

Singlet molecular oxygen by direct excitation

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Received 17th September 2007, Accepted 14th November 2007

First published as an Advance Article on the web 30th November 2007

DOI: 10.1039/b714286b

Direct excitation at 1064 nm and detection of singlet molecular oxygen at 1270 nm is made possible by the availability of powerful YAG-lasers and sensitive NIR photomultipliers. Singlet oxygen was generated in condensed phase at 77 K by direct excitation at 1064 nm (without the use of sensitizers). Several luminescing species were observed by time resolved luminescence spectroscopy and luminescence lifetime measurements, including the single molecule $^1\Delta_g$ and $^1\Sigma_g^+$ states as well as luminescence from the $[\Delta_g]_2$ simultaneous transition. As an application we propose a novel method for obtaining quantitative non-intrusive mapping of the 2-D oxygen concentrations and pressure at cryogenic temperatures, which is of importance in aircraft design for high altitudes.

Introduction

Molecular oxygen is a paramagnetic molecule with an even number of electrons. The prediction by Mulliken^{1,2} that the ground electronic state is $^3\Sigma_g^-$ was one of the early triumphs of molecular orbital theory. The lowest singlet excited states $^1\Delta_g$ and $^1\Sigma_g^+$ lie at 7882 cm^{-1} and 13121 cm^{-1} , respectively, above the ground state. In the free unperturbed molecule, the transitions from the ground state to $^1\Delta_g$ and $^1\Sigma_g^+$ are electric dipole and spin forbidden and gain intensity mainly through magnetic dipole moment. The review by Schweitzer and Schmidt provides a comprehensive discussion of the physical process of singlet oxygen generation and deactivation.³ They report calculated radiative lifetimes of 72 minutes for $^1\Delta_g$ and 11 seconds for $^1\Sigma_g^+$. However, at higher oxygen concentrations and in the presence of other molecular species these transition rates rise up to $\sim 10^4$ times due to intermolecular perturbations, which enhance the radiative processes.^{4,5} The observed lifetimes for $^1\Delta_g$ range from milliseconds in gaseous phase to microseconds in aqueous media. In contrast the lifetime of $^1\Sigma_g^+$ is much shorter since the excited state quickly decays into $^1\Delta_g$. The effect of concentration, solvents and environments on the molecular oxygen transitions has been extensively studied.^{6,7}

Surprisingly for a homogeneous diatomic molecule, in the condensed phase or high gas pressure the absorption spectrum of molecular oxygen spans the UV-NIR spectral range. In addition to the expected single molecule bands for $^1\Delta_g \leftarrow ^3\Sigma_g^-$ and $^1\Sigma_g^+ \leftarrow ^3\Sigma_g^-$ transitions, one observes additional absorption bands that arise from dimer (O_2)₂ configurations and correspond to various pairs of single molecule transitions as shown in Fig. 1. The intensities of these bands have quadratic dependency on the oxygen concentration and are responsible for the blue color of liquid oxygen. This phenomenon is interpreted as an up-conversion process of two oxygen molecules being excited simultaneously by one photon to a virtual state not common to either molecule.⁸ The energy of the up-conversion transition is equal to the sum of the transition energies. This cooperative process was rediscovered in emission by

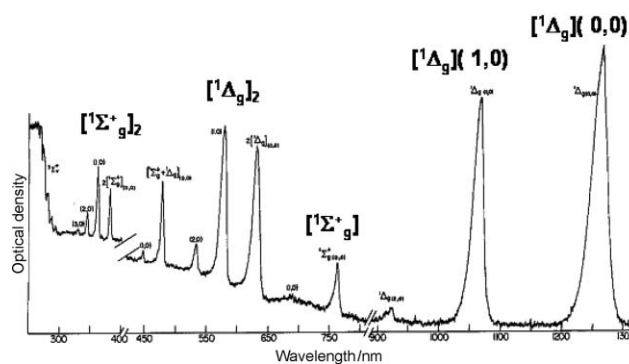
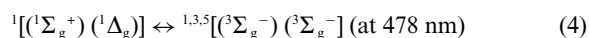
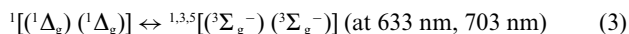
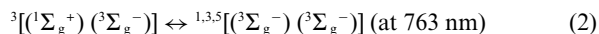


Fig. 1 Absorption spectrum of liquid oxygen (optical cell length is 3.5 cm). Scale is adjusted for plotting purposes. After G. Khalil, PhD thesis, Florida State University, 1978.

Khan and Kasha⁹ by measuring the chemiluminescence reaction (eqn (1)):



These workers observed the following transition bands:



Transition (2) is a single molecule emission event; transitions (3) and (4) are cooperative emission process of two molecules. Combined spin multiplicity notation was used to illustrate the enhancement of the spin selection rule for molecular pair oxygen states. The Ogryzlo group recorded similar emission spectra from an electrical discharge of gaseous molecular oxygen.¹⁰ This pioneering work and others have ignited interest in singlet molecular oxygen research and over the last 30 years several conference proceedings on singlet oxygen and its applications have been published.¹¹⁻¹⁴

Generating singlet oxygen by a photo-sensitizer is the most efficient process and up to 100% $^1\Delta_g$ generation efficiency has been

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reported.^{15,16} Using a platinum porphyrin sensor film we recently demonstrated a new method to measure oxygen concentration on a 2-D surface.¹⁷ The method is based on the porphyrin-sensitized 1270 nm singlet oxygen emission imaged, with an InGaAs camera as a function of surface pressure. Several research groups have previously determined the lifetime of singlet oxygen directly by time resolved spectroscopy.^{3,18}

Generating singlet oxygen by direct excitation became efficient and feasible with the arrival of powerful lasers. Skuja and Güttler detected $^1\Delta_g$ emission from trapped molecular oxygen gas in SiO₂ glass by direct laser photoexcitation.¹⁹ The Krasnovsky research group recently produced the action spectrum of the photo-oxygenation of tetracene and 1,3-diphenylisobenzofuran due to direct formation of the singlet oxygen state $^1\Delta_g$ by laser excitation.²⁰ It was found that the reaction rate is linearly dependent on the laser power and strongly diminished in the presence of singlet oxygen scavengers.

We take advantage of the fortuity that the YAG laser 1064 nm line is a close match to the molecular oxygen transition [$^1\Delta_g(v=1)$] \leftarrow [$^3\Sigma_g^-(v=0)$] absorption band. With the availability of fast sensitive NIR detectors, detection of $^1\Delta_g$ emission becomes much more feasible for direct oxygen concentration measurement and potential surface pressure mapping applications. This present work is a spectroscopic study of the singlet molecular oxygen state generated by direct excitation. Emission spectra and lifetime measurements from the single molecule $^1\Delta_g$ and $^1\Sigma_g^+$ states, as well as from the [$^1\Delta_g$]₂ simultaneous transition are presented for the first time.

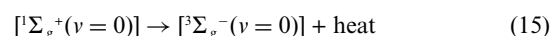
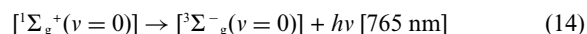
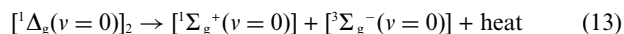
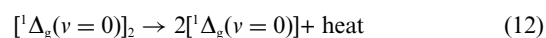
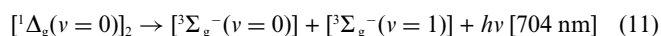
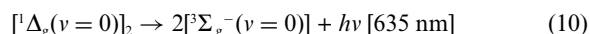
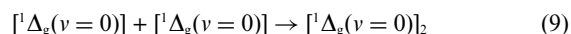
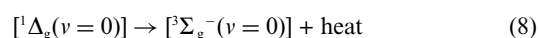
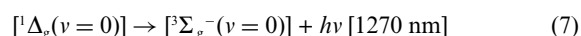
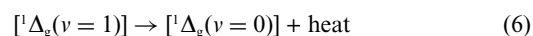
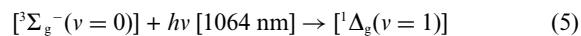
Materials and methods

An empty pyrex NMR tube (4 mm diameter) was placed in a liquid nitrogen filled dewar, which possesses an optically transparent section for spectroscopic measurements. Liquid oxygen or liquid nitrogen–oxygen mixtures were condensed into the NMR tube by flushing the NMR tube with oxygen gas or nitrogen–oxygen gas mixtures prior to the measurements. A temperature of 150 K was obtained by careful addition of liquid nitrogen into n-pentane. For direct excitation of triplet oxygen (condensed oxygen in the NMR tube at 77 K), the pulses from a Spectra Physics Nd-YAG laser (GCR-150-30) at 1064 nm (pulse width ~10 ns; ~100 mJ pulse⁻¹) were used. The molecular oxygen emissions were collected employing a modified Fluorolog 2 spectrometer (Jobin-Yvon Inc.) in conjunction with Hamamatsu photomultiplier tubes (PMT) (R928 for the visible spectral range and H9170-45 for the NIR spectral range). A glass cut-off filter at 800 nm was fitted in front of the sample to eliminate scattered light from laser pump flash-lamps. For recording luminescence decay traces at fixed emission wavelength, the photocurrent from the PMT was amplified (SR 560, Stanford Research Systems) and stored in a digital oscilloscope (TDS 360, Tektronix). For recording time resolved luminescence spectra, the amplified photocurrent from the PMT was time resolved using a boxcar integrator (SR 250, Stanford Research Systems). The time-gated signal from the boxcar integrator was digitized with a DM303 M module (Jobin-Yvon Inc.), then stored and synchronized with the monochromator stepping motor using the software supplied by the Fluorolog 2 spectrometer. Scattering interference from the intense laser line was eliminated by integrating over time periods

of 15 μ s of the emitted signal 35 μ s after the laser pulse. The emission spectra in the visible spectral range were corrected for the wavelength sensitivity of the detector. In a separate measurement, one ml of perfluoro-15-crown-5 (Exfluor Research Corporation) in a 4 mm NMR tube was saturated with oxygen at room temperature by bubbling with oxygen gas. This oxygen saturated solution was shock-frozen in the liquid nitrogen dewar (77 K) and luminescence experiments were performed as described above.

Results and discussion

The excitation of molecular oxygen by the 1064 nm laser pulse produces the following photophysical processes:



Process (5) is the direct excitation to the vibronically excited state [$^1\Delta_g(v=1)$] and its absorption coefficient is known to increase with oxygen concentration.³ Processes ((6), (8), (11), (12), (13) and (15)) are radiationless: decay, intersystem crossing and quenching events. Process (9) is the formation of the molecular pair excited states by collision. In this paper we will focus on radiative processes ((7), (10), (11) and (14)). We carried out spectral measurements on molecular oxygen in condensed phase and in a solution of fluorinated hydrocarbon. All samples were measured sequentially twice: first in the NIR region then in the visible.

Emission measurement

Fig. 2(A) shows the time resolved luminescence spectrum of the condensed phase of oxygen in the NIR region at 77 K. The spectrum is assigned to the emission from the lowest excited state [$^1\Delta_g(v=0)$] to ground state [$^3\Sigma_g^-(v=0)$] and is centered at 1270 nm, (eqn (7)). The band intensity is directly proportional to % oxygen concentrations and no emission was observed in the absence of oxygen (100% nitrogen). The emission from [$^1\Delta_g(v=0)$] to the vibronic ground state [$^3\Sigma_g^-(v=1)$] observed at 1560 nm was not detected due to the lack of response above 1400 nm of the InGaAs photomultiplier model used.

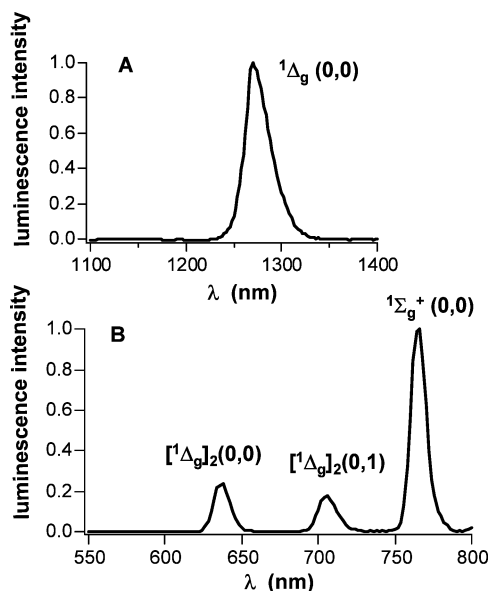


Fig. 2 (A) Time resolved phosphorescence spectrum (30–80 μs) of condensed oxygen at 77 K excited at 1064 nm and detected in the NIR region. (B) The emission spectrum of condensed molecular oxygen excited at 1064 nm and detected in the visible region.

Fig. 2(B) shows the time resolved luminescence spectrum in the visible region. The spectrum has three bands, the 635 nm and 704 nm bands represent the simultaneous electronic transition of two molecules excited at $[^1\Delta_g(v=0)]$ (eqn (9)) emitting a single photon to ground state $[^3\Sigma_g^-(v=0)]$. The two molecules emit at 635 nm if both molecules arrive to the ground state $[^3\Sigma_g^-(v=0)]$ simultaneously as in eqn (10). The two molecules emit at 704 nm if one molecule arrives to the first vibrational ground state $[^3\Sigma_g^-(v=1)]$ as eqn (11). The separation between the two bands is 1543 cm^{-1} which is in good agreement with the ground electronic state vibrational frequency of 1556 cm^{-1} . The emission of the two bands are mirror image to the absorption bands $[^1\Delta_g]_{2(0,0)}$ and $[^1\Delta_g]_{2(1,0)}$ shown in Fig. 1. We observed no emission from the combined simultaneous transition $[^1\Sigma_g^+(v=0)]$ $[^1\Delta_g(v=0)]$ previously reported as weak emission band at 478 nm.⁹ The band at 765 nm (Fig. 2(B)) is assigned to the emission from the single molecule $[^3\Sigma_g^+(v=0)]$ electronic state generated by energy pooling from the $[^1\Delta_g]_2$ simultaneous transition as illustrated by eqn (13) and eqn (14). The relative intensity of the $^1\Sigma_g^+$ band is greater than the intensities of $[^1\Delta_g]_2$ bands, which is in contrast to the band ratio observed in the emission measurement from the chemiluminescence reaction⁹ The differences in the Franck–Condon factors are not understood and similar discrepancies were observed in the singlet oxygen emission generated by electrical discharge of gaseous oxygen.¹⁰

Lifetime measurement

Fig. 3 shows luminescence decay traces measured at 1270 nm, 765 nm, 636 nm and 704 nm. The emission decay curves fitted well to pseudo-first order kinetics. The sharp spikes at the start of the decay curves are attributed to scatter of the laser light. Plot A is the decay curve of the $[^1\Delta_g]$ emission and has a lifetime of 46 μs . Plot B represents the formation of the $[^1\Sigma_g^+]$ state and is followed by the decay process. The emission intensity rise time

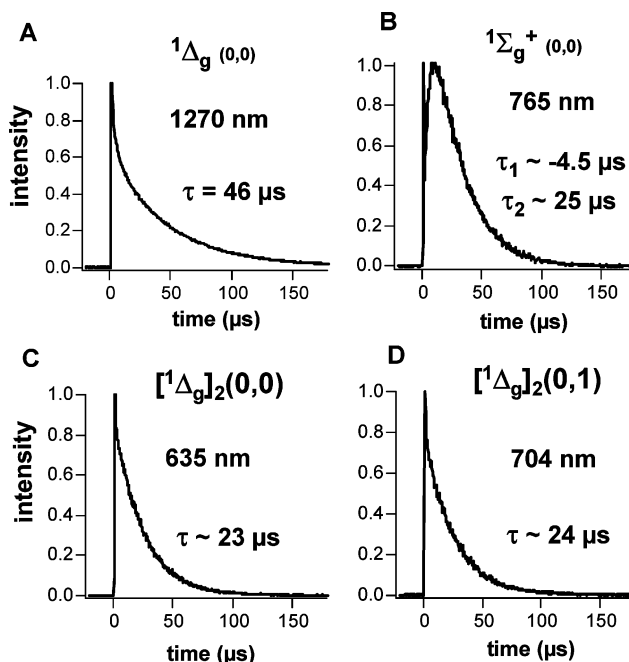


Fig. 3 Luminescence decay traces of condensed molecular oxygen at 77 K excited at 1064 nm and detected at (A) 1270 nm, (B) 765 nm, (C) 636 nm, and (D) 704 nm.

is measured as 4.5 μs and the decay lifetime is 24 μs . Plots C and D are the decay curves of $[^1\Delta_g]_2$ emissions and both have lifetimes of 25 μs . Similar decay lifetimes were observed by Maier and coworkers for $[^1\Delta_g]$ (43 μs) and $[^1\Delta_g]_2$ (22 μs) under similar conditions (excitation at 1064 nm of condensed oxygen at 77 K).²¹ The decay lifetime of $[^1\Delta_g]_2$ is approximately half of the value for $[^1\Delta_g]$, which is in agreement with the studies of Kazakov and Schmidt of luminescence decay kinetics at room temperature in different solvents.²² These authors showed that the factor of two between the decay lifetimes of $[^1\Delta_g]$ and $[^1\Delta_g]_2$ is expected due to the fast equilibrium between 2 molecules of $[^1\Delta_g]$ and $[^1\Delta_g]_2$ in conjunction with the deactivation of $[^1\Delta_g]$ to $[^3\Sigma_g^-]$.

Fig. 4 are the phosphorescence decay traces of the $[^1\Delta_g(v=0)]$ emission detected at 1270 nm at three different oxygen concentrations at 77 K. The lifetime $\tau_{1270\text{ nm}}$ decreases at higher %

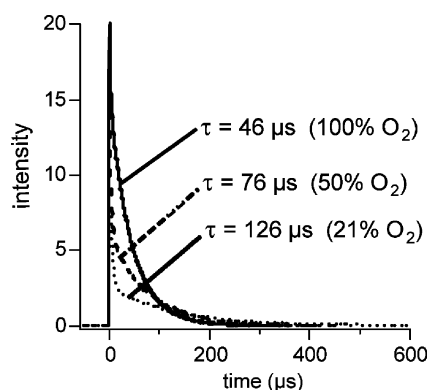


Fig. 4 Luminescence decay traces of condensed molecular oxygen excited at 1064 nm in three oxygen–nitrogen mixtures of different ratios detected at 1270 nm at 77 K.

oxygen as result of the quenching by [$^3\Sigma_g^-$]. It should be noted that the oxygen concentration in the gas mixtures are not the same as in the condensed phase as the ratios are temperature dependent. The short lifetime of singlet oxygen in liquid oxygen of 46 μs is caused by self-quenching. At reduced oxygen concentration in liquid air, a longer lifetime of 126 μs was observed.

Laser power dependence

Using a set of neutral density filters we determined the emission intensity dependency on the laser power. Measurements on the 1270 nm, 765 nm and 635 nm emission bands are plotted in Fig. 5. The results clearly show that for [$^1\Delta_g$] the emission intensity is linearly dependent on the laser power. This is in accord with a one-photon, one-molecule process. On the other hand the emission intensities for [$^1\Delta_g$] $_2$ and [$^1\Sigma_g^+$], exhibit a quadratic laser power dependence. Both transitions require two photons to be absorbed for each photon emitted.

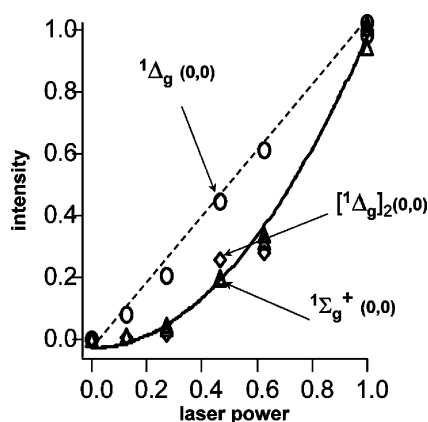


Fig. 5 Laser power dependencies on the emission intensity of $^1\Delta_{g(0,0)}$, $2[{}^1\Delta_g]_{(0,0)}$, and ${}^1\Sigma_g^+(0,0)$, detected at 1270 nm, 636 nm and 765 nm respectively. 100% laser power corresponds to ~ 100 mJ pulse $^{-1}$.

The NIR emission spectrum of shock frozen (77 K) oxygen saturated solutions of perfluoro-15-crown-5 is shown in Fig. 6. The spectrum exhibits a single band centered at 1270 nm. The spectrum is similar to that of condensed oxygen (Fig. 2(A)). The insert of Fig. 6 compares the decay curves of oxygen saturated and argon saturated solutions both monitored at 1270 nm. The oxygen saturated solution show a life time value of 141 μs , whereas the decay trace of the argon saturated solution has no measurable lifetime and follows the laser pulse. To test direct excitation of dissolved oxygen in a perfluorinated polymer film, samples of

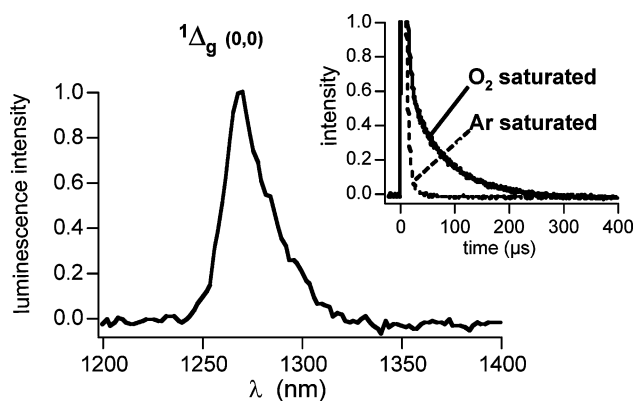


Fig. 6 Time resolved phosphorescence spectrum (30–80 μs) of oxygen saturated perfluoro 15-crown-5 ether solution after excitation at 1064 nm at 77 K. Insert: decay traces of oxygen (—) and argon (---) saturated perfluoro-15-crown-5 ether solutions monitored at 1270 nm following laser excitation (1064 nm) at 77 K.

Teflon tape were equilibrium with 100% gaseous oxygen at 150 K and excited with laser pulses at 1064 nm. A $^1\Delta_g$ emission life time of 530 μs was observed. The longer life time values observed in the samples containing oxygen in the saturated perfluorinated solvent and in the perfluorinated polymer are attributed to lower oxygen concentrations compared to the value measured in the condensed phase at 77 K. All measured lifetimes values are listed in Table 1.

Conclusions

The results contained in this paper have implications for both fundamental and applied aspects of directly photo-excited oxygen luminescence. Recognizing the low quantum efficiency of the proposed process, the approach has certain advantages. (i) It requires no chemical reagents for measuring oxygen concentrations. (ii) Exciting and detecting in the NIR region has low ambient light interference and provides an opportunity for simultaneous measurement in the visible region.

In the area of basic research we will generate the ${}^1\Sigma_g^+$ state directly using known laser line at 760 nm of the condensed molecular oxygen. It should be noted that spectral measurements for the radiative transition from ${}^1\Sigma_g^+$ to ${}^3\Sigma_g^-$ or ${}^1\Delta_g$ were previously reported.^{23–25} We will focus on investigating the following simultaneous transitions:

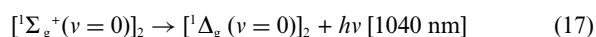
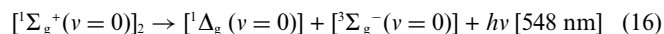


Table 1 Lifetimes of [$^1\Delta_g$], [${}^1\Sigma_g^+$] and $2[{}^1\Delta_g]$ by direct excitation

Solvent	Temperature/K	% Oxygen	$\tau [{}^1\Delta_g]/\mu\text{s}^b$	$\tau [{}^1\Sigma_g^+]/\mu\text{s}^b$	$\tau 2[{}^1\Delta_g]/\mu\text{s}^b$
Nitrogen	77	21 ^a	126		
		50 ^a	76		
		100	46	25	24
Teflon	150	100	530		
Perfluoro-15-crown-5	77	Saturated solution	141		

^a Fraction of oxygen in oxygen–nitrogen gas mixtures, which were used to condense oxygen–nitrogen mixtures at 77 K. The actual oxygen fraction in the condensed phase at 77 K might be different from the gas mixtures. ^b Error limit $\sim 5\%$.

For initial application of direct excitation and detection of singlet oxygen we will focus on its potential use in cryogenic wind tunnel testing.^{26,27} We plan to develop a novel method for obtaining quantitative non-intrusive mapping of the 2-D oxygen/pressure at many points. The image intensity of the 1270 nm luminescence should generate a map whose intensities are proportional to the oxygen concentration which is directly proportional to pressure.

Acknowledgements

The authors at the University of Washington thank the Air Force Office of Scientific Research STTR AF04-T001, Innovative Scientific Solutions Inc. and the National Science Foundation (Grant 0517782) for financial support. The authors at Columbia thank the National Science Foundation for financial support under Grant CHE 04-15516.

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