images of silver-intensified QDs providing a precise localization of the receptors. Altogether our results show that QDs will be invaluable tools for ultrasensitive studies of the dynamics of cellular processes.

PHYS 75 [755084]: NIR-emissive polymersomes: Self-assembled soft matter for in vivo optical imaging

Daniel A. Hammer¹, Peter G. Ghoroghchian¹, Michael J. Therien², Frank S. Bates³, Britton Chance⁴, Paul R. Frail², Kimihiro Susumu², and Dana Blessington². (1) Department of Bioengineering, University of Pennsylvania, 120 Hayden Hall, Philadelphia, PA 19104, hammer@seas.upenn.edu, (2) Department of Chemistry, University of Pennsylvania, (3) Department of Chemical Engineering and Materials Science, University of Minnesota, (4) Department of Biochemistry and Biophysics, University of Pennsylvania

Abstract

Polymersomes are vesicles made of self-assembling block copolymers which spontaneously form lamellar phases in aqueous solutions. The polymersome membrane thickness is set by the polymer molecular weight and architecture, and much larger membrane thicknesses are possible than with typical phospholipid membranes. We use this unique feature of polymersomes to encapsulate large quantities of hydrophobic porphyrinic macrocycles that emit light in the near-infrared part of the spectrum. Light emission in this wavelength range is ideal for biological imaging, due to the strong reduction in tissue absorbance with the wavelength. We show that an entire family of porphyrinic macrocycles, from monomer to pentamer, spontaneously assemble with amphiphilic block co-polymers, with the porphyrins sequestered in the interior of the membrane. Depending on the number of subunits, the side chain chemistries, and the linkage between subunits in the porphyrins, polymersomes can be engineered to emit light across wavelengths from 550 to 1000 nm. We calculate that 150,000 copies of a porphyrin may be stored within a single vesicle, indicating that a high payload, and hence high signal-to-noise may be achieved with emissive polymersomes. We demonstrate the ability of these bright vesicles to image a glioma tumor one centimeter below the skin surface in a rodent.

PHYS 76 [753726]: Recent advances in atmospheric mass independent isotope measurements

Mark H. Thiemens, Chemistry 0356, UCSD, La Jolla, CA 92093-0356, Fax: 858 534 5224, mht@chem.ucsd.edu

Abstract

In recent years the use of mass independent isotopic chemistry has expanded to a most extraordinary range of applications. These applications range in time from the present to 3.8 billion years ago; location, from the Earth to Mars, and sampling to from ground level to the top of the atmosphere. Sulfates and nitrates have proven to be particularly insightful because of their ability to capture oxidative capacity and reaction pathways in the atmosphere. Ice core samples from the Antarctic and Greenland have provided a new way to monitor global oxidative capacity on glacial and inter glacial time periods. Sulfur isotopic measurements of samples from the pre Cambrian have been shown to reflect the origin of life and the evolution of oxygen on billion year time scale. Some of the most recent observations of this new isotopic technique will be presented.

PHYS 77 [752865]: Unusual kinetic isotope effect in ozone formation: New clues for isotope transfer?

Christof Janssen, Atmospheric Physics Department, Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, Heidelberg 69117, Germany, Fax: 0049-6221-516324, c.janssen@mpi-hd.mpg.de

Abstract

Ozone in the atmosphere is known to be strong and anomalously enriched in both the heavy stable oxygen isotopes, ^{17}O and ^{18}O . While consensus on a theory of the origin of this effect has not yet been reached, the kinetics of the ozone forming association reaction $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$ has been clearly identified to be at the heart of the anomaly. Through transfer into other oxygen bearing compounds the ozone anomaly may have far reaching consequences and applications in atmospheric and biogeochemical sciences. Of importance is the position of ^{17}O and ^{18}O in the ozone molecule, forming symmetric or asymmetric isotopomers of $^{49}\text{O}_3$ and $^{50}\text{O}_3$. New, preliminary results from measurements of reactions involving ^{17}O are presented. These provide new constraints for the theoretical description of the ozone isotope effect and for the effectiveness of isotope transfer into other oxygen bearing molecules, such as stratospheric CO_2 .

PHYS 78 [752514]: Ozone isotope effect: What do we really know ?

Reinhard Schinke, MPI Stroemungsforschung, Bunsenstrasse 10, Goettingen D-37085, Germany, Fax: 49-551-5176-712, rschink@gwdg.de

Abstract

The isotope effect in the formation of ozone will be discussed in terms of dynamical calculations using an accurate $\text{O}+\text{O}_2$ potential energy surface and classical mechanics. The difference of the zero-point energies of the two fragmentation channels of ozone are incorporated in an empirical manner into the trajectories. This method has been tested for the isotope dependence of the $\text{O}+\text{O}_2$ exchange reaction by comparison with experimental data. The trajectory calculations do lead to a systematic dependence of (approximate) ozone formation rates on the isotopomers. However, the comparison with the experimental (relative) formation rates still is not satisfactory: the relative rates for the symmetric isotopomers are too large by about 20%. Possible extensions of the calculations as well as general questions (quantum effects, excited electronic states, energy transfer mechanism) will also be discussed.

PHYS 79 [748537]: Quantum origin of anomalous isotope effect in ozone formation

Dmitri Babikov, Chemistry Department, Marquette University, Wehr Chemistry Building, PO Box 1881, Milwaukee, WI 53201

Abstract

The rates of recombination reaction ($\text{O}_2+\text{O}+\text{M} \Rightarrow \text{O}_3+\text{M}$) that forms ozone differ by more than 50% for various isotopic combinations, which is a remarkably large isotope effect taking into account small mass difference. A clear explanation of anomaly is given in terms of the energy transfer mechanism, where the metastable O_3^* states of ozone are formed first and then stabilized by collisions with M. Their energies and lifetimes were obtained from accurate quantum scattering studies. The spectrum of metastable states is anomalously dense below the second dissociation threshold, and these states are accessible only from the lower entrance channel.

They are stabilized very efficiently by collisions because they are energetically close to the bound O₃ states. Such processes significantly enhance the formation rates through the lower channels over the formation rates through the upper channels. This finding finally explains the origin of anomalous isotope effects.

PHYS 80 [752578]: Reaction dynamics of isotope exchange reaction of singlet oxygen atom with carbon dioxide molecule: A crossed molecular beam study

Jim J. Lin¹, Mark J. Perri², Annalise L. Van Wyngarden², Kristie A. Boering³, and Yuan T. Lee⁴. (1) Institute of Atomic and Molecular Sciences, Academia Sinica, P. O. Box 23-166, Taipei 106, Taiwan, Fax: 886-2-2362-0200, jimlin@po.iams.sinica.edu.tw, (2) Department of Chemistry/Boering Group, University of California, (3) Departments of Chemistry and Earth and Planetary Science, University of California, Berkeley, (4) Institute of Atomic and Molecular Sciences

Abstract

The dynamics of the ¹⁸O(¹D) + ⁴⁴CO₂ oxygen isotope exchange reaction has been studied using a crossed molecular beam apparatus at collision energies of 4.2 and 7.7 kcal/mol. Besides isotope exchange together with quenching to ground state O(³P), a new isotope exchange channel in which the product oxygen atom remains on the singlet surface is observed at both collision energies. Electronic quenching of O(¹D) is the major channel at both collision energies, accounting for 84% of isotope exchange at 4.2 kcal/mol and 67% at 7.7 kcal/mol. Isotropic product angular distributions suggest that both channels proceed via a CO₃* complex that is long-lived with respect to its rotational period. Combined with recent ab initio and statistical calculations by Mebel et al., the long complex lifetimes suggest that statistical isotope exchange occurs in the CO₃* complex, although the existence of a small, dynamically-driven unconventional isotope effect in this reaction cannot yet be ruled out. These new molecular-level details may help provide a more quantitative understanding of the heavy isotope enrichment in CO₂ observed in the stratosphere.

PHYS 81 [755520]: Carbon-13 kinetic isotope effects of importance to atmospheric science and their temperature dependence

Hai Lin, Yan Zhao, Benjamin A. Ellingson, Jingzhi Pu, and Donald G. Truhlar, Department of Chemistry and Supercomputer Institute, University of Minnesota, 334 Smith Hall, 207 Pleasant St. SE, Minneapolis, MN 55455, Fax: 612-626-9390, lin@comp.chem.umn.edu

Abstract

The greenhouse gas methane plays an important role in modeling global climate changes. The oxidation of CH₄ by OH radical is the major sink of atmospheric methane in the troposphere. We report a theoretical study of the carbon-13 kinetic isotope effect (KIE) and its temperature dependence for the reaction OH + CH₄ -> H₂O + CH₃. The KIE values at various atmospherically significant temperatures were determined by direct dynamics using variational transition state theory with multidimensional tunneling contributions. The potential energy surfaces were generated at a number of different levels of theory including both explicitly correlated wavefunctions and hybrid and doubly hybrid density functional theory methods. Factorization of the KIE into different contributions (potential energy, translation, rotation,

vibration, and tunneling) provides insights into the origin of the KIE. Our calculated KIEs will be compared to experimental data and theoretical values in literature, and the temperature dependence will be discussed. This work was supported in part by the DOE.

PHYS 82 [753223]: Solvent polarity across weakly and strongly associating liquid/liquid interfaces: Shape matters!

Robert A. Walker, Carmen L. Beildeck, and William H. Steel, Department of Chemistry and Biochemistry, University of Maryland, College Park, Building 091, College Park, MD 20742, Fax: 301-314-9121, rw158@umail.umd.edu

Abstract

Properties at liquid/liquid interfaces can differ significantly from bulk solution limits. To a first approximation, one might assume that interfacial properties should scale with the mutual solubilities of the two adjacent solvents. Liquids that are (slightly) more miscible should create a more diffuse interface than liquids that are less miscible. Using resonance enhanced second harmonic generation and novel surfactants designed to probe interfacial polarity, we show that the "width" of an interface depends much more on an organic solvent's molecular structure than on its miscibility with water. For both weakly associating and strongly associating liquids (i.e. alkanes and long chain alcohols), irregularly shaped solvent molecules create interfaces with water that are much more abrupt than those formed between water and organic solvents that pack efficiently. These results will be discussed in terms of surface induced polar ordering and the intrinsic excluded volume associated with different organic solvents.

PHYS 83 [749331]: Molecular dynamics at aqueous interfaces

Kenneth B. Eisenthal, Shang Xiaoming, Zimdars David, Nguyen Kim, Liu Jian, and Pompano Rachel, Department of Chemistry, Columbia University, 116th St. and Broadway, New York, NY 07450, Fax: 212-932-1289, eisenth@chem.columbia.edu

Abstract

Dynamic processes at aqueous interfaces using the interface selective technique of second harmonic generation will be discussed. A method for measuring the in-plane and out-of-plane ultrafast orientational relaxation motions of molecules at air/water and charged surfactant/water interfaces will be presented. Use of the experimentally determined orientational relaxation times as a measure of interfacial friction and its application to barrierless chemical reactions will be outlined. It will be shown how measurements of the second harmonic signal in real time can be used to investigate the transport kinetics of organic cations across a membrane mimetic bilayer and to determine the effect of an antibiotic on the transport kinetics.

PHYS 84 [767099]: Interfacial acidities, energies and potentials of carboxylic acid-functionalized silica/water interfaces determined by second harmonic generation

Franz M. Geiger, Chris Konek, Michael J. Musorrafiti, and Hind A. Al-Abadleh, Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, geigerf@chem.northwestern.edu

Abstract

In this work, we present the first SHG studies of interfacial acidity, potential and interfacial energy for an acid-functionalized silica/water interface. Two acid-base equilibria, whose pK_a values of 5.6 (2) and 9(1) agree with the ones recently reported by Gershevitc and Sukenik using ATR-FTIR, are observed. By measuring the surface charge densities at pH 6.5 and 11.2, we determined the pH-dependence of the relative interfacial potential and energy. These results provide molecular level information necessary for understanding and predicting how aqueous phase species can interact with liquid/solid interfaces decorated with functionalized organic adlayers at a given pH.

PHYS 85 [754178]: Uptake and chemical dynamics of atmospheric gases in organic films

Douglas J. Tobias, Department of Chemistry, University of California, Irvine, CA 92697-2025, Fax: 949-824-8571, dtobias@uci.edu, and **John S. Vieceli**, Department of Chemistry, University of California, Irvine

Abstract

Organic matter is an important constituent of atmospheric aerosols. Although the composition of organic aerosol components is not known in detail, it is clear that organic particles play an important role in the radiative balance of the atmosphere. Organic molecules are reactive toward oxidants in the atmosphere, and oxidative processing of organic aerosols changes their composition and physical properties. Thus, there has recently been a great deal of interest in the mechanism and kinetics of the oxidation of organic surfaces. This talk will present results from molecular dynamics simulations of model organic aerosols: solid and liquid organic surfaces, and amphiphilic molecules adsorbed at the air/water interface. The structures of these surfaces and their interaction with gaseous oxidants will be discussed in detail and compared with available experimental data. Implications of the results for the kinetics of the processing of organic aerosols will be also discussed.

PHYS 86 [751057]: Computational study of ion binding to the liquid interface of water

Liem X. Dang, Chemical Sciences Division, Pacific Northwest National Laboratory, Battelle Blvd PO Box 999 K1-83, Richland, WA 99352, Fax: 509-375-4381, liem.dang@pnl.gov

Abstract

We have performed extensive classical molecular dynamics simulations to examine the molecular transport mechanisms of the ions across the liquid/vapor interface of water. The potentials of mean force were calculated using the constrained mean force approach and polarizable potential models were used to describe the interactions among the species. The simulated potentials of mean force were found to be different, depending on the type of anion. The larger I⁻ and Br⁻ anions bind more strongly to the liquid/vapor interface of water than did the smaller Cl⁻ ion. We have also studied the transport mechanism of an I⁻ across the water/dichloromethane interface. The computed potential of mean force showed no well-defined minimum as in the liquid/vapor case, but a stabilization free energy of about -1 kcal/mol near the interface with respect to the bulk liquid was observed. The I⁻ anion carried a water molecule with

it as it crossed the interface. This result is in agreement with a recent experimental study on a similar system. Our work differs from earlier contributions in that our potential models have taken many-body effects into account, and in some cases, these effects cannot be neglected.

PHYS 87 [747453]: Molecular dynamics simulations of the liquid/vapor interface of aqueous ethanol solutions

Ramona S. Taylor, Clare Kelleher, and Ethan Stewart, Department of Chemistry, College of the Holy Cross, One College Street, Worcester, MA 01610, Fax: 508-793-3530, rtaylor@holycross.edu

Abstract

Molecular dynamics computer simulations are utilized to study the structural and thermodynamic properties of the liquid/vapor interface of aqueous ethanol solutions as a function of ethanol concentration. The effect of ethanol concentration on both the surface tension and the orientation of the molecules residing at the liquid/vapor interfacial have been calculated. Additionally, the free energy profiles for inserting an ethanol molecule into an aqueous ethanol solution as a function of ethanol concentration are computed using statistical mechanical perturbation theory. Although these profiles predict free energies for solvation that are in agreement with the corresponding experimental data, they exhibit barriers to solvation that are considerably smaller than those predicted by the resistance model for the mass accommodation of ethanol molecules by aqueous aerosols. Non-equilibrium corrections have also been calculated for these free energy profiles. Finally, the orientation of the water molecules at the interface is markedly different for the high concentration ethanol solutions as compared to the low concentration ethanol solutions. The effects of these structural differences on the dynamical properties of the interface are investigated.

PHYS 88 [745255]: Drude oscillators for manybody dispersion and polarization: Quantum oscillators in a classical bath

Glenn Martyna, Physical Science Division, IBM Research, TJ Watson Research Center, PO Box 218, Yorktown Heights, NY 10598, Fax: 914-945-4506, martyna@us.ibm.com, and Troy W. Whitfield, Department of Chemistry, University of Pennsylvania

Abstract

Although Bernal and Fowler first pointed out that polarization effects are important determinants of the properties of liquid water in the 1930's, it wasn't until the 1990's that computers became fast enough to allow polarizable water models to be used to study the bulk. Even today, the vast majority of simulations are carried out using mean field models that fail to describe the complex interfaces of interest in the 21st century. Similarly, Barker first noted the surface tension of simple liquids cannot be treated using an empirical pair potential but rather requires manybody dispersion terms to be introduced explicitly in the 1970's but, even with today's computer power the number of calculations employing manybody dispersion is vanishing small. Given the importance of surface tension in determining the hydrophobic effect, it is clear that neglecting manybody dispersion effects will yield substantial error in the properties of complex interfaces. In order to treat both manybody dispersion and manybody polarization consistently and on an equal footing, a novel path integral solution of the quantum Drude model is presented. Since the

computer time required for the new solution is linear with the number of atoms in the simulation, bulk liquids and solids can be studied easily. Applications to solid and liquid xenon and water are presented.

PHYS 89 [746905]: "Forbidden hops" and detailed balancing in mixed quantum-classical dynamics

Priya Parandekar and **John C. Tully**, Department of Chemistry, Yale University, P. O. Box 208107, New Haven, CT 06520, Fax: 203-432-6144, priya.parandekar@yale.edu, john.tully@yale.edu

Abstract

Mixed quantum-classical procedures have been developed to simulate molecular motions when a classical mechanical description alone is not adequate. A crucial property of such theories is feedback between the classical and quantum motions. Quantum transitions are driven by the time-dependent classical motion and, in turn, the forces governing the classical paths are altered by quantum transitions. Another desired property is satisfying detailed balancing, required to achieve the correct equilibrium state. Two general approaches have evolved for incorporating quantum-classical feedback, the self-consistent-field (SCF) and surface-hopping methods. We present a rigorous analysis of detailed balancing in these methods, supplemented by simulations. We show that with the SCF method the quantum populations approach infinite temperature at long times. By contrast, surface hopping with the "fewest switches" algorithm satisfies detailed balance quite accurately. This is only true, however, when transitions to energy forbidden quantum states are disallowed. Thus "forbidden hops", often considered a failing of surface hopping, are actually essential to achieve equilibrium.

PHYS 90 [755632]: Coherent switching with decay of mixing for non-Born-Oppenheimer trajectories

Chaoyuan Zhu, Shikha Nangia, Ahren W. Jasper, and Donald G. Truhlar, Department of Chemistry and Supercomputing Institute, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455-0431, Fax: 612-626-9390, zhuc@comp.chem.umn.edu

Abstract

A new semiclassical trajectory method, called coherent switching with decay of mixing (CSDM), is presented for the treatment of electronically nonadiabatic dynamics. The new method modifies the semiclassical Ehrenfest (SE) method by including decay-of-mixing terms in the equations for the evolution of the electronic density matrix, and decoherent states (pointer states) are introduced with associated decoherent forces to drive the electronic component of each trajectory toward a pure electronic state. Nonadiabatic transitions are taken into account by switching from one decoherent state to another. The effective potential for nuclear motion is self-consistent in the Ehrenfest sense, and the switching algorithm is coherent for each complete passage through a strong interaction region. The method is tested on both one-dimensional method and full-dimensional triatomic two-state model systems, and the results are compared to the semiclassical Ehrenfest method, to several trajectory surface hopping methods, and to accurate quantum mechanical calculations. The CSDM method is found to be the most accurate of the methods tested. This work was supported in part by the National Science Foundation.

PHYS 91 [742898]: Mixed quantum/classical methods for ultrafast vibrational spectroscopy, with applications to water and aqueous solutions of biologically relevant solutes

James L. Skinner, Department of Chemistry, University of Wisconsin, Madison, WI 53706, Fax: 608-262-9918, skinner@chem.wisc.edu

Abstract

I will discuss the use of two mixed quantum/classical methods (system + bath + coupling, and combined electronic structure/molecular dynamics) for obtaining the fluctuating frequency of a vibrational mode on a solute in solution. The fluctuating frequency is used to compute vibrational line shapes, frequency time-correlation functions, and observables associated with ultrafast spectroscopy. I will present applications to water, and aqueous solutions of biologically relevant molecules.

PHYS 92 [746173]: Quantum features of proton transfer in polar environments

James T. Hynes, Département de Chimie, Ecole Normale Supérieure, UMR 8640 PASTEUR, Department of Chemistry & Biochemistry, University of Colorado, 24, rue Lhomond, 75231 Paris Cedex 05, France, Fax: 303 492 5894, hynes@spot.colorado.edu, and Philip Kiefer, Department of Chemistry and Biochemistry, University of Colorado

Abstract

In this talk we will briefly review aspects of our work stressing the importance of the quantum mechanical character of the proton motion for proton transfer reactions in polar environments. Highlights will include aspects of kinetic isotope effects and an 'inverted region' behavior for proton transfer reactions in solution. Further illustrations of the importance of protonic quantum effects will be given for the first proton transfer in the enzyme system triose phosphate isomerase (TIM).

PHYS 93 [765521]: Molecular dynamics simulations of the formation, stability, and dynamics of the aqueous dielectron

Ross E. Larsen, Department of Chemistry, University of California, Los Angeles, 607 Charles E. Young Dr. East, Los Angeles, CA 90095, and Benjamin J. Schwartz, Department of Chemistry and Biochemistry, University of California, Los Angeles

Abstract

Recent mixed quantum and classical simulations of aqueous electrons in solution have suggested the existence of aqueous dielectrons, paired electrons that both occupy a single cavity in bulk water. We present the results of mixed quantum/classical molecular dynamics simulations of aqueous dielectrons, where the electronic structure of the dielectrons has been treated using full multi-reference configuration-interaction, so the effects of exchange and correlation are included exactly. We use quantum umbrella sampling and thermodynamic charging methods to examine the kinetic and thermodynamic stability of both spin-singlet and spin-triplet dielectrons. We also discuss the stability of dielectrons following photoexcitation and estimate the branching ratio for photodissociation as opposed to geminate recombination. In addition to calculating the

stability of dielectrons, we also predict ultrafast spectroscopic signatures that may be used to identify dielectrons in aqueous solution.

PHYS 94 [747210]: Alternative approaches to large-scale electronic structure calculations

Peter Pulay, Department of Chemistry and Biochemistry, University of Arkansas, Chemistry Building, Fayetteville, AR 72701, Fax: 479-575-4049, pulay@uark.edu

Abstract

Standard quantum chemistry (expansion of the orbitals in Gaussians, and exact evaluation of the integrals) still conforms to computers of the 60s and 70s. The Gaussians description of molecular orbitals is very compact, and the small molecules accessible then did not allow approximations. Physicists, less concerned with precision, have long explored a number of alternatives. Modern computers allow more memory-intensive methods, and the large size currently treated molecules requires low-scaling methods. This talk will review alternative methods for large-scale density functional and Hartree-Fock calculations. The methods include purely numerical representations, plane waves, wavelets, fast multipole methods, density fitting, and dual representations. The purpose of these techniques is to accelerate the calculation of the Coulomb, and sometimes the exact exchange energy. Alternative methods for other bottlenecks: the calculation of the local exchange-correlation energy, and the extraction of the molecular orbitals from the Fock matrix will also be reviewed.

PHYS 95 [748091]: Large scale density functional calculations using the Gaussian and plane wave (GPW) method

Juerg Hutter, Physical Chemistry Institute, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland, Fax: 0041-16353868, hutter@pci.unizh.ch

Abstract

An efficient implementation of density functional theory using the Gaussian and plane wave (GPW) method will be discussed. Kohn-Sham orbitals are expanded with Gaussian basis sets and plane waves are used for the description of the electronic density. This scheme allows for an almost linear build-up of the Kohn-Sham matrix by means of efficient screening techniques and fast Fourier transforms. In addition, it scales nominally quadratic in the basis set size (for a given molecular system) but often shows sub-linear effective scaling. For accurate solutions of the Kohn-Sham equations we have developed an optimization scheme that is linear scaling in the basis set size, guaranteed to converge, and efficient due to pre-conditioning. These new algorithms allow for accurate calculations of large systems with large basis sets.

PHYS 96 [754321]: Reduced scaling using the Cholesky integral representation

Thomas B. Pedersen, Department of Theoretical Chemistry, University of Lund, P.O. Box 124, Lund S-221 00, Sweden, Fax: +46 46 222 4543, Thomas.Pedersen@teokem.lu.se, Alfredo M. J. Sánchez de Merás, Department of Physical Chemistry, University of Valencia, and Henrik Koch, Department of Physical Chemistry, Norwegian University of Science and Technology

Abstract

Forming a positive (semi-) definite symmetric matrix, the two-electron repulsion integrals defining the molecular electronic Hamiltonian may be Cholesky decomposed. The decomposition algorithm exploits the (approximate) linear dependence among the columns of the integral matrix to obtain a highly compressed set of Cholesky vectors containing non-redundant information needed for subsequent quantum chemical calculations. The foremost advantages of the Cholesky integral representation are (1) user-defined accuracy relative to the exact integrals, (2) only a fraction of the total integral matrix needs be calculated, and (3) may be used in conjunction with any electronic structure theory. The fundamental algorithm will be discussed and supplemented with numerical sample calculations demonstrating the potential of the technique.

PHYS 97 [760997]: Fast computation with guaranteed precision: Energies, gradients and response properties for HF and DFT

Robert J. Harrison¹, Takeshi Yanai², Zhengting Gan², and Gregory Beylkin³. (1) U. Tennessee and ORNL, Knoxville, TN 37831, harrisonrj@ornl.gov, (2) Oak Ridge National Laboratory, (3) Department of Applied Mathematics, University of Colorado

Abstract

We will describe our new computational framework MADNESS which is based upon multiresolution analysis in multiwavelet bases using separated representations of operators. The initial development includes implementations of HF and DFT for general, all-electron molecules. The effort to compute total energies to a fixed precision of better than 10 micro-H is observed to scale between linearly and quadratically with the system size depending upon the degree of localization of the orbitals.

PHYS 98 [753571]: Forum Discussion: Prospects and challenges for large scale electronic structure calculations

Ernest R Davidson, Chemistry, University of Washington, Box 351700, Seattle, WA 98195

Abstract

A panel chaired by Prof Ernest Davidson will discuss the merits and challenges of various approaches to perform large scale electronic structure calculations. Local correlation methods, plane wave techniques, density fitting and Choleski decomposition approaches will be topics of discussion.

PHYS 99 [750285]: Angular trapping of microparticles: Torque generation and detection with optical tweezers

Michelle Wang, Arthur La Porta, and Scott Forth, Department of Physics, Cornell University, Ithaca, NY 14853, Fax: 607-255-6428, mdw17@cornell.edu

Abstract

We describe an apparatus that can measure the instantaneous angular displacement and torque applied to a microparticle which is angularly trapped. Torque is measured by detecting the change in angular momentum of the transmitted trap beam. The rotational Brownian motion of

the trapped particle and its power spectral density are used to determine the angular trap stiffness. The apparatus features feedback control that clamps torque or other rotational quantities. The torque sensitivity demonstrated is ideal for the study of known biological molecular motors.

PHYS 100 [740481]: Force-clamp spectroscopy monitors the folding trajectory of a single protein

Julio M. Fernandez, Biological Sciences, Columbia University, 1011A Fairchild Center, MC 2449, 1212 Amsterdam Avenue, New York, NY NY 10027, jfernandez@columbia.edu

Abstract

Abstract text not available.