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Long-Lived, Energetic States of Small Molecules: Spectroscopy, Pattern Recognition, and Formation/Destruction Mechanisms

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Principal Investigator : Robert W. Field

Massachusetts Institute of Technology
Department of Chemistry
77 Massachusetts Avenue
Cambridge, Massachusetts 02139-4307

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14. ABSTRACT

The formation, deactivation, and detection mechanisms of atoms and molecules in metastable electronically excited states are, in general, ill characterized. Yet the chemical and photophysical properties of such states are relevant to Air Force Missions in communication, upper atmosphere modeling, and high-speed vehicle tracking, and identification. The capabilities of a multispectral molecular beam apparatus have been demonstrated on the electronic spectrum of acetylene in the energy region of the first excited singlet state (S_1), which is isoenergetic with high vibrational levels of the metastable triplet states (T_1, T_2, T_3). This apparatus records two kinds of spectra (UV-LIF and SEELEM, respectively UltraViolet Laser Induced Fluorescence and Surface Electron Ejection by Laser Excited Metastables) simultaneously, which sample complementary groups of short- and long-lived rovibronic states. The most remarkable findings are: (i) UV-LIF spectra contain fully assignable eigenstates with dominant S_1 or T_3 character, where the T_3 character acts as a "doorway" into states of dominant T_1, T_2 character that appear in SEELEM spectra; (ii) SEELEM spectra contain eigenstates that are rotationally fully assignable, regular in level pattern and relative intensity, yet *vibrationally ergodic*. Ergodicity in $T_{2,3}$ coexists with doorway behavior in T_1. Ergodicity, contrary to naïve expectations, results in regular appearing spectra.

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I. STAFF SUPPORTED BY AFOSR GRANT

A. Postdocts

1. Adya P. Mishra, currently Scientific Research Officer, Bhabha Atomic Research Centre, India
2. Daniel S. Byun, currently Staff Assistant, Lam Research

B. Graduate Students

1. Ryan Thom (Ph.D. expected 8/05)
2. Kyle Bittinger
3. Serhan N. Altunata (Ph.D. expected 8/05)
4. Selen Altunata (Ph.D. 8/01, currently Staff Scientist, IGEN International)

C. Undergraduate Students

1. Jessica Hagelstein
2. Atanas Pavlov
3. Shervin Fatehi (currently, Ph.D. student, Berkeley)

D. Visiting Scientists

1. Margaret Fackler (summer visiting graduate student, currently, Ph.D. student, University of Texas)
2. Stephen Coy (consultant)
3. Matijs De Groot (visiting graduate student from University of Amsterdam, The Netherlands)

E. Collaborators

1. David Chandler (Combustion Research Laboratory, Sandia, Livermore)
2. Jingsong Zhang (University of California, Riverside)
3. Hideto Kanamori (Tokyo Institute of Technology)
4. Charles Pibel (American University)
5. Timothy Zwier (Purdue University)
6. Marsha Lester (University of Pennsylvania
7. Wybren Buma (University of Amsterdam)
8. Steven J. Lipson (AFRL/VSBT)
9. James A. Dodd (AFRL/VSBT)
10. Steven M. Miller (AFRL/VSBT)
11. Skip Williams (AFRL/VSBT)

II. Research Accomplishments

(1 December 2000 - 30 June 2004)

The following is a slightly edited version of the Accomplishments section (and cited References) of the 3-year Renewal Proposal, submitted in February, 2004, and currently under consideration for support by the AFOSR.

A. Objectives

The objectives of the project "Long-Lived, Energetic States of Small Molecules: Spectroscopy, Pattern-Recognition, and Formation/Destruction Mechanisms" have been to develop experimental methods and analysis techniques in order to detect small molecules in long-lived ($\tau > 100\mu$s) electronically excited states and to determine their structure and excitation, detection, and decay mechanisms. Acetylene has served as the initial test molecule in all completed experiments.

B. Accomplishments

A multispectral, pulsed supersonic-jet, molecular-beam apparatus has been constructed, tested, and refined.[2–4] Three complementary signal channels are simultaneously recorded: Ultraviolet fluorescence detected Laser Induced Fluorescence (UV-LIF), Time-of-Flight Surface Electron Emission by Laser Excited Metastable molecules (TOF-SEELEM), and LIF detected by infrared fluorescence from photofragments (IR-LIF). The UV-LIF channel detects transitions that terminate in an eigenstate that fluoresces in the near UV with radiative lifetime $< 30\mu$s (see Figure 3). The SEELEM channel detects transitions that terminate in an eigenstate that has a vertical excitation energy larger than the work function of the SEELEM detector surface (Au 5.1 eV or Cs 2.1 eV) and remains electronically excited for a time comparable to the 100μs transit time from excitation region to detector surface. No eigenstate can appear in both UV-LIF and SEELEM spectra. The TOF capability distinguishes between SEELEM signals from metastable photofragments and metastable parent molecules.[2] The signal in the IR-LIF channel arises from electronically excited photofragments produced by a two-photon transition, resonant at the one-photon level with a singlet$\sim$triplet mixed eigenstate in the parent molecule and resonant at the two-photon level with a predissociated singlet or triplet Rydberg state. The IR-LIF channel is capable of measuring the fractional singlet or triplet character in each eigenstate.

A general expression for the sampled molecular eigenstates is

$$\psi_j = \alpha_{j,\mathrm{S}_1\underset{\sim}{\mathrm{V}}}\psi_{\mathrm{S}_1\underset{\sim}{\mathrm{V}}} + \beta_{j,\mathrm{T}_3,F_i,\underset{\sim}{\mathrm{V}}}\psi_{\mathrm{T}_3,F_i,\underset{\sim}{\mathrm{V}}} + \sum_{\underset{\sim}{\mathrm{V}}} \gamma_{j,\mathrm{T}_1,F_i,\underset{\sim}{\mathrm{V}}}\psi_{\mathrm{T}_1,F_i,\underset{\sim}{\mathrm{V}}}$$

where α, β, γ are mixing coefficients, S_1 means first excited singlet state, $\underset{\sim}{\mathrm{V}}$ is the set of vibrational quantum numbers, T_3 is an excited triplet state, T_1 is the lowest triplet state, and F_i is the spin-component of a triplet state. When the α, β, γ mixing coefficients for all spectroscopically accessed eigenstates in the explored energy region are measured in our multispectral apparatus, a complete effective Hamiltonian model of the $\mathrm{S}_1 \leftrightarrow \mathrm{T}_3 \leftrightarrow \mathrm{T}_1$ dynamics is obtained.

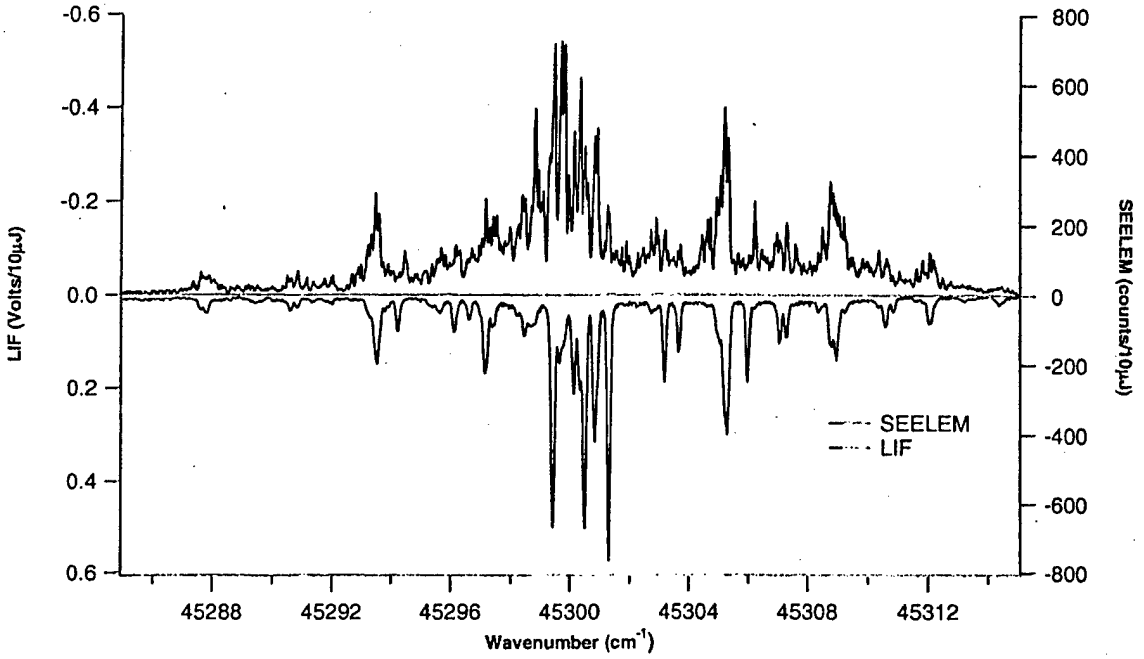

Figure 1: Simultaneously recorded SEELEM (upper trace) and UV-LIF (lower trace) spectra of the HCCH $\tilde{A} - \tilde{X}$ $V_0^3K_0^1$ sub-band. The resolution in the SEELEM spectrum is 0.03 cm^{-1}, a factor of 3 superior to that in the UV-LIF spectrum. The spectra are plotted on a compressed wavenumber scale, which emphasizes their similarity. Although no upper eigenstate appears in both spectra, the 10× more densely-spaced spectral lines in the SEELEM spectrum appear within narrow windows surrounding each line in the UV-LIF spectrum.

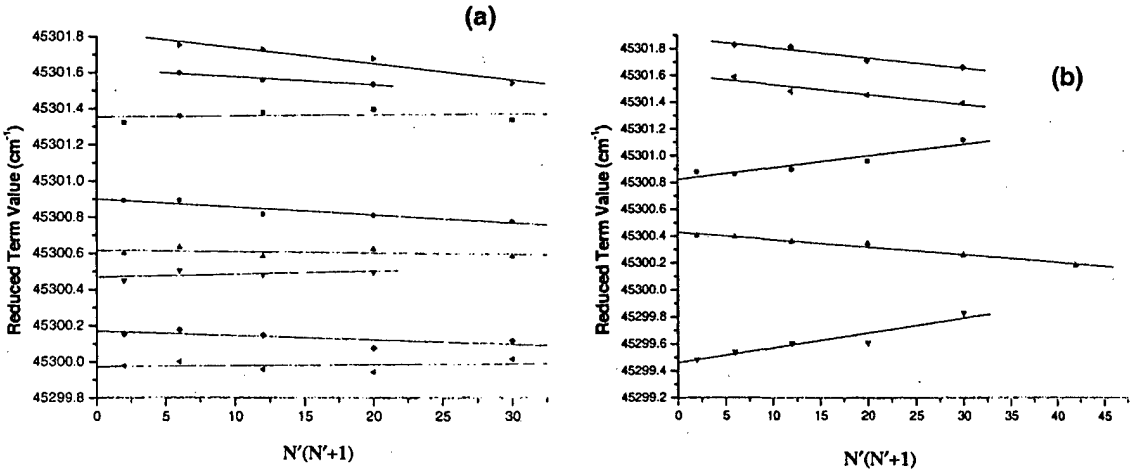

Figure 2: Reduced rotational term value ($E - \overline{B}N'(N'+1)$, $\overline{B} = 1.127$ cm^{-1}) plots of triplet state vibrational levels plotted vs. $N'(N'+1)$. The term values in (a) are e–symmetry levels sampled via R,P branch transitions; those in (b) are f–symmetry levels sampled via Q–branch transitions. The observed vibrational density of states in the SEELEM spectrum is 1.2 states/cm^{-1} and the calculated total symmetry-sorted density of T_1, T_2, T_3 vibrational states is 1.6 states/cm^{-1}.

The ability to distinguish excited triplet from lowest lying triplet state (T_3 vs. T_1) characters is critical to being able to construct a complete (S_1, T_3, T_1) dynamical model. This capability was demonstrated by comparing the absolute signal (counts per laser pulse) when the same region of the SEELEM spectrum was recorded on Yttrium (3.1 eV) and Cesium (2.1 eV) surfaces.[3] In HCCH, only S_1 and T_3 characters in an eigenstate are detectable on a Yttrium surface whereas S_1, T_3, T_2, T_1 characters are detectable on a

Cesium surface. In the energy region examined, the vibrational density of T_1, T_2 states is 10^3 times larger than that on S_1, T_3. The SEELEM spectrum recorded on Cs is 800 times stronger than that on Y.[3] In addition, the relative intensities of features in the two spectra are different, owing to the fact that $T_{1,2}$ are "bright" on Cs but not on Y.

The dynamic range in our Au-SEELEM spectra is $> 10^4$.[4] It turns out that this is sufficient to detect transitions into at least 1/3 of all vibronic-symmetry accessible T_1, T_2 vibrational levels that occur within a ~ 2 cm^{-1} window surrounding each S_1 $3\nu_3$ $K = 1$ level (see Figure 4).[4] Although most of the detected eigenstates are of predominant $T_{1,2}$ character ($> 99.9\%$), the minuscule admixtures of S_1 and T_3 character renders these eigenstates Au-SEELEM detectable. The spin-orbit matrix elements responsible for mixing S_1, T_3 character into predominantly T_1, T_2 states include a vibrational overlap integral as a multiplicative factor.[13] The vast majority of vibrational overlap integrals between highly excited vibrational levels of one potential surface and low vibrational levels of another, similarly shaped surface, are $<< 10^{-3}$. Our observation of $\sim 1/3$ of the T_1, T_2 vibrational levels in the Au-SEELEM spectrum implies that anharmonic mixing on the T_1 surface is close to the ergodic limit at $E_{VIB} = 12,000$ cm^{-1}.[4] This is the strongest spectroscopic evidence ever obtained for ergodic vibrational behavior in a small (4-atom-dihydride) molecule.

But it turns out that these near-ergodic SEELEM spectra are spin-rotationally (J, K_a, N, e/f-symmetry) assignable.[4] Despite the $\sim$10 lines per cm^{-1} in the SEELEM spectra, the vast majority of transitions are assignable using the "lower-state rotational combination difference" method. The assigned rotational levels fall onto smooth, linear, non-intersecting E_J vs. BJ(J+1) term energy plots (see Figure 4) and on linear $\ln(I_J)$ vs. BJ(J+1) Boltzmann intensity plots. Despite the near-ergodic limit mixing of vibrational characters, the rotational levels seem to arrange themselves into smooth, local-perturbation-free "vibrational levels." This combination of vibrational ergodicity and rotational regularity is without precedent.

High resolution is critically important in being able to detect weak lines near strong lines (dynamic range) and in being able to make reliable rotational assignments by the combination difference method. The use of an injection-seeded Nd:YAG laser to excite our dye laser led to a factor of $\sim$3 improvement in dye laser resolution (~ 0.03 cm^{-1} in the UV).[4] This factor of 3 is the difference between spectra that could at best be subjected to statistical measures[135,136] to spectra that can be unambiguously assigned. Another factor of 10 in resolution will soon be available (Coherent 899-29 cw Ti:Sapphire laser at 840 nm cw-doubled in a Spectra Physics WaveTrain to 420 nm and then pulse-amplified and doubled again to 210 nm). We expect this will improve both dynamic range and reliability of rotational assignment and also permit extension of 0.003 cm^{-1} resolution SEELEM spectroscopy to larger molecules.

The dynamic range of the UV-LIF spectrum is also $\sim 10^4$. This has enabled detection of $S_1 \leftarrow S_0$ transitions into previously unobserved vibrational levels of the HCCH S_1 state.[4] Recently, the laser excitation and fluorescence viewing region was moved from the upstream to the downstream side of the skimmer that separates the source from the detector chamber. The resolution went from Doppler-limited 0.08 cm^{-1} upstream to laser-limited 0.03 cm^{-1} downstream. Although the currently achieved 0.03 cm^{-1} resolution in our UV-LIF spectrum is inferior to that achieved by Drabbels *et al*,[137] Figure 5 shows how each improvement of resolution uncovers additional assignable features. A wealth of new information is now laid bare in the UV-LIF spectrum.

C. Collaborations with Research Groups at Air Force Laboratories

We have collaborated with the research group of James A. Dodd (AFRL/VSBT) on the mechanism of predissociation of the OH $B^2\Sigma^+$ state. Owing to the peculiar shape of the B-state potential curve, LIF monitoring of populations in vibrational levels, v″, of the OH $X^2\Pi_i$ state via the B−X transition is far more flexible than via the more familiar and extensively used A−X transition. The reason for this is that Franck-Condon factors for B−X (v′ = 0,v″) transitions permit monitoring of all v′ up to at least v″ = 10, whereas those for the A−X transition restrict observations to v″ < 4. The unique (v′, J′,F_i')-dependent pattern of predissociation rates in the B-state implicates spin-orbit and rotation-electronic interactions with the continuum of the $2^2\Pi$ state as the primary predissociation mechanism. A detailed semi-empirical analysis of the signature of predissociation of a $^2\Sigma^+$ state by the continuum of a $^2\Pi$ state is presented. Relationships are derived between spin-orbit and L-uncoupling interaction parameters, with particular relevance to the electronic configurations of diatomic monohydride molecules.

A collaboration with the research group of Steven M. Miller (AFRL/VSBM) concerning analysis of some perturbations involving the NO $B^2\Pi$, $C^2\Pi$, and $a^4\Pi$ states is under discussion. A nonlinear least squares deperturbation-fitting program, developed by the PIs research group, has been provided (with tutorial in its use) to the Miller group. Possibilities for experiments based on Hg-photosensitized population of the NO $a^4\Pi$ state have been discussed.

There have been discussions, with Dr. Skip Williams (AFRL/VSBXT), of the feasibility and relative merits of various ultra-sensitive optical detection schemes for the O_2 $a^1\Delta_g$ state. It quickly became clear that direct absorption studies via the electric dipole forbidden, electric quadrupole allowed $b^1\Sigma_g^+ \leftarrow a^1\Delta_g$ transition are the best candidate for the required absolute number density measurements. The extant spectroscopic data concerning the $b^1\Sigma_g^+ \leftarrow a^1\Delta_g$ electronic states was examined and found to be of extremely high quality (completeness of states studied, wavenumber precision, reliability of analyses) and free of arcane details that would require knowledge of spectroscopic perturbations and nonstandard effective Hamiltonian models. Two *ab initio* quantum chemical theorists, who use contrasting methods to obtain state-of-the-art quality results, were proposed as likely to be able to compute quadrupole transition probabilities at an accuracy competitive with the most accurate experimental methods: David Yarkony (Johns Hopkins University) and John Stanton (University of Texas). Advice is being provided to Dr. Williams concerning the spectroscopy, rotational linestrengths, and Franck-Condon factors for the O_2 $b^1\Sigma_g^+ \leftarrow a^1\Delta_g$ translation.

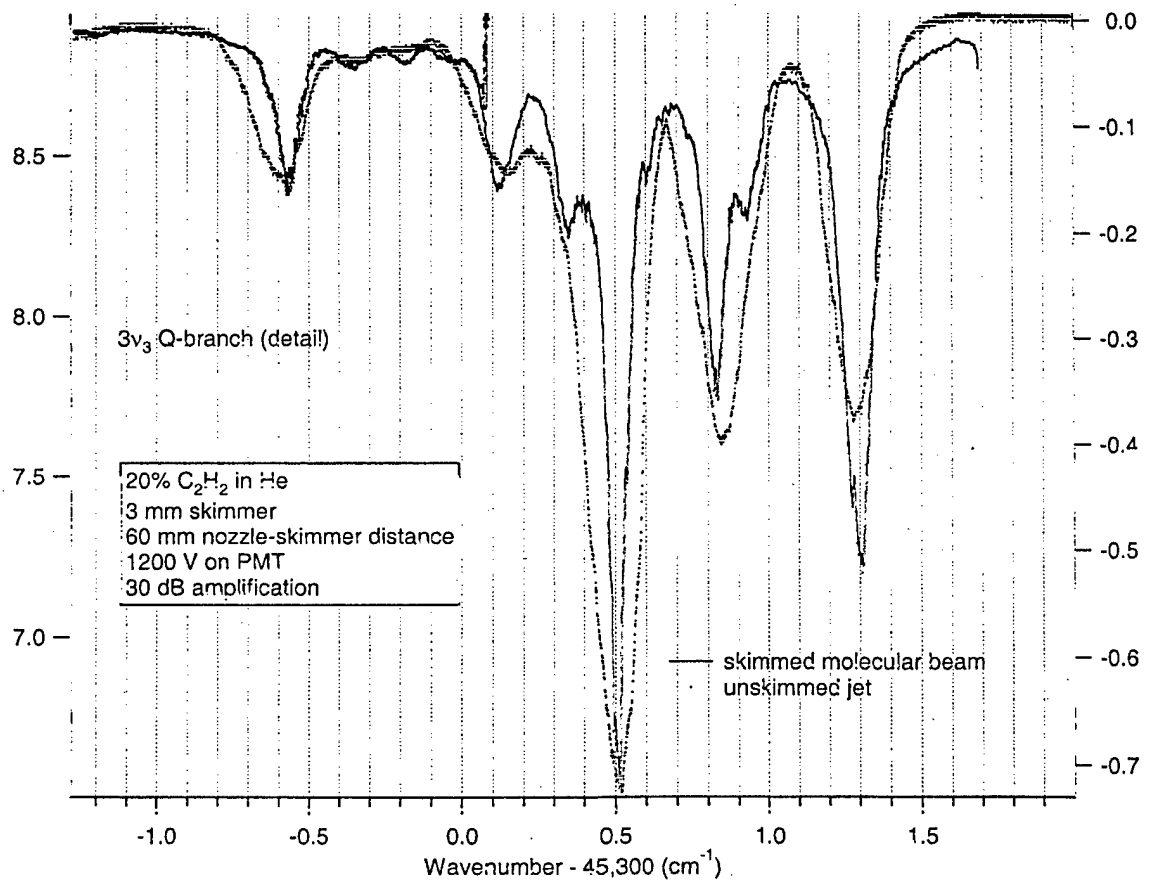

Figure 3: Segment of the UV-LIF spectrum in the HCCH $\tilde{A}-\tilde{X}$ $V_0^3K_0^1$ band. Dotted curve shows Doppler broadened spectrum of unskimmed jet. Solid curve shows laser linewidth limited (0.03 cm^{-1}) spectrum of skimmed (3mm diameter skimmer, 60mm nozzle-skimmer distance) molecular beam.

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III. AFOSR Supported Publications (since 1999)

1. M.P. Jacobson, S.L. Coy, R.W. Field, S.J. Lipson, R.B. Lockwood, D.L. Vititoe, W.A.M. Blumberg, and P.S. Armstrong, "Numerical Pattern Recognition Analysis of CO Atmospheric Simulation Experiments," *J. Chem. Phys.* **104**, 249–257 (2000).

2. H. Ishikawa, R.W. Field, S.C. Farantos, M. Joyeux, J. Koput, C. Beck, and R. Schinke, "HCP→CPH Isomerization: Caught in the Act!," *Annu. Revs. Phys. Chem.* **50**, 443–484 (1999).

3. M. Joyeux, D. Sugny, V. Tyng, M.E. Kellman, H. Ishikawa, R.W. Field, C. Beck, and R. Schinke, "Semiclassical Study of the Isomerization States of HCP," *J. Chem. Phys.* **112**, 4162–4172 (2000).

4. A.F. Ruckstuhl, M.P. Jacobson, R.W. Field, and J.A. Dodd, "Baseline Subtraction Using Robust Local Regression Estimation," *J. Quant. Spectr. Radiat. Transf.* **68**, 179–193 (2001).

5. S. Altunata and R. W. Field, "A Statistical Approach to the Study of the Singlet–Triplet Interactions in the 5.5 – 5.7 eV Region of Acetylene," *J. Chem. Phys.* **113**, 6640–6651 (2000).

6. E. S. Hwang, J. B. Lipson, R.W. Field, and J. A. Dodd, "Detection of OH (X, v) via the $B^2\Sigma^+ - X^2\Pi$ Transition and Properties of the $B^2\Sigma^+$ State," *J. Phys. Chem.* **105**, 6030 - 6037 (2001).

7. M. Silva, R. Jongma, R.W. Field, and A.M. Wodtke, The Dynamics of 'Stretched Molecules': Experimental Studies of Highly Vibrationally Excited Molecules with Stimulated Emission Pumping," *Ann. Rev. Phys. Chem.* **52**, 811–852 (2001).

8. S. Altunata and R. W. Field, "An Assumption–Violating Application of the Lawrance–Kinght Deconvolution Procedure: A Retrieval of Electronic Coupling Mechanisms Underlying Complex Spectra," *J. Chem. Phys.* **114**, 6557–6561 (2001).

9. S. Altunata, K. L. Cunningham, M. Canagaratna, R. Thom and R. W. Field, "The Mechanism of Surface Electron Ejection by Laser Excited Metastable Molecules," *J. Phys. Chem.* **106**, 1122-1130 (2002).

10. A. P. Mishra, R. L. Thom, and R. W. Field, "New S_1 State Vibrational and $T_{3,2,1}$ Spin-Rotational Assignments in the Vicinity of the $\widetilde{A}^1X_u - \widetilde{X}^1\Sigma_g^+$ V_0^3 K_0^1 Band," *J. Mol. Spectrosc.* **228**, 565-579 (2004).

11. A. P. Mishra, R. L. Thom, S. Altunata, and R. W. Field, "Study of Intramolecular Dynamics of Highly Energized Small Molecules Using Laser Spectroscopic Techniques," in *Current Developments in Atomic, Molecular, and Chemical Physics with Applications* (ed. Man Mohan), 2003, Kluwer, New York.

12. A. P. Mishra, R. W. Field, S. V. N. Bhaskara Rao, R. D'Souza, and T. K. Balasubramanian, "Absorption Intensities of the Multipole-Field-Induced Zero-Phonon Transitions in Solid HD, HT, and DT," *Phys. Rev. B.* **67**, 134305:1-9 (2003).

13. A. P. Mishra and R. W. Field, "Absorption Intensities of the Multipole-Field-Induced Double Transitions Involving a Homonuclear-Heteronuclear Pair of Hydrogen Molecules in Condensed Phase," *Phys. Rev. B.* **68**, 184303:1-8 (2003).

14. H. Lefebvre-Brion and R. W. Field, "The Spectra and Dynamics of Diatomic Molecules," Elsevier, 2004.

IV. Interactions/Transitions: Talks

Talks

Talks by RWF on the triplet project at Argonne National Laboratory (10/9/00), University of California Riverside (12/7/00), Pacifichem Honolulu (12/15/00), University of Minnesota (4/11/01), Tsinghua University, Beijing (5/9/01), AFOSR Molecular Dynamics (5/21/01), Molecular Spectroscopy Symposium at Ohio State (6/13/01), University of Pennsylvania (2/28/02), Caltech (6/4/02), EPENS at Montauk (9/24/02).

Talks by Selen Altunata on the triplet project at Wesleyan University (10/31/00), LAM Electronics, IGEN.

Talks By Ryan Thom, Molecular Spectroscopy Symposium at Ohio State (6/12/01 and 6/19/02).

Ph.D. Theses

Selen Altunata, "Intersystem Crossing in Acetylene: A Mechanistic Study"
http://rwf.lms.mit.edu/group/theses/selen_theses.pdf

Kevin Cunningham, "The Surface Ejection of Electrons by Laser Excited Metastables Spectroscopy of Acetylene"
http://rwf.lms.mit.edu/group/theses/kevin_theses.pdf

V. New Discoveries, Inventions, Patents

None.

VI. Honors

Robert W. Field: Elected Fellow of the American Association for the Advancement of Science (AAAS) 2002. AFRL, Space Vehicles Directorate: "Team Publication of the Year" for 2000: (M.P. Jacobson, S.L. Coy, R.W. Field, S.J. Lipson, R.B. Lockwood, D.L. Vititoe, W.A.M. Blumberg, and P.S. Armstrong, "Numerical Pattern Recognition Analysis of CO Atmospheric Simulation Experiments," *J. Phys. Chem.* **104**, 249-257 (2000).)