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ENERGY AND PHASE RELAXATION IN LASER-INDUCED
ADMOLECULAR PROCESSES(U) STATE UNIV OF NEW YORK AT
BUFFALO DEPT OF CHEMISTRY X HUANG ET AL. APR 86
UBUFFALO/DC/86/TR-5 N00014-86-K-0043

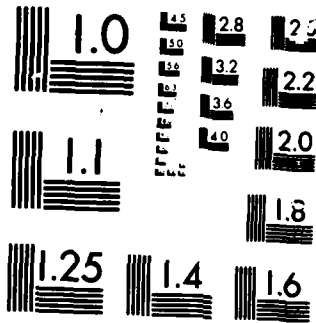
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TECHNICAL REPORT No. 5

Energy and Phase Relaxation in Laser-Induced Admolecular Processes

by

Xi-Yi Huang and Thomas F. George

Prepared for Publication

in

AIP Conference Proceedings

Departments of Chemistry and Physics
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April 1986

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS														
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited														
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE																	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UBUFFALO/DC/86/TR-5			5. MONITORING ORGANIZATION REPORT NUMBER(S)														
6a. NAME OF PERFORMING ORGANIZATION Depts. Chemistry & Physics State University of New York		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION														
6c. ADDRESS (City, State and ZIP Code) Fronczak Hall, Amherst Campus Buffalo, New York 14260		7b. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217															
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract N00014-86-K-0043														
8c. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217		10. SOURCE OF FUNDING NOS. <table border="1"><tr><td>PROGRAM ELEMENT NO.</td><td>PROJECT NO.</td><td>TASK NO.</td><td>WORK UNIT NO.</td></tr><tr><td></td><td></td><td></td><td></td></tr></table>				PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.								
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11. TITLE Energy and Phase Relaxation in Laser-Induced Admolecular Processes																	
12. PERSONAL AUTHOR(S) Xi-Yi Hong and Thomas F. George																	
13a. TYPE OF REPORT Interim Technical		13b. TIME COVERED FROM TO		14. DATE OF REPORT (Yr., Mo., Day) April 1986													
15. PAGE COUNT 3																	
16. SUPPLEMENTARY NOTATION Prepared for publication in the AIP Conference Proceedings																	
17. COSATI CODES <table border="1"><tr><td>FIELD</td><td>GROUP</td><td>SUB. GR.</td></tr><tr><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td></tr></table>			FIELD	GROUP	SUB. GR.										18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) ENERGY RELAXATION PHASE RELAXATION LASER-DRIVEN ADMOLECULE THERMALIZATION ANHARMONIC BOTTLENECK GENERALIZED MASTER EQUATION		
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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☒ DTIC USERS ☐			21. ABSTRACT SECURITY CLASSIFICATION Unclassified														
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson		22b. TELEPHONE NUMBER (Include Area Code) (202) 696-4410		22c. OFFICE SYMBOL													

ENERGY AND PHASE RELAXATION IN LASER-INDUCED ADMOLECULAR PROCESSES

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ABSTRACT

Vibrational excitation and relaxation of a molecule adsorbed on a surface is investigated. The phase relaxation is seen to assist the laser-driving force in overcoming the anharmonic and/or detuning bottleneck. The incoherent thermalization processes in the initial stage of the admoecular multiphoton excitation are evaluated. It is found that phase relaxation (dephasing) due to the surface and admoecular perturbation plays an important role in the thermalization processes.

MODEL

The IR-laser-driven resonant active mode absorbs photons and transfers its energy to other vibrational modes or the surface. Statistical thermodynamical behavior may occur in the resulting desorption/dissociation processes. We confine ourselves to the excitation and relaxation of the active anharmonic vibrational mode which is driven by a nearly resonant coherent field and controlled by both energy (T_1) and phase (T_2) relaxation. We treat the many other inactive modes and surface excitation as a large thermal reservoir, by which dissipation mechanisms are provided.

A generalized master equation which considers the anharmonicity and phase and energy dissipation of the active mode has been derived. For the case of (1) low bath temperatures, i.e., where the average excitation of the bath quantum $\bar{m}_B$ is much less than unity, and (2) where the rate of phase relaxation η is much larger than the energy relaxation κ and the Rabi frequency Ω_R , the generalized master equation leads to the following coupled differential equations:

$$\begin{aligned} \dot{W}_m = & 2\kappa(\bar{m}_B+1)[(m+1)W_{m+1} - mW_m] + 2\kappa\bar{m}_B[mW_{m-1} - (m+1)W_m] \\ & + 2\eta\Omega_R^2(t)\left\{\frac{m(W_m - W_{m-1})}{\eta^2 + [2\kappa(m-1)-\Delta]^2} + \frac{(m+1)(W_m - W_{m+1})}{\eta^2 + (2\kappa m-\Delta)^2}\right\} \quad (1) \end{aligned}$$

Here W_m is the population of the m -th vibrational level, ϵ is the anharmonicity, and Δ is the laser detuning. These equations take both the laser coherent excitation and the thermal excitation and relaxation into account.

Phase relaxation (dephasing) is seen to be more important than energy relaxation in the active-mode thermalization process. We have found that when η is large, such as $\eta = 15$ shown in Fig. 1, the population distribution in the active mode is close to a thermal Planck distribution. We have also found that the energy relaxation constant κ has a minor influence on the thermalization of the driven active mode.

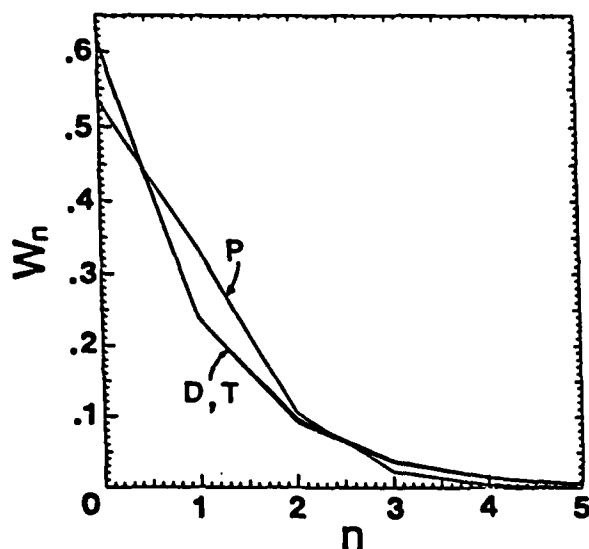


Fig. 1. Level population W_m for : (a) a driven damped anharmonic oscillator (D); (b) Poisson distribution (P); and (c) thermal distribution (T). The same $\bar{m}$ is used for all cases, and $\eta = 15$ is chosen.

ACKNOWLEDGMENTS

This research was supported by the Office of Naval Research and the Air Force Office of Scientific Research (AFSC), the United States Air Force, under Contract F49620-86-C-009.

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