Aromatic hydrocarbons, light, the laser environment and broken glass: A proposed mechanism

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Customer Focused

Employee Owned

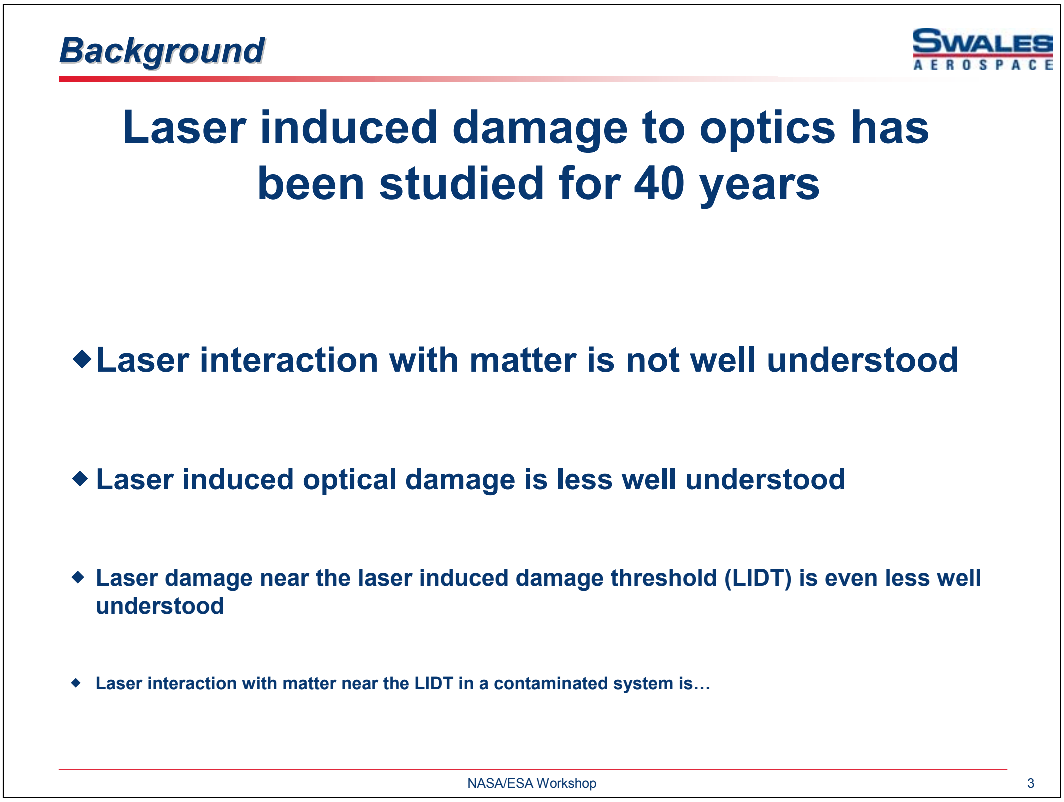
I am proposing a mechanism to describe laser optic damage in the presence of molecular contamination.

This mechanism is based upon knowledge complied from a variety of proven scientific principles and facts.

Understanding of laser damage requires a knowledge of a large number of fields of study.

Introduction

- **Introduction**
  - Background and Knowledge Base
  - Assumptions and Requirements
- **Proposed Mechanism**
  - Precursor – Formation and Annihilation
  - Events – Precipitation
- **Observations**
  - Color Centers – Formation and Annihilation
  - Water – Effects and Surface Roughening
  - Excited States –Formation and Annihilation
  - Local Heating
  - Damage Morphology
- **Application to Other Systems**
- **Summary**
- **Conclusions**



Background

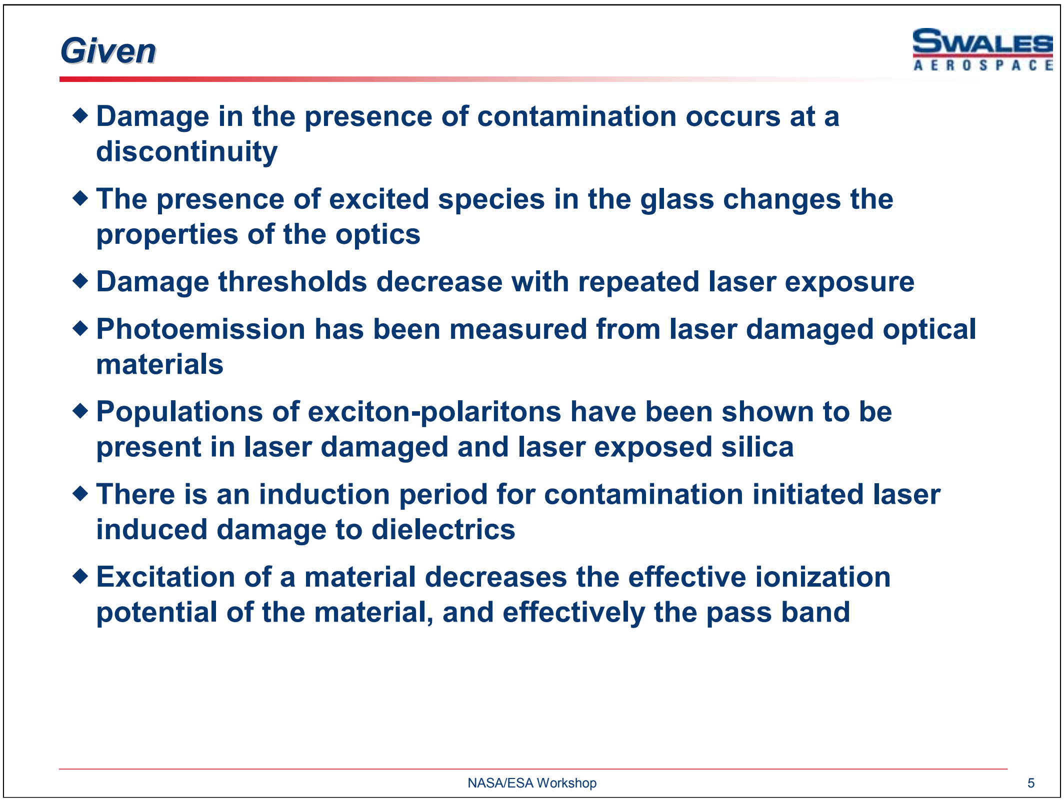
Laser induced damage to optics has been studied for 40 years

- Laser interaction with matter is not well understood
- Laser induced optical damage is less well understood
- Laser damage near the laser induced damage threshold (LIDT) is even less well understood
- Laser interaction with matter near the LIDT in a contaminated system is…

Contamination induced laser optic damage has been the subject of a number of recent studies. While it is known that there are a number of species and classifications of materials that reduce the laser induced damage threshold (LIDT), there has been limited progress in identifying a plausible photochemical mechanism for the initiation of the damage. The propagation rate and final result of the induced damage are of importance; they pale in comparison to the significance of the initiation of the damage process. Without initiation neither propagation nor resultant damage exists.

Understanding Laser Damage

- To adequately study the issue of contamination effects of laser damage, it is required to coalesce knowledge from at least the following areas of study in a unified approach:
  - Experimental laser damage studies
  - Laser damage theory
  - Laser physics
  - Classical Electromagnetic theory
  - Quantum Electromagnetic theory
  - Physical Chemistry
  - Photochemistry
  - Chemical Physics
  - Inorganic Chemistry
  - Organic Chemistry
  - Glass Chemistry
  - Surface Chemistry
  - Surface Physics
  - Contamination engineering
  - Materials engineering
  - Thermal engineering
  - Polymer science
  - Exciton physics
  - Luminescence

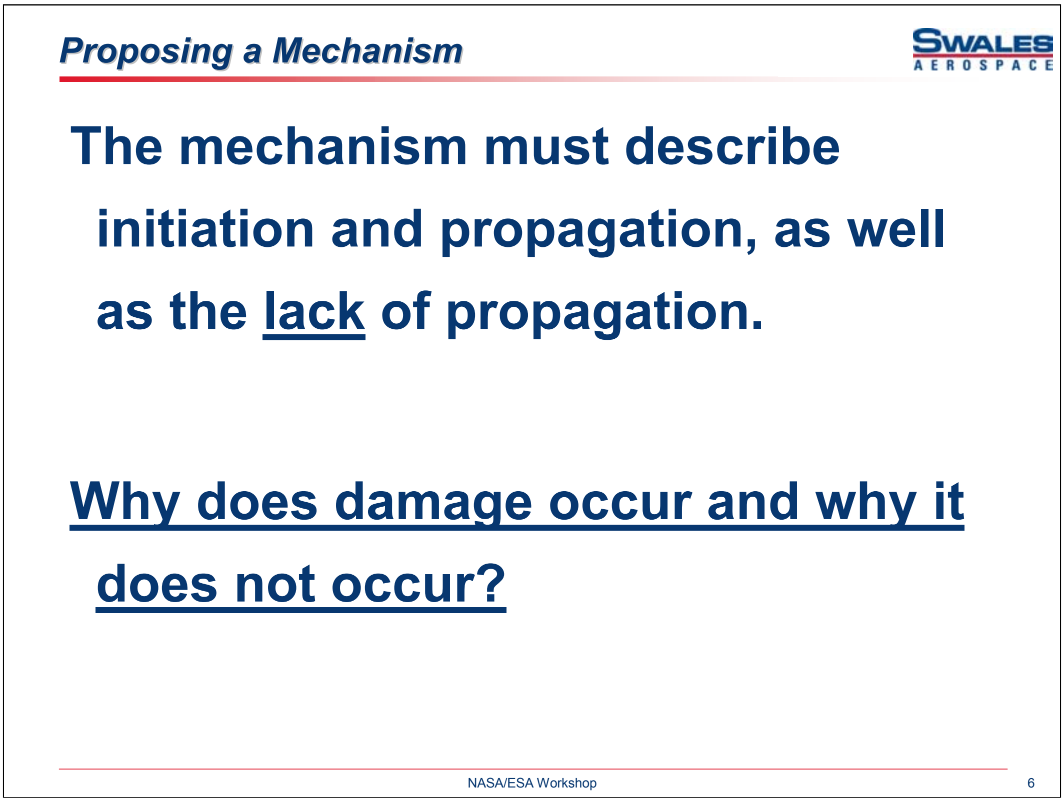


Given

- Damage in the presence of contamination occurs at a discontinuity
- The presence of excited species in the glass changes the properties of the optics
- Damage thresholds decrease with repeated laser exposure
- Photoemission has been measured from laser damaged optical materials
- Populations of exciton-polaritons have been shown to be present in laser damaged and laser exposed silica
- There is an induction period for contamination initiated laser induced damage to dielectrics
- Excitation of a material decreases the effective ionization potential of the material, and effectively the pass band

Hovis, et.al.-1, Sharps2, and Kunz3 studied the effect of numerous materials including solvents on the laser damage process in the early to mid 1990’s. More recently, Scurlock4, Jager5, Becker6, Reide7, and this author8-12, have studied the effects of molecular contamination on laser optic damage. Although the issue is recognized as a significant risk to laser systems, relatively little work has been carried out.

Toluene has been identified as a bad actor in one-micron laser systems. Hovis, et.al1. proposed a polymerization-based mechanism for the laser-induced damage resulting from operation of lasers in the presence of toluene vapor. It was proposed that toluene formed a trimer that strongly absorbed at one micron. This was proposed strictly based upon a third order radiance relationship. From evaluation spectroscopic data of polycyclic aromatic hydrocarbons that could reasonably be formed from toluene and evaluation of functional group addition rules, UV-vis spectral data, and well-documented organic chemistry, this proposed mechanism is bankrupt.



Proposing a Mechanism

The mechanism must describe initiation and propagation, as well as the <u>lack</u> of propagation.

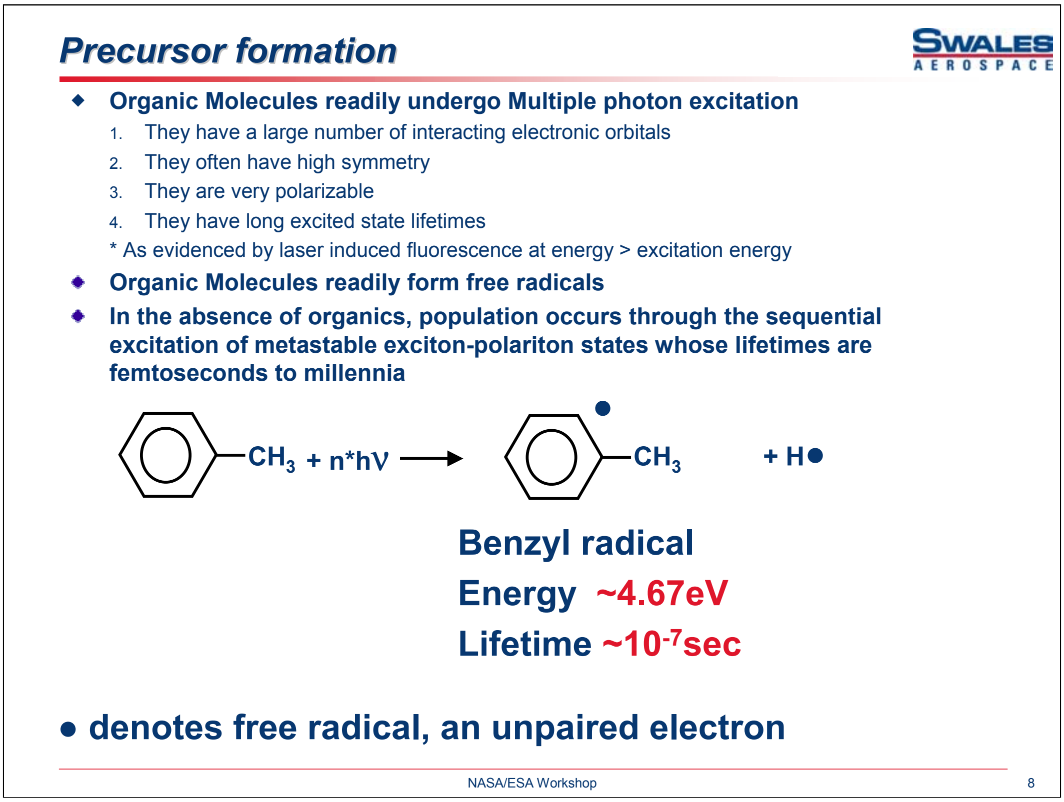
<u>Why does damage occur and why it does not occur?</u>

Not all laser damage scenarios lead to damage.

The parameters affecting laser damage are not well known.

The Proposed Mechanism: For contamination aggravated laser induced damage

This proposed mechanism is based upon a number of phenomena, each well known in certain fields, all of which have been published in open literature.



Precursor formation

- **Organic Molecules readily undergo Multiple photon excitation**
  1. They have a large number of interacting electronic orbitals
  2. They often have high symmetry
  3. They are very polarizable
  4. They have long excited state lifetimes

  * As evidenced by laser induced fluorescence at energy > excitation energy
- **Organic Molecules readily form free radicals**
- **In the absence of organics, population occurs through the sequential excitation of metastable exciton-polariton states whose lifetimes are femtoseconds to millennia**

Benzyl radical

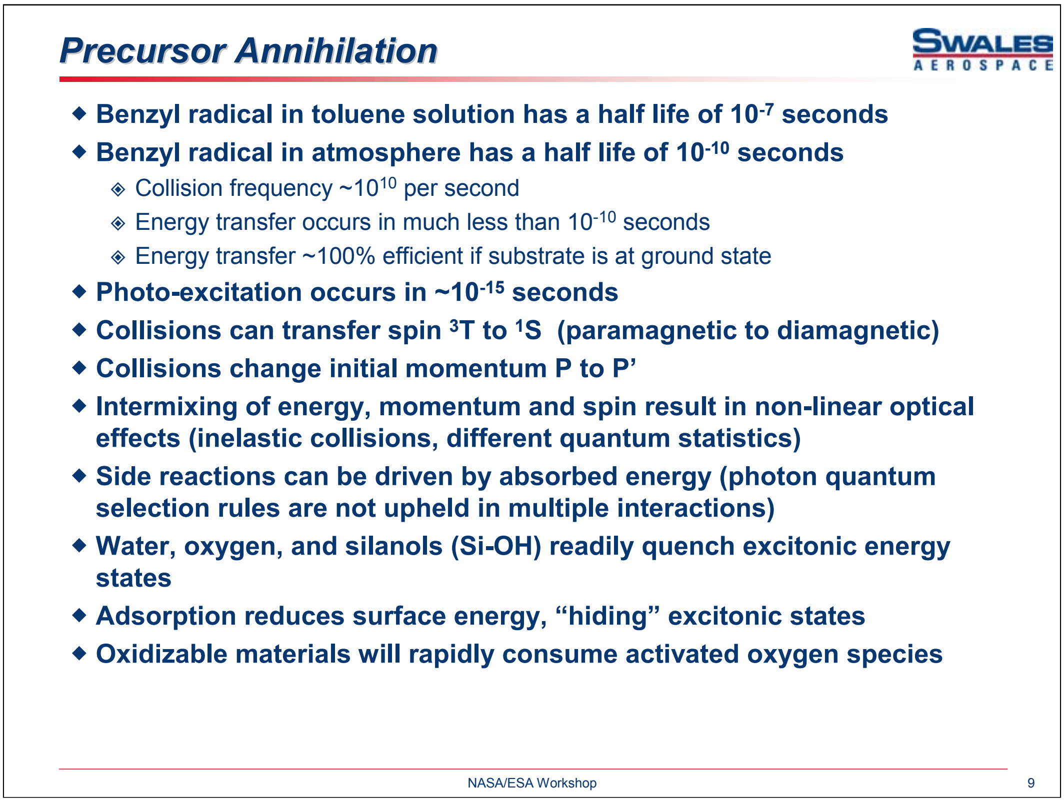
Energy ~4.67eV

Lifetime ~10^{-7}sec

● denotes free radical, an unpaired electron

Precursor Formation

Toluene (in a 1.06um Nd: YAG laser) absorbs approximately 4.7 eV, through a single 4th harmonic photon or multiple photons. This will result in the formation of the benzyl radical (lifetime ~ 10^{-7} sec). The benzyl radical rapidly quenches (rate constant ~ 10^{10}sec-1). The quenching transfers the energy and spin in part or in total to the quenching species. In the case of a metallic surface, where excitonic states are very short lifetime, the energy degrades rapidly either through reaction, emission or absorption. In the case of vitreous dielectric materials, excited states of ~4.7 eV are populated. The excited state populations if trapped will redistribute within the material remaining trapped like exciton



Precursor Annihilation

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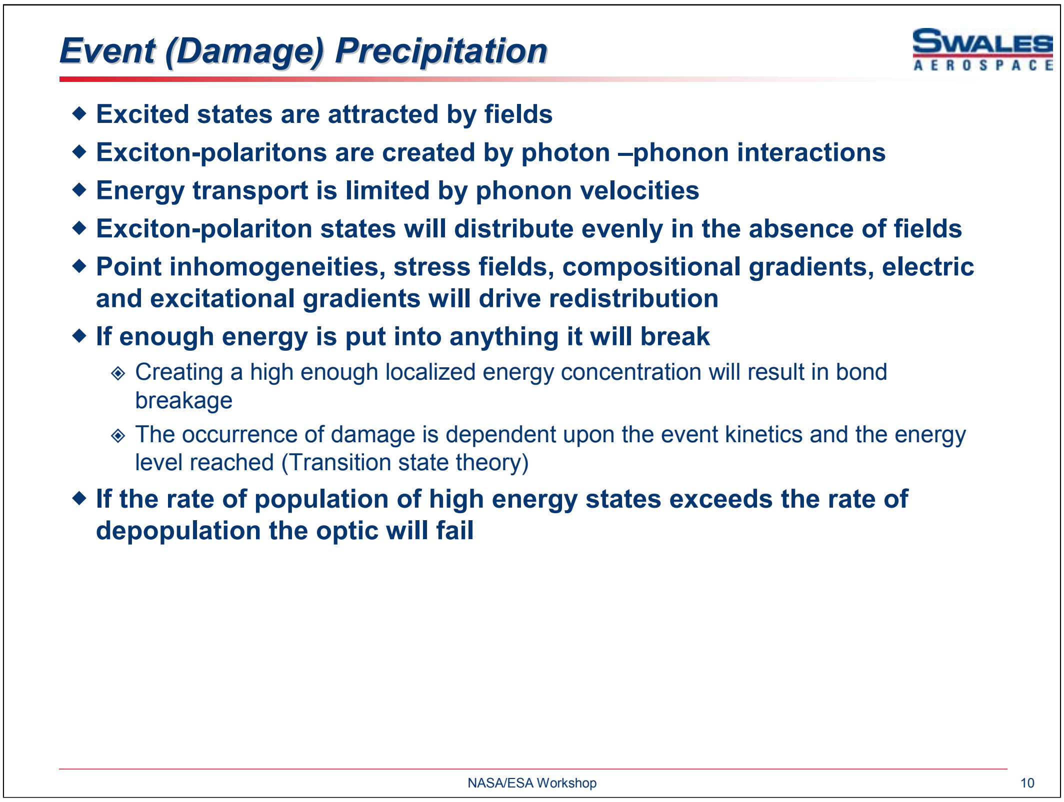
- Benzyl radical in toluene solution has a half life of 10^{-7} seconds
- Benzyl radical in atmosphere has a half life of 10^{-10} seconds
  - Collision frequency ~10^{10} per second
  - Energy transfer occurs in much less than 10^{-10} seconds
  - Energy transfer ~100% efficient if substrate is at ground state
- Photo-excitation occurs in ~10^{-15} seconds
- Collisions can transfer spin ^3T to ^1S (paramagnetic to diamagnetic)
- Collisions change initial momentum P to P'
- Intermixing of energy, momentum and spin result in non-linear optical effects (inelastic collisions, different quantum statistics)
- Side reactions can be driven by absorbed energy (photon quantum selection rules are not upheld in multiple interactions)
- Water, oxygen, and silanols (Si-OH) readily quench excitonic energy states
- Adsorption reduces surface energy, "hiding" excitonic states
- Oxidizable materials will rapidly consume activated oxygen species

Precursor Annihilation

In air the benzyl radical is quenched by both water vapor and oxygen. Quenching of benzyl radical by water vapor forms hydroxyl radical. Quenching of benzyl radical by molecular oxygen forms singlet oxygen. Both hydroxyl radical and singlet oxygen are strong oxidizing agents that will oxidize hydrocarbons to carbon monoxide and/or carbon dioxide. Additionally, hydroxyl radical emission from the hydrated surface layer of silica has been noted in the literature.

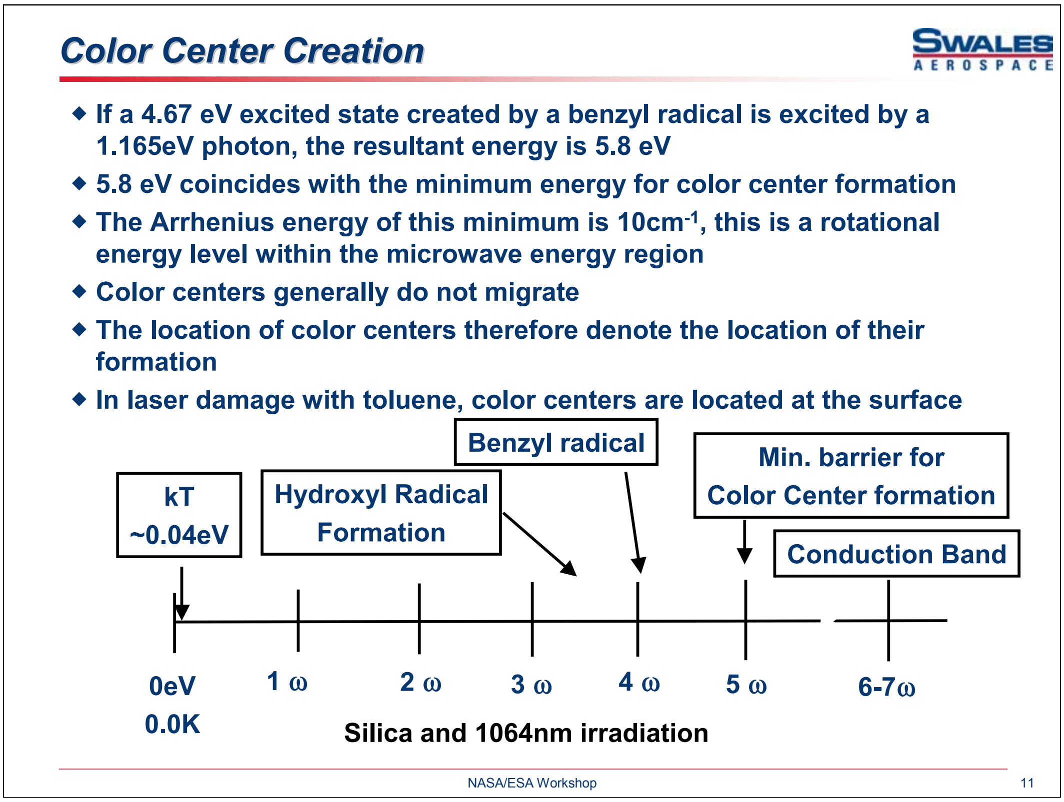


Event (Damage) Precipitation

- Excited states are attracted by fields
- Exciton-polaritons are created by photon –phonon interactions
- Energy transport is limited by phonon velocities
- Exciton-polariton states will distribute evenly in the absence of fields
- Point inhomogeneities, stress fields, compositional gradients, electric and excitational gradients will drive redistribution
- If enough energy is put into anything it will break
  - Creating a high enough localized energy concentration will result in bond breakage
  - The occurrence of damage is dependent upon the event kinetics and the energy level reached (Transition state theory)
- If the rate of population of high energy states exceeds the rate of depopulation the optic will fail

Event Precipitation

The excited states are attracted by field gradients. As phonon transport is required for movement in the trapped state, transport across inhomogeneities is not possible. In the case of an applied field, such as a laser field, the population of the excited states would be drawn toward the laser beam. If the energy density in the optic reaches a critical density, damage will occur. With repeated transfer of energy from the quenching of the toluene, eventually the optic will reach a sufficiently high population that energy transfer would not be favorable, and the excited state toluene lifetime would begin to rise. This can result in the absorption of additional energy.



Color Center Creation

- If a 4.67 eV excited state created by a benzyl radical is excited by a 1.165eV photon, the resultant energy is 5.8 eV
- 5.8 eV coincides with the minimum energy for color center formation
- The Arrhenius energy of this minimum is 10cm^{-1}, this is a rotational energy level within the microwave energy region
- Color centers generally do not migrate
- The location of color centers therefore denote the location of their formation
- In laser damage with toluene, color centers are located at the surface

kT ~0.04eV

Hydroxyl Radical Formation

Benzyl radical

Min. barrier for Color Center formation

Conduction Band

0eV 0.0K

1 ω

2 ω

3 ω

4 ω

5 ω

6-7ω

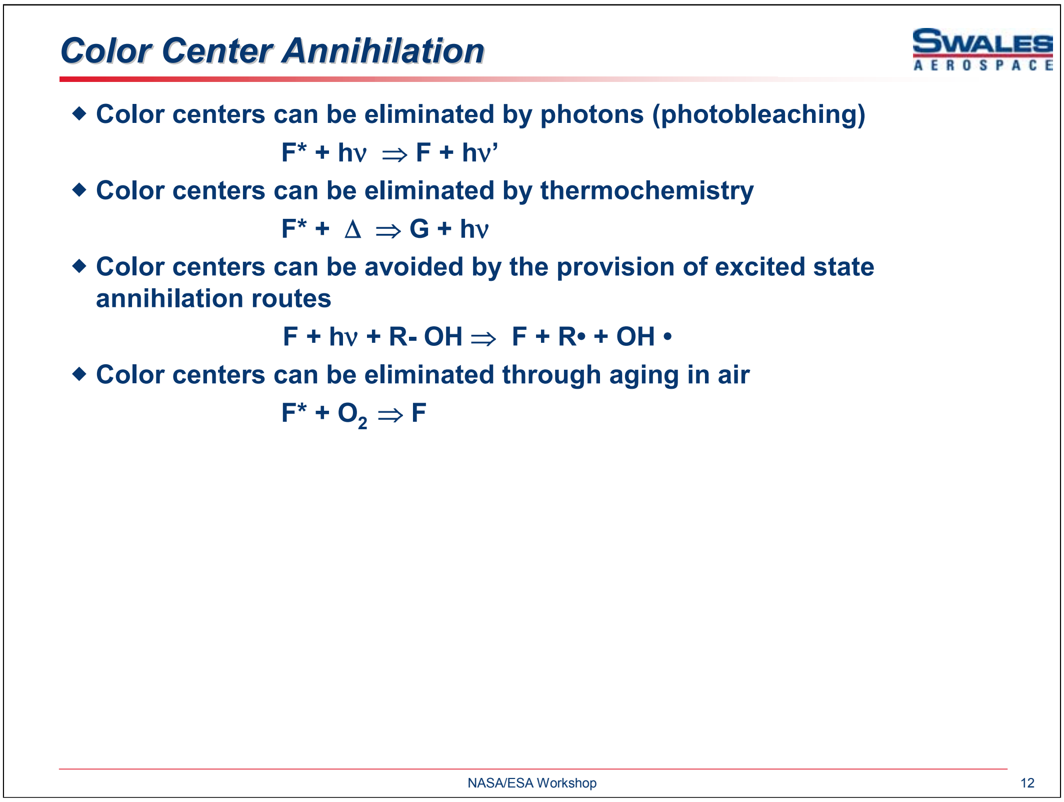
Silica and 1064nm irradiation

NASA/ESA Workshop

Color Center Creation

If the excited state toluene (benzyl radical) is excited by another 1.165eV photon, and then subsequently transfers the energy to silica, the resultant 5.8+eV excited state silica is at an energy at which the activation energy for the formation of color centers is effectively zero (10cm^{-1}). This will result in efficient formation of color centers within the silica surface. This will result in the formation of discolored zones in the silica. Primarily at the surface. This can result in significant surface absorption and damage.

Silica is sufficiently transparent at 5ω to assure color center formation into the bulk.



Color Center Annihilation

- Color centers can be eliminated by photons (photobleaching)

$$F^* + h\nu \Rightarrow F + h\nu'$$

- Color centers can be eliminated by thermochemistry

$$F^* + \Delta \Rightarrow G + h\nu$$

- Color centers can be avoided by the provision of excited state annihilation routes

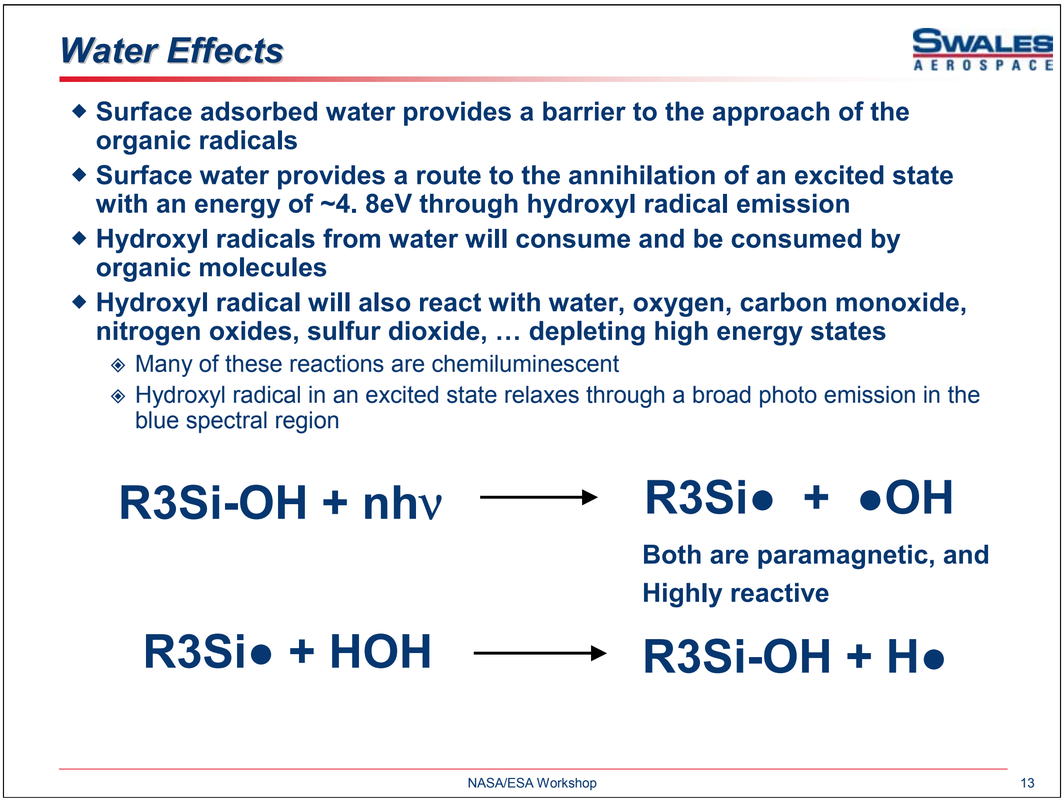
$$F + h\nu + R\text{-}OH \Rightarrow F + R\bullet + OH\bullet$$

- Color centers can be eliminated through aging in air

$$F^* + O_2 \Rightarrow F$$

Color Center Annihilation

It is well known that color centers can be eliminated from optical materials through either photonic or thermal means. The irradiation of glass possessing high color center populations with white light will result in the annihilation of the color centers. Likewise, heating of an optic possessing high color center concentrations can lead to photo bleaching. The same can be said for populations of exciton-polaritons. The radiation-induced defects typically result from a change in the state of the base material, resulting in a population at an energy above that of the Maxwell-Boltzmann described distribution. Providing additional energy to the system will allow re-emission and relaxation.



Water Effects

- Surface adsorbed water provides a barrier to the approach of the organic radicals
- Surface water provides a route to the annihilation of an excited state with an energy of ~4. 8eV through hydroxyl radical emission
- Hydroxyl radicals from water will consume and be consumed by organic molecules
- Hydroxyl radical will also react with water, oxygen, carbon monoxide, nitrogen oxides, sulfur dioxide, … depleting high energy states
  - Many of these reactions are chemiluminescent
  - Hydroxyl radical in an excited state relaxes through a broad photo emission in the blue spectral region

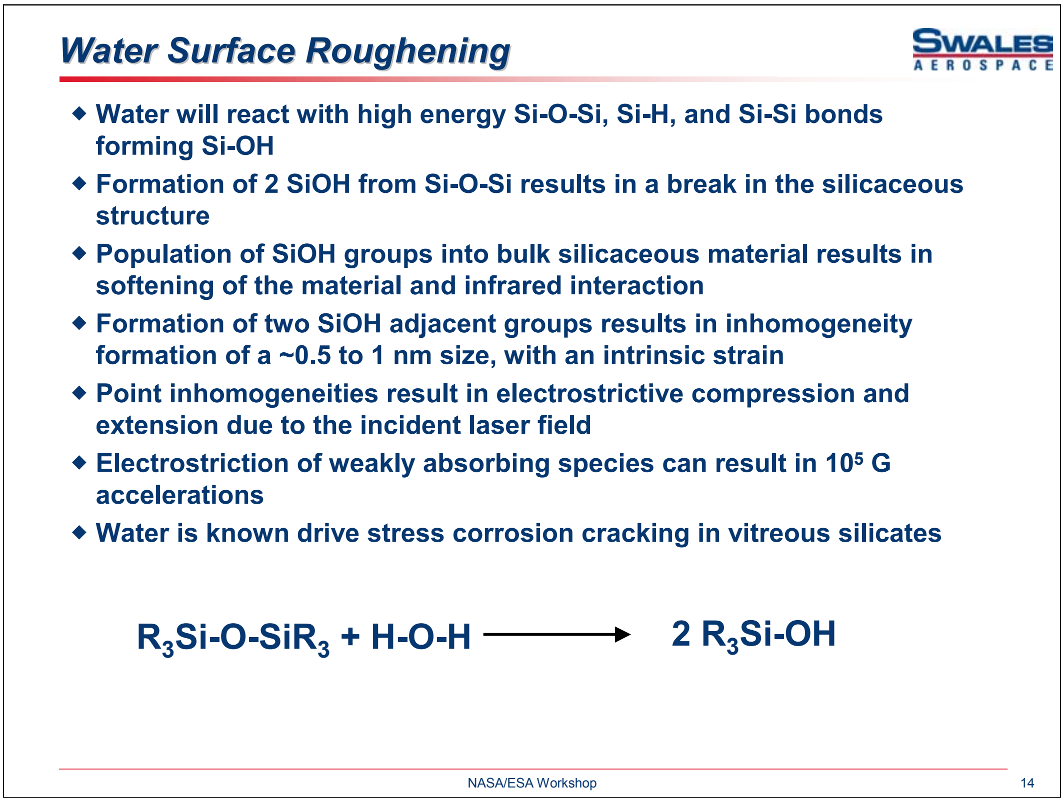
$$R3Si\text{-}OH + nh\nu \longrightarrow R3Si\bullet + \bullet OH$$

Both are paramagnetic, and Highly reactive

$$R3Si\bullet + HOH \longrightarrow R3Si\text{-}OH + H\bullet$$

Water Effects, Conditioning

If the surface is covered with water, the benzyl radical can abstract hydrogen from the water, resulting in the formation of hydroxyl radical. Hydroxyl radical is a highly reactive oxidizing species responsible for many oxidation processes. Abstraction of the hydrogen from water leaves toluene near the ground state. In an excess of water, toluene will be consumed by oxidation by the same process. The water will also effectively screen the energy transfer from the benzyl radical to the silica.



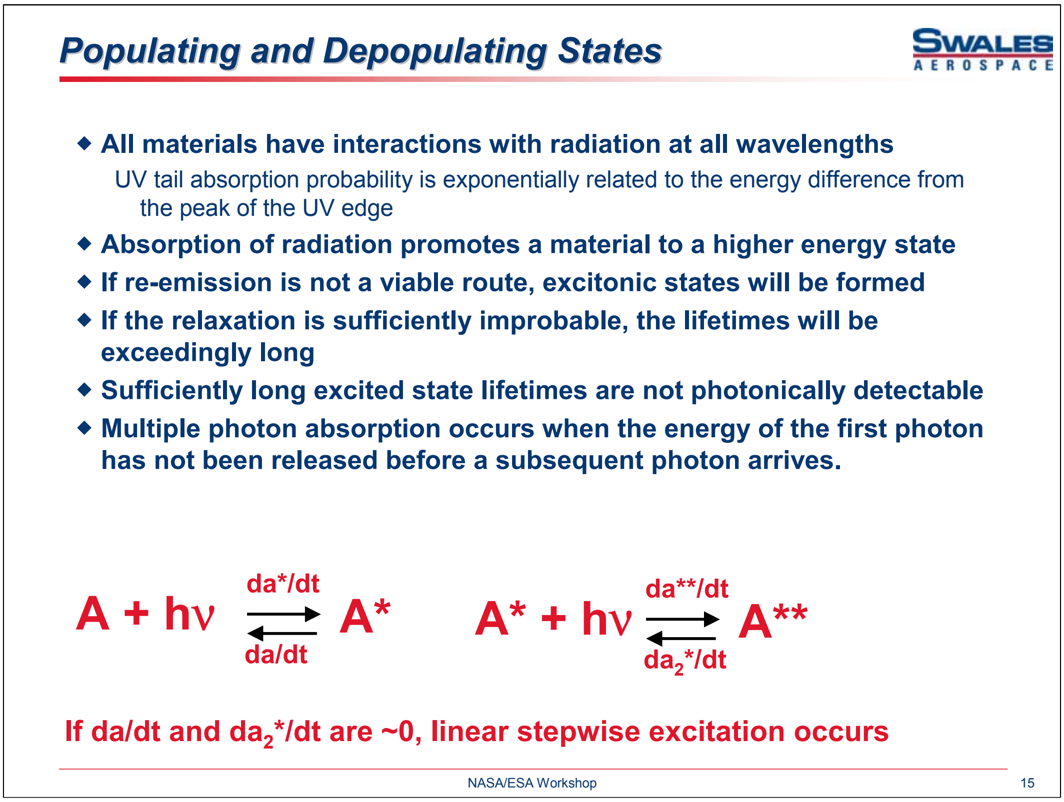
Water Surface Roughening

- Water will react with high energy Si-O-Si, Si-H, and Si-Si bonds forming Si-OH
- Formation of 2 SiOH from Si-O-Si results in a break in the silicaceous structure
- Population of SiOH groups into bulk silicaceous material results in softening of the material and infrared interaction
- Formation of two SiOH adjacent groups results in inhomogeneity formation of a ~0.5 to 1 nm size, with an intrinsic strain
- Point inhomogeneities result in electrostrictive compression and extension due to the incident laser field
- Electrostriction of weakly absorbing species can result in 10^5 G accelerations
- Water is known drive stress corrosion cracking in vitreous silicates

$$R_3Si\text{-}O\text{-}SiR_3 + H\text{-}O\text{-}H \longrightarrow 2\ R_3Si\text{-}OH$$

Water Effects, Surface Roughening

The same hydroxyl radical can abstract hydrogen from the silanols on the surface of the silica as well, leaving the silica in an excited reactive paramagnetic state. The reactive excited state will be more reactive toward hydrolysis than the base silica, and have a larger dielectric response as well. Given an elevated energy, and increased dielectric response, the rate of propagation of micro fractures from the grinding processes will be accelerated. Likewise, the generation of local stresses in the glass will accelerate hydrolysis of the silica at other point inhomogeneities.



Populating and Depopulating States

- **All materials have interactions with radiation at all wavelengths**
  UV tail absorption probability is exponentially related to the energy difference from the peak of the UV edge
- **Absorption of radiation promotes a material to a higher energy state**
- **If re-emission is not a viable route, excitonic states will be formed**
- **If the relaxation is sufficiently improbable, the lifetimes will be exceedingly long**
- **Sufficiently long excited state lifetimes are not photonically detectable**
- **Multiple photon absorption occurs when the energy of the first photon has not been released before a subsequent photon arrives.**

$$A + h\nu \underset{da/dt}{\overset{da^*/dt}{\rightleftarrows}} A^* \qquad A^* + h\nu \underset{da_2^*/dt}{\overset{da^{**}/dt}{\rightleftarrows}} A^{**}$$

If da/dt and da_2^*/dt are ~0, linear stepwise excitation occurs

Populating and Depopulating States

All materials have interactions with incident radiation at all wavelengths. The extinction or absorption phenomenon is related to the index of refraction by Kramers-Kronig relation. As the index of refraction is continuous, the absorption must be also. The presence of a finite intrinsic absorption allows radiation to be absorbed. In many cases, the absorption can lead to formation of excitonic states. If the relaxation of the excitonic stated is sufficiently slow (days, months, years, millennia) with relation to the photon arrival rate, the excited state will behave as a virtual ground state. The stable excited can then be further excited by an independent photon. This eliminates the n-order relationship between an nth level excitation and the photon flux. The limiting factors then become the material’s irradiation history and the intrinsic absorption of the material. Thus, it is not necessary to have high photon flux densities to develop high energy state populations within a material.

Depopulation of excitonic states occurs by a number of well-documented luminescent pathways. Depopulation does not occur significantly by internal decay. As the excitonic states are metastable states, energy is required to overcome the intrinsic barrier energy of the transition. Further, it is necessary for the depopulation transition to provide the requisite energy, momentum, and spin for the emission of a photon. Thus, after forming the excitonic state, the probability of re-emission after an extended duration, is very low. Depopulation can be driven by chemical, radiation, photonic, phononic, mechanical and field induced mechanisms. Chemical, thermal and white light tend to be the primary routes for the depopulation of the excitonic states.

Excited States

- Excited states are distinctly different than unexcited states
- Excited state behavior is entirely different than unexcited behavior

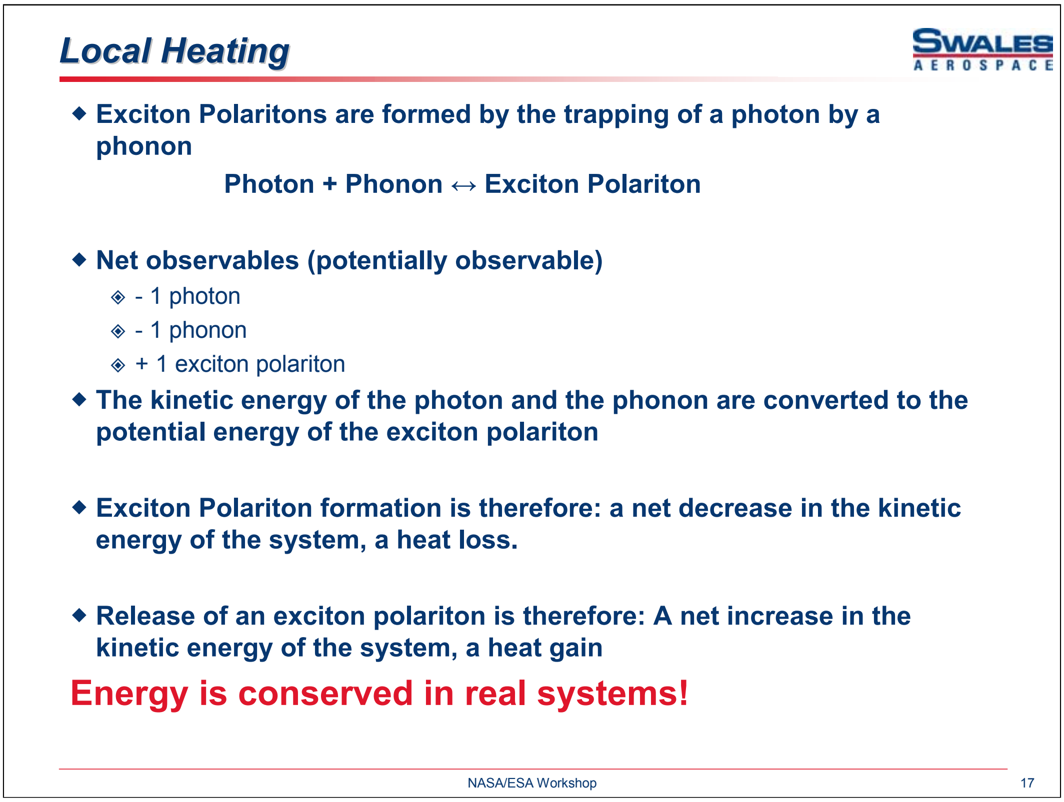
$He + Ne \rightarrow$ No reaction $He^* + Ne \rightarrow HeNe^*$

- Excited states can move up or down in energy

$A + h\nu \leftrightarrow A^*$ $A^* + h\nu \leftrightarrow A^{**}$

- Excited states have higher densities of states and have more energy to interconvert
- Excited states are more polarizable

Higher energy results in weaker attraction of electrons and thus more polarizability and more photo activity



Local Heating

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- Exciton Polaritons are formed by the trapping of a photon by a phonon

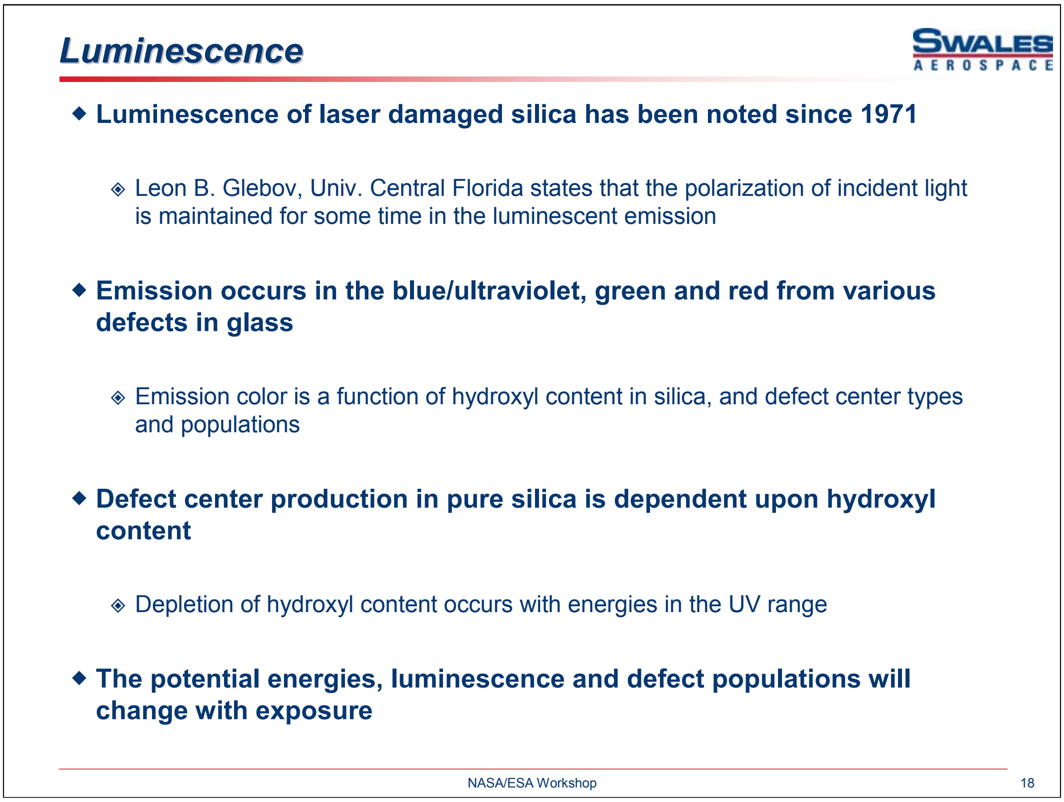
  Photon + Phonon ↔ Exciton Polariton

- Net observables (potentially observable)
  - \- 1 photon
  - \- 1 phonon
  - \+ 1 exciton polariton
- The kinetic energy of the photon and the phonon are converted to the potential energy of the exciton polariton
- Exciton Polariton formation is therefore: a net decrease in the kinetic energy of the system, a heat loss.
- Release of an exciton polariton is therefore: A net increase in the kinetic energy of the system, a heat gain

Energy is conserved in real systems!

Localized Heating

As exciton polaritons are formed from the trapping of a photon by a phonon, the trapping annihilates both a photon and a phonon. In order for the trapping to be long lived, the phonon energy must be well above the ambient energy. This is primarily within the regime of the optical phonons or vibrational regime with optical wavelengths on the order of a few microns. As both the photon and phonon energies are annihilated (as kinetic energy, converted into potential energy) there will be a depletion of kinetic energy during the trapping process, a cooling. This will be a slow cooling based upon the total energy being trapped. In the re-emission of the exciton polariton, it is expected that the release of the trapped photon will release the trapped phonon. The emission will lead to a localized heating in the area due to the creation of phonons from the potential energy, from which the exciton polariton was released.



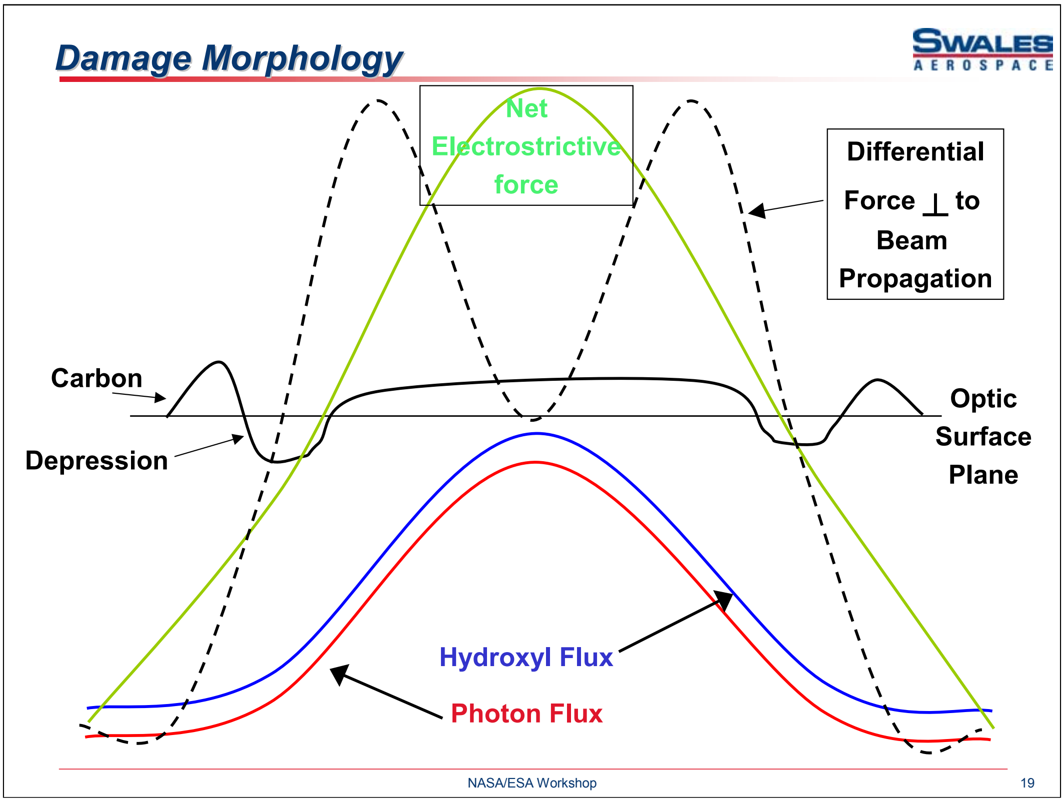
Luminescence

- Luminescence of laser damaged silica has been noted since 1971
  - Leon B. Glebov, Univ. Central Florida states that the polarization of incident light is maintained for some time in the luminescent emission
- Emission occurs in the blue/ultraviolet, green and red from various defects in glass
  - Emission color is a function of hydroxyl content in silica, and defect center types and populations
- Defect center production in pure silica is dependent upon hydroxyl content
  - Depletion of hydroxyl content occurs with energies in the UV range
- The potential energies, luminescence and defect populations will change with exposure

Luminescence

Laser induced optical damage has been noted to result in luminescence. Ginther and Claffy studied this effect to some degree in 1971. Glebov and others have since studied this phenomenon. In previous studies of luminescence and color center formation in solid matrices, it was noted that many different types of absorbed radiation result in very similar luminescent behavior. The emission spectra have been measured both spectrally and temporally for a number of years. It should be apparent that the primary factor in defining the luminescent properties of a material is the material itself, not necessarily the radiation. That is assuming the radiation does not dramatically change the material in a manner inconsistent with the other forms of radiation.

Spontaneous emission and photo-stimulated emission of exciton polaritons have been measured. In addition, in radiation damaged silica, both thermoluminescence and triboluminescence have been detected, as has tribothermoluminescence.



Damage Morphology

In the presence of a photon flux through a dielectric optic, a hydroxyl flux will follow the photonic flux. This is a function of the quantum efficiency and hydroxyl content.

The laser flux will generate an electrostrictive flux proportional to the electric field squared.

The force between adjacent locations will be proportional to the derivative of the electrorestrictive force field. This will result in force regimes resulting in compressive and extensional forces.

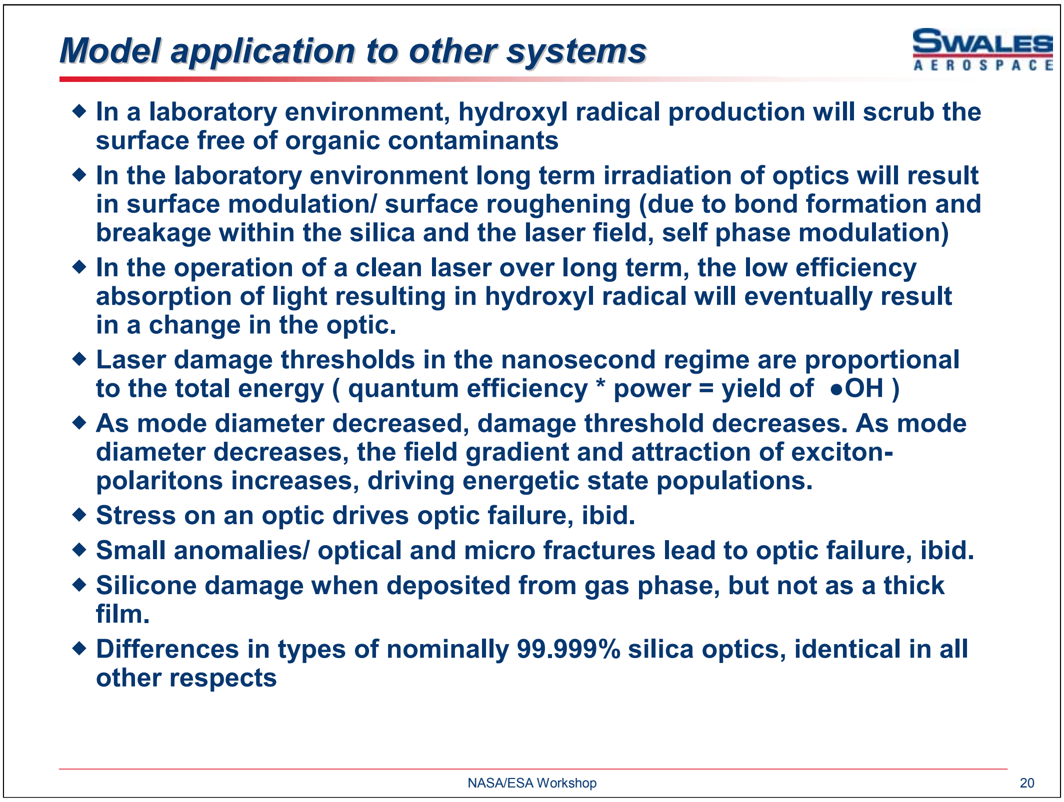
The formation of excited states and hydroxyl fluxes will soften the optical material through the decrease in the electron density between atoms, thereby decreasing the interatomic forces. Adding more energy weakens the molecular structure.

Hydroxyl radical being an energetic oxidizing species, will initiate breakdown of organics.

The exterior region of the beam will attract contaminants. In the exterior region, the hydroxyl radical will be a limiting reactant, driving pyrolytic breakdown.

Moving toward the higher intensity region, the oxidizer concentration will increase, leading to oxidation.

The electrostrictive force will result in the movement of the optical material toward the center of the beam. As the optic's refractive index exceeds that of the ambient environment, the electric field intensity will be higher, resulting in movement toward the lower field, out of the optic.



Model application to other systems

- In a laboratory environment, hydroxyl radical production will scrub the surface free of organic contaminants
- In the laboratory environment long term irradiation of optics will result in surface modulation/ surface roughening (due to bond formation and breakage within the silica and the laser field, self phase modulation)
- In the operation of a clean laser over long term, the low efficiency absorption of light resulting in hydroxyl radical will eventually result in a change in the optic.
- Laser damage thresholds in the nanosecond regime are proportional to the total energy (quantum efficiency * power = yield of ●OH)
- As mode diameter decreased, damage threshold decreases. As mode diameter decreases, the field gradient and attraction of exciton-polaritons increases, driving energetic state populations.
- Stress on an optic drives optic failure, ibid.
- Small anomalies/ optical and micro fractures lead to optic failure, ibid.
- Silicone damage when deposited from gas phase, but not as a thick film.
- Differences in types of nominally 99.999% silica optics, identical in all other respects

Known Behaviors in Silica

Below is a list of known behaviors in the induction of contamination related laser induced optical damage.

Damage does not occur at a uniform constant probability. Hovis

Toluene initiates laser optic damage.

Toluene is found in 3M Scotchweld adhesives, residence time of toluene is long.

Toluene does not interact strongly with 1064nm or 532 nm light, in the first order.

Exciton polariton populations are created in the range of 1,3 & 4 eV when exposed to air. Up to 7eV or more in vacuum in combined 532nm & 1064nm laser.

Energy is required to create damage. Photoemission is seen with damage events.

Degradation of damage thresholds occurs with repeated sub damaging exposure.

Green and UV photoemission is seen from damaged glass.

Polarization of damaging radiation is maintained in the re-emission of the light from the glass.

At least four photoluminescent lifetimes are known for radiation damaged silica. Microsecond, day, week, millennium.

Changes in optical glass due to solar exposure, M. Faraday(1825). Determination of exposure band related to color center formation Duzing (1938),

Color center generation approaches a near zero activation energy at ~ 210nm. Glebov

Toluene and Xylene (benzyl radical) quenching from the first excited state is very fast ~ 1 collision, approximately 10-10seconds at one atmosphere. Quenching is transfer of energy in form of an unpaired electron.

Toluene in the presence of oxygen and/or water does not readily result in damage.

There is an induction period for toluene/contamination induced damage.

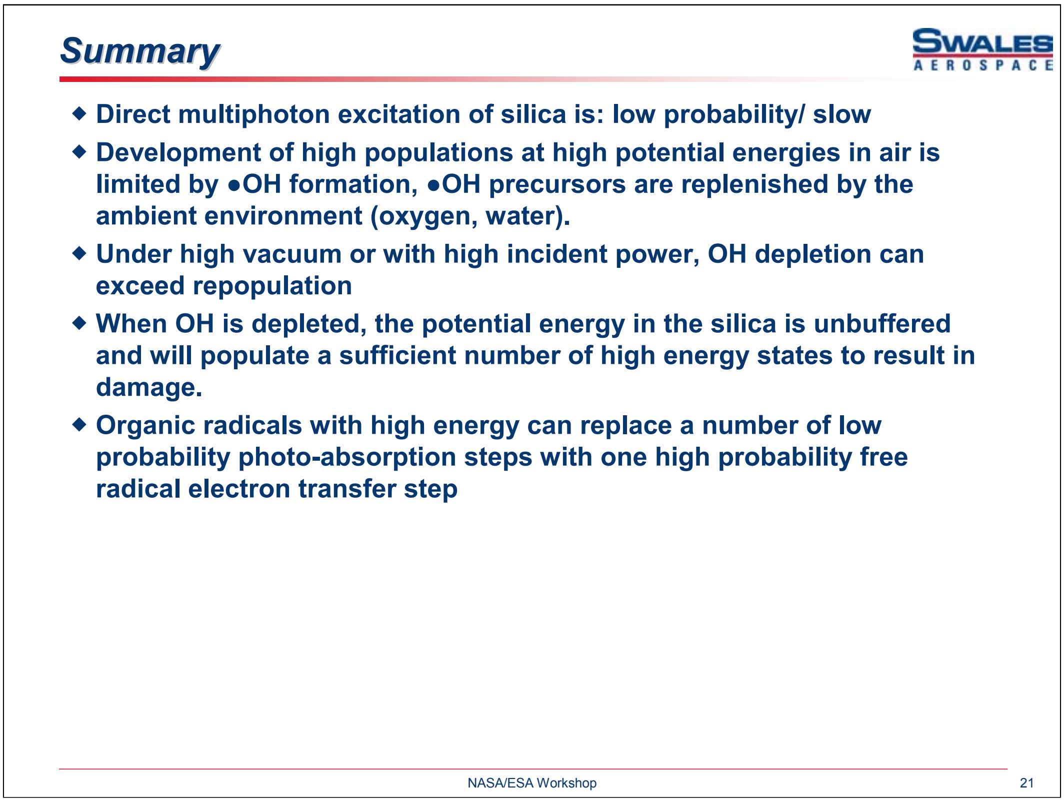
Toluene fluorescence is highly quenched on surfaces.

Benzyl radical formation and quenching provides the formation and transport of 4.66eV quanta at a transition probability at a surface of ~1.

Interaction of 4.66 eV quanta (metastable states) with 1.17eV photons gives 5.83eV which is ~ the minimum for color center formation, and therefore rate maximum.

Organic molecules are highly active in terms of multiple photon absorption.

Aromatic molecules such as toluene and xylene are highly effective in transferring energy from one molecule to another, which is why they are often used in scintillation counting systems.



Summary

- Direct multiphoton excitation of silica is: low probability/ slow
- Development of high populations at high potential energies in air is limited by ●OH formation, ●OH precursors are replenished by the ambient environment (oxygen, water).
- Under high vacuum or with high incident power, OH depletion can exceed repopulation
- When OH is depleted, the potential energy in the silica is unbuffered and will populate a sufficient number of high energy states to result in damage.
- Organic radicals with high energy can replace a number of low probability photo-absorption steps with one high probability free radical electron transfer step

Irradiation of glass by radiation from sources such as UV, x-ray, gamma, electron and laser irradiation affects glass in relation to the radiation absorbed dose (RAD). This dose will result in changes in the physical and chemical properties of the glass. Population of elevated energy states occurs through the population of metastable states in the glass. Including the softening of the glass.

Conclusions

The model appears to fit the contamination aggravated laser induced optical damage.

- **It describes:**
  - Damage composition and morphology
  - Precursor creation and annihilation
  - Propagation and inhibition
  - The chemistry and the physics

It provides coalescence of phenomenological laser damage, materials properties, environmental factors and laser intensity into a relatively concise description.

Raman Spectra