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in Reduction Project (0704-0188), DC 20583.1. AGENCY USE ONLY (Leave Blank)
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2. REPORT

7/29/94

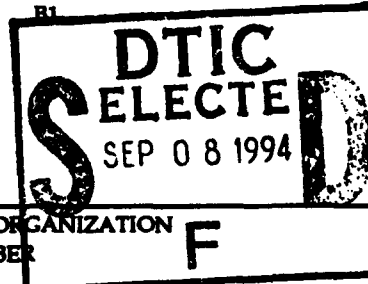
3. REPORT TYPE AND DATES COVERED

Final 1 November 1990 - 31 October 1993

4. TITLE AND SUBTITLE Large Amplitude Motions, Especially
Isomerization and Tunneling in Polyatomic Molecule Spectra: Novel
Experimental, Pattern Recognition, and Theoretical Methods

5. FUNDING NUMBERS

61102 F 2303 B1



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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, MA 021398. PERFORMING ORGANIZATION
REPORT NUMBER

3

9. SPONSORING/MONITORING AGENCY NAME(S) AND
ADDRESS(ES)AFOSR/MONL
BUILDING 410
Bolling Air Force Base
Washington, DC 20332-6448
*Dr. Herman*10. SPONSORING/MONITORING
AGENCY REPORT NUMBER

AFOSR-91-0079

AFOSR-TR- 94 0479

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION IS
UNLIMITED

12b. DISTRIBUTION CODE

A

13. ABSTRACT (Maximum 200 words)

Stimulated Emission Pumping (SEP) spectra of HCP imply surprisingly regular dynamics for a rigid molecule undergoing up to 300° bending vibrations. Optical Optical Double Resonance (OODR) spectra characterize corresponding $(\pi^*)^2 \leftarrow \pi^2$ doubly excited (predissociated) states of HCP and HCCH. The factors governing intensities of nominally forbidden transitions in bent $\rightarrow$ linear SEP spectra are analyzed; this analysis forces the conclusion that transitions into excited CH stretching levels are absent from the $\tilde{A}-\tilde{X}$ SEP spectra of HCN and HCCH. All mystery transitions in Wodtke's SEP spectra of HCN are assigned. An OODR scheme has been devised for distinguishing electric dipole from magnetic dipole transitions. The $J, M \rightarrow J', M'$ rates for $\tilde{J}$ -disalignment in H_2CO^+ / H_2CO^+ collisions have been measured by Transient Gain Spectroscopy and shown to be consistent with a long-range dipole model.

14. SUBJECT TERMS

Laser Spectroscopy, Potential Energy Surface Barriers, Intramolecular Vibrational
Redistribution,Electric Dipole Moment, Symmetry Selection Rules, Rotational Energy Transfer,
Isomerization, Assignment of Isomer Structure.

15. NUMBER OF PAGES

22

16. PRICE CODE

17. SECURITY CLASSIFICATION

UNCLASSIFIED

18. SECURITY CLASSIFICATION
OF THIS PAGE

UNCLASSIFIED

19. SECURITY CLASSIFICATION
OF ABSTRACT

UNCLASSIFIED

20. LIMITATION OF ABSTRACT

UL (UNLIMITED)

SAR (SAME AS REPORT)

NSN 7540-01-280-5500

DTIC QUALITY INSPECTED 5

Standard Form 298 (Rev. 2-89)

Final Report
to
Air Force Office of Scientific Research

**Large Amplitude Motions, Especially
Isomerization and Tunneling in Polyatomic
Molecule Spectra: Novel Experimental,
Pattern Recognition, and Theoretical Methods
AFOSR-91-0079**

94-29028



2308

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Accession For	
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DTIC TAB	☐
Unannounced	☐
Justification _____	
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Distribution /	
Availability Codes	
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Period:

1 November 1990 - 31 October 1993

DTIC QUALITY INSPECTED 3

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TABLE OF CONTENTS

A.	Final Report	2
1.	LIST of PERSONNEL.....	2
a.	Graduate students	
b.	Postdocs and Visitors	
c.	Collaborators	
2.	Report on RESEARCH PROJECTS.....	3
a.	HCP Spectroscopy.....	3
b.	HCN Spectroscopy.....	5
c.	OODR Spectra of HCCH.....	7
d.	A Diagnostic for Magnetic vs. Electric Dipole Electronic Transitions.....	8
e.	$\vec{J}$ -Dealignment in $\text{H}_2\text{CO } \tilde{\text{A}}^1\text{A}_2 v_4=1, K_a=0$	9
f.	Construction of a REMPI-TOF Apparatus.....	9
g.	Statistical Spectroscopy.....	10
h.	2,5-dihydroxy-p-benzoquinone Monomer and Hydrates.....	10
B.	REFERENCES	11
C.	Publications (since 1983) Resulting from AFOSR Support	16

A. Final Report 1 November 1990 - 31 October 1993

1. LIST OF PERSONNEL

a. Graduate Students

David Chasman (Ph.D. 1992)
Sarah-Jane Cohen (S.M. June 1992)
Chris Gittins*
David Jonas[†] (Ph.D. March 1992)
Theresa Kavanaugh (Ph.D. 1992)
James Lundberg* (Ph.D. January 1992)
Jonathan O'Brien
Neme Nnolim
Bhavani Rajaram*
Stephani Solina^{††}
John Wang* (S.M. June 1994)
David Watt^{††} (withdrawn)

[†] AT&T Graduate Scholar

^{††} NSF Graduate Fellow

* Primary support from present grant

b. Postdocs and Visitors

Dr. Joseph Bentley* (now at Delta State University)
Dr. Yit-Tsong Chen* (now at National Taiwan University)
Dr. Stephen Coy
Dr. Alex Golger
Dr. Haruki Ishikawa ^{††}
Prof. King-Chuen Lin (National Taiwan University)
Dr. Yasuhiro Ohshima[†] (University of Tokyo)
Dr. Jean-Paul Pique (University of Grenoble)
Prof. Richard Redington (Texas Tech University)
Dr. Ryuma Takashi (Showa Denko)
Prof. Kaoru Yamanouchi[†] (University of Tokyo)
Dr. David Yaron (now at Carnegie Mellon University)
Dr. Xinsheng Zhao* (now at Peking University)

* Primary support from AFOSR grant

[†] NSF-JSPS International Travel Grant

^{††} JSPS Postdoctoral Fellow

c. Collaborators

Dr. Michael Davis	(Argonne Nat'l lab)	(pattern recognition)
Professor Fritz Grein	(University of New Brunswick)	(HCP <i>ab initio</i>)
Professor Joshua Halpern	(Howard University)	(cyanogen)
Professor Michael Kellman	(University of Oregon)	(theory)
Professor Kevin Lehmann	(Princeton University)	(HCP)
Prof. H.F. Schaefer	(Univ. of Georgia)	(NCNC and triplet HCCH)

Mr. C. David Sherrill	(Univ. of Georgia)	(NCNC)
Professor Jeffrey Steinfeld	(M.I.T.)	(IR-UV Double Resonance)
Professor Soji Tsuchiya	(University of Tokyo)	(SEP)
Professor Alec Wodtke	(UCSB)	(HCN)
Professor Robert Wyatt	(University of Texas)	(<i>ab initio</i> SEP spectra of HCP)
Professor Kaoru Yamanouchi	(University of Tokyo)	(SEP and DF)
Dr. Koichi Yamashita	(Okazaki)	(HCP <i>ab initio</i>)

2. REPORT ON RESEARCH PROJECTS

a. HCP Spectroscopy

This is one of the three most important results from this grant.

Dr. Yit-Tsong Chen (with experimental assistance from Dr. Y. Ohshima, Prof. K.-C. Lin, and John Wang and computational assistance from David Watt) recorded Stimulated Emission Pumping (SEP) spectra of HCP extending up to the pure bending overtone level (0, 42, 0) of the $\tilde{X}^1\Sigma^+$ electronic ground state. Observation of such high excitation ($EVIB = 25,315\text{ cm}^{-1}$) of a bending vibration in a rigid molecule is without precedent. The SEP spectra show a surprisingly regular pure bending overtone progression. The regularity of the bending progression, the Franck-Condon intensity of this progression, and the absence of intensity in combination levels are unexpected. We have attempted to model the HCP SEP spectrum using Prof. Kevin Lehmann's crude *ab initio* $\tilde{X}^1\Sigma^+$ potential surface [LEH85]. Ms. Theresa Kavanaugh collaborated with Dr. K. Yamashita (in Prof. Morokuma's laboratory at the Institute of Molecular Science, Okazaki) to compute a new, more accurate HCP $\tilde{X}^1\Sigma^+$ potential surface. [YAM92] Dr. David Yaron has generalized on the semi-rigid bender model in order to use the SEP spectra to obtain information about a reduced dimension cut (along the bending coordinate) through the potential surface. It appears that the Franck-Condon active bending coordinate deviates from the $\text{HCP} \leftrightarrow \text{HPC}$ isomerization coordinate at about $EVIB = (0,32,0) = 19,800\text{ cm}^{-1}$ where the vibrational fine structure starts to change rapidly. We now believe that rapid changes in vibrational fine structure, polyad structure, and the sudden and intermittent appearance of vibrational perturbations, are the universal spectroscopic signatures of local changes in potential surface topography (e.g., entrance to isomerization valley, top of barrier to isomerization). The HCP SEP spectrum is probably the best example of an interpretable spectrum showing a molecule in the act of isomerizing.

The two-laser PUMP/PROBE spectra of HCP contain both downward (SEP) spectra into high vibrational levels of the $\tilde{X}^1\Sigma^+$ state and upward (OODR) spectra into weakly predissociated levels of a bent excited state.

Sorting out the observed spectral features into SEP and OODR transitions is nontrivial but unambiguous. The predissociated $3^1A'$ state of HCP observed here is analogous (CP bond order of 1) to the $(\pi^*)^2 \leftarrow \pi^2 \tilde{C}'^1A_g$ state of acetylene (CC bond order of 1) observed in similar experiments by Dr. James Lundberg [LUN92a]. The interesting feature of this doubly excited valence state of HCP is that it has a relatively low barrier to linearity. Ms. Bhavani Rajaram is attempting to fit the OODR data to a "quasilinear" model. We expect to be able to determine the shape of the barrier to linearity in the $3^1A'$ bending potential and the effect of CP stretching excitations on the height of this barrier.

At our request, Professor F. Grein has computed *ab initio* potential surfaces for the $\tilde{A}^1A''$, $\tilde{C}^1A'$, and $3^1A'$ states in order to help us interpret our $\tilde{A} \rightarrow \tilde{X}$ and $\tilde{C} \rightarrow \tilde{X}$ SEP spectra and our $3^1A' \leftarrow \tilde{A} \leftarrow \tilde{X}$ OODR spectra [SAN93].

Dr. Chen left MIT in March, 1991 to begin his academic career as an Assistant Professor at the National Taiwan University. Ms. Bhavani Rajaram, Mr. John Wang, and Dr. Haruki Ishikawa have re-started the HCP experiments. Dr. Chen's HCP data are being extended in three important ways: (i) a systematic search is being made for SEP transitions terminating on bend—CP stretch combination levels (especially using the $\tilde{C}^1A'$ -state rather than the $\tilde{A}^1A''$ -state as intermediate, because SEP spectra recorded via the $\tilde{C}$ -state do not seem to exhibit Franck-Condon selectivity toward pure bending overtones); (ii) SEP and OODR spectra are being recorded via $\tilde{A}^1A'' K_a'=0$ intermediate levels, because these spectra sample transitions terminating exclusively on $\tilde{X}^1\Sigma^+ \ell''=1$ (SEP) or $3^1A' K_a=1$ (OODR) levels (which were unobservable in previous experiments) and therefore eliminate assignment and model ambiguities; (iii) spectra of DCP will provide additional information about the potential surfaces of the $\tilde{X}^1\Sigma^+$ and $3^1A'$ states as well as insight into the mysterious regularity and $\tilde{A}-\tilde{X}$ Franck-Condon strength of the $\tilde{X}$ -state bending overtone levels.

Dr. Stephen Coy has applied his Extended Autocorrelation (XAC) [COY94, FIE94] method to the HCP $3^1A' \leftarrow \tilde{A}^1A''$ OODR spectra. This method is capable of picking out *a priori* known patterns [e.g., a 5 line ${}^1R_1(J)$, ${}^1Q_1(J)$, ${}^1P_1(J)$, ${}^3P_1(J)$, ${}^3P_1(J)$ pattern specified by known relative intensities (Hönl-London factors) and splittings ($\bar{B}$ -values)] from a dense manifold of overlapping transitions.

Dr. Joseph Bentley has begun calculations of the $J=0-2$ eigenstates on the full 4-dimensional *ab initio* Yamashita-Morokuma potential for the HCP $\tilde{X}^1\Sigma^+$ state [YAM92]. He expects to compute all of the $J \leq 2$ eigenvalues up to $E_{VIB} = 30,000$ (The HCP $\leftrightarrow$ HPC saddle point is at $E_{VIB} = 26,959 \text{ cm}^{-1}$) by implementing the DVR-DGB (Discrete Variable Representation [LIG85]-Distributed Gaussian Basis [HAM86]) [BAC91] method on the University of

Texas Cray Y-MP8/864 (with a 256 Megaword Solid-State Storage Device), utilizing the "out-of-core" codes provided by the BCSLIB-EXT (Boeing Computer Services Program Product 20462 0520) library. This calculation is very similar to a recent calculation by Bentley et al on the homologous HCN molecule [BEN93]. This HCP calculation initiates the MIT (Field/Silbey)-Texas (Wyatt) collaboration via the unique arrangement of Dr. Bentley's joint MIT/Texas postdoc.

b. HCN Spectroscopy

This is the second of the three most important results from this grant.

David Jonas has made a systematic study of the factors governing the relative intensities of SEP transitions in molecules with bent excited states and linear ground states (e.g., HCN, HCP, and HCCH) [JON92a]. He demonstrated that the dynamic range of SEP spectroscopy is such that transitions can be detected which are 1000 times weaker than the strongest features in the spectrum [JON92b, JON93]. This means that axis-switching effects [HOU65] and systematic resonances (Fermi, Darling-Dennison, Coriolis, ℓ -resonance) [AMA58, PLI72, SMI91] in either the upper or lower electronic state can lend intensity to nominally forbidden transitions. The dynamic range and rotational selectivity of SEP spectroscopy makes SEP superior to higher resolution infrared spectroscopy in providing a complete and detailed picture of the anharmonic mechanisms that destroy the usual vibrational and K or ℓ rotational quantum numbers. A systematic study of resonances provides an explicit short-time picture of where and how fast vibrational energy flows subsequent to any bond-localized excitation in a small polyatomic molecule [JON92b, JON93, KEL90, KEL91, SMI91].

Based largely on his DOE supported study of the Dispersed Fluorescence (DF) [YAM91] and SEP spectra of acetylene [JON92b, JON93], Jonas devised the DF/SEP/superpolyad method for extracting a complete and extrapolable (to higher EVIB and to longer time) picture of intramolecular vibrational dynamics directly from spectra. Low resolution DF spectra [YAM91] identify the Franck-Condon bright states and the earliest stages of energy flow away from these initially prepared bright states. High resolution SEP spectra resolve any ambiguities about the bright state assignments and the mechanism of the first steps of the IVR process [JON92b, JON93]. Perturbation matrix elements are determined which explicitly describe all of the most important resonance mechanisms. A multi-resonance superpolyad model [KEL90, KEL91, SMI91] incorporates all of these resonances in a form that permits extrapolation based on harmonic oscillator matrix-element scaling rules [LEW88, AMR89, QUA90, QUA91]. The superpolyad model, through its representation of a complex web of couplings by a very small number of adjustable parameters, becomes the basis of a sensitive pattern-

recognition scheme for detecting isomerization-related changes in the local topography of a potential energy surface. Ms. Stephani Solina and Mr. Jonathan O'Brien are continuing the study of energy flow in acetylene as part of a DOE supported project. Mr. John Wang had planned to initiate a similar DF/SEP/superpolyad study of the NCNC $\tilde{X}^1\Sigma^+$ state. This would have involved a collaboration with Professor Joshua Halpern at Howard University. However, Mr. Wang unexpectedly decided to withdraw from the Ph.D. program, and the isocyanogen SEP project is suspended pending the interest of a new student. Stimulated by our initial plans to record SEP spectra of isocyanogen, C.David Sherrill proved that the S_1 excited state is nonlinear (essential for SEP access to the highly excited bending levels that are most strongly coupled to the isomerization coordinate) and bound (a lifetime of >20 ns is essential for fluorescence-dip detected SEP spectroscopy) [SHE93].

The conclusions from David Jonas' study of the effects of axis-switching [HOU65] and anharmonic resonances on intensities in SEP spectra [JON92b, JON93] apply to many molecules in addition to acetylene. After careful detective work in the region of $\sim 7,000$ cm^{-1} of vibrational excitation in HCCH, Jonas was able to conclude that bands involving excitations in the CH symmetric stretch have such small intrinsic Franck-Condon intensities that they will be undetectable in the DF and absorption spectra. This means that several previous vibrational and electronic assignments of the HCCH $\tilde{A}-\tilde{X}$ and $\tilde{B}-\tilde{X}$ absorption spectra are questionable. However, the really important result occurred when Jonas looked closely at the unassigned bands in the Wodtke et al SEP spectra of HCN [YAN90]. Jonas assigned all of the remaining unassigned HCN transitions, mostly to axis-switching $K_a' = 1 \rightarrow \ell'' = 1$ transitions [JON92c]. Once again, the C-H stretch is shown to be entirely absent from an $\tilde{A}$ (bent) $\rightarrow \tilde{X}$ (linear) spectrum, this time of HCN.

In addition to completing the assignment picture for Wodtke's SEP spectra of HCN, Mr. Jonas, Ms. Solina, and Dr. Xinsheng Zhao measured the electric dipole moment of the HCN $\tilde{A}^1A''$ state [JON92d].

c. OODR Spectra of HCCH

This is the last of the three most important results from the present grant.

Until the beginning of the present AFOSR grant period, *all* spectroscopic studies of acetylene had been *defined* as part of our DOE-supported project. James Lundberg's OODR studies of the $\tilde{C}'^1A_g$ [LUN92a] and $\tilde{E}^1A$ [LUN92b] predissociated valence states became part of the AFOSR project because of the close relationship between the HCP and HCCH electronic structures revealed in the respective OODR spectra.

Ever since we first began recording SEP spectra of acetylene, we noticed large and broad baseline excursions which were initially dubbed "potatoes" and ignored as instrumental artifacts. Dr. Jean-Paul Pique recorded survey SEP spectra over such a wide energy region that it quickly became clear to Pique and Lundberg that the "potatoes" always occurred at the same energy and could be organized into regular vibrational progressions. Our fluorescence-dip detection scheme enabled us to observe transitions into strongly predissociated (non-fluorescing) states, and our rotationally selective OODR scheme allowed us to resolve coarse (K_a) and fine (J) rotational structure that would have been unresolvable in direct, rotationally non-selected absorption spectra. Complete Nuclear Permutation Inversion (CNPI) group theoretical selection rules [BUN79], elegantly simplified and applied to acetylene OODR spectra by James Lundberg [LUN94], made it feasible to deduce the isomeric form (linear, *trans*-bent, *cis*-bent, vinylidene, nonplanar near-*cis*, nonplanar near-*trans*) and electronic symmetry of each excited electronic state that appeared in our "potato spectra".

Two electronic states were fully characterized. The $\tilde{C}^1A_g$ state is $(\pi^*)^2 \leftarrow \pi^2$ doubly excited (C—C bond order of 1) with respect to the $\tilde{X}^1\Sigma_g^+$ state, and severely predissociated (especially for vibrational levels above the $v=0$ level) [LUN92a]. Only the C—C stretch and trans-bending vibrations are Franck-Condon active. It would be interesting to sample the torsional vibration (via a $v_4 \neq 0$ level of the $\tilde{A}^1A_u$ state, accessible through $\tilde{A}$ -state perturbations [UTZ93, TOB93, SCH86] or IR-UV double resonance excitation [CAR88]) to discover whether the torsional barrier is more like that of a normal C—C σ -single bond or whether the combined effects of a π_{CC} -bond and a π_{CC}^* -antibond lead to an unprecedentedly high torsional frequency.

The $\tilde{E}^1A$ state has been a subject of heated controversy for ~30 years [WIL58, HER66, HER81]. James Lundberg succeeded in proving that the $\tilde{E}$ -state is *nonplanar* near *cis* (the C_2 symmetry axis coincides with the $\tilde{b}$ -inertial axis) [LUN92b]. Conclusive evidence for non-planarity was obtained from the unprecedented odd/even- K_a dependence of the ΔK_a selection rule and the inertial defect ($\delta \propto [1/C - 1/B - 1/A]$) which is definitely negative for the $\tilde{E}$ -state [LUN92b] and $\delta \approx 0$ for the $\tilde{C}'$ -state [LUN92a]. Wilkinson [WIL58] was right about the nonplanarity of the $\tilde{E}$ -state; Herzberg [HER66], Herman [HER81], and several quantum chemists [KAM74, DEM75] were wrong!

Lundberg [LUN92b] also showed that fluorescence-dip detected OODR and REMPI spectroscopies are complementary in acetylene. Fluorescence-dip detected OODR spectra, recorded via the *trans*-bent $\tilde{A}^1A_u$ state, sample primarily bent, predissociated, valence states. REMPI spectra [ASH87, ORL87, TAK92] sample primarily weakly predissociated or predissociation-free, linear, Rydberg states.

d. A Diagnostic for Magnetic vs. Electric Dipole Electronic Transitions

The relative intensities of rotational branches in OODR and SEP spectra were observed to be strongly dependent on the relative polarizations of the PUMP and PROBE laser beams. David Jonas and Stephani Solina realized that since the electric and magnetic fields of electromagnetic radiation oscillate along orthogonal directions, the polarization behavior of an electric dipole transition would be opposite that of a magnetic dipole transition [JON92e]. This scheme was used to prove that the acetylene $\tilde{E}-\tilde{A}$ [LUN92b] and $\tilde{C}'-\tilde{A}$ [LUN92a] transitions in HCCH are electric dipole allowed. A similar diagnostic was recognized earlier by Klemperer et al [LOM67].

e. $\vec{J}$ -Dealignment in $\text{H}_2\text{CO } \tilde{A}^1\text{A}_2 v_4=1, K_a=0$

The Transient Gain Spectroscopy (TGS) technique [VAC85] was used to characterize the microscopic $(J, M_J)_{\text{initial}} \rightarrow (J, M_J)_{\text{final}}$ processes that contribute to the decay of alignment accompanying rotationally inelastic $\text{H}_2\text{CO } \tilde{A}^1\text{A}_2 / \text{H}_2\text{CO } \tilde{X}^1\text{A}_1$ collisions [COY92]. A pulsed PUMP laser selectively populates $\tilde{A}^1\text{A}_2 v_4 = 1, K_a = 0, J=1, |M_J| = 1$ and a cw probe laser monitors the full transient response of the populations and alignments in the $J_{K_a, K_c} = 0_{0,0}, 1_{0,1}, 2_{0,2}, \text{ and } 3_{0,3}$ rotational levels. A master equation fit to the entire TGS data set shows that all of the $(J, M_J)_{\text{initial}} \rightarrow (J, M_J)_{\text{final}}$ rate coefficients are well described by simple electric $\vec{a}$ -dipole transition amplitudes. State-to-state rotationally inelastic rates are found to partition into M_J -resolved collisional transfer rates strictly according to tensor opacity rank $\Lambda = 1$ (with no detectable contribution from $\Lambda = 2$ or 3 terms). We showed that the alignment in the $1_{0,1}$ level decays with no detectable contribution from single-collision direct-elastic events; dealignment is accurately modeled by sequential processes. This is the first clear observation of pure electric dipole alignment relaxation [COY92], perhaps not a very surprising result for a pair of colliders with large permanent electric dipole moments.

f. Construction of a REMPI-TOF Apparatus

Chris Gittins has constructed a pulsed supersonic jet, Resonance Enhanced Multiphoton Ionization-Time of Flight (REMPI-TOF) apparatus. The funds for the construction of this apparatus were provided by an NSF grant (CHE91-20339). This is the first such apparatus to become fully functional in the Field/Silbey research group. Mr. Gittins and Mr. Ryuma Takashi have recorded mass selected REMPI-TOF spectra of Al_2 and Mo_2 . Their initial attempt to record $T_n \leftarrow T_1$ 1+1 R2PI spectra of acetylene, where

the T₁ acetylene is formed by Hg-photosensitization [WEN79] and rotationally cooled by supersonic expansion, was unsuccessful. Mr. Gittins' REMPI-TOF apparatus has subsequently proven to be enormously powerful for Rydberg spectra of the alkaline earth monohalides (an NSF supported project).

g. Statistical Spectroscopy.

Dr. Stephen Coy (in collaboration with David Chasman) has developed two statistical pattern recognition methods for extracting dynamical information from spectra of polyatomic molecules [COY94, FIE94]. These methods are intermediate between the statistical measures borrowed from nuclear physics [POR65, MEH67, BOH84], which deal with the breakdown of a single quantum number, and the elaborate spectroscopic model-based superpolyad [JON93] approach. The key is that the early time energy flow in polyatomic molecules is sequential, owing to hierarchical couplings between several approximately separable internal degrees of freedom.

The Extended Autocorrelation (XAC) method is designed to pick out repeated complex patterns of lines [specified by *a priori* known relative intensities (Hönl-London factors) and splittings ($\bar{B}$ -values)] which are obscured by being embedded in a dense manifold of unassigned transitions. This method has been successfully tested on real [HCP $3^1A' \leftarrow \bar{A}^1A''$ OODR spectra, HCCH $\bar{A}^1A_u \rightarrow \tilde{X}^1\Sigma_g^+$ DF spectra] and synthetic spectra.

The parsimonious trees method [DAV92, DAV93] is designed to identify, in an initially model-free way, the hierarchy of average coupling matrix elements responsible for sequential energy flow. This method has been successfully applied to the NO₂ $\bar{A}^2B_2 - \tilde{X}^2A_1$ spectrum (both band origin and rovibrational data) and to synthetic spectra [COY94, FIE94].

h. 2,5-dihydroxy-p-benzoquinone Monomer and Hydrates

Professor Richard Redington [RED92] has recorded and vibrationally analyzed the fluorescence excitation spectrum of the lowest energy allowed singlet-singlet transition of jet-cooled 2,5-dihydroxy-p-benzoquinone (25Q). The transition is the $S_3 \leftarrow S_0$, $^1B_u \leftarrow ^1A_g$, $\pi^* \leftarrow \pi$ system with 0-0 band at 275.55nm. Our goal was to observe vibrational-mode-specific tunneling splittings associated with intramolecular ---O---H---O= H-atom transfer similar to those we observed in the tropolone spectrum [RED89, RED90]. However, the laser induced fluorescence transitions were observed as structureless peaks with laser intensity dependent bandwidths [RED92].

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C. Publications (Since 1983) Resulting from AFOSR Support

The research of the Co-P.I.'s is supported by AFOSR and DOE grants in the general area of the spectra of vibrationally highly excited polyatomic molecules. The distinction between these two funded projects is discussed in the original research proposals. We list below all of our publications relevant to the research described in the present project; AFOSR support is denoted by (+) and DOE support by (++).

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