

PROJECT ADMINISTRATION DATA SHEET

☒ ORIGINAL ☐ REVISION NO. _____
Project No./(Center No.) G-41-633 (R6243-OA0) GTRC/GIT ^{XXX} DATE 12 / 9 / 86
Project Director: T. Uzer School/Lab ^{XXX} Physics
Sponsor: Research Corporation

Agreement No.: Award Letter dated 10/31/86; Grant No. 10974

Award Period: From 6/30/86 To 10/30/87 (Performance) 6/29/87 Reports

Sponsor Amount: New With This Change Total to Date

Contract Value: \$ _____ \$ 5,500

Funded: \$ _____ \$ 5,500

Cost Sharing No./(Center No.) N/A Cost Sharing: \$ N/A

Title: Theoretical Studies of Mode-Specificity in Intramolecular Energy Transfer

ADMINISTRATIVE DATA

OCA Contact William F. Brown X4820

1) Sponsor Technical Contact:

2) Sponsor Issuing Office:

Robert L. Lichter, Ph.D.

Regional Director-Grants

Research Corporation

44 S. Bayles Avenue

Port Washington, NY 11050-3709

(516) 944-5120

Military Security Classification: N/A

ONR Resident Rep. is ACO: Yes ☒ No

(or) Company/Industrial Proprietary: N/A

Defense Priority Rating: N/A

RESTRICTIONS

See Attached N/A Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval — Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of \$500 or 125% of approved proposal budget category.

Equipment: Title vests with None proposed or anticipated.

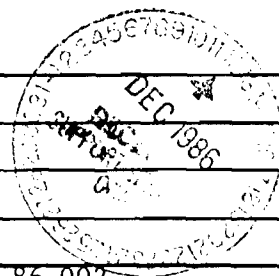
COMMENTS:COPIES TO:

SPONSOR'S I.D. NO. 2.500.021.86.002

Project Director
Research Administrative Network
Research Property Management

Procurement/GTRI Supply Services
Research Security Services
Contract Support Div.(OCA)(2)

GTRC
Library
Project File



GEIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 01/23/91

Project No. G-41-633 _____ Center No. R6243-OAO _____

Project Director UZER A T _____ School/Lab PHYSICS _____

Sponsor RESEARCH CORPORATION/PORT WASHINGTON, NY _____

Contract/Grant No. 10974 _____ Contract Entity GTRC

Prime Contract No. _____

Title THEORETICAL STUDIES OF MODE-SPECIFICITY IN INTRAMOLECULAR ENERGY TRANSFER

Effective Completion Date 901030 (Performance) 901030 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	_____
Final Report of Inventions and/or Subcontracts	N	_____
Government Property Inventory & Related Certificate	N	_____
Classified Material Certificate	N	_____
Release and Assignment	N	_____
Other _____	N	_____
Comments _____		

Subproject Under Main Project No. _____

Continues Project No. _____

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Management	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other _____	N
_____	N

REPORT OF RESEARCH CORPORATION GRANT

10974

(Please check one)

(Submit original and one legible copy)

☒ Interim Report

☐ Terminal Report

Reply to: 44 S. Bayles Avenue

Port Washington, NY 11050

INSTITUTION AND ADDRESS

School of Physics, Georgia Tech

Atlanta, GA 30332-0430

PRINCIPAL INVESTIGATOR Turgay Uzer

PHONE (404) 894-4986

ACADEMIC RANK AND DEPARTMENT Assistant Professor, Physics

SHORT TITLE OF RESEARCH SUPPORTED BY GRANT

Theoretical Studies of Mode-Specificity in Intramolecular Energy Transfer

STARTING DATE 10/31/86

SUMMARY OR PRINCIPAL FINDINGS AND THEIR SIGNIFICANCE (State succinctly in language understandable to one not necessarily expert in this field. Include extent to which original goals have been realized and any changes to original plan made or contemplated.)

Satisfactory progress has been made in the construction of a computer code to provide the numerical data base on which to place subsequent theory. The undergraduate personnel began work on the code in June of 1987, and under my guidance have by now obtained a satisfactory code. The construction of the program could only begin in summer since the undergraduates are free to devote time to project then. They have made remarkable progress in bringing up their physics, chemistry and computing knowledge to a point where they can produce new results. At present, we are testing the code under increasingly stringent conditions, and anticipate to have tested the main novelty of the code, namely the out-of-plane vibrations of benzene, for long running times, by the end of this year.

So far there has been no change in the program outlined in the original application. But instead of employing one graduate student, I decided to employ three talented undergraduates in this project. The one consequence of it was to slow down the progress somewhat. On the other hand, while none of them previously intended to go to graduate school, now all three do, and one of them will probably finish his master's degree on this project at Tech before going on to his PhD.

REPORT OF RESEARCH CORPORATION GRANT

Page 2

STUDENT PARTICIPATION (Give names of students working on the project, their roles in the research, their achievements and their career plans.)

1. Brian MacDonald: Physics senior. In conjunction with Brian Moore, responsible for the calculational aspects of the research. Began to work for the project in summer of 1987 and has made remarkable progress in the construction and running of code. Plans to go to graduate school.
2. Brian Moore: Physics Junior. Role similar to MacDonald's. Plans to go to graduate school.
3. Shane McWhorter: Physics senior. Expert in computer graphics. Has helped research with innovative ways of displaying results. Coauthored a textbook while employed on project. Plans to go to graduate school.

PAPERS AND SCIENTIFIC TALKS (Give titles and references to papers and talks resulting from the work. Attach two copies of any reprints acknowledging Research Corporation support, if not previously forwarded.)

So far, no publications have resulted from this work.

OTHER SUPPORT (List amounts and sources — including institutional—of other contributions received or expected.)

I received an NSF grant of approximately \$120,000, which began on April 1, 1987.

EXPENDITURE OF RESEARCH CORPORATION GRANT FUNDS (List cumulative expenditures.)

a. Equipment, supplies (Itemize major expenditures)

NONE

b. Stipends (Academic status, rates, periods of appointment)

1. Brian Macdonald	Undergraduate	\$5/hr	\$500.-July & August 1987
2. Brian Moore	"	\$5/hr	\$615.-July - Sept. 1987
3. Shane McWhorter	"	\$5/hr	\$740.97

c. Other expenditures (Itemize and give purpose)

\$1855.97

NONE

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Signature of principal investigator

.....10/22/87.....
Date

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Signature of authorized officer of institution (required for terminal report only)

.....
Date

.....
Name and position of authorized officer of institution

The terminal report must be approved by an authorized officer of the institution.

G-41-633

REPORT OF RESEARCH CORPORATION GRANT

(Submit original and one legible copy)

(Please check one)

☒ Interim Report

☐ Terminal Report

Reply to: 6840 E. Broadway

Tucson, Arizona 85710

INSTITUTION AND ADDRESS School of Physics, Georgia Institute of Technology
Atlanta, Georgia 30332-0430

PRINCIPAL INVESTIGATOR Turgay UZER

PHONE (404) 894-4986

ACADEMIC RANK AND DEPARTMENT Assistant Professor, Physics

SHORT TITLE OF RESEARCH SUPPORTED BY GRANT

THEORETICAL STUDIES OF MODE-SPECIFICITY IN INTRAMOLECULAR ENERGY TRANSFER

STARTING DATE 10/31/86

SUMMARY OR PRINCIPAL FINDINGS AND THEIR SIGNIFICANCE (State succinctly in language understandable to one not necessarily expert in this field. Include extent to which original goals have been realized and any changes to original plan made or contemplated.)

The purpose of the current research effort is to find mode specificities in the intramolecular flow of energy. Building up on the programming work that was executed last year with the help of the current grant, we have investigated possible mode-specificities in the overtone-induced dissociation of hydrogen peroxide. This research has resulted in a publication and several invited talks in which the contribution of the Research Corporation was acknowledged.

The scientific problem is as follows: When the Zewail group at Caltech excites the OH stretching modes of the hydrogen peroxide molecule and observes the dissociation rate of the molecules (with a novel technique) they are led to the conclusion that there is mode-specificity in the dissociation: Dissociation from some states is more rapid than from others. At present, their resolution of initial states is insufficient to determine the causes of this mode-specificity. We believe that it is a consequence of mode-specific energy flow by which dissociation energy accumulates in the reactive coordinate at different rates depending on the initial excitation. As soon as these experimental results became available we set off with the program that we had constructed last year to research whether we could understand the cause of this specificity. Our conclusion (as written up in the one accepted paper as well as the more lengthy paper in preparation) is that mode specificity results from the initial excitation of the reactive coordinate vibration (the OO stretching mode) in addition to the OH stretching vibration. If this conclusion could be verified experimentally (and we have very specific suggestions about the design of the experiment) it would be unique in that shifting a very small fraction of the total energy causes this strong mode-specificity. The numerous invited talks have helped to contact experimental groups, two of which are willing to try the experiment.

REPORT OF RESEARCH CORPORATION GRANT

Page 2

STUDENT PARTICIPATION (Give names of students working on the project, their roles in the research, their achievements and their career plans.) (1) Brian D. MacDonald. Main collaboration on the current research. Is a coauthor in the publication describing the research. Started graduate school at UCLA in the fall of 1988.

(2) Brian Moore: Physics Senior. . Is replacing Brian MacDonald as the main student collaborator on the project. Plans to go to graduate school in physics.

(3) Shane McWhorter: Provided software support. Began graduate school in Computer-Aided Design (CAD) in fall of 1988. Still involved with this project.

PAPERS AND SCIENTIFIC TALKS (Give titles and references to papers and talks resulting from the work. Attach two copies of any reprints acknowledging Research Corporation support, if not previously forwarded.)

In the last year one publication has resulted from the current work. "Theoretical Studies of Mode-Specificity in the Dissociation of Overtone-Excited Hydrogen Peroxide" (accepted to Chemical Physics Letters in August 1988). Reprints will be sent when it is published. Talks acknowledging the Research Corporation: (See attached page)

OTHER SUPPORT (List amounts and sources — including institutional—of other contributions received or expected.)

- 1) Received an \$18,000 supplement to my NSF grant under the ROA Scheme.
- 2) Received (together with 2 colleagues) a \$50,000 grant from the Georgia Tech-Israel Exchange Program to investigate laser control of chemical reactions.

EXPENDITURE OF RESEARCH CORPORATION GRANT FUNDS (List cumulative expenditures.)

a. Equipment, supplies (Itemize major expenditures)

None

b. Stipends (Academic status, rates, periods of appointment)

Brian E. Moore, Undergraduate \$6/hr., Nov. 87-Nov.88. Total \$1027.00.

Shane McWhorter, Undergraduate \$6/hr., Nov. 87-Nov. 88. Total \$422.47.

c. Other expenditures (Itemize and give purpose)

None

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Signature of principal investigator

.....
Date

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Signature of authorized officer of institution (required for terminal report only)

.....
Date

.....
Name and position of authorized officer of institution

The terminal report must be approved by an authorized officer of the institution.

Talks Acknowledging the Research Corporation, 1988

1. "Nonlinear Phenomena in Molecular Energy Transfer", UGA Chem. Dept., February 1988.
2. "Overtone-Induced Dissociation of H_2O_2 ", (with Brian McDonald)
Contributed talk at the 17th Southeastern Theoretical Chemistry Assoc. (SETCA) Meeting, Emory University, May 1988.
3. "Theoretical Studies of Overtone-Induced Dissociation of Hydrogen Peroxide", invited talk given at the Third Chemical Congress of North America, Toronto, June 7, 1988.
4. "Dissociation Dynamics of Polyatomic Molecules", invited talk given at the Conference in Honor of Alexander Dalgarno's Sixtieth Birthday on Atomic and Molecular Processes, with Applications to Aeronomy and Astrophysics, Harvard University, June 17, 1988.
5. "Theoretical Studies of Overtone-Induced Dissociation of Hydrogen Peroxide", poster given at the Gordon Conference on Atomic and Molecular Interactions, Plymouth State College, New Hampshire, August 1988.
6. "Theoretical Studies of Overtone-Induced Dissociation of Hydrogen Peroxide", invited talk given at the 196th National Meeting of the American Chemical Society, Los Angeles, September 28, 1988.

6-41-633

REPORT OF RESEARCH CORPORATION GRANT

(Submit original and one legible copy)

10974

Please check one)

☒ Interim Report

☐ Terminal Report

Reply to: 6840 E. Broadway

Tucson, Arizona 85710

INSTITUTION AND ADDRESS School of Physics, Georgia Institute of Technology
Atlanta, GA 30332-0430

PRINCIPAL INVESTIGATOR Turgay Uzer

PHONE (404) 894-4986

ACADEMIC RANK AND DEPARTMENT Assistant Professor, Physics

BRIEF TITLE OF RESEARCH SUPPORTED BY GRANT

THEORETICAL STUDIES OF MODE-SPECIFICITY IN INTRAMOLECULAR ENERGY TRANSFER

STARTING DATE 10/31/86

SUMMARY OR PRINCIPAL FINDINGS AND THEIR SIGNIFICANCE (State succinctly in language understandable to one not necessarily expert in this field. Include extent to which original goals have been realized and any changes to original plan made or contemplated.)

The purpose of our current research is to uncover mode-specificities in intramolecular energy flow and chemical reactions. This year, we have been investigating the effect that a heavy metal atom has on intramolecular energy flow. We are modeling organometallic molecules which contain a variety of bonds and bond strengths: Some bonds are easily and mode-specifically excited by lasers, and others are liable to break when they receive enough energy.

We investigated the intramolecular dynamics in an organometallic in which the excitation site and the reaction site are separated by a heavy metal atom. Our theoretical model addresses an experimental controversy, in which different groups are finding different reactive behavior for similar organometallic molecules. In particular, the controversy concerns the availability of the excitation energy to the entire molecule: If the energy is freely available (the "statistical" case), then one kind of unimolecular reaction should be observed. If, on the other hand, the heavy metal atom imprisons the energy on one side of the molecule, then some reactions are prevented from taking place allowing other, "nonstatistical" processes to happen. Our research (accepted for publication in the Mode-Specific Chemical Reactions issue of Chemical Physics) sets down the conditions for seeing either kind of reactions, and connects them to the initial excitation of the molecule; in other words, infers the conditions for mode-specificity.

REPORT OF RESEARCH CORPORATION GRANT

Page 2

STUDENT PARTICIPATION (Give names of students working on the project, their roles in the research, their achievements and their career plans.)

- (1) William Brower - Provides software support for the research, has just begun his involvement in the project. Plans to go to graduate school in 1990.

PAPERS AND SCIENTIFIC TALKS (Give titles and references to papers and talks resulting from the work. Attach two copies of any reprints acknowledging Research Corporation support, if not previously forwarded.)

In the last year, one publication has resulted from our work: "Dissociation of Remote Bonds by Overtone Excitation: A Model Study of Heavy-Atom Blocking", which will be published in the Mode-Specific Chemical Reactions Issue of Chemical Physics. 2 reprints will be sent when they are available. Talks, acknowledging the Research Corporation appear on the next page.

OTHER SUPPORT (List amounts and sources — including institutional—of other contributions received or expected.)

NONE

EXPENDITURE OF RESEARCH CORPORATION GRANT FUNDS (List cumulative expenditures.)

- a. Equipment, supplies (Itemize major expenditures)

NONE

- b. Stipends (Academic status, rates, periods of appointment)

W. Brower, undergraduate \$6/hour, June 1989. Total \$162.-

- c. Other expenditures (Itemize and give purpose)

Preparation of charts and figures \$474.45

.....
Signature of principal investigator *W*

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Date *8/29/89*

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Signature of authorized officer of institution (required for terminal report only)

.....
Date

.....
Name and position of authorized officer of institution

The terminal report must be approved by an authorized officer of the institution.

TALKS ACKNOWLEDGING THE RESEARCH CORPORATION
NOV. 1988 - PRESENT

1. "The Dynamics of Intramolecular Energy Flow" Joint Seminar of Departments of Physics and Chemistry, The University of Alabama at Birmingham, Dec. 2, 1988.
2. "Beyond The Chirikov Paradigm: A Geometrical View", invited talk at the Texas Dynamics Days, January 5, 1989.
3. "Beyond Chirikov's Pendulum: The Geometry of Vibrational Mixing in Molecules", University of Colorado and JILA Chemical Physics Talk, March 24, 1989.
4. "Beyond Chirikov's Pendulum: The Geometry of Vibrational Mixing in Molecules", Georgia Tech Chemistry Department Colloquium, April 13, 1989.

6-41-633

REPORT OF RESEARCH CORPORATION GRANT

(Submit original and one legible copy)

(Please check one)

☐ Interim Report☒ Terminal Report

Reply to: 6840 E. Broadway

Tucson, Arizona 85710

INSTITUTION AND ADDRESS School of Physics, Georgia Institute of Technology
Atlanta, GA 30332-0430

PRINCIPAL INVESTIGATOR Turgay Uzer

PHONE (404) 894-4986

ACADEMIC RANK AND DEPARTMENT Associate Professor, Physics

SHORT TITLE OF RESEARCH SUPPORTED BY GRANT

Theoretical Studies of Mode-Specificity in Intramolecular Energy Transfer

STARTING DATE ... 10-31-86.....

SUMMARY OR PRINCIPAL FINDINGS AND THEIR SIGNIFICANCE (State succinctly in language understandable to one not necessarily expert in this field. Include extent to which original goals have been realized and any changes to original plan made or contemplated.)

This is the final report for this research grant, the purpose of which was to investigate mode specificities in molecular energy transfer. Since the last annual report, two articles summarizing our findings have been written. One of these is an explicit account of the mode-specificities that we had reported earlier for the near-threshold overtone dissociation of hydrogen peroxide (copies of this predecessor article had been sent last year). Briefly, our findings indicate that the overtone-induced dissociation of the hydrogen peroxide molecule can be very sensitive to the particular mode combination which is excited. According to our research, there seems to be a very strong bifurcation in the dissociation rates of hydrogen peroxide depending on whether the 00 stretching mode is initially excited or not. This finding, now explained in great detail in the article (see below) awaits experimental confirmation.

The research on mode-specification in energy transfer in organometallics (reported on in detail in the last annual report) has now appeared and two copies are enclosed. Briefly our research shows that the heavy metal in an organometallic molecule may act as a blocker to the flow of vibrational energy from one half of the molecule to the other. We have been very excited by a recent article from a group in Princeton (K.K. Lehmann, B. H. Pate, and G. Scoles, J. Chem. Phys. 93, 2152 (1990)), who observe effects reminiscent of the heavy-metal blocking we had predicted. While they have not analyzed their results for all possible factors that might to such an observation, at present the effect predicted by us seem to be the most plausible explanation of their observations.

In conclusion, we feel that we have been able to uncover some systems and situations in which there is mode-selectivity in intramolecular energy transfer and unimolecular reactions; and therefore fulfilled our expectations from this research program which was set up some five years ago.

REPORT OF RESEARCH CORPORATION GRANT

Page 2

STUDENT PARTICIPATION (Give names of students working on the project, their roles in the research, their achievements and their career plans.)

- (1) William Brower: Provides programming support for the research. Because of his previous experience on the project, his involvement has been important. Is currently a graduate student at University of California, San Diego.
- (2) Joshua Boorstein: Has helped me with small theoretical issues that arise during the research. Will go to graduate school in 1991.

PAPERS AND SCIENTIFIC TALKS (Give titles and references to papers and talks resulting from the work. Attach two copies of any reprints acknowledging Research Corporation support, if not previously forwarded.)

Two publications have resulted from this research:

- 1) T. Uzer and J. T. Hynes, Chem. Phys. 139, 163 (1998). 2 reprints are enclosed.
- 2) Y. Guan, T. Uzer, Brian D. MacDonald, and D. L. Thompson, "Dissociation of Overtone-Excited Hydrogen Peroxide near Threshold: A Quasiclassical Trajectory Study. To appear in the 1st Volume of Advances in Molecular Vibrations and Collision Dynamics (edited by J. M. Bowman), 1991. A list of talks acknowledging The Research Corporation is attached.

OTHER SUPPORT (List amounts and sources — including institutional—of other contributions received or expected.)

New NSF grant: \$171,900 (3 years)
NATO Collaborative Grant \$6,800 (2 years)
NSF Research Experience for Undergraduates Grant.
A total of \$130,850 (for 3 years, my share: 1/5).

EXPENDITURE OF RESEARCH CORPORATION GRANT FUNDS (List cumulative expenditures.)

a. Equipment, supplies (Itemize major expenditures)

Supplies: \$302.76
Equipment: \$130 (a modem)

b. Stipends (Academic status, rates, periods of appointment)

W. Brower, undergraduate \$9/hour, \$454.30
J. Boorstein, undergraduate, \$6/hour, \$90

c. Other expenditures (Itemize and give purpose)

Preparation of figures, charts and graphs: \$128.70

.....
Signature of principal investigator *[Signature]*

10/29/90
Date

.....
Signature of authorized officer of institution (required for terminal report only)

10/31/90
Date

.....
Name and position of authorized officer of institution

The terminal report must be approved by an authorized officer of the institution.

TALKS ACKNOWLEDGING THE RESEARCH CORPORATION

1. "Overtone-Induced Dissociation of Hydrogen Peroxide", Chemistry Department, Middle East Technical University, Ankara, Turkey, October 27, 1989.
2. "Beyond Chirikov's Pendulum: The Geometry of Vibrational Mixing in Molecules", Department of Physics, University of Arkansas, Fayetteville, December 1, 1989.
3. "Dynamics of Intramolecular Energy Transfer", Seminar at the Universidad Autonoma de Madrid, May 31, 1990.
4. "Rotation-Vibration Interactions in Molecules and the Asymmetric Top", Colloquium at the Universidad Complutense, Madrid, June 1, 1990.

DISSOCIATION OF REMOTE BONDS BY OVERTONE EXCITATION: A MODEL STUDY OF HEAVY-ATOM BLOCKING

T. UZER

School of Physics, Georgia Institute of Technology, Atlanta, GA 30332-0430, USA

and

James T. HYNES

Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, USA

Received 16 June 1989

We present a classical-mechanical study of model systems which allow the rupture of a weak bond subsequent to excitation of overtones in remote parts of the molecule. Our models are the linear chains HCCCX and HCMCX, where M is a heavy atom and the C–X bond is weak. The ensuing mode-specificities and nonstatistical behavior are strongly affected by the presence of a heavy-atom blocker.

1. Introduction

The course and rate of intramolecular flow of energy leading to dissociation in a vibrationally excited molecule are clearly fundamental – but largely poorly understood – essentials in the molecular-level mechanism of a unimolecular (and bimolecular) reaction [1]. Vibrational overtone excitation, which is in some sense selective, can help reveal how the total internal energy, the excitation state, and the various internal molecular intermode couplings effect and affect the unimolecular reaction induced by the excitation. In consequence the number of experimental overtone-induced reaction studies is growing at a rapid pace [2–4].

Recent theoretical research has revealed the essential role played by nonlinear resonances in effecting intramolecular energy transfer in certain nonreactive systems [5–8]. Here, the critical first step of the overall energy flow from, e.g., an initially excited CH bond is often energy transfer from the excited stretching mode to the adjacent bending mode. This transfer is especially effective when there is a Fermi resonance, i.e. a 2:1 frequency ratio, between the stretching and bending motions. (These mechanisms

have also been implicated in a number of unimolecular reaction studies [9–12].) Most notably, the intramolecular relaxation of excited CH stretches in benzene [6] and in other hydrocarbons [3,7] has been successfully described using this resonance picture. In other cases [3,8], it is instead 1:1 resonant frequency ratios (or combination resonances) for the CH stretches and other molecular modes that are crucial for the flow.

In earlier work, we have modeled the energy flow leading to unimolecular dissociation in overtone-excited hydrogen peroxide [11], and presented a comprehensive picture of energy flow in the molecule and pointed out the possibility of mode-specificity [12] in the unimolecular dissociation following the excitation of combination modes [4].

In contrast to such realistic models, in this article we present a theoretical study of a prototypical model unimolecular chemical reaction induced by overtone excitation. Among the issues here are how and how fast the “molecule” undergoes a specific bond rupture, and whether the course of this rupture can be influenced by initial excitation. Of course, these questions are intimately connected with the manner and rate at which vibrational energy leaves an initial

excitation site and how and how fast it flows into the reaction coordinate [9–21]. A detailed analysis of energy flow is a subtle and intricate issue (as was illustrated recently [11,13,17,20,21]), and we will not analyze the history of energy flow in our trajectories in any detail. We will, however, pay attention to molecular models where the unit separating the remote excitation site and the reactive coordinate contains a heavy metal atom as a potential energy blocker [13,14,17,19,21].

In recent years some attention has been devoted to the question of the efficacy of “blockers” to intramolecular energy flow [13,14,17,19,21–23]. Experimentally the possibility seems to exist [22] that energy may be localized in one reactive portion of an energized molecule by a heavy metal atom; RRKM behavior involving rapid redistribution and reaction remote from the bond excitation site is thwarted. (Statistical behavior has been reported in some molecules with heavy metal “blockers” [23], however.) While there are a number of theoretical studies of potential blocking agents to energy flow for nonreactive model systems [13,14,18], including a very thorough recent study [21], there are fewer studies of explicitly reactive systems [17,19].

The present model has been designed with various factors in mind that are now acknowledged to influence the character and rate of intramolecular energy flow. A preliminary account of some of our findings has been presented previously [19].

2. Model

Our molecular model is an unsymmetrical rigid linear chain of four coupled Morse oscillators and is depicted in fig. 1 with its frequencies and anharmonicities indicated. In this linear “molecule” HCMCX, M is a potential “blocker” atom, and the CX bond (the approximate reactive coordinate) is comparatively weak. The excitation site, namely the CH bond, has approximately the frequency characteristics of a benzene CH bond. M is given the mass of either carbon or mercury in the calculations, and the CM frequency is artificially taken to be independent of M. In the model, the coupling between the motions is entirely kinetic – there is no direct coupling between the excitation site and the reactive remote bond. (In ear-

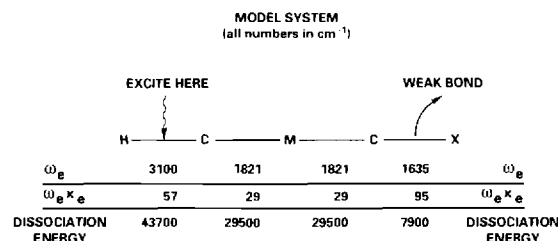


Fig. 1. The model system H-C-M(C)-C-X.

lier work, Swamy and Hase [14] have shown that potential coupling may have a substantial influence on the outcome, as well.) Further, no bending vibrations are included. The effect of bendings has been investigated for a similar model by us [18] and found not to change the picture appreciably because of the generally low bending frequencies in realistic linear systems. We initially deposit energy into the CH bond corresponding to a certain stretching local mode overtone ν_{HC} and examine the resulting energy flow and reactions using quasi-classical trajectories [24]. In all these simulations, zero-point energy has been placed in all the initially unexcited vibrations. The effect of zero-point energy on classical trajectory simulations, and prescriptions to prevent oscillator energies to decrease below it have been reported in two recent publications [25]. Since most of our simulations are for energies well above reaction thresholds, the spurious contribution of the zero-point energy to reactivity is presumably small. The threshold for breaking the weak CX bond is $\nu_{HC}=3$, whereas an overtone of $\nu_{HC}=13$ is required to break the strong CM bond adjacent to the initially excited CH.

The mechanism by which M might act as a blocker relies on two critical features [5,13,14,18,19]: (a) the kinetic coupling [5,13] between the CM and MC bonds will tend to be weak for a large mass of M and (b) there must be sufficient detuning of the 1:1 frequency resonance $\omega_{MC}=\omega_{CM}$ to suppress the flow [19]. This requires a mismatch in the CM and MC bond energies so that anharmonicity can lower one frequency compared with the other.

3. Results

Even in this simple model, we find that generally

valid statements about the energy flow are difficult to make. On the other hand, reaction times provide an objective set of data. In what follows, we will focus on the major indicators and trends, and attempt to correlate these with what is expected on the basis of previous studies. We illustrate these points by histograms of the consequences of overtone excitations in entirely different regions of the H-C excitation range.

3.1. The effect of the HC-CM 1:1 resonance

In table 1, we present the number of reactive events observed in 2 ps in an ensemble of 150 trajectories. When the overtone excitation is below the CM dissociation threshold of $\nu_{\text{HC}} = 13$, all reactive events are CX ruptures. The parameters of the model place the 1:1 resonance between the excitation site and the adjacent CM bond at around $\nu_{\text{HC}} = 11$, and its presence is reflected through the increased reactivity around that overtone. In addition to changes in the number of reacting trajectories, their reaction time distributions (fig. 2) also change markedly as the excitation passes through a resonance shifting towards faster remote bond dissociation.

The center of the resonance zone is a good location where to examine the effect of a heavy atom. For instance, the $\nu_{\text{HC}} = 11$ overtone at the center of the HC-CM 1:1 resonance lacks the energy to break a CM

Table 1
Number of dissociating trajectories (out of an ensemble of 150) for a variety of overtone excitations in HCMCX

Overtone ν_{HC}	Dissociation events (CX ruptures)
8	70
9	92
10	116
11 ^{a)}	118
12	106
13 ^{b)}	93
14	52
15	54
16	43
17	32

^{a)} Approximate location of HC-CM 1:1 resonance.

^{b)} Approximate threshold of C-M dissociation. The overtones with $\nu_{\text{HC}} > 14$ lead mostly to C-M rather than C-X bond rupture.

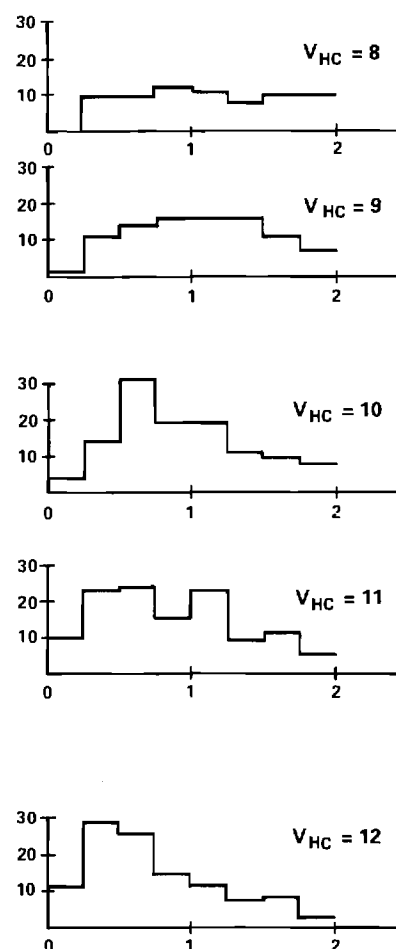


Fig. 2. Reaction time distributions for various H-C stretching overtones. The vertical axis denotes numbers of reactive events.

bond. When the reactivity pattern for HCMCX with M having the mass of mercury, and for HCCCX are compared [19], they are seen to be markedly different (a further example is presented in section 3.2). The HC-CM(C) 1:1 resonance leads to an initial rapid flow of energy to the CM(C) bond in the trajectories, but further flow into the initially cold half of the molecule is hampered. In contrast, in the HCCX species, energy continues to flow rapidly over the entire molecule with negligible apparent blocking ability of the light central C atom (see below).

3.2. $\nu_{\text{HC}} = 13$ excitation

This overtone is the threshold for CM rupture (recall that CM is the bond adjacent to the excitation site, and MC is in the initially cold right half of the molecule). The histogram showing number of reactive events (defined as CX bond ruptures – see below) as a function of time is shown in fig. 3. Out of the 50 trajectories that were followed, 32 dissociated in the heavy metal compound, whereas all dissociated in the carbon compound. For the latter, the reaction histogram has an exponential appearance. But this is not at all the case for the heavy metal atom species. The reaction time scale is noticeably longer, and inspection of the trajectories indicates that this feature arises in considerable part from the detuning of the CM and MC bonds which are only weakly kinetically coupled. The heavy metal atom is acting as a strong retarding agent of the flow (figs. 4a and 4b), whereas in the absence of the blocker, energy flows freely through the molecules (figs. 5a and 5b). Another interesting feature of this excitation in the heavy metal version is the noticeable tendency of the strong C–M bond ($D_e = 29500 \text{ cm}^{-1}$) to break before the weak C–X bond ($D_e = 7900 \text{ cm}^{-1}$), and we turn to this feature next.

3.3. Higher overtones: nonstatistical bond rupture

A remarkable nonstatistical behavior is illustrated in table 2: 150 trajectories were followed for overtones with energies greater than the C–M rupture threshold, and the branching of the dissociative events between CX and CM dissociation was recorded as percentage of reactive events. Note that the improved statistics from our preliminary account [19] has caused virtually no changes in the percentages.

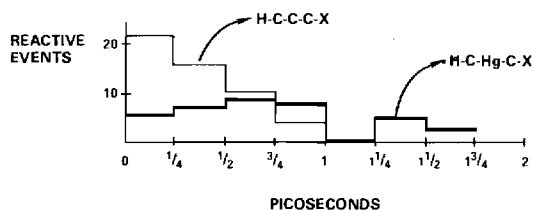


Fig. 3. The distribution of C–X bond rupture times in H–C–M(C)–C–X chains initially excited to $\nu_{\text{HC}} = 13$. See the text.

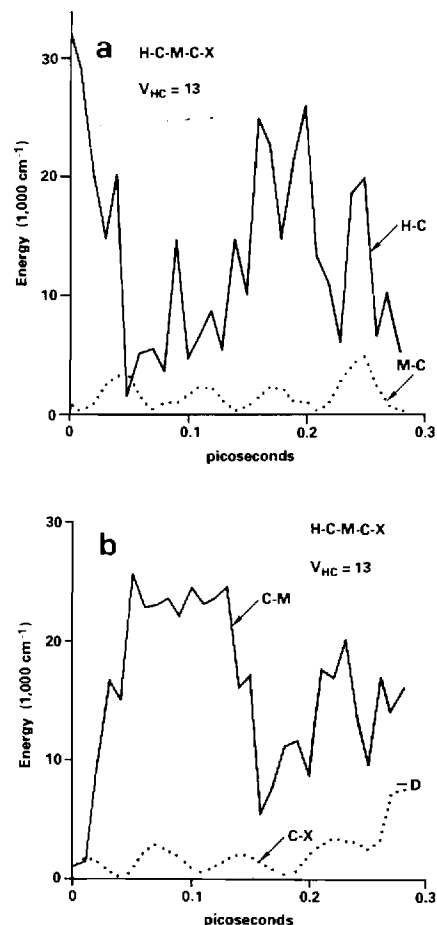


Fig. 4. (a) Vibrational energy in bonds of H–C–M–C–X in a short-lived trajectory with an initial excitation of $\nu_{\text{HC}} = 13$. Shown are the energy contents of the H–C vibration and of the M–C vibration (which is on the right, initially cold side of the molecule). (b) Same conditions as in (a), except that the energies of the C–M bond (on left side of molecule) and the C–X bond (in the right half) are shown. D denotes the dissociation energy of C–X. Note the slow trickle of energy to the right side of the molecule.

There is a marked tendency for the nonstatistical dissociation of the strong CM bond as opposed to the heavily statistically favored rupture of the remote weak CX bond. No MC ruptures were observed. Our interpretation is as follows: The center of the 1:1 resonance between the HC bond and the adjacent CM bond is approximately $\nu_{\text{HC}} = 11$, and considerable energy can flow into CM. But the same energy drastically lowers the CM frequency, via that bond's anharmonicity, detuning it from that of the adjacent

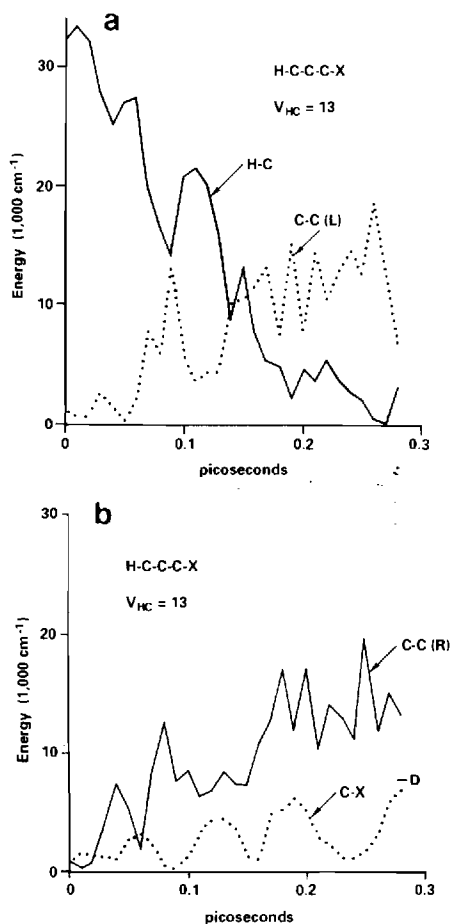


Fig. 5. (a) The bond energies in a short-lived trajectory of H-C-C-C-X excited to $\nu_{\text{HC}} = 13$. Shown are the bond energies on the left half of the chain, i.e. of H-C and the C-C (L). (b) Same conditions as in (a), except the right-hand side of the molecule is shown. Note that the energy accumulates in the right-hand side C-C bond in a similar manner to the left C-C bond, i.e. in contrast to the situation in fig. 4, energy is not prevented from travelling swiftly inside the molecule. As before, *D* denotes the C-X dissociation energy.

initially unexcited MC bond in the initially cold half of the molecule, i.e. one resonance is working against the other. Together with the weak CM-MC kinetic coupling, this feature evidently isolates the left half of the molecule sufficiently to cause the striking non-statistical bond rupture. Indeed, a mode-by-mode inspection of individual trajectories indicates that in many of them, the molecule behaves as two half-molecules separated by the heavy atom (figs. 6a and 6b).

Table 2

The branching of dissociation events between CM and CX ruptures in HCMCX as a function of overtone. Given figures are percentages of an ensemble of 150 trajectories

ν_{HC}	CX rupture	CM rupture
13	62	38
14	35	65
15	36	64
16	29	71

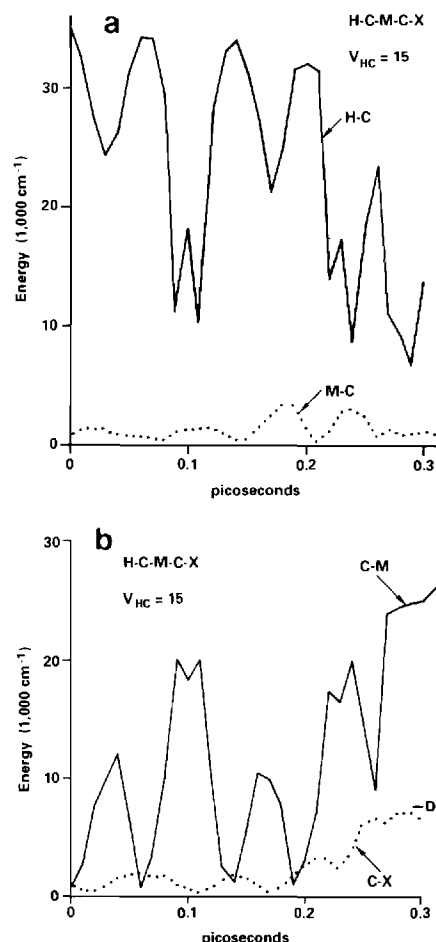


Fig. 6. (a) The energy flow picture for H-C-M-C-X excited to $\nu_{\text{HC}} = 15$. Shown are the H-C energy content and the vibrational energy in the M-C bond, which is on the right-hand side of the molecule. (b) Same conditions as in (a). Shown are the C-M bond energy (left side of the molecule) and the energy in C-X. Considering this and fig. 5 together, it is clear that the molecule has been separated by the blocker into two poorly communicating halves.

A similar two-scale relaxation mechanism, one being rapid relaxation in the side chains, and others being slow energy transfer across the heavy central mass, has also been observed by Schranz et al. [17] for their chains containing a heavy mass.

3.4. $\nu_{\text{HC}}=4$ excitation

The reactivity behavior is quite different in this low overtone excitation, which is only slightly above the threshold for CX rupture. Out of 100 trajectories in this case, 62 dissociated for the carbon compound, compared to 16 dissociations for the heavy metal version.

The reaction histograms are shown in fig. 7. Inspection of the individual dissociating trajectories shows a variety of behaviors: In the heavy metal compound, a slow and bond-to-bond sequential energy flow is seen (figs. 8a and 8b). In the carbon-containing species energy travels all over the molecule very rapidly (figs. 9a and 9b), except that for some trajectories the HC and adjacent CC are detuned and the molecule behaves like separate HC and CCX species. The energy in the HC motion takes a long time to disperse, even in the carbon-containing variety.

4. Concluding remarks

These results indicate strongly that the heavy metal atom in the linear model compound serves to moderate the rate of energy transmission through the molecule and in certain cases leads to pronounced nonstatistical behavior. This observation is in harmony with the results of Schranz et al. [17] who found that the validity of RRKM theory is adversely

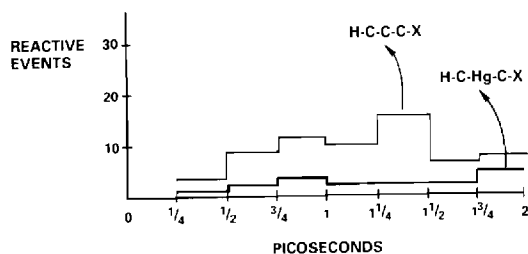


Fig. 7. Histogram of reaction times for H-C-M(C)-C-X chains excited to $\nu_{\text{HC}}=4$. See the text.

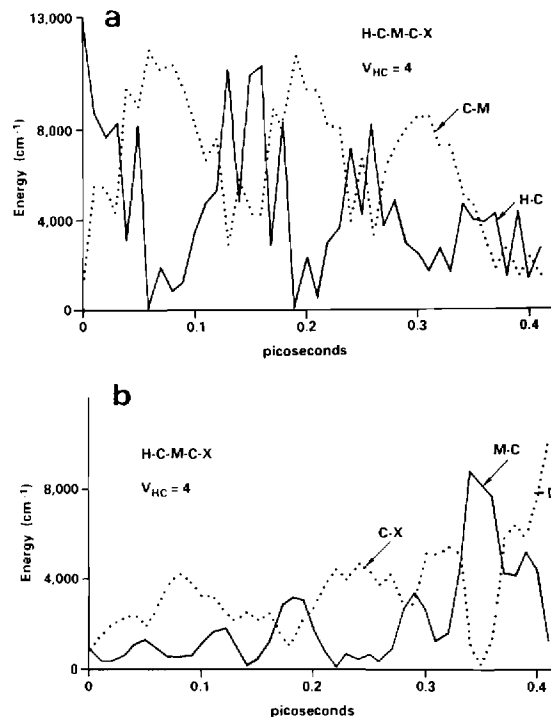


Fig. 8. (a) Energy transfer in a short-lived H-C-M-C-X trajectory corresponding to excitation of $\nu_{\text{HC}}=4$. Note how energy is transferred within the left side of the molecule among H-C and C-M bonds. (b) Same conditions as for (a). Shown are the energy transfer events in the right side of the molecule. Note that again the two halves of the molecule are communicating poorly, and energy transfer takes place mainly inside the two segments, as evidenced by the beating pattern.

affected by nonuniformities (such as heavy masses) in chain molecules. But more generally, they also show that the initial flow route of the energy out of an excited bond is specific, and that specificity has important consequences for reactions. These flow rates and mechanisms can be comprehended, at least qualitatively, in terms of nonlinear resonance ideas. Our previous experience [11] indicates however, that with increasing realism, and with more internal degrees of freedom, the flow routes become increasingly complex, in a manner similar to the onset of statistical behavior in nonlinear oscillator systems due to the proliferation of couplings as well as increasingly wider resonances [26]. Thereby, one begins to see how RRKM behavior can eventually result. But even in that limit, intramolecular flow rates are finite

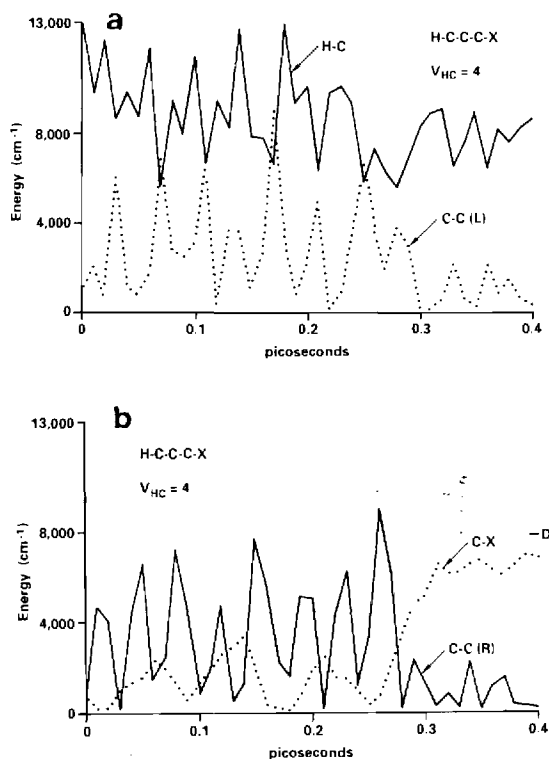


Fig. 9. Energy transfer in a short-lived H-C-C-C-X trajectory corresponding to excitation to $v_{HC}=4$. The dynamics in left side of the molecule is shown. (b) Same conditions as in (a). Shown is the energy transfer dynamics of the right side of the molecule. Comparison with fig. 8 shows that when the blocker is absent, energy spreads more evenly.

and energy transfer paths are not random, as is being revealed by detailed quantum-mechanical studies [21,27].

Acknowledgement

This research was supported by a grant from the Research Corporation (to TU), NSF grant CHE86-19298 (to TU); as well as CHE84-19830 and CHE88-07852 (to JTH). Acknowledgement is also made to the Donors of the Petroleum Research Fund, as administered by the American Chemical Society, for partial support of this work.

References

- [1] D.W. Noid, M.L. Koszykowski and R.A. Marcus, *Ann. Rev. Phys. Chem.* 32 (1981) 267; W.L. Hase, in: *Dynamics of Molecular Collisions*, Part B, ed. W.H. Miller (Plenum Press, New York, 1976); N. Bloembergen and A.H. Zewail, *J. Phys. Chem.* 88 (1984) 5459; J. Manz, in: *Molecules in Physics, Chemistry and Biology*, ed. J. Maruani (Kluwer, Dordrecht, 1989).
- [2] F.F. Crim, *Ann. Rev. Phys. Chem.* 35 (1984) 657; J.W. Wong and C.B. Moore, *J. Chem. Phys.* 77 (1982) 603; J.W. Perry and A.H. Zewail, *J. Phys. Chem.* 86 (1982) 5197; D.W. Chandler, W.E. Farneth and R.N. Zare, *J. Chem. Phys.* 77 (1982) 4447; K.V. Reddy, D.F. Heller and M.J. Berry, *J. Chem. Phys.* 78 (1983) 2817; T.R. Rizzo, C.C. Hayden and F.F. Crim, *Faraday Discussions Chem. Soc.* 75 (1983) 112; J.M. Jasinski, J.K. Frisoli and C.B. Moore, *Faraday Discussions Chem. Soc.* 75 (1983) 289; M.-C. Chuang, J.E. Baggot, D.W. Chandler, W.E. Farneth and R.N. Zare, *Faraday Discussions Chem. Soc.* 75 (1983) 301; T.R. Rizzo, C.C. Hayden and F.F. Crim, *J. Chem. Phys.* 81 (1984) 4501; S.D. Peyerimhoff, M. Lewerenz and M. Quack, *Chem. Phys. Letters* 109 (1984) 563; H.R. Dubal and M. Quack, *J. Chem. Phys.* 81 (1984) 3779; C.I. Manabares, N.L.S. Yamasaki, E. Weitz and T. Knudsen, *Chem. Phys. Letters* 117 (1985) 477; J.E. Baggot, M.-C. Chuang, R.N. Zare, H.-R. Dubal and M. Quack, *J. Chem. Phys.* 82 (1985) 1186; T.M. Ticich, T.R. Rizzo, H.-R. Dubal and F.F. Crim, *J. Chem. Phys.* 84 (1986) 1508; L.J. Butler, T.M. Ticich, M.D. Likar and F.F. Crim, *J. Chem. Phys.* 85 (1986) 2331; X. Luo, P.T. Rieger, D.S. Perry and T.R. Rizzo, *J. Chem. Phys.* 89 (1988) 4448; J.H. Gutow, D. Klenerman and R.N. Zare, *J. Phys. Chem.* 92 (1988) 172; J. Segall and R.N. Zare, *J. Chem. Phys.* 89 (1988) 5704; R. Marquardt and M. Quack, *Infrared Physics* 29 (1989) 441.
- [3] P. Hofmann, R.B. Gerber, M.A. Ratner, L.C. Baylor and E. Weitz, *J. Chem. Phys.* 88 (1988) 7434.
- [4] N.F. Scherer, F.E. Doany, A.H. Zewail and J.W. Perry, *J. Chem. Phys.* 84 (1986) 1932; N.F. Scherer and A.H. Zewail, *J. Chem. Phys.* 87 (1987) 97.
- [5] E.L. Sibert III, W.P. Reinhardt and J.T. Hynes, *J. Chem. Phys.* 77 (1982) 3583; C. Jaffe and P. Brumer, *J. Chem. Phys.* 73 (1980) 5646; M.S. Child and L. Halonen, *Advan. Chem. Phys.* 57 (1984) 1.

- [6] E.L. Sibert III, W.P. Reinhardt and J.T. Hynes, *Chem. Phys. Letters* 92 (1982) 455; *J. Chem. Phys.* 81 (1984) 1115, 1135;
D.L. Clarke and M.A. Collins, *J. Chem. Phys.* 86 (1987) 6871; 87 (1987) 5312;
D.-H. Lu and W.L. Hase, *J. Phys. Chem.* 92 (1988) 3217;
A. Garcia, J. Santamaria and G.S. Ezra, *J. Chem. Phys.* 89 (1988) 801.
- [7] J.S. Hutchinson, J.T. Hynes and W.P. Reinhardt, *J. Phys. Chem.* 90 (1986) 3528;
E.L. Sibert III, J.S. Hutchinson, J.T. Hynes and W.P. Reinhardt, in: *Ultrafast Phenomena*, Vol. 4, eds. D.H. Auston and K.B. Eisenthal (Springer, Berlin, 1984) p. 336.
- [8] J.S. Hutchinson, W.P. Reinhardt and J.T. Hynes, *J. Chem. Phys.* 79 (1983) 4247;
J.S. Hutchinson, J.T. Hynes and W.P. Reinhardt, *Chem. Phys. Letters* 108 (1984) 353.
- [9] T. Uzer and J.T. Hynes, *Chem. Phys. Letters* 113 (1985) 483;
T.A. Holme and J.S. Hutchinson, *J. Chem. Phys.* 83 (1985) 2860.
- [10] B.G. Sumpter and D.L. Thompson, *J. Chem. Phys.* 82 (1985) 4557; 86 (1987) 2805;
C. Getino, B.G. Sumpter, J. Santamaria and G.S. Ezra, *J. Phys. Chem.* 93 (1989) 3877.
- [11] T. Uzer, J.T. Hynes and W.P. Reinhardt, *Chem. Phys. Letters* 117 (1985) 600; *J. Chem. Phys.* 85 (1986) 5791.
- [12] T. Uzer, B.D. MacDonald, Y. Guan and D.L. Thompson, *Chem. Phys. Letters* 152 (1988) 405.
- [13] V. López and R.A. Marcus, *Chem. Phys. Letters* 93 (1982) 2132;
S.M. Lederman, V. López, G.A. Voth and R.A. Marcus, *Chem. Phys. Letters* 124 (1986) 93;
V. López, V. Fairén, S.M. Lederman and R.A. Marcus, *J. Chem. Phys.* 84 (1986) 5494;
C. Sloane and W.L. Hase, *J. Chem. Phys.* 66 (1977) 1523.
- [14] K.N. Swamy and W.L. Hase, *J. Chem. Phys.* 82 (1985) 123.
- [15] H.W. Schranz, S. Nordholm and B.C. Freasier, *Chem. Phys.* 108 (1986) 69.
- [16] H.W. Schranz, S. Nordholm and B.C. Freasier, *Chem. Phys.* 108 (1986) 93.
- [17] H.W. Schranz, S. Nordholm and B.C. Freasier, *Chem. Phys.* 108 (1986) 105.
- [18] T. Uzer and J.T. Hynes, *J. Phys. Chem.* 90 (1986) 3524;
R.A. Marcus and M.S. Child, *Faraday Discussions Chem. Soc.* 75 (1983) 157.
- [19] T. Uzer and J.T. Hynes, in: *NATO ASI Series C*, Vol. 200. *Stochasticity and Intramolecular Redistribution of Energy*, eds. R. Lefebvre and S. Mukamel (Reidel, Dordrecht, 1987) p. 273.
- [20] T.A. Holme and J.S. Hutchinson, *J. Chem. Phys.* 84 (1986), 5455;
B.G. Sumpter and D.L. Thompson, *J. Chem. Phys.* 87 (1987) 5809;
J.S. Hutchinson, *J. Phys. Chem.* 91 (1987) 4495;
L.G. Spears Jr. and J.S. Hutchinson, *J. Chem. Phys.* 88 (1988) 250.
- [21] S.M. Lederman, V. López, V. Fairén, G.A. Voth and R.A. Marcus, *Chem. Phys.* 139 (1989) 171.
- [22] P.J. Rogers, D.C. Montague, J.P. Frank, S.C. Tyler and R.S. Rowland, *Chem. Phys. Letters* 89 (1982) 9;
P.J. Rogers, J.I. Selco and F.S. Rowland, *Chem. Phys. Letters* 97 (1983) 313.
- [23] S.P. Wrigley and B.S. Rabinovitch, *Chem. Phys. Letters* 98 (1983) 386;
S.P. Wrigley, D.A. Oswald and B.S. Rabinovitch, *Chem. Phys. Letters* 104 (1984) 521.
- [24] L.M. Raff and D.L. Thompson, in: *Theory of Chemical Reaction Dynamics*, Vol. 3, ed. M. Baer (CRC Press, Boca Raton, 1985) p. 1.
- [25] J.M. Bowman, B. Gazdy and Q. Sun, *J. Chem. Phys.* 91 (1989) 2859;
W.H. Miller, W.L. Hase and C.L. Darling, *J. Chem. Phys.* 91 (1989) 2863.
- [26] G.H. Walker and J. Ford, *Phys. Rev.* 188 (1969) 416;
J. Ford, *Advan. Chem. Phys.* 24 (1973) 155;
M. Tabor, *Advan. Chem. Phys.* 47 (1981) 73;
S.A. Rice, *Advan. Chem. Phys.* 47 (1981) 117;
P. Brumer, *Advan. Chem. Phys.* 47 (1981) 201.
- [27] S.M. Lederman, S.J. Klippenstein and R.A. Marcus, *Chem. Phys. Letters* 146 (1988) 7;
S.M. Lederman and R.A. Marcus, *J. Chem. Phys.* 88 (1988) 6312.