

OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/
HONORS/STUDENTS REPORT

for

Contract N00014-J-1761

DTIC
ELECTE
JUN 15 1992
S A D

R&T Code 413n001

Nanocrystals on Inert Substrates

Robert L. Whetten, Principal Investigator

*Department of Chemistry and Biochemistry
University of California, Los Angeles, California 90024*

June 1992

Reproduction in whole or in part is permitted for any purpose of the
United States Government.

This document has been approved for public release and sale; its
distribution is unlimited.

92-15277



92 6 11 008

AD-A251 486



2

Part I

- Papers submitted to refereed journals

- Reactions in Cluster-surface Collisions: F⁻-transfer in scattering of alkali-fluoride nanocrystals from silicon*, P. M. St.-John, R. D. Beck, R. L. Whetten, submitted to J. Chem. Phys., revised version submitted to Phys. Rev. Lett. (1992).
- Recoil Velocity Distributions of Surface-Scattered C₆₀ by Re-ionization*, C. Yeretdzian, K. Hansen, R. D. Beck, R. L. Whetten, Chem. Phys. Lett. submitted (1992).
- Stability Islands for Doubly-Charged Clusters: Secondary Ionization of Alkali-Halide Clusters by Ultraviolet Radiation*, X. Li, R. D. Beck and R. L. Whetten, Chem. Phys. Lett., (1992).
- Scattering of Mass-selected Alkali-Halide Clusters from Solid Surfaces* R. D. Beck, P. St. John, and R. L. Whetten; submitted to J. Chem. Phys.
- Alkali-halide nanocrystals* R. L. Whetten, submitted to Acc. Chem. Res. (1992).
- Collisional Probes and Possible Structures for La₂C₈₀* C. Yeretdzian, K. Hansen, M. M. Alvarez, E. G. Gillan, K. Holczer, R. B. Kaner, K. S. Min, R. L. Whetten, Chem. Phys. Lett. in press (1992)
- Fragmentation of C₆₀: A thermally forbidden process*, R. D. Beck, C. Yeretdzian, F. Diederich, R. L. Whetten, Nature, submitted.
- Persistence of Electron Pairing in Cold Metal-Atomic Clusters*, J. L. Persson, M. L. Homer, E. C. Honea, R. L. Whetten, Chem. Phys. Lett. submitted (1992).
- Magnetization and Susceptibility of Ferromagnetic Clusters*, J. L. Persson, B. J. Salisbury, R. L. Whetten, Europhys. Lett. submitted (1992)

- Papers published in refereed journals

- Impact-induced cleaving and melting of alkali-halide nanocrystals* R. D. Beck, P. St. John, M. L. Homer, R. L. Whetten Science **253**, 879 (1991).
- De-metallization of excess-electron alkali-halide clusters* R. D. Beck, P. St. John, M. L. Homer, and R. L. Whetten, Chem. Phys. Lett. **187**, 122 (1991).
- Photon-stimulated ejection of atoms from alkali-halide nanocrystals* X. Li, R. D. Beck, R. L. Whetten, Phys. Rev. Lett. **68**, 8 June (1992).
- Resilience of All-Carbon Molecules C₆₀, C₇₀, C₈₄: A Surface-Scattering, Time-of-Flight Investigation* Beck, R. D.; St. John, P.; Alvarez, M. M.; Diederich, F.; Whetten, R. L. J. Phys. Chem. **95**, 8402-9 (1991).
- Delayed emission of electrons from C₆₀ following energetic impact against graphite*, C. Yeretdzian and R. L. Whetten, Z. Phys. D in press (1992).
- Hyperthermal scattering of SiN[±] Clusters From Solid Surfaces*, P. St. John and R. L. Whetten, Chem. Phys. Lett. in press (1992).
- Structure-dependence of ammonia adsorption on alkali-halide clusters* M. L. Homer, F. E. Livings-ton, R. L. Whetten, J. Am. Chem. Soc. in press (1992).
- Evidence for Electron Shells in Metal-Atomic Cluster with 100-1300 Electrons* J. L. Persson, R. L. Whetten, H.-P. Cheng, and R. S. Berry, Chem. Phys. Lett. **186**, 215 (1991) [Also NSF-PYI, and ONR to RSB]
- Ionization energies and stabilities of Na_n, n < 25* M. L. Homer, J. L. Persson, E. C. Honea and R. L. Whetten, Z. Phys. D **22**, 441-7 (1991)

A-1

Electronic Structure and Binding Energies of Aluminum Clusters H-P. Cheng, R. S. Berry, and R. L. Whetten, Phys. Rev. B **43**, 10647 (1991)
Complete Statistical Thermodynamics of the Cluster Solid-Liquid Transition H-P. Cheng, X. Li R. L. Whetten and R. S. Berry, Phys. Rev. A in press (1992).

A number of papers published or in press on molecular carbon have cited ONR support, including the following:

- Isolation of D₂-C₇₆: A Chiral Allotrope of Carbon* Ettl, R.; Chao, I.; Diederich, F.; Whetten, R. L. Nature **352**, 149-153 (1991).
- Fullerene Isomerism: Isolation of C_{2v}-C₇₈ and D₃-C₇₈* Diederich, F.; Whetten, R. L.; Thilgen, C.; Ettl, R.; Chao, I.; Alvarez, M. M. Science **254**, 1768 (1991).
- La₂C₈₀: a soluble dimetallofullerene* M. M. Alvarez, E. G. Gillan, K. Holczer, R. B. Kaner, K. S. Min, and R. L. Whetten, J. Phys. Chem. **95**, 10561-3 (1991)
- Beyond C₆₀: The higher fullerenes* F. Diederich and R. L. Whetten, Acc. Chem. Res. **25**, 119 (1992).
- Endohedral Rare-Earth Fullerene Complexes*, E. G. Gillan, C. Yeretizian, K. S. Min, M. M. Alvarez, R. L. Whetten, R. B. Kaner, submitted to Nature, revised version in preparation (1992).
- Alkali-Fulleride Superconductors: Synthesis, Composition, and Diamagnetic Shielding* Holczer, K.; Klein, O.; Huang, S.-M.; Kaner, R. B.; Fu, K.-J.; Whetten, R. L., Diederich, F. Science **252**, 1154-1157 (1991).
- Structure of Single-Phase Superconducting K₃C₆₀* Stephens, P. W.; Mihaly, L.; Lee, P. L.; Whetten, R. L.; Huang, S.-W.; Kaner, R.; Diederich, F.; Holczer, K. Nature **351**, 632-634 (1991).
- Pressure Dependence of Superconductivity in Single-Phase K₃C₆₀* Sparn, G.; Thompson, J. D.; Huang, S.-M.; Kaner, R. B.; Diederich, F.; Whetten, R. L.; Gruner, G.; Holczer, K. Science **252**, 1829-1831 (1991).
- Atomic Force Microscope Studies of Fullerene Films: Highly Stable C₆₀ fcc (311) Free Surfaces* Snyder, E. J.; Anderson, M. S.; Tong, W. M.; Williams, R. S.; Anz, S. J.; Alvarez, M. M.; Rubin, Y.; Diederich, F. N.; Whetten, R. L. Science **253**, 171-173 (1991).
- Critical Magnetic Fields in the Superconductive State of K₃C₆₀* Holczer, K.; Klein, O.; Gruner, G.; Thompson, J. D.; Diederich, F.; Whetten, R. L. Phys. Rev. Lett. **67**, 271-274 (1991).
- Magnetic-field penetration depth in K₃C₆₀ measured by muon spin relaxation* Uemura, Y. J.; Keren, A.; Le, L. P.; Luke, G. M.; Sternlieb, B. J.; Wu, W. D.; Brewer, J. H.; Whetten, R. L.; Huang, S. M.; Lin, S.; Kaner, R. B.; Diederich, F.; Donovan, S.; Gruner, G.; Holczer, K. , Nature **352**, 605-607 (1991).
- Pressure and Field-Dependence of Superconductivity in Rb₃C₆₀* Sparn, G.; Thompson, J. D.; Whetten, R. L.; Huang, S.-M.; Kaner, R. B.; Diederich, F.; Gruner, G.; Holczer, K. Phys. Rev. Lett. **68**, 1228 (1992).
- Isolation of the T_c = 29.6 K superconducting compound fcc-Rb₃C₆₀* Holczer, K.; Chalmers, G. R.; Wiley, J. B.; Huang, S.-M.; Kaner, R. B.; Strouse, C. E.; Diederich, F.; Whetten, R. L. Synthetic Metals, in press.
- Giant vibrational resonances in A₆C₆₀ compounds* K.-J. Fu, W. L. Karney, O. L. Chapman, S.-M. Huang, R. B. Kaner, F. Diederich, K. Holczer, R. L. Whetten, Phys. Rev. B in press (1992).
- Normal-State Magnetic Properties of K₃C₆₀* W. H. Wong, M. Hanson, W. G. Clark, G. Gruner, J. D. Thompson, R. L. Whetten, S.-M. Huang, R. B. Kaner, F. Diederich, P. Petit, J.-J. Andre, K. Holczer Europhysics Lett. **18**, 79 (1992).
- Time-Resolved Degenerate Four-Wave Mixing in Thin Film C₆₀ and C₇₀ Films using Femtosecond Optical Pulses*, M. J. Rosker, H. O. Marcy, T. Y. Chang, J. Khoury, K. Hansen, and R. L. Whetten, Chem. Phys. Lett. submitted.

Normal-State and Superconducting Properties of A₃C₆₀ Compounds, K. Holczer and R. L. Whetten, submitted to (1992).

- Book Chapter Published

Soft-Landings, Hard Rebounds, and Fracture of Alkali-Halide Nanocrystals
Rainer D. Beck, Pamela St. John, Margie L. Homer, and Robert L. Whetten
Clusters and Cluster-Assembled Materials, Mat. Res. Soc. Symp. Proc. 206, 639 (1991)

- Invited Presentations at Conferences

1. Fall Meeting of the Materials Research Society, Special Session on Buckyballs: New Carbon Materials, [A. Kaldor, organizer] Boston MA (30 November 1991)
2. Telluride Summer Research Center Workshop on Clusters, [R. L. Whetten and D. Ray, co-organizers] Telluride CO (24 June - 7 July 1991)
3. ONR Contractor's Meeting, [R. DiMarco and M. Ross, organizers], Alexandria VA, (18-20 July 1991)
4. Workshop on Fullerene Compounds, [J. Fischer organizer], Philadelphia, PA (2-3 August 1991)

Since early autumn (1991), the PI has presented about ten (10) invited talks at major conferences. An updated list will be forwarded shortly.

- Contributed Presentations at Conferences

1. Gordon Research Conference on Metal and Semiconductor Clusters, [M. Mandich, organizer], Wolfesboro NH (5-9 August 1991)
2. Gordon Research Conference on Organic Superconductors, Irsee, Germany, September 1991.

- Number of Students and Postdoctoral Fellows Receiving Support

Three graduate students
Two postdoctoral fellows

The following is a complete list over the last five years under ONR support.

Margie L. Homer	Chemistry, 5th year	Swarthmore College
Xiuling Li	Chemistry, 4th year	Beijing University
Joseph Khoury	Chemistry, 3ndyear	Northwestern Univ. (M.S.)
Pamela St. John	Chemistry, 3nd year	SUNY-Stony Brook
Dr. Rainer Beck (89-91)	Assistant Professor (Habil. Cand.), Universität Karlsruhe	[Ph.D. Oregon State Univ. (89)]
Eric C. Honea, Ph.D. Physics 1990, AT&T Bell Laboratories		Univ. of Calif.-Irvine
	<i>Localization of Excess Electrons in Alkali Halide Clusters</i>	
Dr. David Hales (90-)	Ph.D. UC-Berkeley (90)	
Dr. Chahan Yeretizian (91-)	Ph.D. Universität Bern	

Part II

- a. **Principal Investigator:** Robert L. Whetten, Professor
Department of Chemistry, UCLA
- b. **Cognizant ONR Scientific Officer:** Dr. John Pazik
- c. **Telephone Numbers:** (310) 825-2836
(310) 206-7655 (FAX)
- d. **Brief Project Description:**

The interaction of clusters with surfaces is under investigation with regard to the following:

- (i) deposition of neutral or charged clusters beams as a method for growth of highest quality thin films
- (ii) deposition of size-selected cluster beams for creating novel cluster-assembled materials;
- (iii) consequences of energetic collisions of large clusters with solid surfaces; and
- (iv) use of collision phenomenology for determining cluster structure and energetics.

Our approach consists of two parallel efforts: (i) We use size-selected, energy-resolved charged cluster beams in collisions with crystalline surfaces for measurements of the mass-, angle- and energy-distributions of scattered clusters and fragments. (ii) We characterize the states of clusters deposited under well-defined conditions by surface-analysis methods.

The clusters investigated are larger atomic and compound clusters, such as larger fullerenes, silicon, and I-VII and II-VI compounds. The surfaces are graphite or silicon crystals, polycrystalline gold, and self-assembled monolayers.

- e. **Significant Results During Last Year:**

The year June 1991 through May 1992 included the end of the earlier project, "Cluster-Surface Processes and Interactions" and the beginning of a renewal project entitled "Scattering, Deposition and Spectroscopic Investigation of Nanocrystals on Inert Substrates." All the published or submitted reports pertain to work initiated in the former project, with emphasis on cluster-surface collisions, scattering, and energization phenomena. At the same time, we have implemented plans to carry

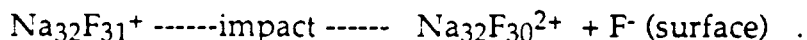
out the experiments on the special, larger clusters ("nanocrystals") after they are mass-selected and deposited on inert substrates. The progress in this direction is mostly concerned with the assembly of the surface chamber. The first results from this newer work are expected in late summer.

In the final full year of the earlier project, there have been several major developments, now reported in complete manuscripts or accepted papers.

Found that low-energy impact (< 1 eV per atom) of alkali-halide nanocrystals against graphite or silicon surfaces results in *cleavage* of the nanocrystals -- an unique process not identified previously. This process was found for clusters of many different compositions and charge-states ($\pm$). At higher energies the impact transforms the cluster into a molten or disordered state. These investigations have been accepted for publication as a Research Article (ie. one describing a major development in its field) in *Science*.

(iii) Found evidence for transient adsorption-desorption phenomena in the alkali-halide nanocrystal / graphite-surface system. This serves as indirect evidence for the 'soft-landing' regime.

(iv) Found that low-energy impact of larger alkali-halide nanocrystals (> 60 atoms) results in a reactive channel with the silica surface -- transfer of a halide ion to the surface. This process is detected by collection of the doubly-charged clusters, ie.



This novel channel is also under further investigation.

(v) Discovered that larger carbon clusters (fullerene molecules $\text{C}_{60}^{\pm}$, C_{70}^{+} , C_{84}^{+}) are able to survive highly energetic collisions with graphite or silicon surfaces. [This was in parallel to the experiments at NRL establishing the same conclusion, and has been interpreted in terms of the resilience of the fullerene bonding network in accord with the NRL theory-group simulations of C_{60} -diamond scattering.]

(vi) Directly demonstrated other features of the $\text{C}_{60}^{\pm}$ surface-scattering process, including: (a) the important role of impact-induced neutralization (e-transfer), as demonstrated by re-ionization of scattered neutrals; (b) existence of an electron-ejection threshold (perhaps associated with thermionic emission) in C_{60}^{-} scattering; (c) the scattered C_{60} is strongly heated by impact, as demonstrated by direct photofragmentation subsequent to the collision event.

(vii) Performed the first measurements of the recoil velocity distribution of a surface-scattered cluster, for the case of 'bouncing buckminsterfullerene.' These provide a sensitive comparison with the theoretical simulations (Mowrey et al. of NRL) of the impact-scattering process.

(viii) Employed the impact excitation method to study a number of other interesting cluster systems, including excess-metal alkali-halides (F-center clusters -- see paper in press), and charged water clusters.

In addition to this main activity, ONR support has been used to assist in the area of molecular carbon research at UCLA. Particularly important in this regard are support of the following:

(i) The development of an apparatus for high-yield production of C_{60} and larger fullerenes. Purified samples of C_{60} , C_{70} and larger fullerenes, all obtained in this apparatus, supplied the UCLA research activities and were also supplied to researchers in many other laboratories during the crucial, initial stage (September through December).

(ii) The analysis of molecular carbon samples by laser-desorption/nozzle-jet/time-of-flight mass spectrometry.

(iii) The large-scale production and separation of fullerenes as required for solid-state reaction studies leading to the first single-phase alkali-fulleride superconductors, and ultimately to their full characterization.

A final additional activity supported by ONR has been the investigation of the optical and excited-state properties of alkali-halide nanocrystals. These systems serve as models for the processes occurring at the surfaces of insulator systems and ultrafine particle composites. We have demonstrated that excitation to the conduction (charge-transfer) band of these systems results quantitatively in the ejection of a neutral halogen atom. This process has not yet been observed from crystalline surfaces.

f. Plans for Next Year

We have begun the investigation of the scattering and deposition of silicon clusters ($Si_N^\pm$) from a number of surfaces. These systems are important from the standpoint of deposition, and also because of the novel properties of nanostructure silicon/silica as light-emitters. However, they remain very poorly understood. A major assault on these systems could lead to a breakthrough in understanding, so we would like to contribute. With continued support, we intend to continue this effort, and perhaps examine the II-VI materials (CdS etc.) in the same way. Also with continued or renewed support, we intend to complete the upgrade of our capabilities to include better surface characterization, both prior to and following cluster scattering or deposition.

g. Graduate Students

Pamela St. John	Chemistry
Margie L. Homer	Chemistry
Joseph T. Khoury	Chemistry
Xiuling Li	Chemistry

h. Postdoctoral Fellow

Dr. Chahan Yeretzian
Dr. David C. Hales

Part III

Research Highlight:

Reactions in Cluster-Surface Collisions

Background: Cluster-surface interactions are important in the process of thin-film growth by the ionized cluster beam (ICB) or natural cluster beam (NCB) methods, and also in the formation of novel cluster-assembled materials (CAM) by deposition of size-selected clusters. These interactions can be studied by : (i) surface collisions of cluster beams under well-defined conditions, combined with (ii) characterization of the properties of supported clusters that have been deposited under these conditions. This project pursues both paths. Secondly, the measurement of collision outcome observables (such as fragment, energy and angular distributions) can give vital information on cluster structure and energetics, while the ability to vary the cluster-size over a wide range enables tests the scaling predictions from the atomic to 'droplet' projectile regimes.

Our approach is to collide mass-selected, charged atomic or compound clusters at well-defined incident velocities against a crystalline surface of various materials, either clean or with a particular overlayer. By varying the collision energy and angle, we are characterizing the 'soft-landing' regime by examining the scattering yield of neutral and charged clusters and the properties of the surface-supported clusters.

Our early efforts have focussed on the scattering processes. In the past year we have constructed, tested and implemented the collider instrument, [which controls the energy and angle of the incident cluster, the surface parameters (temperature and cleanliness), and the scattering detector] and the cluster beam and mass-selector, [consisting of a laser-vaporization/supersonic helium nozzle source, a pulsed ion accelerator, and a fast mass-gate]. This instrument has been thoroughly characterized by carrying out collision-fragmentation experiments with standard molecular ions in place of the charged-cluster beam. And new experiments using carbon cluster ions and graphite surfaces have begun to yield insight into the sticking, energy transfer, angular distribution, and fragmentation patterns of these processes.

The following research highlight provides a specific example of the state of this research project. Papers cited above provide more detailed information.

Caption for accompanying figure

Time-of-flight profile for the $\text{Na}_{53}\text{F}_{52}^{+}$ (3x5x7 nanocrystal, inset) at the impact energies 15 eV (1.1 km/s, upper trace) and 50 eV (2.1 km/s, lower). The important process, besides intact scattering, is the F⁻-transfer channel, giving $\text{Na}_{53}\text{F}_{51}^{2+}$; at the higher energy the probabilities of these processes are nearly equal.

Cluster-Surface Reactions

*Pamela St. John, Chahan Yeretdzian, Rainer D. Beck, and
Robert L. Whetten*

Department of Chemistry
University of California, Los Angeles

Significance: Cluster-surface impact is important in--

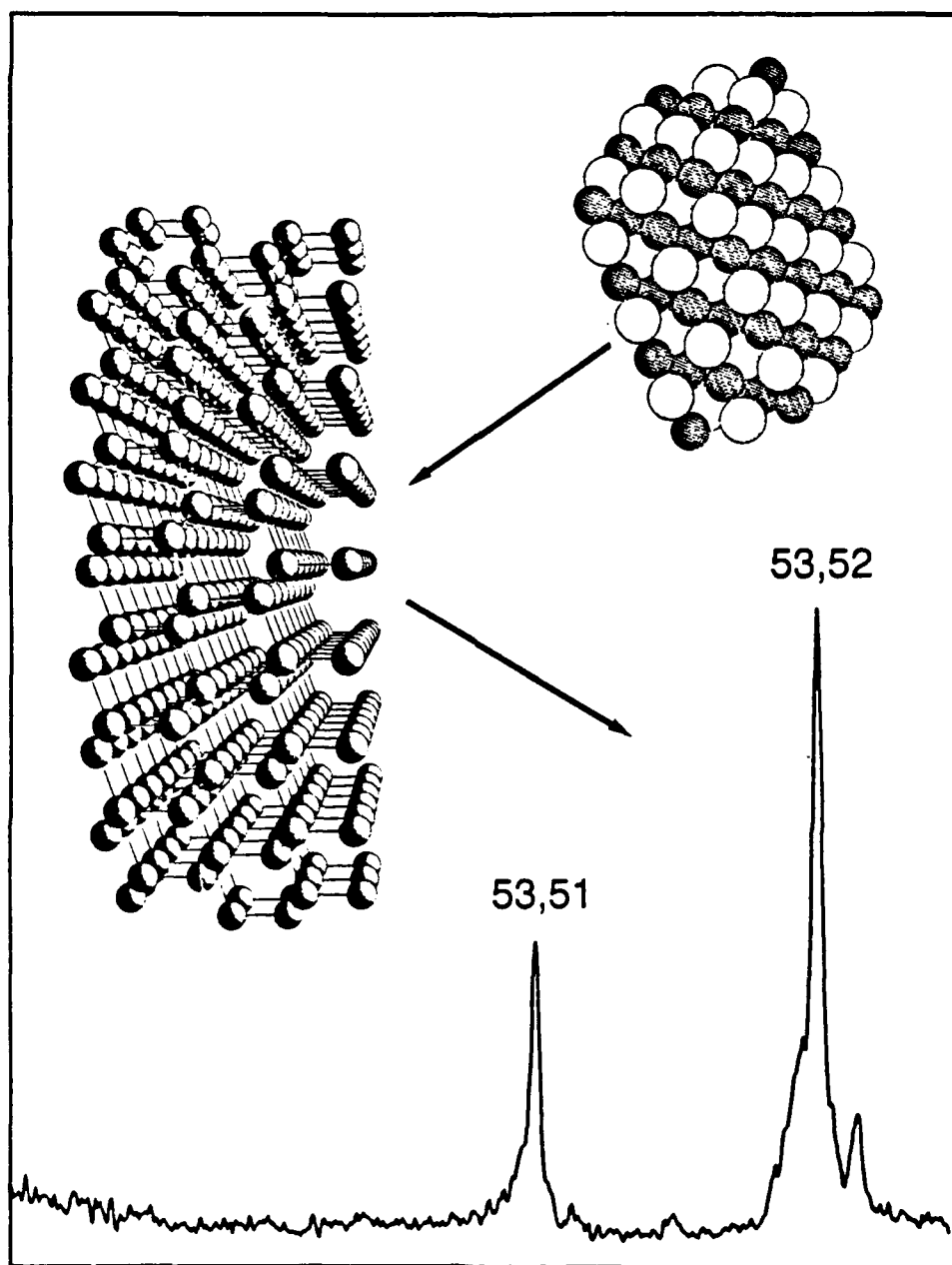
- (1) Surface modification
- (2) Forming cluster-assembled materials (CAM)
- (3) Phenomena resulting from energetic-beam/solid interactions
- (4) Novel reactions in compressed nanomatter

Approach taken--

- (1) Mass-, energy-, and angle-resolved collisions of cluster beams with crystalline surfaces and overlayers.
- (2) Characterization of clusters deposited under well-defined conditions

Example- Reactive collisions between NaF nanocrystals and Si(111) surfaces

**Funding provided by Office of Naval Research*



Time-of-flight