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Ions and Radicals in Condensed Media

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NOTICE

FOREWORD

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13. ABSTRACT (MAXIMUM 200 WORDS)

Twenty-five publications have been wrritten covering energetics and dynamics of ions and radicals in condensed media. Abstracts of five of these publications are included. This report is a summary of some of the subjects with significance to the High Energy Density Materials (HEDM) program and a list of scientific accomplishments achieved during the program.

Optical methods for in-situ generation of radicals and ions in solids has been the main method used in these studies. To this end, we have concentrated on understanding photon induced dissociation, and subsequent photo- and thermal-induced dynamics.

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The contract period, 1990–1993, has been a rather productive one. This is best summarized by the 25 publications that have resulted to–date, on subjects entirely dedicated to the energetics and dynamics of Ions and Radicals in Condensed Media. Abstracts of five of these publications, two of which have been accepted for publication, the other three were recently submitted. The details of the work performed are included in the articles themselves. This report is a summary of some of the subjects with significance to the High Energy Density Materials (HEDM) program and a list of scientific accomplishments achieved during the program.

Optical methods for in–situ generation of radicals and ions in solids has been the main method utilized in our studies. To this end, we have concentrated on understanding photon induced dissociation, and subsequent photo– and thermal–induced dynamics. Understanding these processes in the greatest of rigor has been the motivation in coupling experiments with theory, with simulations, and most recently resorting to time resolved measurements on subpicosecond timescales. Among the most original contributions in our work have been the studies under high pressure. Although several papers have resulted concerning such studies, a significant portion of the completed work is not yet published. A manuscript is now in preparation.

I. Highlights of Main Accomplishments

Time resolved measurements of bond breaking and bond making in condensed matter has been a long standing challenge to chemical physics. Accordingly, Papers 19 and 24 I believe will become landmarks, as they report the first observations of their kind. In Paper 19 we reported the first observation of bond formation in a bimolecular process in the liquid phase. It was shown that the bond between solvent Xe atoms and Xe^+Cl^- forms in 330 fs. Moreover, it was shown that the process could be interrupted by stimulated radiative dissociation of the intermediate. Thus in addition to observing the most fundamental chemical process in real time, the element ot control was also demonstrated. This paper is also significant in demonstrating the coherent nature of cooperative laser induced harpoon reactions –– a two–photon two–electron transition. Paper 25 describes the first time resolved observation of bond–breaking and making in the solid phase. The measurements show that the photodissociation and subsequent cage induced recombination of atoms preceeds without strong dephasing of the initially prepared wavepacket, moreover, it shows that the population coherence can survive extensive vibrational relaxation. This fascinating result opens up a new era in solid state reactive dynamics. For the first time detailed molecular dynamics calculations can be directly compared with experiments. In this paper, we have already demonstrated that the dynamics not only probes the chromophore, but also the cage of isolation, in the form of feedback on the isolated molecule dynamics. Such experiments will pave the way for the future in developing a full understanding of many–body dynamics.

Energetics of radicals in many–body media is perhaps the most mundane information required in devising energetic materials. The difficulty in treating such energetics is due to the open shell nature of radicals. This minimally leads to angular anistropic pair interactions, and more seriously, is expected to have many–body contributions. In order to correctly predict behavior of radicals doped in solids, it is necessary to at least approximately guess these interactions. Exact calculations are in principle possible, but in practice not available. The issue has been discussed in

Paper 22, and detailed test cases were presented in Papers 23 and 25, in which spectral simulations were carried out for open shell atoms and compared with experiment. Additionally in Paper 23 global surfaces were constructed in an attempt to at least rationalize the thermal mobility of atomic oxygen in rare gas solids. In Paper 25 we treated the simplest case, the open shell, one-hole I atom, isolated in crystal Kr and Xe. In this paper we also introduced the method for treating not only the non additive potentials, but also of spectral simulations of coupled electron-nuclear systems in solids. The important result was the determination that at least in stable trap sites, the many-body contributions to potential energy surfaces of open shell systems is less than 5%. The same conclusion was reached in the case of the two-hole atomic oxygen, trapped in Kr and Xe. We were able to reproduce site specific spectra, without adjusting pair interaction parameters. More importantly, it was shown that while the global surfaces are in qualitative agreement with the observed thermal diffusion of O atoms in these solids, they are not refined enough to make quantitative predictions. It is clear that advance in this front is crucial for the predictability of dynamics of radicals in solids.

As an example of bulk metastability, we had suggested in our original proposal the possibility of making ionic Xe^+F^- crystals. We have failed at this task although a significant effort was exerted. Papers 18 and 19 describe the progress we have made in understanding the condensed phase energetics and dynamics of Xe^+F^-, but a detailed reading of these papers will show that more questions have been raised than answered. We now believe that the precursor to ionic crystals, FXe^+F- has been observed, but we have not been able to observe the signature of pairing between the charge transfer centers. We hope in the future to return to this null result. It is entirely possible that the open shell nature of the Xe^+ prevents the formation of a Coulomb lattice. A possible method to overcome this would be to consider the closed shell ion Xe_2^+ as the building block cation. To generate a stable lattice from such a bulky ion, a large counterion, such as I^-, will have to be considered. Due to their large sizes, the reduced Coulombic contribution per pair may not be enough to stabilize this system in the ground state, however, a low lying band-gap may be possible to observe.

High Pressure Studies carried out under this program, have been reported in part, in Publications 6, 8, 12 and 17. This involves both theoretical simulations of constant pressure ensembles, 17, and experiments 6, 8 and 12. The papers published in journals involved Cl_2 and showed reorientation and caging dynamics. The work on F doped solids has been published as HEDM proceedings, however the definitive paper is not complete even though the experimental work is complete. The important result with respect to HEDM applications is the fact that we have been able to stabilize F atoms in solid Ar and solid Kr, at room temperature and for periods of many weeks. The significance of this result is that F atoms are the most mobile species in rare gas solids. They diffuse and recombine in crystal Kr at 17 K, in a matter of seconds. While at pressures of 90 kbar, they are stabilized at room temperature for days. Another aspect of the stability is that it depends greatly on the photogeneration history of the atoms. Thus, at a given pressure, atoms photogenerated at high temperature are stable, however, atoms generated at low temperature undergo catastrophic recombination during warm-up. These solids are clearly under strain, and once the recombination is initiated, it becomes auto-catalytic. Photodissociation has also been clearly demonstrated at pressures as high as 60 kbar. This result is not predictable when simple pair potentials are considered. It is clear that under high pressure the potentials are greatly modified, and a likely picture to use for understanding fragments generated at high kinetic energy is that they may acquire significant ionic character when they pass over cage barriers. It will be a serious challenge to theory to begin understanding these interactions under extreme pressure and kinetic energy conditions. On the other hand, it is clear that studies under moderate pressures, pressures below 10 kbar should be carried out, to enable an understanding based on existing databases.

Multiphoton accessed, exciton mediated dissociation in condensed media has been demonstrated in Papers 11 and 14. These are significant in that they rely on excitation of the bulk for in-situ generation of radicals. This was proposed as a method for preparing radicals in solids under high pressure. Indeed the mechanism relies on exciton trapping of an impurity, accessing ion-pair or charge transfer states. The latter will lead to facile dissociation even in high pressure media since as we had shown in the past, the separation of fragments involves an inverse cage effect. The method was proposed as a viable scheme to produce such solid as H doped H_2, or O doped O_2 under high pressure. It has been recently implemented in Tokyo for the preparation of N doped N_2 (S. Koda, Univ. of Tokyo, private communications).

Photogeneration and subsequent dynamics of some of the most important radical atoms, H (**7, 15, 16, 15**), O (**9, 11, 21, 22, 23**), F (**1, 2, 3, 18, 20**) in solids has been demonstrated and characterized in significant detail. These are first row elements, potentially suitable as dopants that can enhance the energy content of propellants. It is noteworthy that all three of these radical atoms should be possible to isolate in solid H_2 since in all cases a substantial activation barrier prevents reaction at cryogenic temperatures. The lowest barrier is that of F, which is activated by 850 K in the formation of HF + H. Among the aspects for which a firm understanding has emerged in rare gas solids, are: photon induced dissociation probabilities, their dependence on energy, temperature, and intermolecular potentials; photomobilities of fragments; thermal stability of fragments. These, coupled with our relative success in simulations, gives us a rather reliable database for the predictability of behaviors of these radicals in the solid state. The novel aspect of dynamics that has to be characterized, is that of the quantum nature of solid H_2 as a host. We hope that the Phillips Lab will take this consideration in serious account in their future research plans -- there is little understanding of the quantum solid hosts.

Ions in solids have received a secondary interest, since they are suspected to be of little value as energetic materials. Accordingly, they have been for the most part delegated to other groups to study. The work described in Paper 7 has been the basis of a long series of papers from the groups of H. Kunttu and T.F. George. The dynamics of these systems — charge delocalization, mobility, recombination, separation, trapping at impurity sites — is fascinating and will remain of great fundamental interest.

II. Training of Students and Postdoctoral Fellows

Six graduate students were trained under this program. Three have already graduated, and three remain in the graduate program. Four postdoctorals were trained, only one remains in the group. Of the two undergraduates, Ashjian has already been accepted in a medical school, while Sudnik is trying to decide which graduate program to follow. Below is a list of the personnel, including the present positions of those who have already left the group.

Graduate students:

H. Kunttu	Ph.D. 1990	Faculty member at U. of Helsinki
W.G. Lawrence	Ph.D. 1991	Postdoc at U. of Emory
G. Valero	M.S. 1991	Research technician at NASA Ames
J. Zoval	1990–1993	

M. Hill	1991-	
A. Danilychev	1991-	
Postdoctorals:		
E. Sekreta	1990-1992	Postdoc in U. of Kyoto
G.J. Hoffman	1990-1992	Faculty member College of William & Mary
D. Imre	1991-1992	Research staff Brookhaven
R. Zadoyan	1991-	
Undergraduates:		
P. Ashjian	1990-	
L. Sudnik	1991-1991	Grad. School of Chemistry

Publications (1991-1993)

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Patent

Apkarian, V.A.; Fajardo, M.E.; Wiedeman, L.; and Schwentner, N.

Condensed Phase Exciplex Lasers

U.S. Patent 5,134,625 Issued 28 Jul 92

Spectroscopy of XeF in Ar and Ne Matrices

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ABSTRACT

Spectroscopic constants for the $B^2\Sigma^+$ and C2Π charge transfer states of XeF in Ar and Ne matrices are derived from vibrational progressions in excitation and emission spectra. Polarization effects on the T_e values are discussed and Rittner potentials are fitted to the constants. Emissions at 3889 and 411 nm in Ne and Ar respectively are attributed to a distorted B state as B* with a strong red shift of T_e and an about 30% larger ω_e. B* is assigned to XeF center with an additional F atom which can be a precursor to XeF_2 according to a comparison with Xe_2F spectra and the concentration dependence of the intensities. The B* vibrational bands display 2 well resolved fine structure progressions with a common ω_e of 60 cm^{-1} in Ar and Ne which is close to maximum matrix phonon density and one with 30 cm^{-1} in Ne and 15 cm^{-1} in Ar. A reversible change in the Ne finestructure pattern with temperature can be correlated to a fcc-hcp phase transition.

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Temperature induced mobility and recombination of atomic oxygen in crystalline Kr and Xe: I. Experiment

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ABSTRACT

Recombinant molecular spectra of O_2 in crystalline Kr and Xe, obtained from sudden recombination induced by laser pumping of the predissociative B state, and by adiabatic recombination induced thermally, are reported. All electronic states that correlate with $O(^3P)$ + $O(^3P)$ are populated by both methods in Kr. The excited triplet states are strongly perturbed in Xe. Laser induced fluorescence spectra of atomic O are also reported. Two emissions are observed in Kr, one at 563 nm with a radiative lifetime of 11 μs. These are assigned to emissions from neutral $O(^1S)$ trapped in substitutional and interstitial octahedral sites, respectively. O atoms are generated in situ by photodissociation of either O_2 of N_2O. The subsequent thermally induced recombination of atoms is followed using LIF from atomic centers, and molecular thermoluminescence. The recombination follows first order kinetics, from which it is inferred that atomic mobilities are characterized by long-range migration, with migration lengths of $\geq$300A. Site specific Arrhenius rate constants are extracted from the analysis of glow curves. Only two sites, interstitial and substitutional O_h, contribute to the glow curves in crystalline Kr. A third site is present in crystalline Xe. A broad distribution of activation energies is observed in vapor deposited matrices.

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Atomic oxygen in crystalline Kr and Xe:
II. Adiabatic Potential Energy Surfaces

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ABSTRACT

The potential energy surfaces of atomic oxygen, O(^{3}P, ^{1}D, ^{1}S), trapped in crystalline Kr and Xe are developed based on known angularly anisotropic pair interactions. The electrostatic limit, with the neglect of exchange and spin-orbit interactions, is assumed. Using a classical statistical treatment for the simulation of spectra the surfaces are shown to reproduce the experimental O(^{1}S ---- ^{1}D) emissions in substitutional and interstitial sites of crystalline Kr. The surfaces are also in accord with charge transfer emission spectra of O/Xe solids. With lattice relaxation, the Xe-O(^{1}D)-Xe insertion site becomes the global minimum, and can therefore act as a stable trap site. This is in accord with experimental observations of a third trapping site in Xe. To rationalize the recently reported long-range mobility of O atoms in these solids [A.V. Danilychev and V.A. Apkarian, *J. Chem. Phys* (in press)], the topology of various electronic surfaces are presented. It is shown that the minimum energy paths connecting insterstices on the triplet and singlet surfaces are quite different. The triplet path is strongly modulated and proceeds along body diagonals of the unit cell. The singlet path is more gently modulated and proceeds along face diagonals. These features are consistent with the postulated thermal mobility as proceedings via triplet-singlet conversion. However, on a qualitative basis, the electrostatic surfaces fail to support the model. The site specific crossing energies, including lattice relaxation, are calculated to range between 1.2 and 1.7 eV in Xe and Kr, which is an order of magnitude larger than the observed experimental activation energies of migration. Inclusion of spin-orbit and charge transfer mixing in these surfaces, absent in the present treatment, should reduce this discrepancy.

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Coherent photodissociation-recombination dynamics of I_2 isolated in Matrix Ar

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ABSTRACT

Time-resolved studies of photodissociation-recombination dynamics of I_2 isolated in matrix Ar are reported. The experiments consists of pump-probe measurements with a time resolution of 180 fs. The data are analyzed by comparisons with molecular dynamics simulations of the system. A simple treatment, based on the reflection approximation, is employed for the conversion of the classical trajectories to observable signals that can be directly compared to experiment. When I_2 is prepared on the $A(^3\Pi_{1u})$ surface at energies of 3500 cm^{-1} to 1000 cm^{-1} above dissociation, it recombines on the A/A' surfaces and undergoes coherent oscillations in the immediate Ar cage. The wavepacket prepared by the pump pulse recombines coherently and retains its coherence even after extensive loss of energy to the lattice. The observed oscillations are a sensitive function of excitation energy and location of the probe windows; these dependences can be well-understood by analysis of trajectories calculated using a single (A) electronic surface. Vibrational relaxation of the recombinant pair on the A/A' surfaces is completed in 12 ps, in good agreement with the simulations.

Published in *Chem. Phys. Lett.*

Many-Body Potentials of an Open Shell Atom: Spectroscopy of Spin-Orbit Transitions of Iodine in Crystalline

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ABSTRACT

Temperature dependent emission spectra of spin excited iodine in crystalline Xe and Kr are presented and analyzed in terms of non-additive anistropic pair interactions. In the octahedral trap site, the atomic ^2P states split into $E_{1/2}$ and $G_{3/2}$ groups of the double valued representation. The fourfold degenerate $G_{3/2}$ state is subject to strong Jahn-Teller instability and further splits by coupling to phonons into $E_{1/2}$ and $E_{3/2}$ Kramers pairs. Accordingly, the observed emission spectra are composed of two bands: $2E_{1/2} \rightarrow 1E_{1/2}$, $2E_{1/2} \rightarrow E_{3/2}$ transitions. Two pairs of bands are observed each in Xe and Kr. The long-lived pairs (at 15 K, $\tau = 250$ μs and 930 μs in Xe and Kr respectively) are assigned to the isolated atom, while a short lived pair of bands (at 15 K, $\tau < 1$ μs in Xe, and $\tau = 2.2$ μs in Kr) are assigned to I atoms trapped as nearest neighbor to a localized charge, identified as $(HRg)^+$. The isolated atom spectra are simulated by Monte Carlo methods which assume classical statistics in the heavy atom coordinates, and adiabatic following of the electronic coordinate. Angle dependent, gas phase pair interactions are used as a starting point. Minor modifications to the pair interactions, and a temperature dependent spin-orbit splitting constant, adequately reproduce the experimental spectra. Many-body contributions to the effective pair potentials can be estimated to be smaller than 5%.

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