

Surface Absorption Polarization Sensors (SAPS)

Final Technical Report

Laser Probing of Immobilized SAPS Actuators Component

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Executive Summary

A novel hypothesized detection scheme for the detection of chemical agents was proposed: SAPS “Surface-Adsorbed Polarization Sensors”. In this technique a thin layer of molecular rotors is adsorbed to a surface. The rotors can be energized by light absorption, but are otherwise locked in position or alternatively rotate slowly. Using polarized light, the adsorbed rotors are turned as an ensemble. Chemical agent (analyte) binding that alters the rotary efficiency would be detected by sensitive polarized absorption techniques. The mechanism of the SAPS detection can be mechanical, chemical, or photochemical: only a change in rotary efficiency is required.

To achieve the goal of SAPS detection, new spectroscopic technique, polarized Normal Incidence Cavity Ringdown Spectroscopy (polarized NICRDS), was developed. The technique employs very sensitive and general Cavity Ringdown absorption spectroscopy along with the ability to perform polarized absorption measurements. Polarized absorption offers the ability to measure the angular position of molecular chromophores. In the new experiments a thin layer of SAPS sensors (roughly corresponding to a monolayer coverage on a surface) immobilized in PMMA. The PMMA layer is less than 100 nm thick and is spin-coated onto a flat fused-silica substrate.

The new technique was applied to study the photoisomerization-driven rotary motion of a family of SAPS actuators based on a family of substituted dibenzofulvene rotors based upon 9-(2,2,2-triphenylethylidene)fluorene. By varying the substitution to include moieties such as nitro, amino, and cyano the absorption spectrum and the quantum efficiency of photoisomerization can be varied. This SAPS effect was readily detected by polarized NICRDS.

The amino substituted SAPS actuator binds H^+ to form an ammonium species which was shown to have a much larger quantum efficiency for photoisomerization. A thin layer of immobilized amino actuators were then shown by polarized NICRDS to have a propensity for the angular control of rotary motion to be strongly influenced by the presence of the H^+ analyte: the SAPS actuators can readily detect the presence of a H^+ analyte at 1 equivalent concentration. Because the total number of SAPS actuators in the probe volume of the film is small, the amount of analyte detectable can be very low.

A variety of SAPS actuator structures based on dibenzofulvene rotors are possible that could bind other analytes. It appears that analyte binding that alters the electron density in the dibenzofulvene ring is sufficient to create a detectable change in the rotary efficiency. If the analyte is strongly bound to the rotor, the SAPS actuator behaves in a dosimeter mode. Weak, reversible binding would allow for monitoring of varying concentrations.

1 Original Hypothesis

1.1 Operational concept

The proposed SAPS actuators were envisioned to consist of two components, a planar rotor chromophore (depicted in red in Fig. 1) and a tripod base unit (depicted in blue in Fig. 1). The molecular structure of the SAPS actuators is designed so that the plane of the rotor chromophore is inserted between “teeth” on the tripod base. The gearing interaction of the rotor into the teeth of tripod can be made sufficiently strong such that the unenergized rotor chromophore is stationary on the timescale of detection of its angular orientation. The rotor can be functionalized so that it reacts with and covalently binds targeted analyte molecules.

Upon absorption of light of the correct wavelength, the SAPS actuator is energized and its rotor chromophore undergoes a photoisomerization process which changes the angular orientation of the rotor with respect to the base unit. This change is depicted on the top line of Fig. 1 below. Binding of an analyte molecule to the SAPS actuator will hinder or prevent photoisomerization of the rotor chromophore, as depicted on the lower line of Fig. 1.

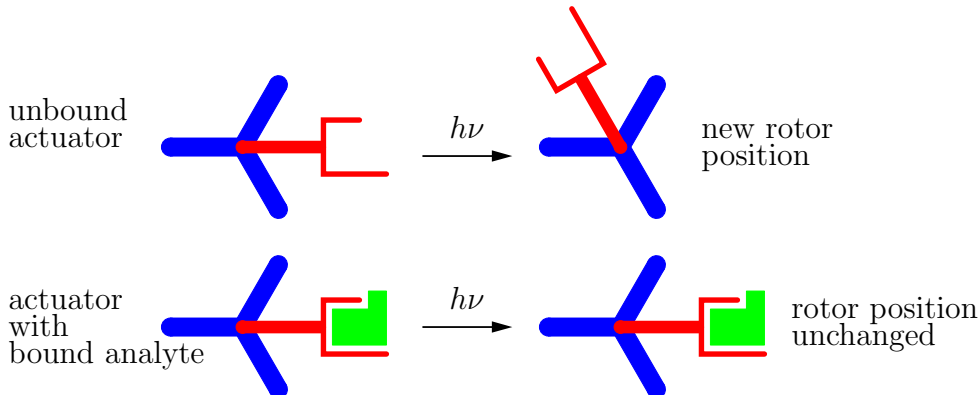


Figure 1: SAPS actuator operation.

This change in the photoisomerization efficiency upon analyte binding is measured by polarized excitation and absorption spectroscopy and provides a direct indication of the presence of the analyte. In a SAPS device the tripod bases of actuator molecules will be immobilized onto an optical substrate surface with random rotor chromophore orientations. In Fig. 2, the initial random angular distribution of actuator positions is depicted as the array of red lines on the left. A polarized laser beam energizes those rotors aligned with the light polarization, creating a temporary angular “hole” in the orientational distribution, as shown on the right side of Fig. 2.

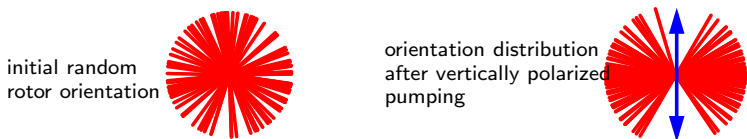


Figure 2: Orientational hole burning due to absorption of polarized light.

1.2 Surface absorption cavity ringdown detection

The rotary motion describe above was to be detected by cavity ringdown absorption spectroscopy (CRDS), an extremely sensitive absorption technique that has been pioneered in gas phase experiments over the last 20 years.^{1,2,3,4} This technique utilizes a high- Q optical resonator cavity. The intensity of a short laser light pulse injected into the resonator decays exponentially and has a long residence lifetime (typically microseconds). The lifetime, τ , is shortened if an absorber (such as an analyte molecule) is inserted into the cavity. The change in lifetime is directly related to the absorption per pass according to

$$\tau = \frac{t_r}{2[(1-R) + \alpha l_s]} \quad (1)$$

where t_r is the round-trip time for light in the cavity, l_s is the cavity length, R is the fractional reflectivity of the cavity mirrors, and α is the absorption coefficient of the sample. The ring-down lifetime is therefore a direct measure of the absorption of the sample. The key feature of the technique is that source amplitude noise is of no concern, because the lifetime of the ringdown is independent of the amplitude of the laser pulse injected into the cavity. Absorptions of 3×10^{-7} *per pass* can be detected in a single measurement using gas-phase samples.⁴

Prior to our work, CRDS had been extended to surface adsorbed species. One scheme for using the technique is to study the absorption spectroscopy of surface-adsorbed analyte molecules on a special prism inserted into the cavity. The light in the cavity undergoes total internal reflection from the prism and its evanescent wave excites the adsorbed molecules.^{5,6,7,8,9,10} The evanescent wave cavity ringdown technique can match or surpass the sensitivity of ATIR methods, but still requires a special, and potentially expensive prism on which the sample is adsorbed. Alternatively a substrate optical flat can be attached to the prism using an index-matching compound, however this introduces additional losses into the ringdown cavity, thereby lowering the sensitivity of the measurement.

More sensitivity and experimental simplicity can be obtained if the sample is directly mounted in the resonator cavity in such a way that the ringdown light travels directly through the a transparent substrate on which the analyte is adsorbed. The difficulty with this approach is reflective losses from the surface of the substrate.

If the substrate is positioned at the center of the cavity and aligned perfectly orthogonal to the cavity axis, there are sufficiently low reflection losses to enable CRDS spectroscopy.^{11,12} However this requires extremely careful alignment. A much easier approach is to position the optically transparent substrate at Brewster’s angle. Then p -polarized light in the cavity suffers no reflective losses and no special alignment are is required. This technique has been demonstrated for both the infrared¹³ and visible¹⁴ wavelengths. In the infrared this technique offers two orders of magnitude better sensitivity than the best ATIR methods with a fractional absorption sensitivity of 2×10^{-7} with signal averaging of 10^4 decays.¹³ For visible wavelengths, the sensitivity has been previously reported for one monolayer of a visible chromophore.¹⁴

1.3 Detection of angular position of surface immobilized actuators

As discussed in Sec. 1.1, the function of the receptor relies upon the change in efficiency of light-induced rotary motion upon analyte binding. In order to detect this efficiency, we originally pro-

posed to use Brewster-angle cavity ringdown spectroscopy (see Sec. 1.2) to detect the angular position of the rotors. As part of this project we ultimately utilized a new polarized version of the “perfectly orthogonal” detection geometry mentioned above^{11,12} to probe the rotor angular position distribution. Here we refer to this new technique as polarized “Normal Incidence Cavity Ringdown Spectroscopy” (polarized NICRDS). However the original microscopic picture remains valid.

To understand how the detection scheme works, we consider relative angular orientation of three vectors, depicted in Fig. 3 for surface-adsorbed SAPS receptors:

Transition dipole moment vector of actuator rotor. This vector, μ , lies in the plane of the dibenzofulvene rotor chromophore of the SAPS receptor. The transition dipole μ for the (π, π^*) transition of the rotor chromophore is expected to be polarized perpendicular to its molecular plane, and therefore nearly parallel to the surface.

Electric vector of drive light. This is the electric vector, $\mathbf{E}_{ex}$ of the exciting laser beam that drives the photoisomerization of the actuator. The angular probability, P_{ex} , for excitation of the actuator is given by

$$P_{ex} \propto \cos^2(\hat{\mathbf{E}}_{ex} \cdot \hat{\mu}) \quad (2)$$

Electric vector of the probe light. This is the electric vector, $\mathbf{E}_{abs}$, of the probe laser beam that measures the angular position of the actuator rotor. The angular probability, P_{abs} , for probe absorption of the actuator is given by

$$P_{abs} \propto \cos^2(\hat{\mathbf{E}}_{abs} \cdot \hat{\mu}) \quad (3)$$

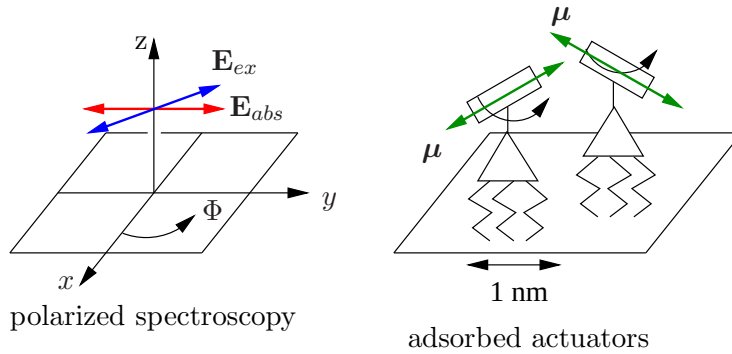


Figure 3: Polarized excitation and absorption spectroscopy of surface adsorbed actuators.

Those actuator rotors having transition dipoles aligned parallel to the electric vector of the light polarization have a higher absorption cross section. To detect the rotor positions, our strategy is to create an anisotropy in the population of the immobilized actuator rotors using a train of linearly polarized laser pulses. The laser polarization is then changed so that the anisotropy evolves as subsequent laser pulses are delivered. The absorption polarized in a particular direction is be detected by CRDS spectroscopy. Prior to this project, the device in Fig. 4 was in use in the Cline laboratory. The key elements are shown in Fig 5 for clarity. They consist of the Brewster Plate

(BP) on which the SAPS actuators have been immobilized, along with the ringdown cavity defined by the two spherical mirrors. The drive laser beam is shown in blue, and its polarization state can be controlled by standard techniques. The polarization of the trapped probe laser pulse in the ringdown cavity is vertical, and its trajectory is shown in red. Other optics, lasers, and detectors are not shown in Fig. 5 for simplicity. The experiment then consists of measuring the ringdown lifetime (and hence SAPS actuator absorption) as a function of the polarization state of the drive laser beam.

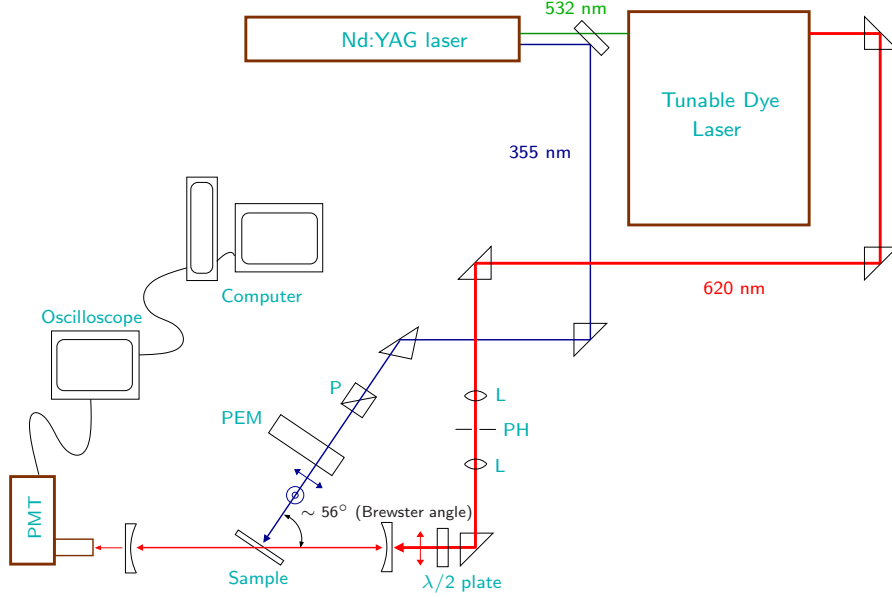


Figure 4: Apparatus for absorption measurements of surface adsorbed chromophores by Brewster-angle cavity ringdown spectroscopy. PEM = photoelastic modulator, PMT = photomultiplier detector.

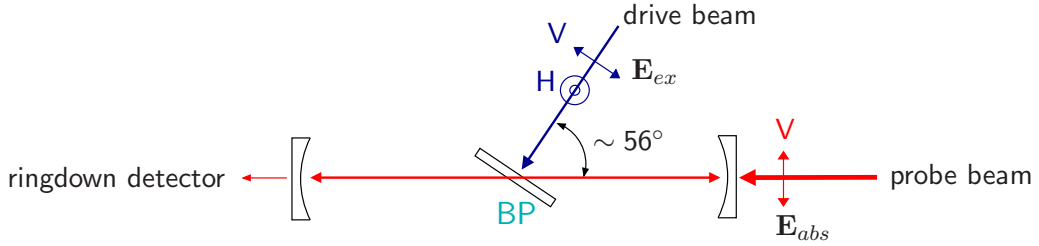


Figure 5: Schematic representation of cavity ringdown detection apparatus.

We model such an experiment using an ensemble of 10^5 rotors with random base orientations on the surface. Initially the actuator rotor is thermally locked into any of the three equivalent sites of the base. Therefore, prior to exposure to the drive laser radiation, the angular population of the rotors is isotropic. Figure 6 shows evolution of the angular distribution of actuator rotors as the polarization of the drive wavelength is changed. Each panel in Fig. 6 represents the angular probability of rotor orientations on the surface xy -plane as a radial polar plot.

Step 0 In Fig. 6, the isotropic initial distribution is depicted as a circularly symmetric polar plot

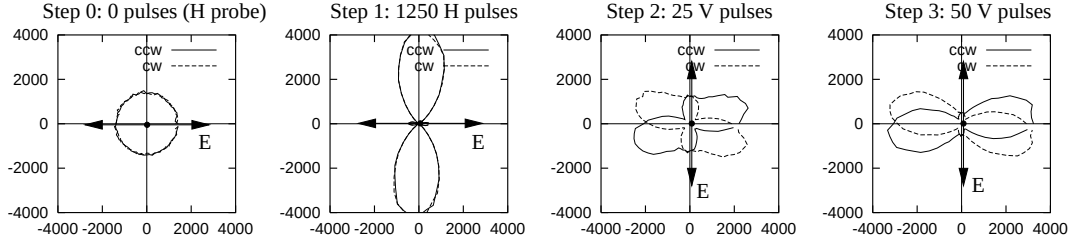


Figure 6: Rotor angular orientation population distribution for adsorbed actuators.

of the angular population about the azimuthal angles of the SAPS rotors with respect to the surface normal. (Fig. 7 depicts azimuthal angle Φ of a single adsorbed SAPS actuator.)

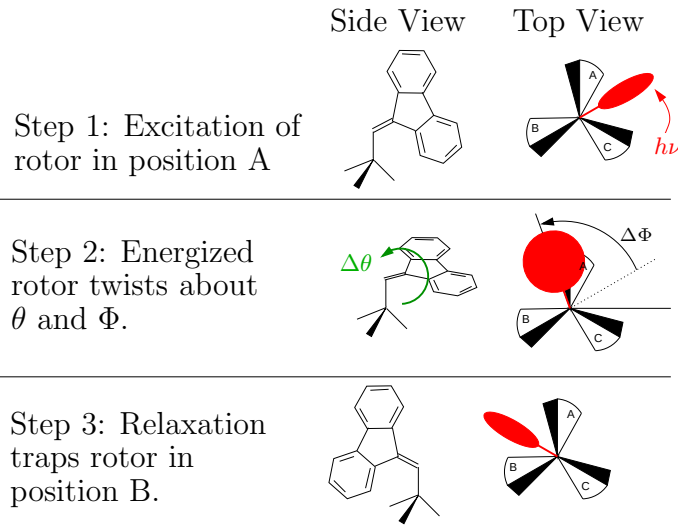


Figure 7: Photoisomerization dynamics of SAPS actuator rotor geared into immobilized trityl “stator” base. For simplicity the trityl base structure is not explicitly shown.

Step 1 Drive laser pulses energize the immobilized SAPS rotors, with an arbitrary 5% overall probability per molecule per absorbed photon for a successful rotation by 120° depicted in Fig. 7. In this Monte Carlo simulation, 1250 H -polarized drive laser pulses energize the SAPS actuators. (H -polarized drive pulses in Fig. 5 are polarized along the x -axis in Figs. 3 and 6.

As rotors with transition dipoles aligned along the x -axis selectively absorb and rotate, the angular probability of the ensemble along the x -axis is depleted. Ultimately, the angular probability of transition dipoles becomes directed along the y -axis, preferentially perpendicular to the drive polarization (where the actuator rotors become “stuck” due to the perpendicular orientation of $\mathbf{E}_{ex}$ and $\boldsymbol{\mu}$.) The angular distribution of chromophore transition dipoles approximately has a $\sin^2 \Phi$ dependence, where Φ is the azimuthal angle in the xy -plane, measured from the x -axis in Figs. 3 and 6. The distribution in the Step 1 panel of Fig. 6 is a steady-state angular population that would not evolve if additional horizontally polarized drive pulses were delivered. This angular distribution would cause a dramatic decrease in the ringdown lifetime, because the rotors have been selectively oriented so that their transition dipoles, $\boldsymbol{\mu}$, are now vertical and parallel to the probe beam, resulting in a large absorption

(cavity loss).

Steps 2 and 3 Now the drive polarization is set to V and drive pulses are applied to disturb the alignment created in Step 1. Some SAPS rotors move clockwise, and others counter-clockwise, but the ultimate result is that the ringdown lifetime will dramatically increase, as the transition dipoles, μ , of the SAPS rotors become directed orthogonal to the V -polarization of the light trapped in the ringdown cavity. Ideally, in this case there is no absorption by the actuator rotors and therefore low cavity loss. The ultimate steady-state angular distribution will have an approximate $\cos^2 \Phi$ functional form that is being approached in the right panel of Fig. 6.

This process can be thought of as creating a “polarization hole” and then subsequent refilling of the hole. (Such experiments are sometimes called hole-burning experiments.) **The rate with which the hole can be created (or refilled) as a function of the number of drive laser pulses gives the relative rotary efficiency of the actuator.**

2 Project Accomplishments

We have studied a family of substituted dibenzofulvene rotors based upon 9-(2,2,2-triphenylethylidene)fluorene or “TEF” with a generic structure shown in Fig. 8. These structures can be divided into a dibenzofulvene “rotor” moiety and a triphenylmethane “stator” moiety. These components are connected by an exo-cyclic double bond, which plays the key role in actuation by photoisomerization. The family of “TEF” molecules has been synthesized at Nevada by the group of Prof. Thomas Bell, as a separate DOE component of this project. Our group previously reported that the tert-butyl substituted dibenzofulvene rotors “TTEF”.¹⁵ In this project we showed that the amino (-NH_2) substituted dibenzofulvene rotor “ATEF” is a SAPS actuator with an efficiency that depends upon the proton concentration in its environment.

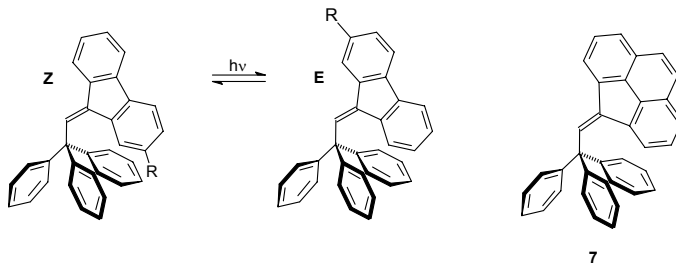


Figure 8: Generic structure of a SAPS rotor with a substituent R . Photon absorption causes photoisomerization that exchanges the Z and E isomers. The structures with $R = t\text{-butyl}$, $R = \text{NH}_2$, $R = \text{NO}_2$, and $R = \text{CN}$ are abbreviated TTEF, ATEF, NTEF, and CTEF, respectively. The structure on the right shows an alternative rotor structure (not reported on here).

These results of the project can be categorized into two components, the demonstration that the amino SAPS rotor efficiency can be altered by binding with H^+ , and the polarized detection of that binding by surface-adsorbed SAPS rotors.

2.1 Photoisomerization upon proton binding by an amino-substituted SAPS rotor

We have previously reported measurements of the photoisomerization efficiency of *t*-butyl substituted rotors TTEF ($R = t$ -butyl in Fig. 8).¹⁵ Here we use similar methods to measure the photoisomerization quantum yield ϕ of the SAPS actuator “ATEF” that is amino substituted ($R = \text{NH}_2$ in Fig. 8).

The effect of protonation was examined for the molecules ATEF, NTEF ($R = \text{NO}_2$), and CTEF ($R = \text{CN}$). The molecules were studied at room temperature in acetonitrile solvent, and the Z and E isomer populations followed by high-pressure liquid chromatography.

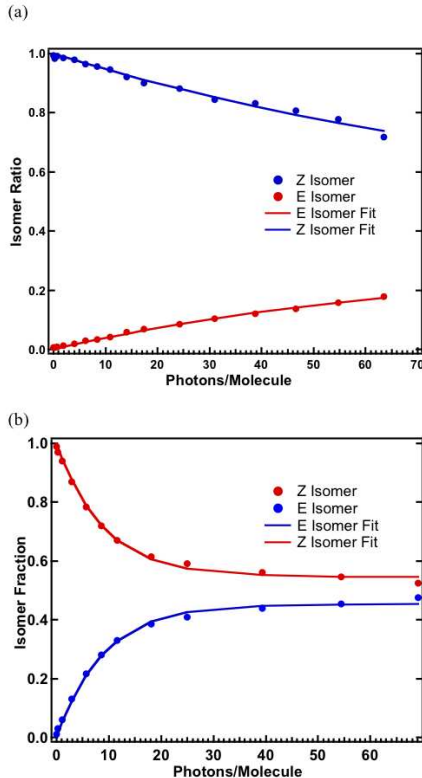


Figure 9: Mole fractions of Z and E ATEF isomers measured by high-pressure liquid chromatography as a function of the average number of photons absorbed at 266 nm. (a) Results in acetonitrile solvent. (b) Results in acetonitrile with 1.5 equivalents of trifluoroacetic acid.

Figure 9 shows the photoisomerization kinetics of ATEF measured when a solution initially containing only the Z-ATEF isomer is irradiated at 266 nm. The photoisomerization kinetics are dramatically faster when 1.5 equivalents of trifluoroacetic acid (TFA) are present in solution. Kinetic modelling of the unprotonated ATEF data in Fig. 9(a) gives a $E \rightarrow Z$ quantum yield of $\phi_{EZ} = 0.76 \times 10^{-2}$ and a $Z \rightarrow E$ quantum yield of $\phi_{EZ} = 0.41 \times 10^{-2}$. Protonated ATEF with 1.5 equivalents of TFA gives quantum yields of $\phi_{EZ} = 8.94 \times 10^{-2}$ and $\phi_{EZ} = 5.49 \times 10^{-2}$, more than an order of magnitude increase. Preliminary results in our laboratory using the extremely

strong triflic acid gives quantum yields that are approximately 4 times larger than protonation by TFA. This strong dependence on H^+ concentration is only observed with the amino substituted ATEF compound, for example, addition of acid to solutions of NTEF and CTEF has no effect on photoisomerization efficiency within experimental error.

The origins of the increased ATEF photoisomerization quantum yield upon protonation were analyzed. A study of a sequence of R groups in Fig. 8 shows that more electron donating substituents exhibit lower photoisomerization quantum yields. The lone pair on the amino substituent in ATEF makes it highly electron donating, and consequently it has a low photoisomerization quantum yield. Protonation of NH_2 to create an ammonium, NH_3^+ , creates an electron withdrawing substituent. The photoisomerization quantum yield is then observed to increase.

The dependence of the ATEF photoisomerization quantum yield with protonation is therefore an ideal simple test case for SAPS detection of an analyte. In this case the analyte is H^+ .

2.2 Surface Immobilized Results

The photoisomerization of ATEF, NTEF, and CTEF were all studied by polarized NICRDS when immobilized in a thin polymethyl methacrylate polymer (PMMA) film. The film was prepared from a 1 mg/mL solution of PMMA (average MW = 1200 g/mol) in spectroscopic grade toluene solvent. The typical concentration of NTEF in the coating solution is (1:10) (NTEF:PMMA) by mass. A 50 μ L sample of this solution was spin-coated (1500 rpm for 60 s) onto high quality, flat, fused silica substrates (CVI, surface flatness = 10-5, 5 seconds deviation between the two surfaces). The thickness of the polymer layer is expected to be in the range 10-50 nm, based on previous studies of films prepared with the same spin-coating recipe.

Prior to coating, substrates were cleaned by wiping with methanol, and then sonicated for one hour in an aqueous soap solution, rinsed with distilled water, sonicated in an aqua-regia solution for one hour followed by rinsing with doubly distilled water, concentrated ammonia solution, and dried in an oven at 100 $^{\circ}$ C. The coated fused silica substrate was placed in the center of the cavity ringdown spectrometer. The cavity consists of two parallel, highly reflective mirrors (Los Gatos Research, $R = 0.9995$ at 355 nm, radius of curvature = 1.0 m). The substrate was aligned to be normal to the cavity axis using precision rotary stages. Achieving a normal incidence geometry is critical to maximizing the lifetime of photons trapped in the optical cavity, and hence the sensitivity of the absorption measurements. The distance between the two mirrors was 75 cm.

All measurements were made at room temperature in ambient air. The experimental apparatus is shown in Fig. 10. The experiments are of the “pump-probe” type. A linearly polarized “drive” laser pulse was used to excite the sample with pulse energies between 12.0 μ J and 300.0 μ J. The probe beam consists of a circularly-polarized pulse injected into the NICRDS cavity to measure polarized absorption. Both pulses were obtained from the third harmonic (355 nm) of a 5 ns pulse, 10 Hz repetition rate, Nd:YAG laser. As shown in Fig. 10, the drive beam direction is $\hat{k}_d$ and the probe beam direction is $\hat{k}_p$. The two beams intersect at the coated surface of the fused silica substrate. On the substrate drive beam spot size had diameter of 0.3 mm, the probe beam was smaller in diameter and hits the center of the drive beam spot. In our NICRDS apparatus the drive and probe beams can not be completely collinear, so the drive beam, $\hat{k}_d$, is not perfectly normal to the substrate. In our apparatus the deviation from normal is 7 $^{\circ}$. The polarization of the drive beam was linear and the laboratory frame polarization angle was controlled by a half-wave plate, $\lambda/2$. The probe pulse passed through a pinhole spatial filter to improve its transverse mode

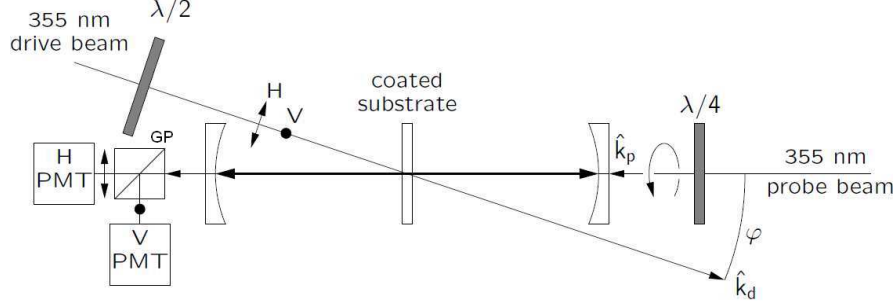


Figure 10: The NICRDS apparatus and associated polarization and detection optics. The vector $\hat{\mathbf{k}}_p$ is the direction of the circularly-polarized probe light and $\hat{\mathbf{k}}_d$ is the direction of the linearly-polarized drive light. The optics $\lambda/2$ and $\lambda/4$ are half- and quarter-wave plates, respectively. GP is a Glan prism.

quality, and then converted to circular polarization by a quarter wave plate, $\lambda/2$, immediately prior to entering the cavity. Following the second cavity mirror, a Glan polarizing prism separated the escaping probe light into its horizontal “H” and vertical “V” polarization components, which were measured by separate photomultiplier detectors. The individual H and V ringdown decay transients were simultaneously recorded by separate channels of a two-channel digital oscilloscope and individually transferred to a computer. Individual decay transients were fit to an exponential decay to obtain the cavity lifetime, τ . A “blank” cavity lifetime, τ_b , was measured for each channel the start of the experiment, prior to the irradiation by drive pulses. The reflectivity of the cavity mirrors, scattering by the PMMA matrix, and substrate scattering all contribute to τ_b , in addition to the initially isotropic absorbance of the NTEF molecules immobilized in the PMMA film. After irradiation by the drive pulse the cavity lifetime, τ , is converted to a change in absorbance relative to the “blank”, making use of the relation¹⁴

$$a = \frac{l}{c} \left(\frac{\tau_b - \tau}{\tau_b \tau} \right) \quad , \quad (4)$$

where l is the cavity length, c is speed of light, τ_b is the blank lifetime, τ is the measured lifetime.

Using Eq. 4, the initial absorbance of the initially isotropic NTEF ensemble, a , is defined as zero. Following irradiation by the drive beam, a change is observed in both the vertical and the horizontal absorbance.

To focus on the polarization difference the difference absorbances, $\Delta a(V)$ and $\Delta a(H)$, measured in each polarization channel subtracted from the average of the two channels:

$$\Delta a(V) = \frac{a(V) - a(H)}{2} \quad , \quad (5)$$

$$\Delta a(H) = \frac{a(H) - a(V)}{2} \quad , \quad (6)$$

Figure 11 shows the results of a polarized NICRDS experiment on NTEF in a PMMA matrix.

The transition dipole vector, μ , of NTEF lies in the plane of the two benzene rings of 2-nitrofluorene actuator moiety. The linearly polarized drive light preferentially energizes molecules having rotor moieties parallel to $\hat{\epsilon}$, the electric vector of the drive light. Absorption of light results in moving μ to a new direction. This results in reversible “hole burning” in the angular distribution of the molecular transition dipoles. Changing the polarization of the drive beam refills the existing hole and create a new hole in the direction parallel to the new polarization, as shown in Fig. 11. Alternating the drive beam polarization (vertical and horizontal) yields multiple cycles of hole burning and refilling. The overall average of both probing polarizations shows a first order decay, which we attribute to some photodecomposition of the NTEF. This is evident in the decreasing amplitude of the envelope containing the Δa oscillations in Fig. 11.

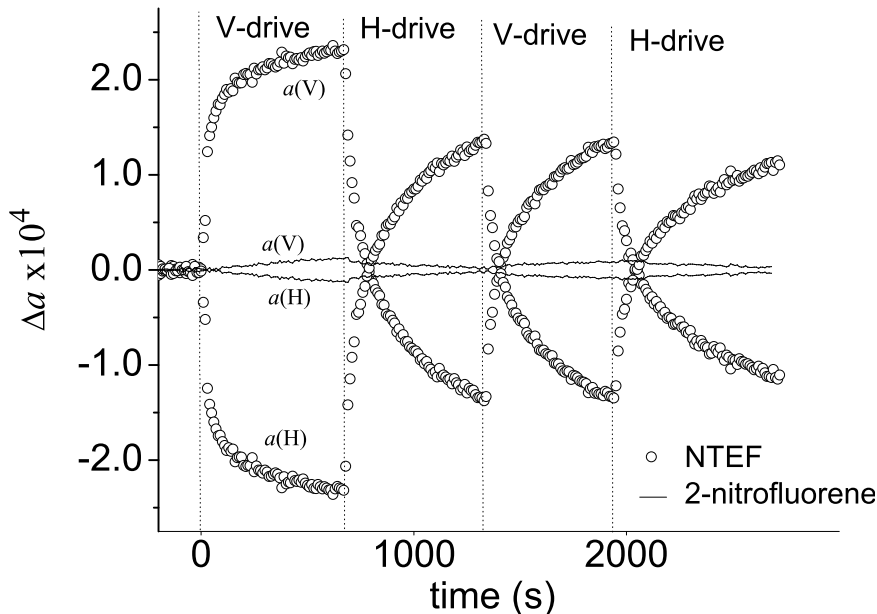


Figure 11: A comparison of the polarization effect for NTEF molecule and the 2-nitrofluorene, under the same experimental conditions; the weight ratio of either molecule to the PMMA is (1:60), drive energy pulse equal to 100 $\mu\text{J}/\text{pulse}$.

An important question is whether photoisomerization is essential to angular hole burning, or is the effect primarily due to local heating by absorption of the drive light. To investigate this issue we studied PMMA films containing the molecule 2-nitrofluorene, a similar chromophore which cannot photoisomerize. After accounting for the molar absorptivity of 2-nitrofluorene (about half that of NTEF) and its molecular weight relative to NTEF, films of 2-nitrofluorene and NTEF having the same mass concentration have nearly the same optical density. Fig. 11 shows a comparison of the angular hole burning observed for 2-nitrofluorene and NTEF molecules with same concentration to PMMA (1:60); in the first oscillation the polarization difference in 2-nitrofluorene is about 6% of that obtained in the NTEF experiments. Moreover, in the longer term irradiation of 2-nitrofluorene the polarization effect becomes even smaller (less than 2%) and changing the drive light polarization cannot destroy the initially created hole.

The experiments on NTEF actuator angular hole burning demonstrate the SAPS hypothesis that

was the basis for the proposed work. To demonstrate the detection capabilities of SAPS actuators we studied the ATEF actuator immobilized in PMMA. In these experiments a 1:10 solution of ATEF:PMMA by mass in toluene solvent was spin-coated onto a fused silica substrate. Varying amounts of TFA were added to the spin-coated solution. The resulting surface-adsorbed matrix was then studied by polarized NICRDS to evaluate the efficiency of hole-burning with H^+ concentration.

The results of these experiments are shown in Fig. 12. Protonation by TFA dramatically increases the magnitude of the angular hole burning and also the rate at which the hole is created. Similar experiments conducted on the NTEF rotor show no such dependence on H^+ concentration. Experiments of this type have also been performed in vacuum on a PMMA matrix containing ATEF but no TFA. This unprotonated matrix show a rapid acceleration in angular hole burning with dosed with a vapor containing HCl.

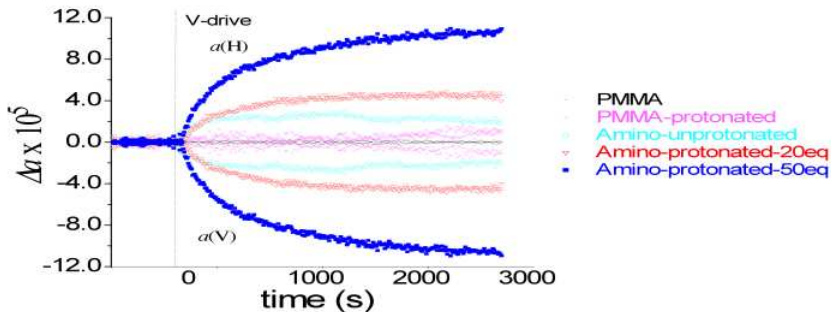


Figure 12: Angular hole burning for the ATEF rotor in a PMMA matrix irradiated at a drive wavelength of 266 nm and probed by polarized NICRDS at 355 nm. Color-coded traces show the magnitude of holes burned in a PMMA matrix with no ATEF (with and with TEA), with ATEF but no TEA, and with ATEF and 20 and 50 equivalents of TFA. The results show that ATEF must be present to observe angular hole burning, and that the hole burning is a strong function of the number of equivalents of TFA present in the matrix.

3 Summary and Conclusions

A new spectroscopic technique, polarized Normal Incidence Cavity Ringdown Spectroscopy, was developed to probe a thin layer of SAPS sensors immobilized in PMMA. The technique offers the ability to probe the angular distribution of molecular chromophores by highly sensitive polarized absorbance measurements.

The new technique was applied to study the rotary motion of a family of SAPS actuators based on substituted dibenzofulvene chromophores, shown in Fig. 8. The NTEF, ATEF, and protonated ATEF experiments validate the SAPS hypothesis. SAPS actuators can readily detect the presence of a H^+ analyte at 1 equivalent concentration. If the analyte is strongly bound to the rotor, the SAPS actuator behaves in a dosimeter mode. Weak, reversible binding would allow for monitoring of varying concentrations. Because the total number of SAPS actuators in the probe volume of the film is small, the amount of analyte detectable can be very small. A variety of SAPS actuator structures based on dibenzofulvene rotors are possible that could bind other analytes. It appears that analyte binding that alters the electron density in the dibenzofulvene ring is sufficient to create

a detectable change in the rotary efficiency.

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