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ABSTRACTS

of talks to be presented at the

International CNLS Conference

on

Intramolecular Vibrational
Redistribution and Quantum Chaos

October 3 - 5, 1985

University of Rochester
Rochester, N.Y.

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

A workshop on intramolecular vibrational redistribution and quantum chaos, was held at the University of Rochester, NY, in October 2-5, 1985, with thirty-five participants - four Europeans and thirty-one Americans. The purposes of the workshop were: 1) to review critically the current status of experimental and theoretical studies of highly vibrationally activated molecules and molecular clusters; 2) to discuss the ranges of applicability of the classical, quantum and semiclassical methods currently employed in the calculations of intramolecular relaxations and spectral lineshapes; 3) to compare various criteria used to characterize either classical or quantum chaos and to discuss their relevance to intramolecular dyanamics; 4) to examine the available information on distributions of energy levels and other statistical measures of molecular spectra and to explore their relevance to intramolecular dynamics and quantum chaos; 5) to allow theorists and experimentalists a free exchange of information and ideas and to discuss future directions. Keywords:

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INTERNATIONAL WORKSHOP
on
Intramolecular Vibrational Redistribution and Quantum Chaos
October 3 - 5, 1985
Rochester, N.Y.

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INTERNATIONAL WORKSHOP

on

Intramolecular Vibrational Redistribution
and Quantum Chaos

SPONSORS:

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THE UNIVERSITY OF ROCHESTER
THE EXXON CORPORATION
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Organized by:

Shaul Mukamel, University of Rochester
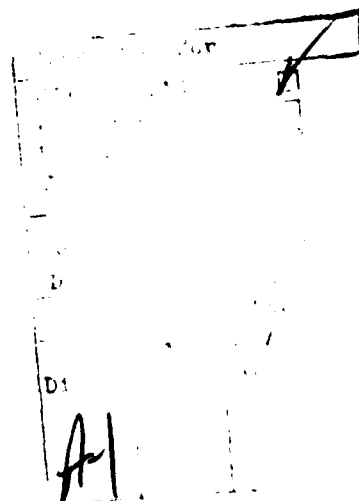and
Roland Lefebvre, Universite de Paris-Sud

SESSION 1

SELECTIVE PHOTOCHEMISTRY

Gowen Room

Thursday, October 3rd, from 8:45 A.M. until 12:30 P.M.

Chairman: J. Kommandeur

S. A. Rice
James Franck Institute
The University of Chicago

"COHERENCE VS. CHAOS: CONTROL OF SELECTIVITY
OF A CHEMICAL REACTION"

A time-dependent formulation of two photon spectroscopy is

employed to show that slectivity of reactivity can be

achieved via coherent two-photon processes. The problem of

finding the optimum wave form that will maximize the

formation of a desired chemical species is formulated as a

problem in the simple cases and numerically for models which

carry the major characteristics of a chemical reaction.

Examples of selectivity and pulse shape determination will

be discussed.

C. B. Moore
University of California at Berkeley

"SPECTROSCOPY OF THE VIBRATIONAL LEVELS OF FORMALDEHYDE
IN THE ENERGY RANGE OF THE TRANSITION STATE TO H_2 + CO"

"SPECTRALLY RESOLVED IVR - THE CH STRETCH - CH BEND COUPLING
IN TRIHALOMETHANES"

"SINGLE-PHOTON VIBRATIONAL PHOTOCHEMISTRY -
OPTICALLY ACCESSIBLE UNIMOLECULAR REACTION COORDINATES?"

(Three short subjects involving IVR)

V. E. Bondybey
AT&T Bell Laboratories

"INFRARED-INDUCED ISOMERIZATIONS AND REARRANGEMENTS
IN LOW-TEMPERATURES MATRICES: EVIDENCE FOR MODE SELECTIVE
CHEMICAL REACTIONS"

W. H. Miller
University of California at Berkeley

"DYNAMICS OF HYDROGEN ATOM TRANSFER IN VINYLIDENE
AND MALONALDEHYDE"

Reaction surface models -- i.e., two-degree-of-freedom systems coupled to

a harmonic bath -- are used to describe the vinylidene → acetylene

isomerization,

$$H_2C=C: \rightarrow HC\equiv CH \quad ,$$
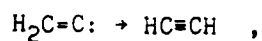
and the tunneling splitting in malonaldehyde that is caused by hydrogen atom

transfer,
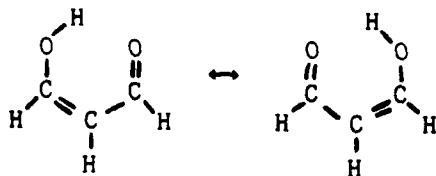
SESSION 2

PHOTOPHYSICS AND PHOTOCHEMISTRY OF OVERTONE LINESHAPES

Gowen Room

Thursday, October 3rd, from 2:00 until 5:30 P.M.

Chairman: C. Parmenter

Michael Berry
William Marsh Rice University

"NONCHAOTIC BEHAVIOR IN HIGHLY VIBRATIONALLY EXCITED MOLECULES"

After studying the spectroscopy and reaction dynamics of approximately seventy gas phase polyatomic molecular systems by single photon vibrational activation techniques, we believe that the following conclusions can be reached to support the argument that highly vibrationally excited molecules are often very orderly in their behavior:

1) mixing decreases as a function of increasing vibrational energy (e.g., acetylene),

2) specific doorway states lead to IVR (e.g., alkynes, benzenes), and

3) strong nonstatistical effects govern the dynamics of both nonreactive (e.g., benzene) and reactive (e.g., formyl fluoride, hydrazoic acid, allyl isocyanide) systems.

Based on these conclusions, it appears that new theoretical approaches are needed to understand the nature and dynamics of highly vibrationally excited molecules.

M. Quack
Eidgenössische Technische Hochschule
Zürich, Switzerland

"THE DYNAMICS OF THE ISOLATED CH-CHROMOPHORE
AND THE EMERGENCE OF GLOBAL VIBRATIONAL STATES
AND INTRAMOLECULAR RELAXATION IN POLYATOMIC MOLECULES"

The concept of the *global vibrational state* (as opposed to
normal and *local* vibrational states) and its relationship to
the spectroscopy and quantum dynamics of polyatomic molecules
has been put forward some time ago[1]. In the talk a survey
of our experimental work on the isolated CH-chromophore will
be presented[2] and the present status summarized in relation
to recent theoretical developments. If time permits, the
relationship to the pioneer work of Berry and coworkers[3] on
the benzene CH overtone spectra will be discussed as well as
the more recent theoretical work on benzene[4] and experiments
on acetylene[5], which seem to conform closely to some of the
concepts presented in 1).

1) M. Quack, Faraday Disc. Chem. Soc. 71, 359 (1981) see also
    in particular pages 3 and 325 of this volume and M. Quack
    in "Energy Storage and Redistribution in Molecules" Pro-
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    Plenum Press, New York; and J. Chem. Phys. 69, 1282 (1978)

2) H.R. Dübal and M. Quack, Chem. Phys. Lett. 72, 342 (1980);
    K. von Puttkamer, H.R. Dübal and M. Quack, Faraday Disc.
    Chem. Soc. 75, 197, 263 (1983); S.D. Peyerimhoff, M. Lewerenz
    and M. Quack, Chem. Phys. Lett. 109, 563 (1984); H.R. Dübal
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    (1985); A. Amrein, H.R. Dübal and M. Quack, Mol. Phys.
    in press (1985)

3) M.J. Berry and R.G. Bray, J. Chem. Phys. 71, 4909 (1979)

4) E.L. Sibert, W.P. Rinehart and J.T. Hynes, Chem. Phys.
    Lett. 92, 455 (1982)

5) E. Abramson, R.W. Field, K.K. Innes and J.L. Kinsey,
    J. Chem. Phys. 80, 2298 (1984)

J. T. Hynes
University of Colorado

"MECHANISMS OF INTRAMOLECULAR ENERGY FLOW
IN VIBRATIONALLY ACTIVATED MOLECULES"

We will briefly describe some mechanisms (vibrational and rotational) and rate

of intramolecular energy flow in energized and reactive molecules that have

emerged in our theoretical studies.

· R. L. Woodin and C. F. Meyer
Exxon Research & Engineering Co.

"EFFECTS OF MOLECULAR STRUCTURE ON INFRARED MULTIPLE PHOTON EXCITATION"

A fundamental question which remains unclear for infrared laser induced multiple photon processes is the mechanism of excitation through the dense "quasicontinuum" of states of a vibrationally excited molecule. Results from several different experiments suggest that the quasicontinuum is not structureless, but rather that particular states of the excited molecule can enhance the multiple photon absorption process. Understanding the energies and couplings of excited molecular states provides new insight into the ir multiple photon excitation process.

Energy deposition spectra have been measured for a variety of molecules using tunable, intense 3μm infrared radiation. Comparison of energy deposition spectra taken under focused (2-5 J/cm^2, >100MW/cm^2) conditions to spectra taken with an unfocused beam locates the spectral features which most readily undergo multiple photon excitation, while deuterium substitution identifies those molecular groups which are necessary for the excitation process but may not be initially resonant with the excitation frequency. Data for propylene (C_3H_6) indicate that specific "doorway" states can be particularly effective in promoting 3μm multiple photon excitation, and that these states are associated with distinct features of molecular structure.

Data from isobutene spectra ($CH_2C(CH_3)_2$) are in agreement with the picture of coupled doorway states that emerges from the propylene data. In benzene (C_6H_6) enhanced multiple photon absorption is similarly observed in a portion of the spectrum where doorway states are predicted from vibrational overtone spectra.

An alternative method of exploring the degree of coupling which exists between vibrational modes is by measuring saturation of absorption features using intense radiation. The intensity dependent saturation behavior of several molecules have been measured at 3μm, including CH_4, C_3H_6, c-C_3H_6 and C_6H_6. C-H vibrational modes which are expected to have fewer couplings to other molecular vibrations are observed to saturate more readily than modes which are expected to be highly coupled. This has been observed both when comparing vibrational modes in molecules of different structure, and when comparing different absorption features of one molecule. In some cases, effects of rotational structure on saturation behavior can be observed.

SESSION 3

STATISTICAL SPECTROSCOPY

The Rose Mansion

Thursday, October 3rd, from 8:00 until 9:30 P.M.

Chairman: C. B. Moore

L. Leviandier, M. Lombardi, R. Jost, and J. P. Pique
CNRS, Grenoble, France
Session 3, 8:00-8:45 P.M.

"LEVEL STATISTICS: FROM FREQUENCY TO TIME DOMAIN"

Preliminary experimental examples, showing the influence on time-resolved experiments of going from Poisson to Wigner level statistics, will be displayed using Fourier Transform techniques. We discuss to what characteristics of level statistics are most sensitive time-resolved experiments. Possibility to use these techniques to extract useful information out of badly resolved spectra will be discussed.

Yongquin Chen, Evan Abramson, Robert L. Sundberg,
George Scherer, James L. Kinsey,
and **Robert W. Field** –

STRUCTURE, ISOMERIZATION, AND QUANTUM ERGODICITY IN S_0 ACETYLENE: REAL SPECTRA OF A REAL MOLECULE."

We have used the technique of Stimulated Emission Pumping (SEP) to examine the vibration-rotation structure of HCCH $\tilde{X}^1\Sigma_g^+$ at 9500-16000cm^{-1} and 27900 cm^{-1} of vibrational excitation. The levels accessed by SEP show much larger and more frequent perturbations than those observed in the C-H stretch high overtone spectra in the same energy region. The $\ell=2$ levels lose their almost good quantum numbers (V, ℓ_4, ℓ_5) at lower energy than the $\ell=0$ levels. $\ell=0$ (σ_g^+) remains a good quantum number to at least 27900 cm^{-1}, but $\ell\neq0$ becomes undefined by 13000 cm^{-1}. At 27900 cm^{-1} the spectra consist of clumps of vibrational lines. The clumps can be assigned vibrational and ℓ quantum numbers but the lines cannot. The observed density of σ_g^+ vibrational levels significantly exceeds that predicted by the best anharmonic density of states calculation. Statistical tests for quantum ergodicity imply that, on the 100 ps time scale sampled by the clump fine structure, only J and σ_g^+ remain good quantum numbers. High resolution spectra can tell us how many almost conserved observables remain defined after a time interval set by the spectral resolution. In order to talk about "quantum ergodicity" it would be useful to specify what phase space we consider to be accessible and how long we are prepared to give the molecule to access it. The combination of traditional methods of assigning spectra and statistical tests borrowed from nuclear physics holds the promise of obtaining, from high resolution spectra, dynamical information about the molecular mechanisms of intramolecular energy flow.

SESSION 4

SEMICLASSICAL METHODS -
REGULAR VS. CHAOTIC SPECTRA

Gowen Room

Friday, October 4th, from 8:30 A.M. until 12:45 P.M.

Chairman: W. H. Miller

R. Lefebvre
Universite de Paris-Sud, France

"BOX QUANTIZATION AND INTRASYSTEM DYNAMICS"

Enclosure of a quantum system in a box allows for the identification of resonance states which are less sensitive to a variation of box size than the quasi- scattering states [1]. It has been shown recently [2] that the graphs giving the energies as a function of box size may be exploited to extract the resonance parameters even when the coupled channel expansion of the wave funtions yields more than one open channel in the energy range of interest. The case of the collinear reactive collisions $H + H_2$ and $H + MuH$ is considered in this context, with a box shape suggested by the hyperspherical (polar) coordinates. The resonances are easily identified on the energy graphs. Comparison of these graphs with those obtained by applying box quantization to the different diagonally corrected hyperspherical adiabatic channels [3] indicates the increasing validity of the adiabatic separation of variables as one goes toward heavy-light-heavy mass combinations and allows for the interpretation of avoided crossings in terms of channel interactions. The "boxed" reactive systems can also be considered as a special type of billiard to which it is possible to apply various criteria for detecting the transition to a stochastic regime (overlap of avoided crossings, lack of single adiabatic configuration dominance).

1.   A.U. Hazi and H.S. Taylor, Phys. Rev. A1, 1109 (1970)

2.   R. Lefebvre, J. Phys. Chem. in press.

3.   J. Römelt, Chem. Phys. 79, 197 (1983).
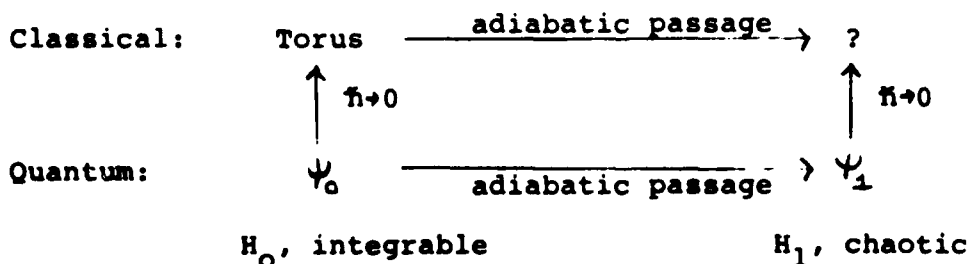
P. Pechukas
Columbia University

"QUESTIONS ABOUT CLASSICAL ADIABATIC PASSAGE AND SEMICLASSICAL BOUND-STATE CALCULATIONS"

The method of choice for semiclassical bound-state calculations on systems with more than two degrees of freedom is based on classical adiabatic passage from an invariant torus of a reference Hamiltonian H_O to the corresponding torus of the Hamiltonian of interest, H_1. There are a number of interesting questions about the foundations of the method.

1. The multidimensional adiabatic hypothesis--that corresponding tori of H_O and H_1 are connected by adiabatic passage--is most likely to be true if not only H_O and H_1, but also all the Hamiltonians encountered during the passage, are integrable. What further conditions are necessary, or is this enough?

2. Suppose H_O and H_1 are integrable, but some fraction of the Hamiltonians one runs through during the adiabatic passage are not. What happens?

3. A variant of question 2: Suppose H_O is integrable but H_1 is not. A torus of H_O remains a torus, under passage from H_O to H_1 at any non-zero rate, but likely becomes convoluted and misshapen, the more so the slower the passage. In what sense, if any, does this increasingly deformed torus have a well-defined phase space set as its adiabatic limit? Is that then the phase space set associated, in the semiclassical limit, to the corresponding "chaotic" eigenfunction? In other words--mathematicians' words--is the following diagram commutative?

Classical: Torus $\xrightarrow{\quad \text{adiabatic passage} \quad}$?

$\uparrow \hbar \to 0$ $\qquad\qquad\qquad\qquad\qquad$ $\uparrow \hbar \to 0$

Quantum: $\psi_0 \xrightarrow{\quad \text{adiabatic passage} \quad} \psi_1$

$\quad H_O$, integrable $\qquad\qquad\qquad\qquad$ H_1, chaotic

These questions will be discussed, but most likely not answered. The content of the discussion will depend on what my brilliant student Frank Johnston discovers in the next two months.

H. Taylor
University of Southern California

"REGULAR MOTION; BORN OPPENHEIMER APPROXIMATION AND
ENERGY LOCALIZATION"

G. S. Ezra
Cornell University

"CLASSICAL AND SEMICLASSICAL MECHANICS OF MOLECULES"

In this talk we review two aspects of our recent work on classical and semiclassical mechanics of molecules.

First, we discuss a method for EBK quantization of molecular bound states, based upon a Fourier representation of invariant tori. A key feature is the direct determination of good action variables from Fourier transforms of trajectories. The method has been successfully applied to systems with up to four vibrational degrees of freedom. An important point is that the technique can easily be applied to quantize strongly resonant trajectories. Results are presented for several resonant systems, and future applications outlined.

Second, we describe our investigations of the classical dynamics of vibration-rotation (VR) interaction. We have treated a simplified rigid-bender model for a triatomic molecule: that is, a single bending vibration interacting with 3-dimensional rotation. Use of a canonical transformation that eliminates angles conjugate to the conserved quantities j and m reduces the problem to one involving two degrees of freedom. The resulting 'rotational surface of section' provides considerable insight into the effects of VR coupling. We show that, even for a purely harmonic bending mode, the rigid bender displays the full range of dynamical behavior expected for a nonlinear system: near-separable quasiperiodic motion; resonant tori (a large 2:1 resonance is of particular importance); VR chaos. These phase space characteristics can be correlated with the rate and extent of VR energy transfer.

There is no Coriolis coupling in our rigid-bender model. The VR interaction is due solely to the dependence of the moments of inertia on the bending coordinate. There have been several recent studies of the effects of Coriolis interaction on the vibrational dynamics of two-mode systems rotating in a plane. A synthesis to yield a complete picture of VR interaction has yet to be achieved.

A. Warshel
University of Southern California

"SIMULATING INTRAMOLECULAR DYNAMICS OF RADIATIVE AND RADIATIONLESS
PROCESSES IN LARGE MOLECULES AND SOLUTIONS"

Significant progress has been made in recent years in simulation of molecular
spectra. It appears, however, that the available methods do not offer a
reliable and practical way for simulation of the vibronic lineshapes of large
anharmonic molecules. Our effort in attacking this problem concentrates in two
main directions: on the one hand, we treat systems with a few degrees of
freedom with a Semiclassical Green's function (SGF) approach that generates
quantized vibronic transitions between electronic surfaces of anharmonic
molecules. This method reproduces the quantum mechanical lineshape but (in its
present form) cannot be used as a practical way for studying many-dimensional
systems. On the other hand, we study large molecules and molecules in solutions
by a less rigorous semiclassical approach that uses the time-dependent energy
gap along the trajectories of the system. This seemingly ad hoc approach
appears now to reproduce the correct quantum lineshape in the high temperature
limit. More importantly, this method allows one to go beyond the harmonic
approximation in treating radiationless transitions of large molecules
(including electron transfer reactions). Thus, we can study the dependence of
rate processes on free energy rather than energy differences and obtain a
practical microscopic description of frictional effects.

SESSION 5

SPECTRA OF ULTRACOLD MOLECULES

Friday, October 4th, from 2:00 until 6:15 P.M.

Chairman: M. Quack

J. Kommandeur
University of Groningen, The Netherlands

"PYRAZINE AND PYRIMIDINE, THE CHAOTIC AND THE WELL-BEHAVED BROTHER?"

By the use of skimmed molecular beams and high resolution cw lasers the molecular eigenstate (ME) spectra of pyrazine and pyrimidine were obtained. Fourier transforming these spectra give the decay behaviors as observed by using narrow or broad laser excitations.

The pyrazine spectra are complex since the rotational states of the singlet are intimatly coupled to the ro-vibronic states of the triplet. In a few cases the ro-vibronic triplet manifold can be reconstructed and the various couplings can be found. They both have chaotic aspects, but too few data are obtained to apply a reasonable statistical analysis.

On the contrary pyrimidine, which differs only in the density of the ro-vibronic triplet manifold at the energy of S_1 appears to be a rather well-behaved molecule. The ME-spectra show rotational states, which can be fairly well interpreted on the basis of an axis-switched a-symmetrical top. Nevertheless, here also "perturbation" of some states occurs, but the effects are minor, at most leading to magnetic sensitivity of the absorption lines.

Since the pyrazine spectra can be understood as an "extrapolation" of the pyrimidine data, it is questionable whether a "chaotic" analysis would yield more insight.

D. W. Pratt
University of Pittsburgh

"PYRAZINE (AND PYRIMIDINE), REVISITED"

Much controversy has recently been generated over the proper interpretation of both time and frequency domain experiments on the first excited "singlet" states of the diazabenzenes, particularly pyrazine. In this talk, we will review the data and present a model which accounts for all of the observations to date, including several unpublished ones. We will also comment on the relevance of this work, and similar experiments on other systems, to problems in intramolecular energy flow, ergodicity, and "spectral" chaos.

A. Amirav and J. Jortner
AT&T Bell Laboratories

"EXCITED STATE DYANMICS AND IVR IN DIPHENYLBUTADIENE AND PYRAZINE".

Excited state dynamics of diphynylbutadiene (DPB) and pyrazine as well as over thirty other polyatomic molecules was probed by the simultaneous measurement of their absorption and light-induced fluorescence spectra, resulting in their emission quantum yield. In DPB, quantum yield measurements over the range $E_x=0-7000$ cm^{-1} above the izomerisation threshold could be nicely fitted both to RRK and RRKM. The pure radiative filetime τ_r of DPB's strongly scrambled $S_2(1B_u)-S_1(2A_g)$ MES was found to be vibrational energy independent and surprisingly short. Quantum yield measurements in pyrazine showed an inverse rotational state dependence, and markedly decreased with vibrational energy. An attempt is made to explain the wealth of experimental results in pyrazine in terms of K selective (due to coriolis interaction) rotationally mediated IVR between its MES and other background triplet states.

P. M. Rentzepis
AT&T Bell Laboratories

"UNRELAXED EMISSION OF LARGE MOLECULES
IN LOW-TEMPERATURE MATRICES"

C. S. Parmenter
Indiana University

"STATE-SELECTED IVR DYNAMICS IN TWO RELATED MOLECULES, p-DIFLUOROBENZENE AND p-FLUOROTOLUENE"

Psec IVR dynamics have been characterized experimentally from a variety of selected levels in S_1 pDFB and pFT. The experiments are based on time-resolved $S_1 \rightarrow S_0$ fluorescence spectra obtained by the method of chemical timing. The results reveal a high dependence of IVR time scales on the mode initially selected, but a smooth transition occurs from intermediate case to statistical case dynamics as the state density near the excited level increases. pFT displays IVR dynamics that are accelerated relative to those in pDFB. Comparison of IVR in the two molecules comments on the roles of vibrational symmetries, molecular rotations, methyl group internal rotation and ergodicity. The experiments are those of two Ph.D. students, both now finished, Karl W. Holtzclaw and Brad K. Stone. Financial support was provided by NSF and by PRF.

SESSION 6

THEORETICAL METHODS

Gowen Room

Saturday, October 5th, from 8:45 A.M. - 12:15 P.M.

Chairman: R. Lefebvre

S. Mukamel, Y. Yan, J. Sue, K. Shan
University of Rochester

"REDUCED DESCRIPTION OF MOLECULAR LINESHAPES AND NONLINEAR SUSCEPTIBILITIES"

Green function techniques are used to develop a simple and
efficient method towards the direct calculation of
absorption and fluorescence spectra of large polyatomic
molecules without having to sum over individual eigenstates.
Applications are made to the supersonic-beam spectra of
Anthracene and to a model system with Dushinsky rotation.
The absorption, excitation, and dispersed fluorescence
spectra of β carotenes in condensed phases are analyzed,
using a stochastic model of line broadening. This formalism
is used also to calculate nonlinear optical susceptibilities
such as $\chi^{(3)}$, four-wave mixing, and coherent transients in
polyatomic molecules.

FIGURE CAPTIONS

Figure 1 - Dispersed Fluorescence of supercooled Anthracene. The excess vibrational energy in the excited state (in cm) is shown in each panel.

      (A) Experimental (W. R. Lambert, P. M. Felker, and A. H. Zewail, J. Chem. Phys, **81**, 2209 (1984))

      (B) Calculated for a harmonic 17-mode model using the Green function technique.

Figure 2 - Same as Fig. 1 but for larger values of the excess vibrational energy.

Figure 3 - Raman spectra of a model harmonic system with 10 modes.

Mode No.	1	2	3	4	5	6	7	8	9	10
Ground State Frequencies	755	1015	220	300	380	520	860	1180	1280	1340
Excited State Frequencies	745	985	200	280	380	540	840	1160	1260	1320
Dimensionless Equilibrium Displacement	1.5	1.2	0.5	0.3	1.0	0.5	1.0	0.7	0.35	0.5

Modes 1 and 2 are mixed by a Dushinsky rotation. The rotation angle (from bottom to top) is 0°, 30°, 60°, 90°, 120°, 150°. Fig. A shows the Raman transition in which mode 1 starts at v"=1 and ends at v"=2 as a function of the excitation frequency. Fig. B shows the same spectra where mode 2 is initially in v"=1 and ends in v"=2. All other modes are in v"=0.

Figure 4 - Absorption spectrum of the molecule of Fig. 3 with Dushinsky rotation of 45°, as a function of temperature. The right column is with a higher resolution.
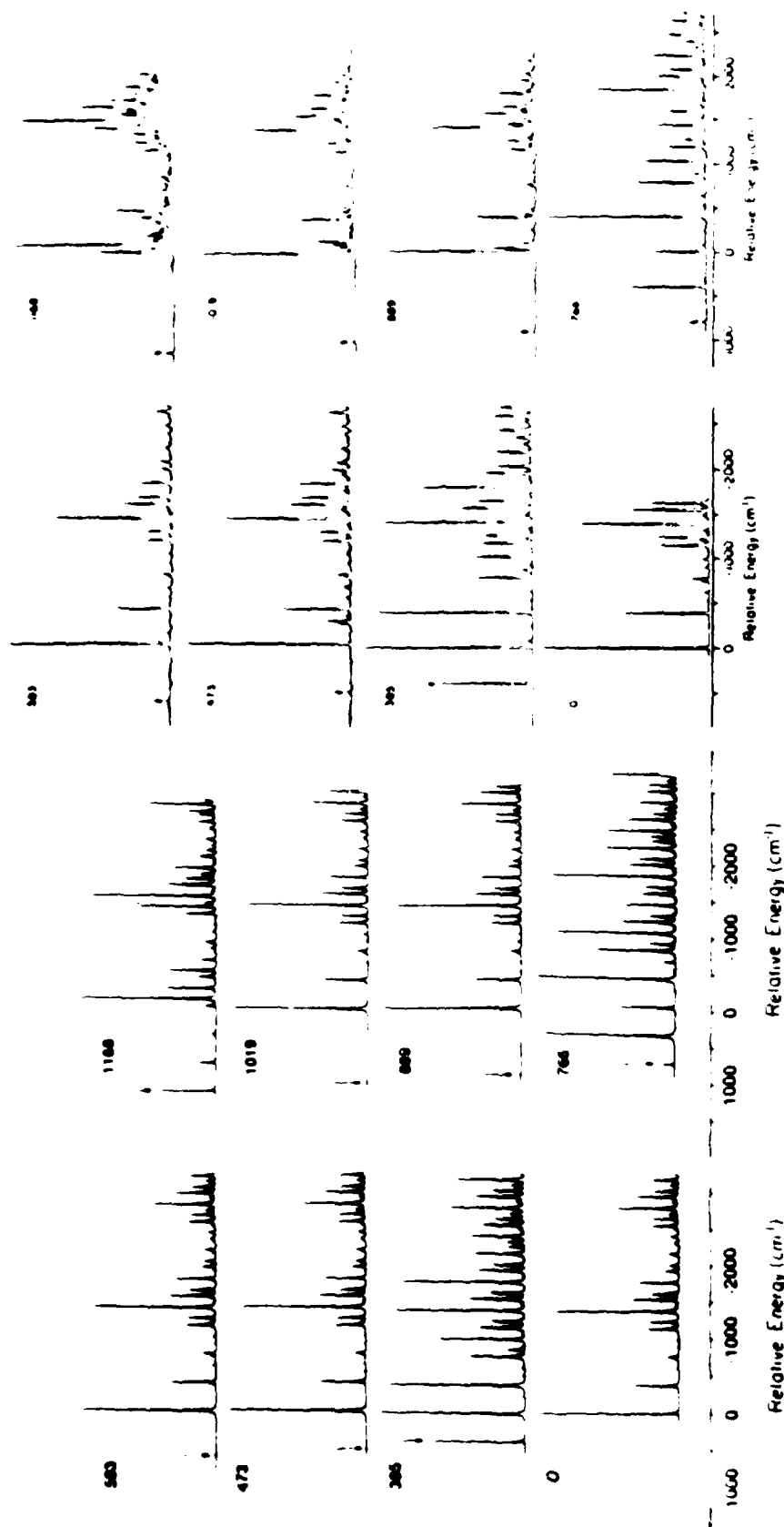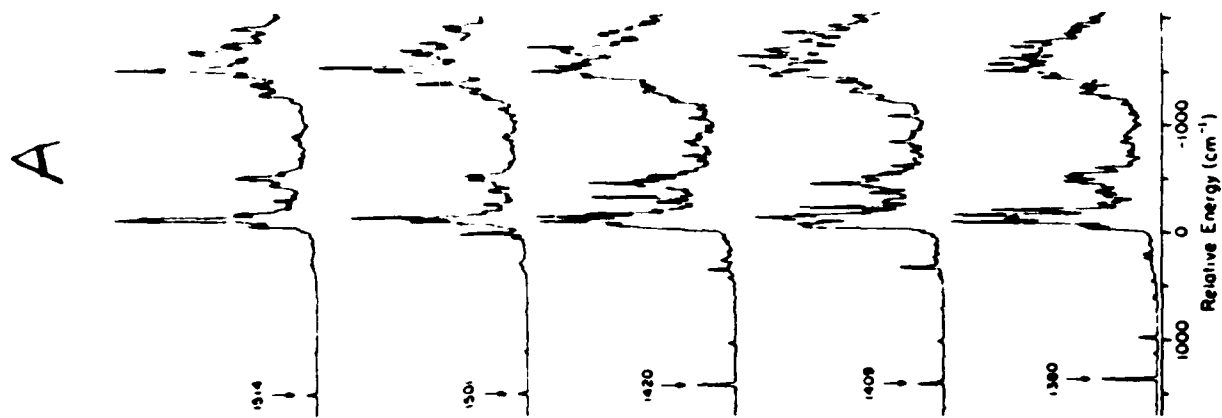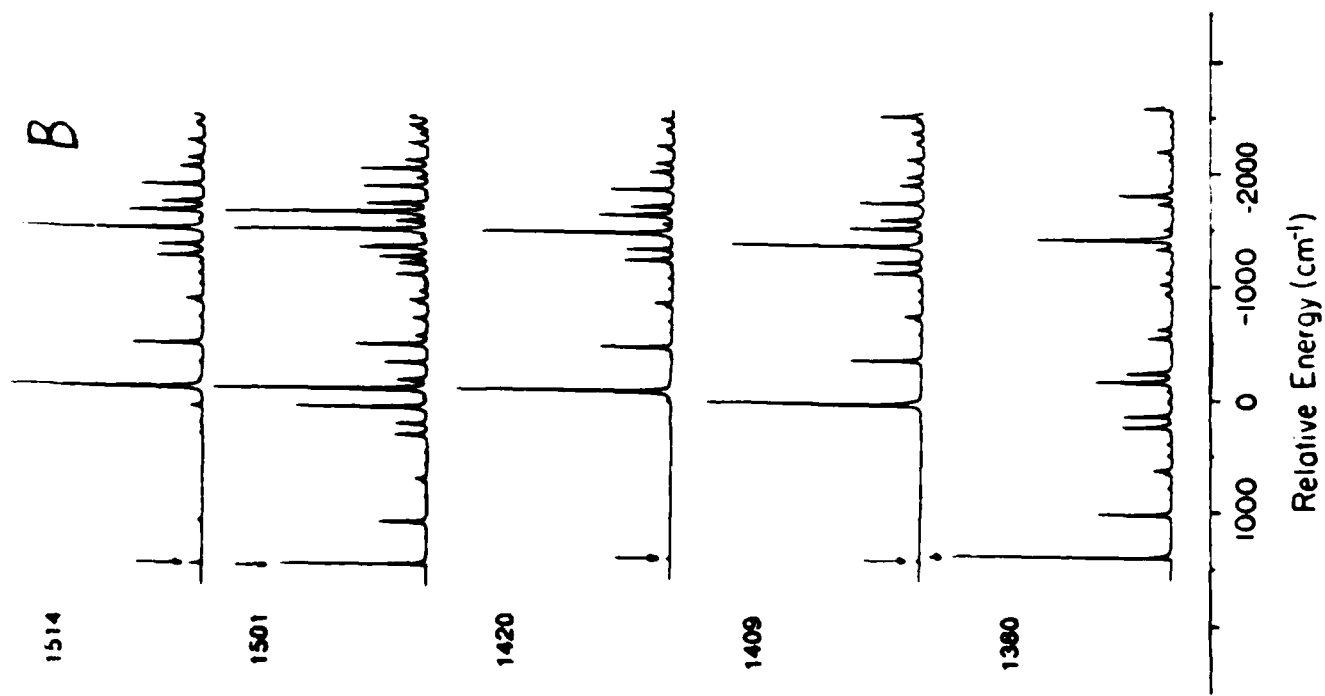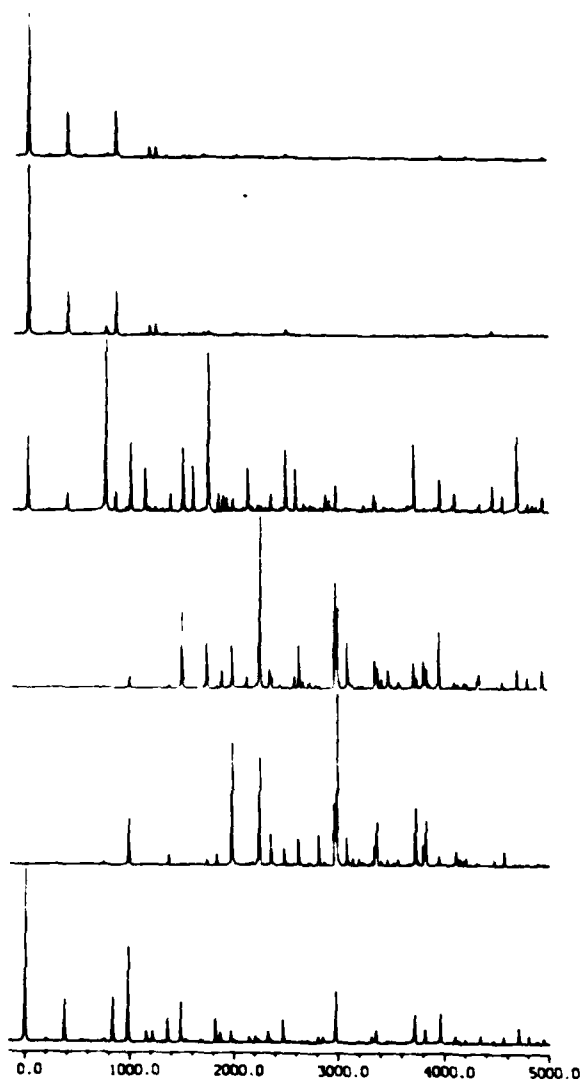
A

B

Relative Energy (cm⁻¹)

Relative Energy (cm⁻¹)

JCB/01Aug84/OH6/FIG 1/SC:

Fig 1

A

Relative Energy (cm⁻¹)

1514
1501
1420
1409
1360

JCP/O/A, 84/046/EEL-9/7511.

B

Relative Energy (cm⁻¹)

1514
1501
1420
1409
1360

Fig 2

A   B

0.0 1000.0 2000.0 3000.0 4000.0 5000.0   0.0 1000.0 2000.0 3000.0 4000.0 5000.0

$|\langle \cdot 0 | G | 2 0 \rangle|^2$ $|\langle 0 \cdot | G | 0 \cdot \rangle|^2$

Fig 3

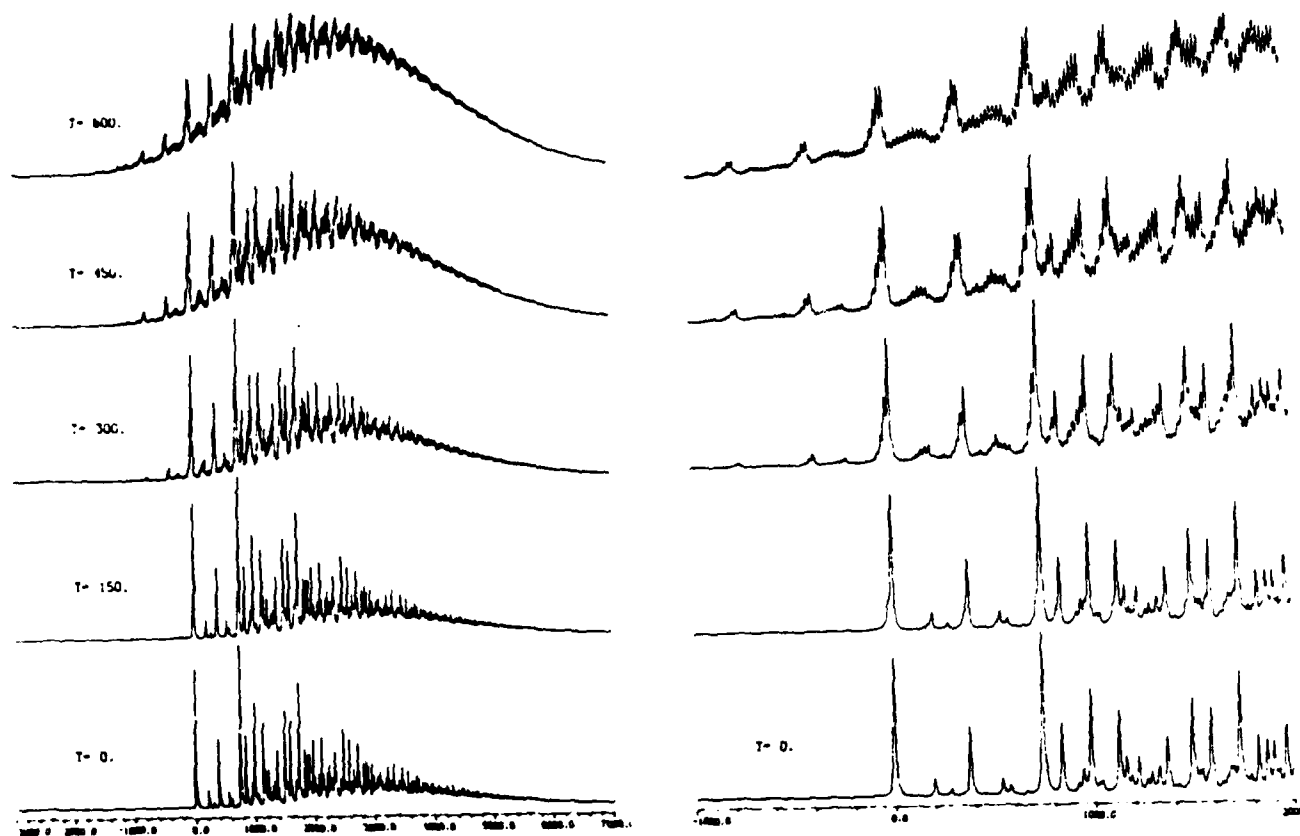Fig 4

R. B. Gerber
The Hebrew University, Jerusalem, Israel
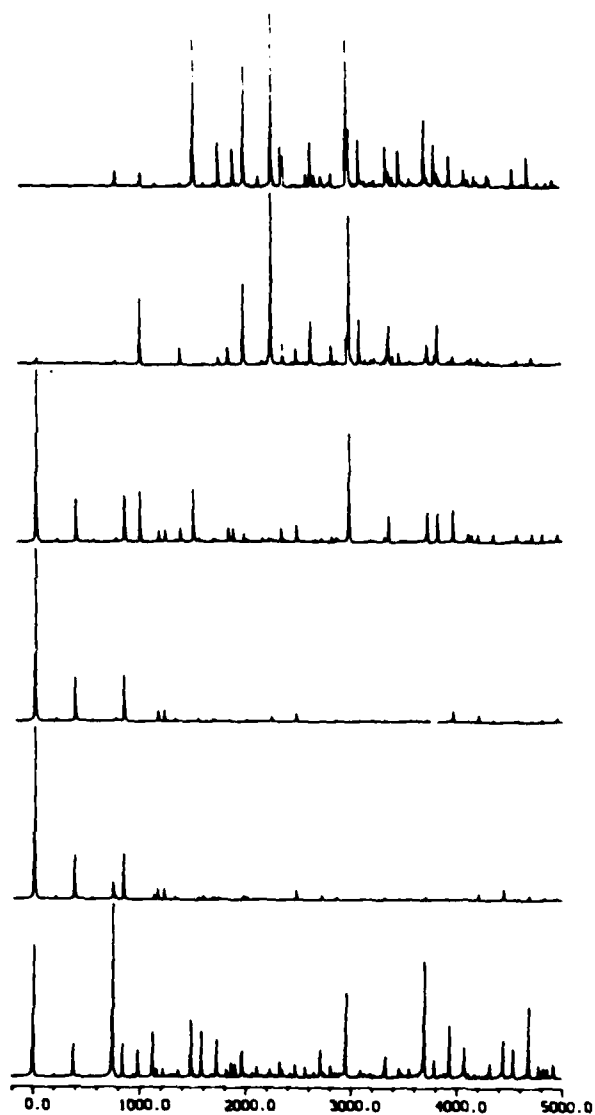
"HIGHLY EXCITED VIBRATIONS OF POLYATOMIC MOLECULES AND CLUSTERS: A MEAN FIELD APPROACH"

Energy level structure and energy transfer dynamics in vibrationally excited polyatomic molecules and van der Waals clusters is explored within the framework of a mean field treatment. In this approach each mode is described as moving in an effective potential being the average field due to the other modes. The effective potentials for the various modes are determined by a self-consistency requirement. There are versions of the approach for: (i) Calculation of energy levels and other stationary properties (Self Consistent Field - SCF method); (ii) Intramolecular energy transfer (Time-Dependent Self Consistent Field method - TDSCF); (iii) Thermodynamical and structural properties (Temperature-Representation Self-Consistent Field method -TRSCF). Calculations are presented indicating that: (a) The self-consistent field methods may be applicable in cases of very strong anharmonic coupling between the modes (validity conditions are discussed). (b) These methods are relatively easily applicable also to systems with a substantial number of degrees of freedom, thus they provide useful insight on *dependence of intramolecular-dynamics upon system size.*

Specific results of interest include:

(1) The SCF provides a convenient route to spectroscopic assignment of excited levels (when possible), for identification of "good modes" in the strong anharmonic regime, and for the explicit inversion of measured vibrotational levels of polyatomics to yield the (multidimensional) potential energy surface. (Applications: CO_2, HCN).

(2) TDSCF describes with good accuracy the vibrational predissociation dynamics of clusters, both such corresponding to the weak coupling regime (e.g. $I_2(v)Ne$) and those pertaining to strong coupling, RRKM-type dynamics (e.g. Ar_3).

(3) TDSCF calculations offer interesting insight on the variations of vibrational relaxation dynamics with cluster size, in systems of the type $I_2(v)[Ne]_N$. Results in the range $N = (1,16)$ are provided.

R. E. Wyatt
University of Texas, Austin

"QUANTUM DYNAMICS WITH ULTRA-LARGE BASES: THE RECURSIVE RESIDUE-GENERATION METHOD"

The Recursive Residue Generation Method (RRGM) allows the computation of state-to-state time-dependent transition amplitudes in systems with thousands of states.[1,2,3] Applications have recently been made to multiphoton excitation,[4] electronic absorption spectra,[5] thermally averaged time-correlation functions,[6] and the computation of rates of chemical reactions.[7] The RRGM will be reviewed, recent formal analysis in terms of moment diagrams will be described,[8] and current molecular applications will be illustrated.[9]

1. A. Nauts and R. E. Wyatt, Phys. Rev. Lett. **51**, 2238 (1983).
2. A. Nauts and R. E. Wyatt, Phys. Rev. A**30**, 872 (1984).
3. R. A. Friesner and R. E. Wyatt, J. Comp. Phys., to be published.
4. J. Castillo and R. E. Wyatt, J. Comp. Phys. **59**, 120 (1985).
5. R. A. Friesner and R. E. Wyatt, to be published.
6. R. A. Friesner and R. E. Wyatt, J. Chem. Phys. **82**, 1973 (1985).
7. R. E. Wyatt, Chem. Phys. Lett., to be published.
8. I. Schek and R. E. Wyatt, J. Chem. Phys., to be published.
9. J. Chang and R. E. Wyatt, to be published.

J. Brickmann and R. D. Levine
The Hebrew University, Jerusalem, Israel

"SENSITIVITY ANALYSIS FOR QUANTUM EIGENVALUES OF BOUND SYSTEMS"

The sensitivity of the eigenvalues E_i of a nonintegrable Hamiltonian measured by their second differences or the second derivatives $d^2E_i/d\lambda^2$ with respect to a coupling parameter λ is studied for the regular and the irregular part of the spectrum as well as for the range of *isolated* avoided crossings. In the regular part the $(d^2E_i/d\lambda^2)$-values are expected to be arranged on branches in a plot *vs.* energy; in the avoided crossing range there should be a drastic increase and for the irregular part a decrease and a breakdown of the branching is predicted.

SESSION 7

IVR AND CHEMICAL REACTIVITY

Gowen Room

Saturday, October 5th, from 1:45 - 6:30 P.M.

Chairman: M. J. Berry

A. Zewail
California Institute of Technology

Session 7, 1:45-2:30 P.M.

"IVR AND CHEMICAL REACTIVITY - AN OVERVIEW"

A. Kaldor
Exxon Research & Engineering Co.

Session 7, 2:30-3:15 P.M.

"THE REACTIONS OF TRANSITION METAL CLUSTERS"

R. M. Hochstrasser
University of Pennsylvania

"RELAXATION PROCESSES INVOLVED IN PHOTO-ISOMERISM"

GENERAL DISCUSSION

THE FUTURE OF THE FIELD

Gowen Room

Chairman: A. Zewail

Saturday, October 5th, from 4:30 - 6:30 P.M.