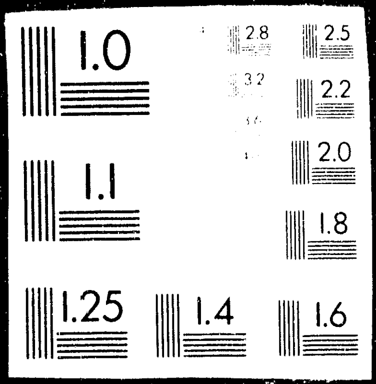
006504

1 OF 1



DOE/ER/13671--10

DE93 006504

## II. TECHNICAL PROGRESS REPORT 2/1/90 - 6/30/92

### A. SEP Spectroscopy of Acetylene

1. Pattern Recognition Schemes Based on Statistics. SEP made it possible to look at eigenstate-resolved and rotationally pre-sorted spectra of small polyatomic molecules at such high levels of vibrational excitation that traditional spectroscopic eigenstate-by-eigenstate assignment methods seemed both infeasible and inappropriate. Surely our SEP spectra would manifest some quantum mechanical version of classical chaos and "therefore" the eigenstates in the energy region, above which the classical dynamics is predominantly chaotic, would be *intrinsically unassignable.* Thus we sought to develop statistical measures [BER77, PEC83, BRO81, MEH67, PIQ87] which, when applied to *pure sequence*[5] fully resolved-eigenstate spectra, would reveal whatever is left of *almost good quantum numbers* (i.e., vibrational-quantum numbers, rotational projection quantum numbers $K_a$ or $K_c$, or a specific bonded network $H_aC_bC_cH_d$ vs. $H_dC_bC_cH_a$) or localization in a restricted region of symmetry- and energetically-accessible phase space.

Our initial SEP experiments on acetylene were therefore directed at two targets: (i) the evolution toward global chaos [ABR84, ABR85, SUN85, PIQ87, CHE88b]; (ii) detection of acetylene↔vinylidene isomerization resonances [CHE89]. We elected to skip over the relatively low-energy region, which, as we found in the $E_{VIB} < 8000\ cm^{-1}$ SEP spectra of $H_2CO$ [REI84, DAI85], we expected would be assignable in terms of traditional spectroscopic quantum numbers and effective Hamiltonian fit models [AMA58, PLI72a, PLI72b]. Our conviction that the traditional approach to low-energy vibration-rotation spectra could not be extended, at an acceptable level of effort, to the high energy region, led us to temporarily abandon what has turned out to be the most fruitful ($E_{VIB} \approx 7000\ cm^{-1}$) region for investigation.

The statistical approach to SEP spectra was not entirely unrewarding. Yongqin Chen was awarded the 1990 "Nobel Laureate Signature Award" for

---

[5] A pure sequence contains only eigenstates belonging to the same value of the quantum numbers corresponding to all rigorously conserved quantities (J, parity, and g, u symmetry for the HCCH $X\ ^1\Sigma_g^+$ state).

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED his (entirely DOE-supported) attempt to locate acetylene↔vinylidene isomerization resonances in the 15,000-15,900 cm$^{-1}$ energy region [CHE88a, CHE89]. The crucial idea was that the transition state for interconversion of two chemically equivalent bonded networks, $H_aC_bC_cH_d \leftrightarrow H_dC_bC_cH_a$, lies in the vinylidene region of phase space and that the tunneling rate between the two acetylene bonded networks will be enhanced at energies near "vinylidene resonances". Chen invented a method for detecting the effect of these resonances on the SEP spectrum that combined CNPI (Complete Nuclear Permutation-Inversion) group theory and SCC (Spectral Cross-Correlation), a statistical pattern recognition scheme. In SCC two SEP spectra, recorded from two $\tilde{A}$-state intermediate rotation-vibration levels *which belong to the same rigorous symmetry class* but are carefully selected to *give Franck-Condon access to two disjoint sets of $\tilde{X}$-state vibrational levels*, are cross-correlated. If the cross-correlation is abnormally high in a particular energy region, this indicates that some kind of mode-mixing in the $\tilde{X}$-state has destroyed the normally preserved Franck-Condon distinction. Chen devised a CNPI-based group theoretical test to identify mode-mixings induced by tunneling through the vinylidene region of phase space. If a high cross-correlation were actually caused by a vinylidene resonance, then this correlation would be absent in another pair of SEP spectra, recorded from an $\tilde{A}$-state intermediate level belonging to a CNPI symmetry species in which the acetylene↔vinylidene resonance is symmetry forbidden. One resonance, at $E_{VIB} = 15{,}525 \pm 150$ cm$^{-1}$, was identified that passed the SCC-CNPI tests [CHE88a, CHE89].

The SCC statistic is superior to the nearest neighbor level spacing [ABR84], long-range spectral rigidity [SUN85, PIQ87], and intensity distribution [PIQ88] statistics that we used previously because SCC is based on the breakdown of one, *a priori*-specified, almost-conserved dynamical quantity rather than merely the survival of any unspecified approximate constants of motion. SCC was a step back toward traditional spectroscopy. Yongqin Chen suggested another, even better structure-targeted statistic: the appearance of resolvable $H_aC_bC_cH_d \leftrightarrow H_dC_bC_cH_a$ tunneling doublings near each vinylidene resonance [CHE88a]. These doublings will be present in SEP spectra of $H^{13}C^{13}CH$ [$I(^{13}C)=1/2$] but not $H^{12}C^{12}CH$ [$I(^{12}C)=0$]. We had planned to search for these $H^{13}C^{13}CH$ doublings during the present grant period, but postponed those experiments in order to complete a more promising study of the SEP spectrum in the $E_{VIB} = 7000$ cm$^{-1}$ region (discussed below). It is fortunate that we did so, because we now know how to select specific zero-order "bright states" from which the short-time dynamics points directly toward the vinylidene region of phase space.

2. <u>A Pattern Recognition Scheme Based on Traditional Spectroscopic Models</u>. The crucial push away from statistical pattern recognition and back toward traditional spectroscopic pattern recognition was the result of a long-term collaboration with Professors Kaoru Yamanouchi and Soji Tsuchiya (Department of Pure and Applied Sciences, University of Tokyo). Low resolution (30 cm$^{-1}$ FWHM) dispersed fluorescence spectra of $H^{12}C^{12}CH$ were recorded at the University of Tokyo [YAM91]. These spectra contained long progressions in the two $\tilde{X}$-state vibrational modes expected to be Franck-Condon active: mode-2 (CC stretch) and mode-4 (*trans*-bend). However, many progressions were built on a vibrational level involving excitation in either mode-1 (symmetric CH stretch) or even quanta of mode-5 (*cis*-bend). Mode-1 was naively expected to be weakly Franck-Condon active, but mode-5 should have been completely inactive. The assignment ambiguity was based on the accident that $v_1 \approx v_2 + 2v_5$.

We were initially uncomfortable even with the idea of "assigning" vibrational quantum numbers to *features* in a low resolution spectrum which, at high $E_{VIB}$, would certainly not be *single vibrational eigenstates*. So we decided to do some high resolution SEP detective work. Our primary goal was to resolve the $v_1$ vs. $v_2 + 2v_5$ ambiguity by examining the rotation-vibration fine structure [PLI72a and b] under the lowest energy observed feature state in one of the mystery DF progressions [YAM91]. These experiments led to the following observations and conclusions.

(i) The lowest energy members of assigned feature state progressions were in fact single vibrational eigenstates known [by their vibrational energy, $G(\underset{\approx}{V})$, rotational constant, $B(\underset{\approx}{V})$, $\ell$=0,2 splitting ($g_{44}$), and $\ell$=2 $\ell$-type doubling ($q_4$)] from high resolution infrared [PLI92a and b] and Raman spectroscopy.

(ii) As a progression continues to higher energy, the feature states are observed to split into a steadily increasing number of subfeatures.

(iii) By comparing SEP spectra recorded from two different intermediate levels ($\tilde{A}$ $v_3'$=2 and $\tilde{A}$ $v_3'$ = 3), it was possible to distinguish the overall $\tilde{A}$-$\tilde{X}$ Franck-Condon envelope (of no relevance to dynamics on the $\tilde{X}$-state) from hierarchical clusterings into features, sub-features, sub-sub-features that are *bona fide* consequences of $\tilde{X}$-state dynamics [YAM91].

(iv) Each of the feature states in the low resolution DF spectrum corresponds to a single Franck-Condon bright state, and the vibrational quantum numbers of this bright state specify the t=0 early-time localization that would be produced if the entire feature were prepared by a sufficiently short DUMP pulse.

(v) The mystery progressions in the DF spectrum are built on two or four quanta of mode-5. The *cis*-bend ($v_5$) is lit up, even after the shortest time (~200 fs) sampled by the 30 cm$^{-1}$ resolution of the DF spectrum, by a Darling-Dennison [DAR40] interaction with the *trans*-bend [($v_4$, $v_5$) ~ ($v_4$–2), ($v_5$+2)].

(vi) The subfeatures under each feature state arise from a now nearly completely characterized combination of Darling-Dennison ($2v_4$~$2v_5$ and $2v_1$~$2v_3$), anharmonic ($v_2 + v_4 + v_5$~$v_3$: "2345 Fermi"), and vibrational $\ell$-resonance ($\Delta\ell_4 = -\Delta\ell_5 = \pm 2$, $\Delta v_4 = \Delta v_5 = 0$) interactions [AMA58, PLI72a and b, JON92a, JON93]. This multi-resonance picture completely describes how the vibrational energy, initially localized in a single Franck-Condon bright state, flows in a *sequential* manner throughout the entire *super-polyad* to which that bright state belongs. Kellman's ARQ (Algebraic Resonance Quantization) scheme [KEL86, FRI87, KEL91] assigns a superpolyad number, $N' = 5v_1 + 3v_2 + 5v_3 + v_4 + v_5$, to the restricted region of phase space explored by the bright state. [For example, the feature state at $E_{VIB}$ = 11,554 cm$^{-1}$, ($v_2$=2, $v_4$=10, $v_5$=2) belongs to N'=18, which consists of 22 members ignoring the $\ell_4$, $\ell_5$, $\ell$ fine structure!]

(vii) The enormous number of intra-superpolyad coupling matrix elements are expressed in terms of a small number (~4) of adjustable parameters scaled by simple functions of vibration-rotation quantum numbers (derived from textbook coordinate and momentum matrix elements evaluated in a harmonic oscillator basis set [AMA58, PLI72a and b, JON92a, JON93, LEH92]). The sequential and restricted Intramolecular Vibrational Redistribution (IVR) process in the acetylene $\tilde{X}\ ^1\Sigma_g^+$ -state can be described by a *very elaborate* effective Hamiltonian matrix model which is expressed in terms of a *very small number* of adjustable parameters. These parameters can be determined by detailed spectroscopic examination of a small subset of one superpolyad, or again taking advantage of harmonic oscillator matrix element scaling laws, determined from analysis of a simpler, lower energy superpolyad.

(viii) David Jonas and Stephani Solina have concentrated on SEP spectra in the $6{,}900 < E_{VIB} < 7{,}130$ cm$^{-1}$ region that contains the $(v_1, v_2, v_3, v_4^{\ell_4}, v_5^{\ell_5})^{\ell} = (0,1,0,8^0,0)^0$ and $(0,1,0,8^2,0)^2$ Franck-Condon bright and $(0,1,0,6^0,2^0)^0$, $(0,1,0,6^2,2^0)^2$, and $(0,1,0,6^{\pm 2},2^{\mp 2})^0$ Darling-Dennison brightened states (the SEP-bright part of the $N'=11$ superpolyad). By combining their multi-resonance analysis with previous analyses [STR76] of high resolution Raman, infrared [PLI72a and b], and high overtone spectra [SCH83, SMI91, HER92], all of the intra-superpolyad coupling parameters needed to describe the time evolution of any SEP bright state have been determined, provided that no change in the topography of the potential energy surface destroys the $N'=5v_1 + 3v_2 + 5v_3 + v_4 + v_5$ superpolyad structure. One such topographical change is certain to occur near $E_{VIB} \approx 15{,}000$ cm$^{-1}$, where the top of the acetylene↔vinylidene isomerization barrier is located [CHE89, ERV92, GAL92].

(ix) The Jonas-Solina multi-resonance model [JON92a, JON93] is therefore a sophisticated structural-model-based pattern-recognition scheme, vastly superior to crude chaos-based statistics, which is capable of detecting the onset of isomerization as a subtle deviation of the structure on the (N′+m)-th superpolyad from predictions based on extrapolation from the N′-th superpolyad. *The stage is now set to use changes in the coarse structure of a superpolyad to detect chemically interesting topographical features on a potential energy surface.*

(x) In the course of their multi-resonance modeling of the $E_{VIB} \sim 7000$ cm$^{-1}$ region, Jonas and Solina[6] discovered that the dynamic range of SEP was much larger than we had expected; SEP transitions spanning an intensity range of a factor of $\sim 10^3$ from strongest to weakest are detectable [JON92a]! This means that we can see much deeper into a superpolyad (i.e. detect much weaker transitions into nominally dark vibrational levels) than is possible in high resolution Raman, infrared, or high overtone spectra. This is important because the weakest transitions typically carry the most valuable information about the coupling parameters that control IVR rates and patterns. *Where does the energy go? How fast? Why?*

(xi) An especially important class of nominally forbidden transitions appears in our SEP spectra via the "axis-switching" mechanism [HOU65]. For example, in the HCCH $\tilde{A}$-$\tilde{X}$ transition, the principal inertial axes $(\hat{a},\hat{b},\hat{c})_{\tilde{X}}$ in the linear $\tilde{X}$-state ($\hat{a}$ along the $C \equiv C$ bond) are oriented differently than $(\hat{a},\hat{b},\hat{c})_{\tilde{A}}$ in the *trans*-bent $\tilde{A}$-state ($\hat{a}$ tipped slightly away from the C≡C bond and toward the H···H axis). As a result, simple c-type rotational selection rules ($\Delta K_a=\pm1$, $\Delta K_c$=even) are not strictly valid for acetylene $\tilde{A}\rightarrow\tilde{X}$ SEP spectra. Nominally forbidden $K_a'-\ell''=0,\pm2$ transitions are expected to appear in the SEP spectra with *a priori* calculable intensities. This is especially significant for a bent→linear transition, because in a linear molecule the vibrational angular momentum for mode-s, $\ell_s$, varies in steps of 2 from $\ell_s^{max} = v_s$ down to $\ell_s^{min}=0$ or 1. Thus, $K_a'-\ell''$=even axis-switching transitions from $K_a'=1$ terminate in different $\tilde{X}$-state vibrational levels (odd $v_4'' + v_5''$) than the nominally allowed transitions (even $v_4'' + v_5''$)!

(xii) David Jonas' recognition of the importance of axis-switching transitions in acetylene led him to conclusive assignments for all of the unassigned mystery bands in Alec Wodtke's HCN $\tilde{A}\rightarrow\tilde{X}$ SEP spectra [JON92b].

---

[6] Stephani Solina reported on this work at the 1992 International Molecular Spectroscopy Symposium at Ohio State University. Her talk was selected as one of the three best "first talks by a graduate student" and she will be awarded the "1992 Rao Prize" at the 1993 Symposium.

(xiii) The absence of SEP transitions terminating on $v_{CH} > 0$ vibrational levels of HCN led Dave Jonas to compute the v=1:v=0 Franck-Condon factor ratios for SEP transitions terminating in $v_{CH}=1$ levels of HCN and $v_1$ (symmetric CH stretch) = 1 levels of HCCH. He found that, in the spectral regions examined, the Franck-Condon factors for all transitions terminating in $v_{CH} > 0$ and $v_1 > 0$ levels were below the detection threshold [JON92b, JON93].

(xiv) In all of our pre-1991 acetylene-SEP publications [ABR84, ABR85, SUN85, PIQ87, CHE88b] we claimed to be able to sort the observed transitions into pure sequences. We claimed that the density of $\ell=0$ ($\Sigma_g^+$) vibrational levels that actually appear in our SEP spectra was a factor of ~3 larger than the total calculated density of $\Sigma_g^+$ states [CHE88b]. This led us to suggest that standard methods for computing vibrational densities of states might be systematically underestimating the true density of states. We also applied several chaos-based statistical measures to our SEP spectra [ABR84, SUN85, PIQ87, PIQ88], but these tests are only meaningful when applied to pure sequences. We now know, primarily due to the previously unsuspected large dynamic range in our SEP spectra, that *the observed density of $\ell=0$ levels is not larger than the calculated density* [JON92a, JON93]. David Jonas has devised a *rigorous* procedure for extracting statistically useful pure $\Sigma_g^+$, J=0 sequence data sets from SEP spectra. Although this procedure will require *six* separate SEP scans through each targeted energy region, it will produce interloper-free, reasonably complete, pure sequences of J=0 levels (J=0 levels are invariably preferred by theoreticians).

(xv) The minimum energy path from acetylene to vinylidene involves simultaneous large amplitude local CCH bend and local C-H stretch motions of one H atom [CAR84]. The multi-resonance model shows that certain SEP-bright states are directly coupled to states with significant local bend, local stretch character [JON92a, JON93]. Therefore we know which SEP-accessible members of each superpolyad are most strongly coupled to the acetylene↔vinylidene reaction coordinate. This will enable us to devise excitation schemes that will optimally display vinylidene resonance energies and lifetimes.

## B. SEP Spectroscopy of the Formyl Radical via the $\tilde{B}^2A' \leftrightarrow \tilde{X}^2A'$ Electronic Transition

HCO is produced in a flow cell by photolysis of acetaldehyde at either 308nm (XeCl excimer laser) or 266nm (Nd:YAG laser).

We have recorded fluorescence excitation spectra of the HCO $\tilde{B}^2A' \leftrightarrow \tilde{X}^2A'$ system [SAP90, COO92] and performed a rotational analysis of the $0_0^0$ band. The rotational structure of the $\tilde{B}$-$\tilde{X}$ $0_0^0$ band proves that the transition is of hybrid **a**,**b**-type and that the $\tilde{B}$-state is of $^2A'$ symmetry. Detailed measurements of relative **a**-type and **b**-type rotational branch intensities imply that the electric dipole transition moment, $\vec{\mu}_{\tilde{B}-\tilde{X}}$ lies in the plane of the HCO molecule at an angle of 31(4)° away from the **a** principal inertial axis. Whether $\vec{\mu}_{\tilde{B}-\tilde{X}}$ lies more nearly parallel or perpendicular to the C-H bond axis remains to be determined from a more detailed study of intensity interference effects. The rotational structure of the band previously thought to be the $\tilde{C}^2A''-\tilde{X}^2A'$ $0_0^0$ band [DIX69, TAN79] is also hybrid **a**,**b**-type (and not **c**-type as would be required if the upper state were of $^2A''$ symmetry), which implies that all bands previously assigned to the $\tilde{C}-\tilde{X}$ system are actually transitions to levels of the $\tilde{B}$-state with $v_{CH}=1$. Some irregularities in the spacings between $K_a'=0,1,2$ manifolds in the $\tilde{B}^2A'$ (0,0,0) level suggest a perturbation by an unknown quartet state.

The primary objective of our HCO experiments has been to record SEP spectra, via the $\tilde{B}^2A' \leftrightarrow \tilde{X}^2A'$ system, of quasibound vibrational levels ("resonances") of the $\tilde{X}^2A'$-state. We have examined the rotational structure and rotational level widths in the $\tilde{B}$-$\tilde{X}$ (0,0,0) → (0,5,0) band [in the $\tilde{X}$-state the conventional normal mode numbering is $v_1''$ = CH stretch, $v_2''$ = CO stretch, $v_3''$ = bend]. We found that, even though the (0,5,0) level is ~4000 cm$^{-1}$ above the $H{-}CO \rightarrow H(^2S) + CO(X^1\Sigma^+)$ dissociation limit [MUR86, CHO90b], the rotational structure is that of a textbook asymmetric top and the rotational level widths appear to be independent of N, $K_a$, $K_c$, and J. This $\tilde{B}$-$\tilde{X}$ $2_5^0$ band is also of hybrid **a**,**b** type, and $\vec{\mu}_{\tilde{B}-\tilde{X}}$ lies 35(5)° away from the **a** inertial axis.

We have measured the widths of six quasibound $\tilde{X}$-state vibrational levels in the $8{,}000 \le T_v \le 11{,}000$ cm$^{-1}$ energy region. Levels with 1 or more quanta of the bending vibration are invariably shorter-lived than pure $v_{CO}$ overtone levels (with $v_{bend}=0$). Levels with $v_{CH} \geq 1$ are apparently too broad to be detected in our present SEP spectra. This $\Gamma_{CH} > \Gamma_{bend} > \Gamma_{CO}$ mode specificity in the resonance widths is consistent with theoretical predictions, but all of the published theoretical width predictions are for resonances at lower energy than those observed in our SEP spectra [LEE86, GAZ87, GAZ91, GAZ92].

With the exception of one SEP band into a mystery level near $T_v = 9335\ cm^{-1}$, the SEP linewidths do not vary with rotational quantum numbers within a vibrational band.

Since our initial HCO $\tilde{B} \to \tilde{X}$ SEP spectra were recorded, the HCO SEP set-up has been completely rebuilt. George Adamson can now generate a complete SEP data set for a single $\tilde{X}$-state vibrational level in ~ 2 days. Deconvolution programs for extracting linewidths from raw SEP spectra have been written and tested.

Dispersed fluorescence and PUMP-DUMP-PROBE experiments are being designed to measure the widths of very broad $v_{CH} \geq 1$ levels and very narrow near-threshold levels.

## C. Publications and Theses Resulting from DOE Sponsorship (Since 1985)

### 1. Refereed Journals

E. Abramson, R.W. Field, D. Imre, K.K. Innes, and J.L. Kinsey, "Fluorescence and Stimulated Emission $S_1 \to S_0$ Spectra of Acetylene: Regular and Ergodic Regions," J. Chem. Phys. 83, 453-465 (1985).

R. L. Sundberg, E. Abramson, J.L. Kinsey, and R.W. Field, "Evidence of Quantum Ergodicity in Stimulated Emission Pumping Spectra of Acetylene", J. Chem. Phys. 83, 466-475 (1985).

G.J. Scherer, Y. Chen, R.L. Redington, J.L. Kinsey, and R.W. Field, "An Unsuspected Fermi Perturbation in the Acetylene $\tilde{A}\ ^1A_u\ 3v_3$ Level", J. Chem. Phys. 85, 6315-6323 (1986).

C.E. Hamilton, J.L. Kinsey, and R.W. Field, "Stimulated Emission Pumping: New Methods in Spectroscopy and Molecular Dynamics," Ann. Rev. Phys. Chem. 37, 493-524 (1986).

J.P. Pique, Y. Chen, R.W. Field and J.L. Kinsey, "Chaos and Dynamics on 30fs-1ns Time Scales in Vibrationally Excited Acetylene: Fourier Transform of Stimulated Emission Pumping Spectrum", Phys. Rev. Letts. 58, 475-478 (1987).

J.P. Pique, Y.M. Engel, R.D. Levine, Y.Chen, R.W. Field, and J.L. Kinsey, "Broad Spectral Features in the Stimulated Emission Pumping Spectrum of Acetylene", J. Chem. Phys. 88, 5972-5974 (1988).

P.G. Green, J.L. Kinsey, and R.W. Field, "A New Determination of the Dissociation Energy of Acetylene", J. Chem. Phys. 91, 5160-5163 (1989).

Y. Chen, D.M. Jonas, J.L. Kinsey, and R.W. Field, "High Resolution Spectroscopic Detection of Acetylene ↔ Vinylidene Isomerization by Spectral Cross-Correlation" J. Chem. Phys. 91, 3976-3987 (1989).

J. Vander Auwera, T.R. Huet, M. Herman, C. Hamilton, J.L. Kinsey, and R.W. Field, "The $\tilde{A}\ ^1A''$ Electronic State of Monodeuterated Acetylene", J. Mol. Spectrosc. 137, 381-395 (1989).

C.E. Hamilton, R.W. Field, T.R. Huet, and M. Herman, "Low Energy Vibrational Levels in the $\tilde{A}\ ^1A_u$ Electronic State of $C_2D_2$", J. Mol. Spectrosc. 137, 427-429 (1989).

Y. Chen, S.D. Halle, D.M. Jonas, J.L. Kinsey, and R.W. Field, "Stimulated Emission Pumping Studies of Acetylene $\tilde{X}^1\Sigma_g^+$ in the 11,400-15,700 $cm^{-1}$ Region: the Onset of Mixing", J. Opt. Soc. Am. B 7, 1805-1815 (1990).

P. Dupré, R. Jost, M. Lombardi, P.G. Green, E. Abramson, and R.W. Field, "Anomalous Behavior of the Anticrossing Density as a Function of Excitation Energy in the $C_2H_2$ Molecule", Chem. Phys. 152, 293-318 (1991).

K. Yamanouchi, N. Ikeda, S. Tsuchiya, D.M. Jonas, J.K. Lundberg, G.W. Adamson, and R.W. Field, "Vibrationally Highly Excited Acetylene as Studied by Dispersed Fluorescence and Stimulated Emission Pumping Spectroscopy: Vibrational Assignment of Feature States", J. Chem. Phys. 95, 6330-6342 (1991).

J.K. Lundberg, R.W. Field, C.D. Sherrill, E.T. Seidl, Y. Xie, and H.F. Schaefer III, "Acetylene: Synergy Between Theory and Experiment," J. Chem. Phys.

D.M. Jonas, S.A.B. Solina, B. Rajaram, R.J. Silbey, R.W. Field, K. Yamanouchi, and S. Tsuchiya, "Intramolecular Vibrational Relaxation and Forbidden Transitions in the SEP Spectrum of Acetylene," J. Chem. Phys., 97, 2813-2816 (1992).

D.M. Jonas, S.A.B. Solina, B. Rajaram, S.J. Cohen, R.J. Silbey, R.W. Field, K. Yamanouchi, and S. Tsuchiya, "Intramolecular Vibrational Relaxation in the SEP Spectrum of Acetylene," J. Chem. Phys.

## 2. Conference Proceedings

E. Abramson, H.-L. Dai, R.W. Field, D.G. Imre, J.L. Kinsey, C. Kittrell, D.E. Reisner, and P.H. Vaccaro, "Laser Population of Highly Excited Vibrational Levels of Molecules," Reactants and Probes in Chemistry, W.M. Jackson and A.B. Harvey, eds. pp. 393-404 Howard University Press, 1985.

R.W. Field, "High Resolution Spectroscopy of Small Molecules", Conference Laser M2P, 1987, J. de Physique C7, 17-28 (1987).

Y. Chen, D.M. Jonas, C.E. Hamilton, P.G. Green, J.L. Kinsey, and R.W. Field, "Acetylene: Isomerization and Dissociation," Berichte der Bunsengesellschaft für Physikalische Chemie, 92 329-336 (1988).

J.P. Pique, Y. Chen, R.W. Field, J.L. Kinsey, and M. Lombardi, "New Order Out of the Chaotic Bath of Highly Excited Vibrational States of $C_2H_2$", Berichte der Bunsengesellschaft für Physikalishe Chemie 92, 422-424 (1988).

R.W. Field, "Pathologically Complex Spectra of Small Molecules: High Resolution Techniques for Displaying Vibrational Chaos and Electronic Simplicity", Conference on Quantum Electronics and Laser Science, 1989 Technical Digest Series, Vol. 12 (Optical Society of America, Washington, DC), pp. 160-162 (Talk THHH2), 1989.

R.W. Field, "Statistical Spectroscopy: Insight or Nonsense?", ILS-IV, 1988, Am. Instit. of Phys. Conf. Proc. 191, 673-682 (1988).

## 3. Theses (Since 1988)

Yongqin Chen, "Spectroscopic Studies of Highly Excited Acetylene",* Ph.D. September, 1988, Chemistry

Peter G. Green, "Acetylene Near Dissociation: Novel Effects of External Fields", Ph.D. September, 1989, Chemistry

James K. Lundberg, "Double Resonance Studies of Electronically Excited Acetylene", Ph.D. February, 1992, Chemistry

David M. Jonas, "Spectroscopy of Vibrationally Hot Molecules: Hydrogen Cyanide and Acetylene", Ph.D. June, 1992, Chemistry.

---

* The research presented in this Thesis resulted in the "1990 Nobel Laureate Signature Award" of the American Chemical Society to Dr. Chen and to his co-preceptors, James L. Kinsey and Robert W. Field.

Sarah Jane Cohen, "The Use of Stimulated Emission Pumping Spectroscopy to Examine the Molecular Dynamics of Acetylene", M.S., June, 1992, Chemistry.

# END

---

DATE
FILMED

02/19/93