Effect of Simple Aliphatic Alcohol Thin Films on the Laser Induced Excimer Fluorescence Decay of Naphthalene on $\alpha$-Alumina During Temperature Programmed Desorption

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Abstract

The effect of a homologous series of simple aliphatic alcohols on the laser induced fluorescence decay of naphthalene that had been vapor deposited on a crystal of $\alpha$-alumina during temperature programmed desorption was observed. At temperatures before the desorption of the alcohol, thermally induced percolation caused the formation of molecular naphthalene possibly due to solvation. Concurrently, a relatively unstable excimer species was observed that had a much
smaller laser induced fluorescence decay rate constant than at deposition. In the presence of the alcohol thin film, thermally irreversible rearrangement of the naphthalene adlayer occurred that resulted in excimers that have increased rate constants and are postulated to be energetically more stable than the excimer formed at deposition.

**Keywords:** excimer, naphthalene, fluorescence, laser induced fluorescence, temperature programmed desorption, deposition, decay rate constants, lifetimes

### Introduction

Some years ago, excimers of aromatic molecules were observed in solutions [3] and more recently they have also been detected in vapor deposited molecular adlayers [4-7,12]. Recently, the effect of several aliphatic hydrocarbons on the spectral intensity of naphthalene excimers during temperature programmed desorption (TPD) was communicated [6,12]. In this paper, the effect that the homologous series of simple aliphatic alcohols has on the laser induced fluorescence (LIF) decay of vacuum deposited naphthalene is given.

### Experimental

The fluorophore, naphthalene, was purchased from Sigma-Aldrich (St. Louis, MO). The alcohols, methanol, ethanol, n-propanol, n-butanol, n-pentanol, and n-hexanol were also purchased from the same source. The samples were placed in stainless steel ampoules, outgassed by freezing-pump-thaw cycles, and introduced into the vacuum chamber through leak valves.

Details of the experimental set-up have been previously published [4-7,12], and only a brief outline is given here. For the wavelength resolved TPD, the adlayer of fluorophore was excited by a high pressure Hg lamp, and detected with a diode array spectrometer. The heating of the α-alumina crystal for the TPD was accomplished by sending current through the electrically resistive tantalum foil that had been placed in thermal contact with the crystal. The temperature was monitored with a thermocouple that was in direct contact with the crystal and provided the feedback for the linear temperature ramp that was programmed at 2 K/s.

A quadrupled Nd:YAG laser that was pulsed at 10 Hz was the excitation source for the LIF measurements. The decays were detected with a very fast digitizing oscilloscope that exported individual decays to a computer. In the analysis, the decays were assumed to be a simple first-order exponentially decaying function and as such, the natural logarithm of the waveform should yield a straight line. A least square
curve-fitting program was used to determine the slope, i.e. the rate constant, and intercept of this line in real time. The exponential of the intercepts represents the initial intensities of the LIF decay. The fit was continuously monitored visually throughout the TPD experiment to ensure that it was qualitatively good. Subsequent to the end of a run, the rate constants and intercepts were plotted as a function of temperature with a spreadsheet software. The run-to-run error in the LIF decay rate constants during replicate TPDs was found to be about ± 30%.

A variation of the LIF decay TPD experiment involved the annealing of the adlayer at a preset temperature. Then the adlayer was allowed to cool back down to the deposition temperature. The TPD was then done through desorption in the usual manner. Changes from the un-annealed LIF decay TPD would indicate dynamic processes on the surface adlayers that were thermally irreversible.

Experimental hardware integration and control for the TPD, residual gas analyzer, oscilloscope and spectrometer was done with a system design software. The wavelength-resolved TPD figures were created with a software that manipulated the large array of spectra versus wavelength and temperature.

The adlayer coverages were determined by using a diode laser that was directed at the α-alumina surface during deposition [4]. The resulting optical interference was used to calibrate the integrated mass spectral peaks in the TPD in terms of the surface coverage with units of monolayers (ML). The error in the coverage was about ± 20%. In the TPD experiments described in this study, attempt was made to hold the coverage of naphthalene constant at about ~200 ML with a reproducibility of about ± 200 ML deemed acceptable. The thin film coverages for the alcohols were ~20 ± 20 kML.

The activation energy for desorption, $E_a$, was calculated by Redhead analysis by assuming a first-order desorption kinetics as described by King and is based on the mass spectral peak desorption temperature, $T_p$ [8-9,11]. The uncertainties in the desorption temperatures and the propagated error in the activation energies were ± 2%.

**Results and Discussion**

The wavelength-resolved TPD of multilayer of naphthalene is shown as an inset in Figure 1. Although it’s difficult to see from the figure, the $\lambda_{\text{max}}$ was observed to be ~ 400 ± 2 nm by rotating the plot to directly view intensity versus wavelength. The peak desorption temperature, $T_p$, of naphthalene occurred at ~ 274 K. By assuming that the desorption occurred as a first-order process, $E_a$ was calculated to be 71.6 kJ/mol [8-9,11]. When methanol was deposited below naphthalene and the resulting bilayer was optically pumped, the wavelength-resolved TPD of the excimer fluorescence appeared almost indistinguishable from that of the multilayer. In order
to emphasize the effect that methanol has on the spectral features of naphthalene during the TPD, the wavelength resolved TPD of the difference between that of the bilayer of methanol and naphthalene, and the naphthalene multilayer is plotted in Figure 1.

Shown in Figure 2 are the LIF decay rate constants for the bilayer of methanol and naphthalene and the intercept of the least squares fit during the TPD that are observed at the excimer $\lambda_{\text{max}}$. For comparison, the lower inset shows the same two plots for multilayer naphthalene with the same relative graphical scales. The LIF decay rate constant of naphthalene at deposition, is initially $5.4 \times 10^6 \text{ s}^{-1}$, and the increase begins at around 27 K below desorption. The LIF decay rate constants are consistent with published lifetimes of naphthalene and its excimer [1,3,10]. The increase in rate constant is attributed to thermal quenching, and the maximum in the rate peaks at almost $15 \times 10^6 \text{ s}^{-1}$. The intercept decreases with temperature due to thermally induced non-radiative processes and mirrors the LIF decay.

For the bilayer of methanol and naphthalene in Figure 2, the solid black up arrow points to $T_p$ of naphthalene. For reference, the black dashed arrow is the $T_p$ for multilayer methanol. The rise in the LIF rate constant at 210 K is attributed to the thermally induced surface dynamics of the methanol. The cause for the decrease in the rate constant that is shown in dashed blue up arrow at 262 K can be postulated. (Cf. Table 1, $T_{\text{min. rate}}$). One possibility is the thermally induced solvation of naphthalene by methanol. This idea is supported by the observed complex kinetics exhibited by the raw waveform of the LIF decay during the decreased rate constant at 262 K. (Cf. upper inset). Analysis of the build up in the intensity subsequent to the laser pump indicates a possible appearance of a second excimer type that serves as an energy acceptor. From the rising portion of the waveform, the formation of the excimer species and the energy transfer occurs with a rate constant of $\sim 1 \times 10^6 \text{ s}^{-1}$. The subsequent decay in the waveform occurs at a rate consistent with the minimum in the LIF decay rates during the TPD, viz., $\sim 2 \times 10^6 \text{ s}^{-1}$. The fact that the intensity of this excimer is relatively high (blue down arrow) means that this excimer is formed in significant quantity. (Cf. Table 1, $T_{\text{max.intercept}}$).

The idea that another excimer type is formed is further supported by the wavelength resolved TPD difference plot that was shown in Figure 1, in which the negative going excimer intensity (solid up arrow) appears at the same temperature as this minimum in the LIF decay rate, and as well, the appearance of the molecular fluorescence (solid down arrow). In the difference plot, a negative going intensity means that the excimer intensity is less at the temperature of interest for the bilayer when compared to that of the multilayer. After the bulk of the methanol has desorbed, the intensity of the bilayer is higher than that of the multilayer for a short temperature interval just prior to desorption (dashed and dotted down arrow, for the molecular and excimer fluorescence, respectively).

In a series of experiments, the bilayer of methanol/naphthalene was annealed to 250 K and then allowed to cool. Then the LIF decay of the bilayer was observed as a
function of temperature in the usual TPD experiment. This procedure was repeated in increments beyond $T_p$ of methanol. (No changes were observed when the bilayer was annealed below 250 K). Shown in Figure 3 is the series of LIF decay constants during TPD as a function of the annealing temperature. What is noteworthy is that the starting rate constants for the bilayer increased with annealing temperature (Cf. right inset in Figure 3), an effect that is not observed for multilayer naphthalene (Cf. left inset in Fig. 3). The conclusion is that the percolation of the methanol causes a thermally irreversible rearrangement within the amorphous naphthalene adlayer that is characterized by shorter lifetimes. Also, a close examination has shown a slight spectral red-shift in the excimer emission and such red-shift has been reported to be evidence for a more stable excimer [3].

When the adlayer is annealed to 265 K, most of the methanol has desorbed, and the minimum in the LIF decay rate constant is no longer observed because of the loss of solvation. (Cf. Figure 3) After the desorption of the bulk of the methanol in the bilayer at annealing temperature $\geq$ 265 K, (the last 3 upper points on the right inset) the LIF decay rate constants during the TPD begin to resemble that of the multilayer naphthalene as the effect that the methanol adlayer has on the naphthalene decreases.

The LIF decay rate constants as a function of TPD temperatures were determined for naphthalene in a bilayer with a series of other homologous alkanols and are shown in Figure 4. To unravel the cluster of curves before desorption, the inset shows the temperatures at which the minimum in the LIF decay rate occurs ($T_{\text{min. rate}}$ in Table 1) as a function of the alcohol. ($T_p$ and $E_a$ for these alcohols are also given in Table 1). In the table, $T_{\text{min. rate}}$ and $T_{\text{max. intercepts}}$ are the features analogous to those of the bilayer of methanol/naphthalene shown as dashed blue up arrow and solid blue down arrow in Figure 2, respectively. To emphasize the fact that the minimum in the rate does not occur exactly at the same temperature as the maximum in the intercept, the difference in the two are given in the column so labeled. Furthermore, the difference between the multilayer $T_p$ and the bilayer $T_{\text{min. rate}}$ is quite significant, and attests to the strong interaction of the naphthalene adlayer with the alcohol thin film that decreases with the length of the carbon chain. Finally, the plots yield an average LIF decay rate of about $2 \times 10^6$ s$^{-1}$ at $T_{\text{min. rate}}$. This shows that the solvation is relatively independent of the alcohols’ property.

In conclusion, the LIF decay rate constant for vapor deposited naphthalene is about $6 \times 10^6$ s$^{-1}$. The TPD experiments on the bilayers of naphthalene and aliphatic alcohols generated an excimer species whose rate constant is about $2 \times 10^6$ s$^{-1}$. Surface dynamics begin at a temperature much before desorption of the thin film, for example, about 55 K before desorption for methanol. Annealing experiments revealed that irreversible thermally induced rearrangement of the excimer occurs in the presence of the alcohol, and that the excimer that is formed is characterized by a shorter lifetime and increased stability than the excimer at deposition.
References


Table 1. Summary of observed trends in the alcohol multilayers and bilayers with naphthalene. \( T_p \) = peak desorption temperature and \( E_a \) = desorption energy of the alcohol multilayer. \( T_{\text{max. intercept}} \) and \( T_{\text{min. rate}} \) are the maximum observed in the intercept and the minimum in the rate constant of the least square fit, respectively, in the LIF decay during the TPD of the bilayer with naphthalene. \( T_{\text{max. intercept}} - T_{\text{min. rate}} \) and \( T_{\text{min. rate}} - T_p \) are observed trends described in the text.

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<th>( T_p ) (K)</th>
<th>( T_{\text{max. intercept}} ) (K)</th>
<th>( T_{\text{min. rate}} ) (K)</th>
<th>( T_{\text{max. intercept}} - T_{\text{min. rate}} ) (K)</th>
<th>( T_{\text{min. rate}} - T_p ) (K)</th>
<th>( E_a ) (kJ/mol)</th>
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<td>271.5</td>
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<td>1.5</td>
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<td>-1.6</td>
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Figure 1. The difference of the plots of the wavelength-resolved TPD of the bilayer and multilayer fluorescence TPD’s. Wavelength resolved TPD of multilayer naphthalene is shown as an inset; the axis labels are the same. Solid down arrow points to the molecular fluorescence that appears concurrently with the negative going intensity in the excimer (solid up arrow). The molecular luminescence (dashed arrow) and the positive going intensity in the excimer (dotted arrow) occur simultaneously in the TPD just prior to desorption.
Figure 2. LIF decay rate constants (lower plot, scale on left) and intercepts (upper plot, scale on right) as a function of temperature for the bilayer of naphthalene and methanol. The lower inset is the corresponding LIF decay and intercept for naphthalene. The solid and dashed up arrows are the $T_p$ of multilayers of naphthalene and methanol, respectively. The blue dashed arrow points to the $T_p$ of methanol in the bilayer. The upper inset is the non-exponential waveform observed at $T_p$ of methanol in the bilayer (dashed blue up arrow).
Figure 3. LIF decay rate constants as a function of temperature for the bilayer of methanol and naphthalene. The numbers on the graph refer to the annealing temperature in K. The left inset is the corresponding LIF decay plots with the same scale and similar annealing temperatures for naphthalene. The right inset shows the LIF rate constants as a function of annealing temperatures for methanol (in purple diamonds) and naphthalene (in black circles). The dashed down arrow is the $T_p$ for methanol, the solid up arrow is the minimum in the LIF decay rate constant, and the solid down arrow is the $T_p$ for naphthalene.
Figure 4. LIF decay rate constants for the homologous series of linear alcohols. The inset shows the temperature at which the minimum in the LIF decay rate constant is observed for a particular alcohol. The color used in the inset is the legend for the plots in the larger graph.

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