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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: D-1	2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): Annual Progress Report of Contract: Photoactivation and Dissociation Kinetics.	5. TYPE OF REPORT & PERIOD COVERED: 4-1-78 - 3-31-79
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Edward K.C. Lee	8. CONTRACT OR GRANT NUMBER(s): N-000 14-75C-0813
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, University of California, Irvine, California 92717	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: Phys. Program, NR014-506, Phys. Sci. Div., ONR, DOE
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, 1030 E. Green St., Pasadena, California	12. REPORT DATE: Nov. 20, 1978 13. NUMBER OF PAGES: 4
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Unlimited

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Unlimited

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

18. SUPPLEMENTARY NOTES

Annual progress rept. 1 Apr 78 - 31 Mar 79,

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Photoactivation, Dissociation Kinetics, Selected Rotational and Vibrational States

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This is a short annual progress report on the present contract, for which a renewal to continue the project one more year has been submitted. A publication list is accompanied.

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S/N 0102-LF-014-6601

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ANNUAL REPORT OF CONTRACT

N-00014-75C-0813

"Photoactivation and Dissociation Kinetics"

by

Edward K. C. Lee

Department of Chemistry
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Irvine, California 92717

November 20, 1978

1. Contract Description (April 1, 1979 - March 31, 1980)

The electronic relaxation (radiative and nonradiative transitions), decomposition, and reaction kinetics of the small, electronically excited molecules formed by laser excitation will be studied in the gas phase.

2. Scientific Problem

The broad scientific aim of this research is to investigate intramolecular electronic relaxation processes, related vibrational and rotational energy redistribution, and dynamics of photodissociation. More specifically, the experimental effort of the forthcoming year will be directed toward (1) the preparation of the laser-excited small molecules (3 and 4 atoms) in a specified rotational, vibrational, and electronic state (single rovibronic level, SRVL), (2) the measurement of the energy disposal of the excess internal energy, and (3) the probing of the fate and the time-evolution of the prepared excited state. This experimental information will then be used to find suitable theoretical description for the relaxation mechanism and justifications for the observed rates of relaxation. Since the molecules of interest are important to atmospheric chemistry, laser isotope separation, and combustion chemistry, the experimental data obtained on the primary photochemical and kinetic processes on these molecules are very desireable.

We will carry out detailed studies on HNO, SO_2 and H_2CO. Our recent studies on the rotationally and vibrationally selected states of formaldehyde have shown dramatic effects of Coriolis coupling, singlet-triplet perturbation, Fermi resonance and other interactions on the photochemical transformation mechanism. Therefore, we will extend the studies to other small molecules such as HNO and SO_2. Because of the strict conservation of the angular momentum, the rotation plays a greater mechanistic role than the vibration. The importance of rotation to the energy migration involved in the mode selectivity of chemical processes will be examined.

3. Scientific and Technical Approach

Our photoactivation studies involve (1) preparation of a specified rovibronic state, (2) steady-state spectroscopic measurement, (3) time-resolved spectroscopic measurement, and (4) final product analysis. The preparation of the SRVL involves finely tuned dye laser excitation of low pressure samples under collision free condition. The steady-state spectroscopic measurement involves either or both of excitation spectroscopy and emission spectroscopy. The time-resolved study involves the decay time measurements by either pulsed or modulated excitation. The final product analysis is achieved by either chromatographic or spectroscopic measurement involving chemiluminescence. In order to improve the sensitivity of our laser induced fluorescence measurements, a multiple path

absorption/fluorescence cell with the White cell optics for absorption and the Welsh cell optics for fluorescence collection is being used. A use of a digital signal averager also improves the sensitivity of the electronic instrumentation.

4. Progress (April 1, 1978 - Present).

We have made a substantial progress in improving the sensitivity of the overall fluorescence emission apparatus by the use of a multiple reflection cell thereby permitting the collision-free, low pressure studies possible. Using this instrumentation, recently we have measured the absolute quantum yield of the fluorescence emission (Φ_F) from a number of SRVL of H_2CO. It was found that for the 4^1 ($\nu_i' = 1$; $E_{vib} = 1125\ cm^{-1}$) level the values of Φ_F steadily decreased with the increase of the K' quantum number but irregularly varied with the J' quantum number. This appears to support a mechanism involving a weak Coriolis coupling between the 4^1 and the 4^0 level.

We are extending the above studies to other SVL's and to HNO and SO_2. For the HNO study we are designing a flow reactor/cell, since HNO is a transient species. For the SO_2 study, we are using a larger multiple path cell than the one used for the H_2CO study.

We have completed our ozone photolysis study between 250-300 nm to show that the relative quantum yield of the $O(^1D)$ atom formation is constant throughout. We have used a NO_2 chemiluminescence technique to determine the $O(^1D)$ atom yield.

5. Publications

From ONR supported research program this contract year, two papers have been published (a, b), three papers have been accepted for publication (c, d, e), and two review articles are in press (f, g).

(a) A Novel Electrode Adaption for N_2 Lasers.
Review of Scientific Instruments, 49, 395 (1978).
Amnon Fischer, Jon R. Peacock, and Edward K.C. Lee.

(b) Single Vibronic Level Photochemistry of Formaldehydes in the $\tilde{A}\ ^1A_2$ State: Radiative and Non-Radiative Processes in H_2CO, HDCO, and D_2CO.
Journal of Chemical Physics, 68, 4448 (1978).
Richard G. Miller and Edward K.C. Lee.

(c) Relative Quantum Yields of O (^1D) in Ozone Photolysis in the Region Between 250 and 300 nm.
Chemical Physics Letters, accepted for publication.

(d) Rotational Dependence of the Fluorescence Quantum Yields of H_2CO and D_2CO ($\tilde{A}\ ^1A_2$): Single Rovibronic Level Values and Their Average Values for the 4^1 Level.
Kazuhiko Shibuya and Edward K.C. Lee.
Journal of Chemical Physics, accepted for publication.

(e) Laser Induced Photodecomposition of Formaldehyde ($\tilde{A}\ ^1A_2$) From Its Single Vibronic Levels: Determination of the Quantum Yields in H-Atom by HNO ($\tilde{A}\ ^1A''$) Chemiluminescence.
Journal of Physical Chemistry, accepted for publication.
Kenneth Y. Tang, Paul W. Fairchild, and Edward K.C. Lee.

(f) Photochemistry of Simple Aldehydes and Ketones in the Gas Phase
in Advances in Photochemistry, Vol. 12, in press.
Edward K.C. Lee and Roger S. Lewis.

(g) Experimental Measurement of Electronic Relaxation of Isolated Small Polyatomic Molecules from Selected States
in Radiationless Transitions, edited by S.H. Lin, Academic Press, in press.
Edward K.C. Lee and Gary L. Loper.