Arkansas University Chemistry and Biochemistry

ONR CONTRACT INFORMATION

Contract Title: Time-Resolved Elec Diff
Contract Number: N00014-85-C-0757
Work Unit Number: 4327-864
Scientific Officer: R. S. Miller

Annual Technical rept.

Enclosure (1)
a. Description of Scientific Research Goals.

It is the goal of this research to construct an instrument for Time-Resolved Electron Diffraction (TRED) studies of the structures of short-lived, energetic molecular states and of the dynamics of primary dissociation processes found in molecules of energetic materials.

The TRED experiments will be performed by focusing the 193 nm output of a pulsed ArF excimer laser (pulse duration 10-20 nanoseconds) onto the cold photocathode of a high voltage electron gun, where electron pulses will be generated by field-assisted photoelectric emission. These electron pulses will be scattered off the gas-phase molecules in an effusive molecular beam after some fraction of the beam population has been excited by a pulse from a XeCl excimer-pumped dye laser. Electron diffraction intensities will be recorded using the real-time gas electron diffraction (GED) technology developed at the University of Arkansas[1,2]. By synchronizing the dye laser excitation pulse and the diagnostic electron pulse, intensity data can be obtained from molecules which all have the same age relative to the time of excitation. Thus, time-resolved observations of excited molecular states and of transient reaction products should be possible.

b. Significant Results of the Past Year.
b.1. Design and Construction of the Pulsed Photocathode.

Construction of the photocathode (PC) unit, begun last year, was completed. That is, PC vacuum chamber was assembled and put into operation; electron gun construction for space-charge limited pulsed electron emission was completed after thorough theoretical analysis; a second excimer laser was installed, tested, and the first excimer laser overhauled (converted to 3-phase electrical power with an improved thyratron); laser synchronization mode was selected and the synchronizer obtained; PC chamber was HeNe laser-aligned with the ArF excimer and the optical system for delivery of the 193 nm laser light onto PC emitting surface was installed; PC vacuum system was successfully tested and the first photoemitted pulsed electron beam was obtained.

Preliminary results indicate 1) that space-charge limited electron pulses can be easily obtained by our procedure; 2) that the pulsed electron beam can be readily focused with a magnetic lens to a diameter suitable for GED experiments; and 3) that the duration of the electron pulses is comparable to that of the ArF excimer-pump laser pulses.
b.2 Attempts to Improve Angular Detection Range and Detector Sensitivity.

To improve the existing detection mode, as described last year, a fiber optic detector system was designed and constructed. The system consists of a vacuum fiber window, a fiber coupler (1:1 or 2:1 imaging), and a Tracor Northern fiber optic covered photodiode array. The new detector was interfaced to an IBM personal computer, and its characteristics are currently being tested.

A considerable part of the funds needed for the ongoing detector improvement research is covered by an NSF grant ($115,000, starting date 4/1/87) which supports attempts to employ our real-time GED data recording technique as a detector for gas chromatography. High detector sensitivity is needed for this application as for the TRED studies in preparation.

b.3 GED Studies of the Products of Pyrolytic Reactions.

During the last year the first successful identification was reported [3] of photochemical reaction products observed by using our procedures. In these experiments, cis-1,2-dichloroethene (CDCE) and trans-1,2-dichloroethene (TDCE) were irradiated with 193 nm excimer laser light shortly before their GED patterns were recorded. TDCE was found in the diffraction pattern of irradiated CDCE, and CDCE was found in the pattern of irradiated TDCE. Experiments of this kind, albeit time-unresolved and involving stable molecular species, are directly useful for the TRED studies in preparation, because they provide us with the opportunity to gather experience in the analysis of GED data of mixtures containing several components.

In a variation of these experiments, a CO$_2$ laser (on loan from NRL) was restored. A special quartz inlet system was built for the electron diffraction instrument (in collaboration with W.Braun at NBS). A laser delivery system (contained beam) was designed and installed by which the CO$_2$ laser output can be focused onto the tip of the GED inlet system, thus heating a small area to temperatures of up to 1500K. In the diffraction chamber, the heated tip is less than 1 mm away from the electron beam. Thus, GED patterns can be obtained of gases immediately after they have traversed the high temperature region, and pyrolysis products can be observed before they can undergo collision-induced secondary reactions. First experiments were performed with CF$_3$I heated in this way. Temperature dependent changes in the diffraction intensities are clearly visible. Attempts at quantitative analysis are underway.
c. Plans for Next Year's Research.

During the next year we plan to continue the project by taking as many of the following steps as time will allow:

1.) Build a collimating and focusing system for the PC pulsed electron beam. Characterize the electron pulses (current and duration), measure laser and electron pulse temporal correlation, and determine correlation between irradiation intensity and photoemission intensity. Design and construct a gas inlet system for the PC-connected diffraction chamber, and expand the existing pumping system of the latter to make gas-phase experiments possible. Record first GED patterns with the new PC beam (solid state and gas phase samples). Construct the dye laser delivery system, implement and test the prepared excimer laser synchronization procedure, and initiate first studies of transient species.

2.) Develop data acquisition software for the fiber optic detector system, integrate the new detector with a diffraction chamber, and perform test GED experiments.

3.) Perform pyrolysis experiments using the CO₂ laser-heated inlet system in attempts to record GED data of energetic and reactive molecular species.

List of Publications/Reports/Presentations

1. Papers Published in Refereed Journals:


3. Presentations:
   a. Invited:


   b. Contributed:


4. Books: none
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Enclosure (3)
h. List of Participants.

At the University of Arkansas:

1. Dr. John D. Ewbank, promoted to tenure-track Assistant Professor of Chemistry, as of August 1987.
2. Dr. David L. Monts, Assistant Professor.
3. Dr. David W. Paul, Associate Professor.
4. Dr. Lothar Schafer, Professor.
5. Dr. Khamis Slam, postdoctoral research assistant.
6. Susan Kulp, graduate student.
7. Stephen Bowling, undergraduate research participant.

At NRL:

   Dr. W. L. Faust, Optics Division.

1. Other Sponsored Research:


Proposals Submitted: none.
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT
(Number Only)

Papers Submitted to Refereed Journals (and not yet published): none
Papers Published in Referenced Journals: one
Books (and sections thereof) Submitted for Publication: none
Books (and sections thereof) Published: none
Patents Filed: none
Patents Granted: none
Invited Presentations at Topical or Scientific/Technical Society Conferences: one
Contributed Presentations at Topical or Scientific/Technical Society Conferences: one
Honors/Awards/Prizes: none

Enclosure (4)
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