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14. ABSTRACT

Principles of quantum computing using molecular vibronic states and time-frequency resolved coherent anti-stokes Raman scattering (TFRCARS) were demonstrated through, and the execution of standard algorithms were elaborated alongwith measures of fidelity. These proof-of-principle implementations are on ensembles ofmolecules in the gas phase, unlikely to be a realistic architecture in practicalimplementations. We have therefore focused on solid-state implementations of the same,where now the understanding and control of decoherence of systems in intimate contactwith their surrounding environment is the key scientific challenge. Very significantprogress in this regard has been made in a) developing the tools to probe quantumcoherence and decoherence of vibronic states in phase space, b) developing semiclassical methods for the analysis of the mechanics of decoherence, c) demonstratingmesoscopic coherence ("cat"-states) and complete arrest of decoherence in stationarynon-eigenstates prepared by environmentally induced coherence. Also, significantprogress has been made in approaching the single molecule limit in TFRCARSimplementations - a crucial step in considering scalable quantum computing using themolecular Hilbert space and nonlinear optics.

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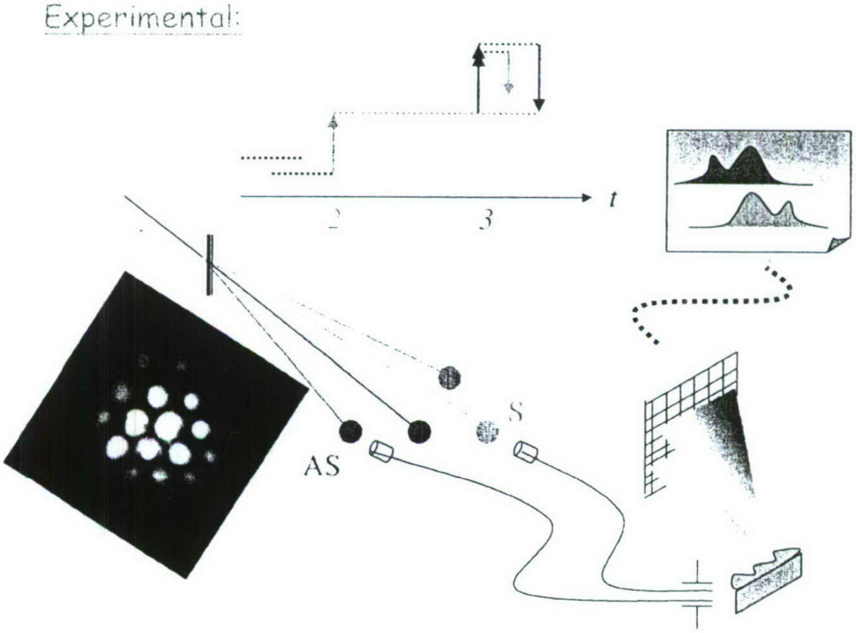
ABSTRACT

Principles of quantum computing using molecular vibronic states and time-frequency resolved coherent anti-stokes Raman scattering (TFRCARS) were demonstrated through, and the execution of standard algorithms were elaborated along with measures of fidelity. These proof-of-principle implementations are on ensembles of molecules in the gas phase, unlikely to be a realistic architecture in practical implementations. We have therefore focused on solid-state implementations of the same, where now the understanding and control of decoherence of systems in intimate contact with their surrounding environment is the key scientific challenge. Very significant progress in this regard has been made in a) developing the tools to probe quantum coherence and decoherence of vibronic states in phase space, b) developing semi-classical methods for the analysis of the mechanics of decoherence, c) demonstrating mesoscopic coherence ("cat"-states) and complete arrest of decoherence in stationary non-eigenstates prepared by environmentally induced coherence. Also, significant progress has been made in approaching the single molecule limit in TFRCARS implementations – a crucial step in considering scalable quantum computing using the molecular Hilbert space and nonlinear optics.

The original concept of quantum computing in the molecular Hilbert space through Time-Frequency Resolved Coherent Ant-Stokes Raman Scattering (TFRCARS) was proposed by us, and universal computing through this scheme was experimentally demonstrated in an early paper.[1] The elements of universal computing are the single qubit logic gates, consisting of the full set of Pauli matrices operated on ro-vibrational coherences, and the two-qubit C-NOT gate, for which the product of vibrational and electronic states, |v,e> was used as basis. We followed the demonstration of logic gates, by demonstrating algorithms. First, we showed how the Deutsch-Jozsa algorithm could be implemented in the vibronic basis set, along with analysis of fidelity improved through the use of shaped pulses.[2] More recently we outlined the implementation of the Grover search algorithm, now using the ro-vibronic basis, with a detailed analysis of gate fidelities.[3] There have since been other proposals of Q-computing in the molecular Hilbert space, now of polyatomics in which various normal modes are used as qubits. While these approaches have been of significant value conceptually and for proofs-of-principle, none is likely to become practical for two mundane reasons: a) Although decoherence can be kept under control in the gas phase, it is unlikely that Q-computers will have tube architecture (gas phase); b) The implementations are in ensembles, subject to dephasing, and limited quantum determinism, unless taken to the single molecule limit. These two considerations have driven the rest of our research thrusts: a) understanding vibronic decoherence of molecules trapped in solid matrices; b) pursuing experimental developments to perform TFRCARS measurements on single molecules.

Our program in characterizing decoherence relies on variants of TFRCARS, with significant development in both methods and discovery of mechanisms. In a set of studies on the ground electronic state of molecular iodine isolated in rare gas matrices, we have generated the most comprehensive data base of vibrational dephasing in the solid state, in Ar,[4,5] and in Kr,[6,7,8,9,10] for v = 1 through v = 19,[8] and for T = 2.6 K to 32 K.[10] These studies are testing grounds for theories on the subject, and we have provided one of the more crucial analysis of the role of vacancy imperfections and thermal phonons in inducing dephasing.[11,12] Vibrational decoherence in the ground electronic state of iodine can be classified as the weak coupling regime, where dephasing is dominated by Raman scattering of phonons, and for v ~ 1 the molecule may oscillate for 10^3 periods prior to damping. The more surprising findings are in the strong coupling regime, where no general theoretical framework exists for treating the quantum dynamics of a dissipative system. Our first important report on the subject was through six-wave mixing on $I_2(B)$ in Ar, along with the only viable method for atomistic analysis of the mechanics of decoherence through semiclassical forward-backward propagation of many-body dynamics.[13] To fully characterize the nature of evolving coherences in the strong coupling limit, we implemented spectrally resolved 3-and 4-color 4-wave mixing studies. The complete set of these studies is the subject of the PhD thesis of D. Segale.[14] Only part of the more significant discoveries in this work has been published: the preparation and the characterization of Schrodinger "cat" states.[15] Since already published, we succinctly note the essence of the discovery. By preparing two distinct wavepackets on a single electronic state of a molecule, the observation of cross-coherence after dissipation implies, through entanglement, coherence in the bath. Through classical MD simulations it is possible to show that the bath coherence is non-trivial, consists of ~12 orthogonal modes in superposition – hence a significant kitten if not a cat. The two remaining papers that are under preparation are on "phase-space probe of vibronic dynamics through multicolor four-wave mixing" and "Arrested decoherence and dissipation in a spiral coherent state of an oscillator strongly coupled to its environment", we expand on these developments below.

The experimental approach for phase-space measurements is illustrated in figure 1.



Three noncolinear fs pulses of three different colors are used to prepare two distinct packets on the electronically excited state of molecular iodine in solid Kr, and to probe their cross-coherence. The two signals, along two distinct directions:

$$k_{AS} = k_3 + (k_1 - k_2) \quad \text{and} \quad k_S = k_3 - (k_1 - k_2) \qquad (1)$$

are simultaneously collected with two fibers, dispersed in a monochromator and the spectra are collected as a function of the two delays between the three input pulses. A very large, multidimensional data set is generated. An example of the simultaneously recorded AS and S signals for fixed $t_{12} = 100$ fs, and as function of probe delay, t_{13}, is shown in Figure 2.

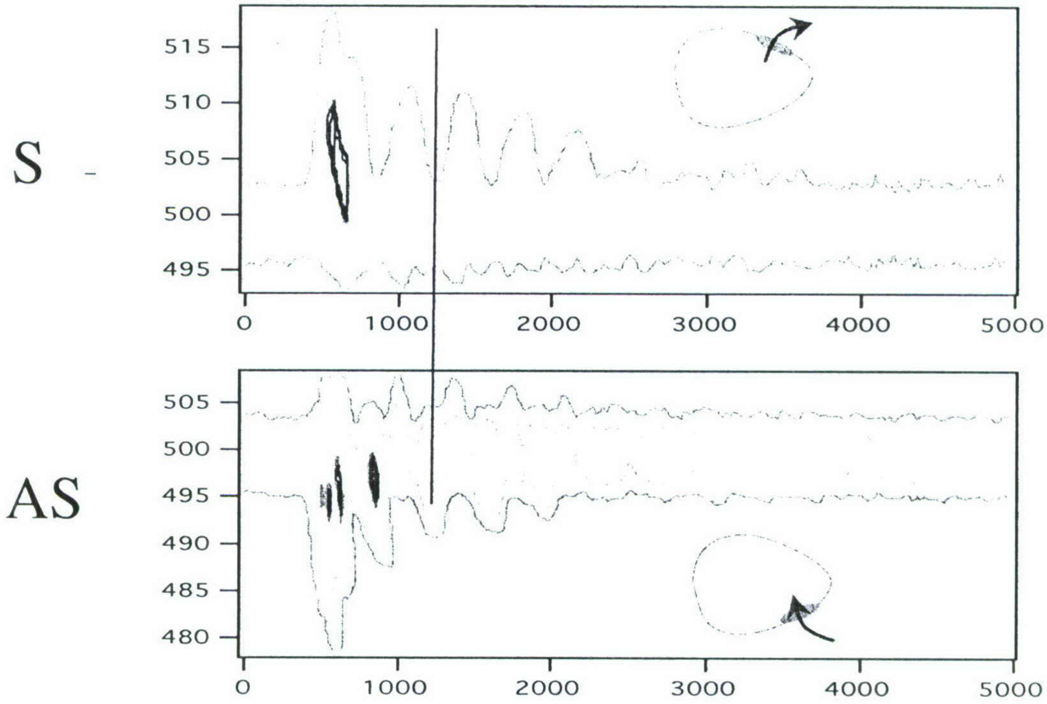


Fig. 2: *The S- and AS- spectra as function of t_{13}(fs) is shown. The probe is at 500 nm. The red-shifted S-signal and the blue-shifted AS-signal are shifted in time by a half period. This can be understood by the phase space plots shown in the inset, the AS-signal arises by projecting the green packet onto the red, while the S-signal arises by the red-green projection, following the blue trajectory (arrow) on the ion-pair state.*

To the extent that coherence is maintained in the system, energy conservation dictates the spectral window in which signal can be detected:

$$\omega_{AS} = \omega_3 + (\omega_1 - \omega_2) \quad \text{and} \quad \omega_S = \omega_3 - (\omega_1 - \omega_2) \qquad (2)$$

In the absence of resonances, say in glass, such a signal can only be observed when all three pulses overlap in time. Indeed, this is used as a means for characterizing ultrashort pulses. The observation of signal past the pulse overlap implies coherence, and the latter is more surprising when the system can be verified to have undergone dissipation. Dissipation in this case is verifiable through the contraction of recursion periods (Morse oscillator), and of course has previously been carefully characterized through pump-probe measurements. Identifying the two packets by their energies:

$$\varepsilon_i = \langle \varepsilon_i \rangle = \langle \varphi_i | H | \varphi_i \rangle \qquad (3)$$

the condition (2) reduces to:

$$\varepsilon_{AS} = \hbar\omega_3 + (\varepsilon_1 - \varepsilon_2) \quad \text{and} \quad \varepsilon_S = \hbar\omega_3 - (\varepsilon_1 - \varepsilon_2) \qquad (4)$$

By convention, $\varepsilon_1 > \varepsilon_2$, as such the AS-signal is blue shifted relative to the probe, while the S-signal is red shifted as in Fig. 2. Since the probe is resonant with a real electronic state (the E ion-pair state), the color-shifted signals appear from the two different momentum branches of the packet, as illustrated by the phase space plots. Note, (4) is the condition based on the mean energy of packets, the spectra reflect the full distribution, namely the density $\rho_{\varepsilon\varepsilon'}$:

$$\rho_{\varepsilon\varepsilon'} = |\varepsilon\rangle\langle\varepsilon|\varphi\rangle\langle\varphi|\varepsilon'\rangle\langle\varepsilon'| \qquad (5)$$

The diagonal density, $\rho_{\varepsilon\varepsilon}$, occurs under the probe spectrum, while the shifted spectra are strictly the off-diagonal densities, $\rho_{\varepsilon\varepsilon'}$, as a function of the energy separation $\varepsilon - \varepsilon'$. Note, the off-diagonal densities represent strictly quantum coherence, and should be clear from the figure that spectra collapse as a function of time, to the limit of the probe pulse – the coherence decays to the diagonal density, i.e., to population. The decoherence half-life in the shown example can be directly read as ~ 1.2 ps, namely four periods of oscillation. These considerations should clarify the power of the method:

a) the signal identifies position and momentum of packets
b) dissipation is distinctly determined from period contraction
c) decoherence is directly measured as a function of energy separation, and as a function of phase-space separation between packets

The observation coherent dissipation is remarkable as argued above in terms of "cat" states. The more significant novel finding in these detailed measurements is that for a given color separation, therefore energy separation as in (4), different decoherence rates are obtained for different preparations of the packets (pulse width and chirp). Spectrally broad, short pulses generate longer-lived coherences. This is the most direct demonstration of quantum nonlocality in interactions – the distribution of the packet in energy (in phase space) determines its coherence, the wave nature of the atomistic dynamics is revealed in a fundamental way. The ultimate "arrest" of decoherence we see in states that are prepared by system-bath interaction into packets that wrap around themselves, into "spiral coherent states". The measured signal from such a preparation is shown in Fig. 3. Note, the period of vibration is 400 fs, while the length of the packet is 600 fs (length of the leafs) the packet wraps around itself by 1.5 turns in phase space. The probe is at 530 nm (blue band), therefore the entire signal is the off-diagonal quantum coherence. In energy (y-axis), the packet stretches from 530 nm to 495 nm, i.e. an energy separation of 1300 cm^{-1}, more than 10 vibrational quanta. The extracted phase space portrait of the spiraling packet is shown in Fig. 4. It is directly recognized that the coherence in this state is maintained for the duration of the population, which leaks through pre-dissociation on a time scale of 2 ps!

The implications and generalizations of the discovery of effectively stationary non-eigenstates (stationary distribution of position and momentum, or marginals of the packet) in strongly coupled systems are tantalizing. The most fundamental way of understanding the arrest of decoherence and dissipation is in the general statement that fluctuation leads to dissipation, in stationary states the absence of fluctuation in position or momentum leads to arrest of dissipation. Such states can be expected to play a major role in all quantum manipulation, control and information transfer, and learning how to prepare them in arbitrary systems should be of great interest.

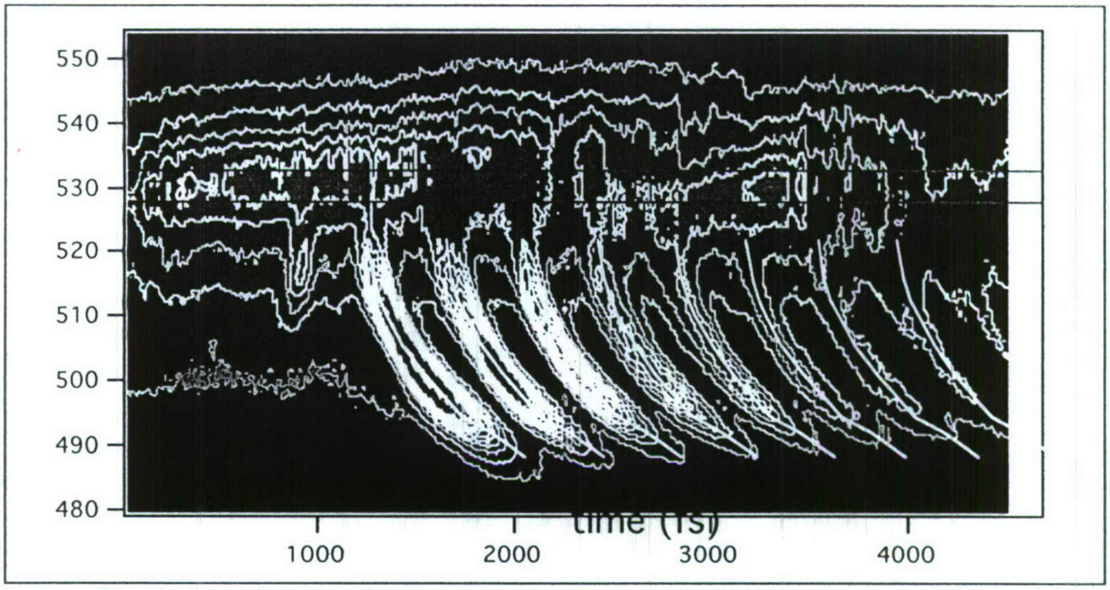


Fig. 3: Decoherence free wave packet prepared with non t-transform limited 25 fs pulses of ~800 cm^{-1} bandwidth, Note, the leafs highlighted with the white lines are entirely off diagonal densities that evolve with a period of 400 fs. The length of the packet is 600 fs, and therefore it has wrapped around itself by 1.5 turns. The packet spirals down with fixed pitch.

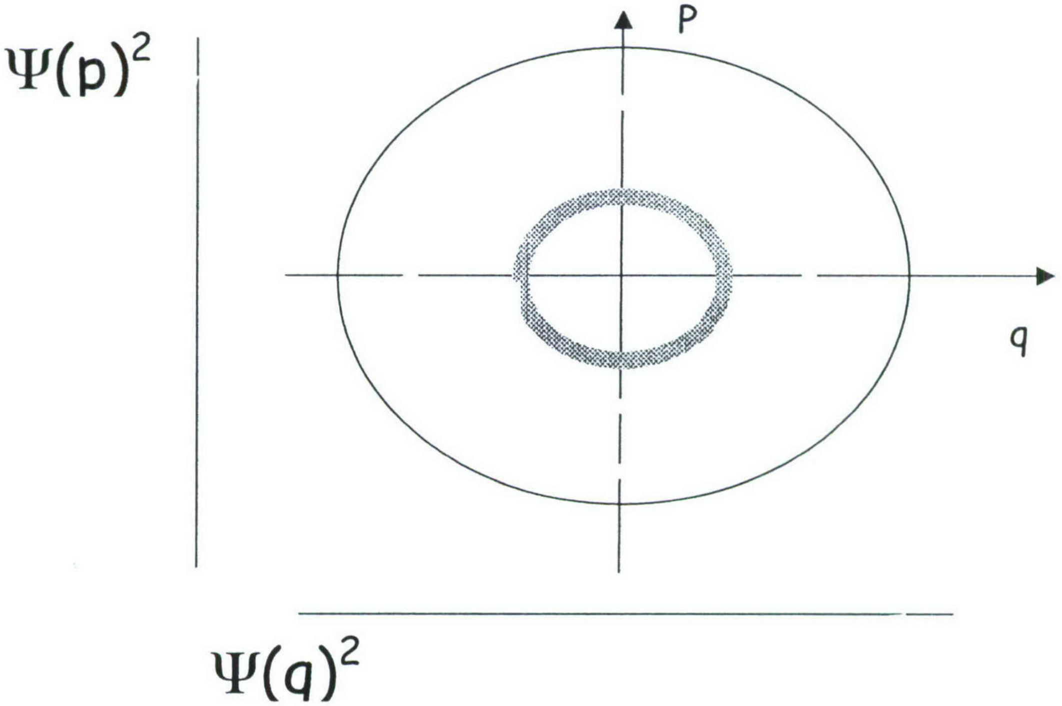


Fig. 4: The phase portrait of the decoherence free packet is a closed spiral. Its marginals, as illustrated, are stationary both along the position and momentum coordinates.

We have also made significant progress toward four-wave mixing studies in single molecules. Indeed, a second PhD thesis was completed on this theme, by H. Seferyan.[16] One of the approaches is collaborative, designed to couple an optical STM with ultrafast NLO. This effort remains in the stage of instrumental development. In parallel, we have expended a significant effort to design systems that may enable single molecule nonlinear optical measurements under ambient conditions. To accomplish such measurements on molecules, it is essential to rely on antennae as both condensers and broadcasters of radiation. Collective electron oscillations – plasmons – provide such antennae, as best known in molecular spectroscopy in the form of surface enhanced Raman scattering (SERS). A molecule that carries its own antenna is a single walled carbon nanotube (SWCNT), as recently literally demonstrated by constructing a single nanotube radio. Given the fact that Raman scattering can be carried out on SCNT, we can be sure that 4-wave measurements are possible. We have carried out such measurements, now transient grating measurements on nano-Molar SWCNT, to establish the excitonic nature of their electronic states, and to fully characterize the energy cascade in both metallic and semiconductive tubes.[17] In parallel, we initiated investigations on metallic nano-particle plasmons as antennae. In the chemically tailored structure of a distyryl benzene tethering two silver (or gold) nano particles of 15 nm radius, we have succeeded in recording Raman spectra from single molecules (see fig. 5). We are now confident that we will be able to carry out TFRCARS measurements on such units, and with it, we should complete the circle to demonstrate truly quantum logic.

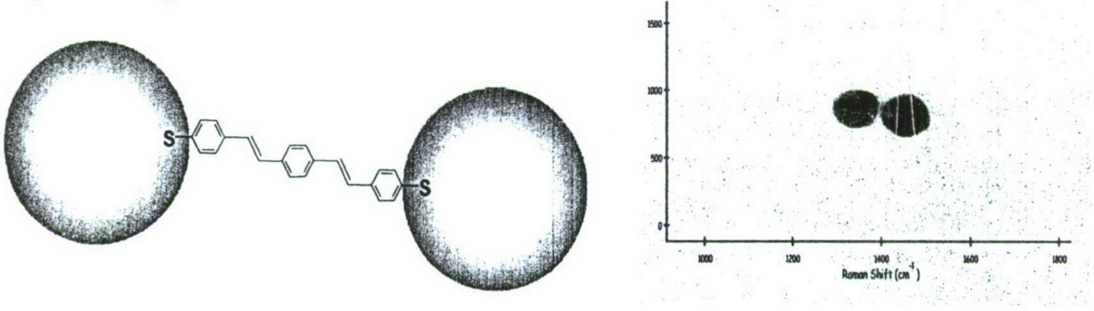


Fig. 5: Two Ag nano-particles (15 nm radius) act as plasmonic antennae to couple radiation into the tethering molecule, distyril benzene. The local field enhancement allows the recording of Raman spectra of the single molecule, as shown in the right panel along with the TEM of the tailored plasmonic molecule.

Personnel:

The personnel directly supported from the grant are:

- V. A. Apkarian, PI, (2 summer months)
- I. Y. Goldschleger, postdoctoral fellow
- R. Zadoyan, research associate
- Darren Segale, principal graduate student, PhD, 2007
- V. Senekerimyan, graduate student, PhD, 2007

Many more have contributed to the project, supported through fellowships.

- Z. Bihary, graduate student, PhD 2005, through DoE-GAANN fellow
- M. Petterson, postdoc, Academy of Finland
- M. Karavitis, graduate student, prior AFOSR and GAANN

Collaborators:

- D. Lidar, Prof. U. of Toronto and USC
- D. Glenn, graduate student, U. of Toronto

Invited presentations by PI:

2/04	Third International Meeting on Photodynamics (Havana, Cuba) *Quantum Coherent Dissipation – a glimpse of the 'cat'*
3/04	Seventh Symposium on Molecular Reaction Dynamics in Condensed Matter (Laguna Beach, CA) *Quantum Coherent Dissipation – a glimpse of the 'cat'*
6/04	Sophia University (Japan) *The manipulation of Quantum Coherence in Condensed Phase*
6/04	Japanese Chemical Society Meeting (Tokyo, Japan) *Quantum Coherent Dissipation: A Glimpse of the "cat"*
6/04	University of Tokyo (Japan) *Multi-linear Spectroscopy in the Condensed Phase*
9/04	5th International Conference on Low Temperature Chemistry (Berlin) *Quantum Coherent Dissipation: A Glimpse of the "cat"*
9/04	Physics Institute (Prague) *Quantum Coherent Dissipation: A Glimpse of the "cat"*
9/04	CNRS (Orsay, France) *Quantum Coherent Dissipation: A Glimpse of the "cat"*

3/05	OC Section of ACS (Concordia, Irvine) *Making of Schrodinger's cat: Would you know it if you saw it*
5/05	AFOSR Molecular Dynamics and Theoretical Chemistry Contractor's Meeting (Monterey, CA) *Quantum computing in the molecular Hilbert space*
6/05	Theoretical Physics Spring School (Mochima, Venezuela) *Coherences and decoherence in condensed phase*
11/05	1st French-Syrian Meeting on Physics (Homs, Syria) *1. Nonlinear Optical Spectroscopy & Quantum Computing* *2. Manipulating Coherence in the Condensed Phase*
3/06	231st ACS National Meeting (Atlanta, GA) *Phase-space probes of vibronic dynamics in condensed media*
3/06	SFB III Workshop (Berlin, Germany) *Imaging and manipulation of molecular coherences in condensed phase*
7/06	GRC, Atomic & Molecular Interactions (Colby-Sawyer College, NH) *Electronically resonant four-wave mixing: a phase space probe of molecular dynamics*
8/06	6th International Conference on Low Temperature Chemistry (Chernogolovka, Russia) *The making of Schrodinger's cats and their observation in phase space*
9/06	Sixth International Conference on Cryocrystals and Quantum Crystals (Kharkov, Ukraine) *The making of Schrodinger's cats and their observation in phase space*
8/07	CECAM Workshop (Dublin, Ireland) *Portraits of dissipative quantum oscillators: recoherence & arrested decoherence*
9/07	Zcheck Academy, Prague Cat states, decoherence, and arrested decoherence in condensed phase
9/07	Retreat of Optics Center of Oregon (Eugene, Oregon) *Portraits of dissipative quantum oscillators: recoherence & arrested decoherence*

Honors and Awards:

2004	Fellow AAAS
2004-2007	Chair, Department of Chemistry
2005	UCI Distinguished Faculty Award for Teaching
2006	USC Distinguished Alumnus Award

Cited Publications based on AFOSR supported research

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1. Zadoyan, R.; Kohen, D.; Lidar, D.; Apkarian, V. A. *Chem. Phys. 266*, 323-351 (2001). "The manipulation of massive ro-vibronic superpositions using time-frequency-resolved coherent anti-Stokes Raman scattering (TFRCARS): from quantum control to quantum computing"

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13. Bihary, Z., Karavitis, M., Apkarian, V. A., *J. Chem. Phys. 120*, 8144 (2004). "Onset of Decoherence: Six-wave Mixing Measurements of Vibrational Decoherence on the Excited Electronic State of I_2 in Solid Argon"

14. "Phase space probe of dissipative vibronic dynamics: spectrally resolved multicolor four wave mixing studies of I_2(B) in solid Krypton", Darren Segale, PhD thesis, UCI (Irvine, 2007).

15. Segale, D., Karavitis, M., Fredj, E., Apkarian, V. A., *J. Chem. Phys. 122,* 111104 (2005). "Quantum Coherent Dissipation: A glimpse of the 'cat'"

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