

# FORMATION OF A TRANSIENT BIPHENYL-CUMENE COMPLEX DURING TEMPERATURE PROGRAMMED DESORPTION ON AN $\text{Al}_2\text{O}_3$ SUBSTRATE

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## Abstract

Biphenyl that is vapor deposited on  $\text{Al}_2\text{O}_3$  at 110 K is in the twisted conformation with a  $\lambda_{\text{max}} \approx 320$  nm, while deposition at 138 K allowed biphenyl to overcome the activation barrier to planarity and the adlayer was sufficiently amorphous for the biphenyl to form excimer with a characteristic fluorescence with  $\lambda_{\text{max}} \approx 370$  nm.<sup>1</sup> When a thin layer of cumene was deposited adjacent to the  $\text{Al}_2\text{O}_3$  and beneath the biphenyl a new biphenyl peak with  $\lambda_{\text{max}} \approx 315$  nm was observed during the TPD that appeared briefly at 147 K. This peak was identified as a complex of biphenyl and cumene whose composition depended on the conformer of biphenyl. The biphenyl:cumene complex was determined to be  $3 \pm 1$  biphenyl molecules to one cumene molecule if the biphenyl was deposited in the twisted conformation and  $1.4 \pm 0.2$  biphenyl to one cumene if the biphenyl was deposited in the planar form.

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## Introduction

Vapor deposited biphenyl on a single crystal of  $\text{Al}_2\text{O}_3$  at 110 K is in the twisted conformation with  $\lambda_{\text{max}} \approx 320$  nm.<sup>1</sup> Deposition at 138 K caused biphenyl to take on a planar conformer and the morphology was sufficiently amorphous for the biphenyl to form excimer with a characteristic  $\lambda_{\text{max}} \approx 370$  nm.<sup>1</sup> The optimum deposition temperature for the formation of the biphenyl excimer was detailed in a previous paper.<sup>2</sup> When biphenyl was deposited at 160 K, the thermal energy was sufficient to undergo the disorder-to-order transition such that the adlayer was composed of biphenyl in the planar conformation with  $\lambda_{\text{max}} \approx 345$  nm as in an ordered crystal.<sup>1</sup> The transition was accompanied by a decrease in the fluorescence intensity due to energy transfer within the ordered matrix.<sup>1</sup> In a previous study biphenyl analogs that had the rings fixed in planar or twisted conformers were found to exhibit characteristic spectra that can serve to distinguish the two conformers of biphenyl.<sup>3</sup>

Other studies that made use of biphenyl's spectroscopic signature have included epitaxial ordering by aromatic hydrocarbon substrates such as xylene<sup>4,5</sup> and other alkyl substituted benzenes.<sup>6</sup> Homoepitaxy was observed by annealing a substrate of biphenyl first, followed by the deposition of the overlayer at 110 K.<sup>7</sup> Finally resonance energy transfer from alkylbenzenes to biphenyl and biphenyl to naphthalene were reported in earlier studies.<sup>8</sup>

Cumene was found to energy transfer to naphthalene, but the formation of a heteromolecular complex was not observed.<sup>9</sup> In this study a bilayer of biphenyl in either the planar or twisted conformer was found to form complexes when cumene was deposited below it. The stoichiometry of cumene to biphenyl depended on the specific conformer of biphenyl and is reported here.

## Experimental

Biphenyl and cumene were of the highest purity that are commercially available (Sigma-Aldrich, St. Louis, MO). These compounds were placed in separate sample holders and vapor deposition was accomplished with adjustable precision leak valves. Details of the experimental set up have been previously published<sup>1,6</sup> and a brief summary is given here. The ultra-high vacuum chamber had a background hydrogen base pressure of  $1 \times 10^{-9}$  Torr. A single crystal of  $\text{Al}_2\text{O}_3$  (0001) (Crystal Systems, Inc., Salem,

MA) was suspended on the lower end of a liquid nitrogen cryostat via copper post on either side of the  $\text{Al}_2\text{O}_3$  with a sapphire spacer for electrical and thermal isolation. The sapphire spacer thermally isolated the liquid nitrogen from the crystal so that the lowest temperature that was routinely achieved was about 110-115 K. In order to deposit the biphenyl excimer, the deposition temperature was controlled to within  $\pm 1$  K by a feedback algorithm. The sample was then cooled to 110-115 K prior to the epilayer deposition and then the temperature programmed desorption (TPD) was performed. During the TPD experiment, the temperature was linearly ramped at 2 K/s by resistively heating the  $\text{Al}_2\text{O}_3$  by sending current through a thin tantalum foil that was in thermal contact with it. A type-K (chromel/alumel) thermocouple (Omega, Norwalk, CT) that was also in thermal contact with the  $\text{Al}_2\text{O}_3$  monitored the temperature. Process control during the TPD experiment was accomplished by a program written in LabVIEW (National Instruments, Austin, TX) that incorporated a PID (proportional-integral-derivative) feedback algorithm that linearly incremented the temperature of the  $\text{Al}_2\text{O}_3$  crystal.

Additionally during the TPD, the program took the fluorescence spectra from an Ocean Optics USB4000 spectrometer (Ocean Optics, Dunedin, FL) in real time every 300 ms. The program also scanned the residual gas analyzer for the masses of the compounds that had been deposited onto the  $\text{Al}_2\text{O}_3$ . Manipulation of the array of spectra as a function of temperature by a MATLAB (Mathworks, Natick, MA) template yielded the wavelength-resolved TPDs that are shown in the figures. In the inset, the top view is given so that the wavelength can be more easily observed. To ensure a clean surface, the  $\text{Al}_2\text{O}_3$  was heated to 300 K after each run.

The activation energy for desorption,  $E_a$ , was calculated by Redhead analysis<sup>10</sup> in which a first-order desorption kinetics as described by King was assumed and is based on the mass spectral peak desorption temperature,  $T_p$ .<sup>10-12</sup> The uncertainties in the desorption temperatures and the propagated error in the activation energies were  $\pm 2\%$ .

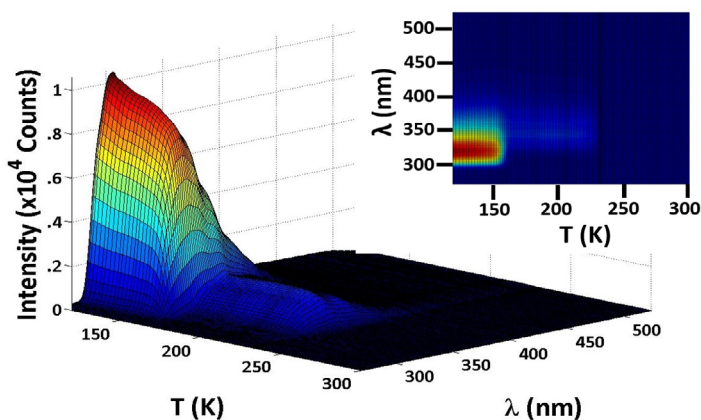
The surface coverages,  $\Theta$ , in monolayers (ML) were calculated by calibrating the integrated mass spectral peaks to an optical interference experiment. The interference experiment yielded

accurate rate of deposition with coverage error of  $\pm 30\%$ , and is described in detail elsewhere.<sup>13</sup>

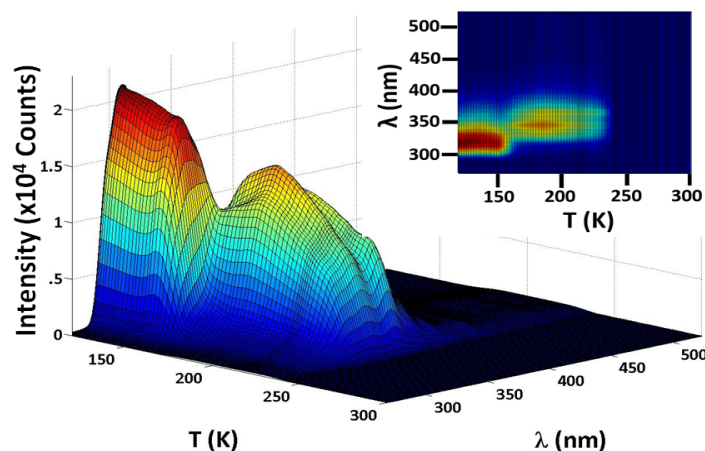
## Results and Discussion

### Multilayer biphenyl

The peak desorption temperature of neat biphenyl at low coverages ( $\sim 20$  ML) was 222 K. First-order desorption was assumed and the activation energy for desorption,  $E_a$ , was calculated to be 57.6 kJ/mol.<sup>1,6,10-12</sup> The wavelength-resolved TPD of biphenyl with  $\Theta_{\text{biphenyl}} \approx 98$  ML that was deposited at 110 K is shown in Figure 1. A summary of the main features that are observed in these plots are: *a.* With a  $\lambda_{\text{max}} \approx 320$  nm, the fluorescence of the amorphous adlayer at a deposition temperature of 110 K was previously characterized to be the twisted conformer.<sup>1,3</sup> *b.* The disorder-to-order transition occurred at  $160 \pm 1$  K at which temperature biphenyl assumes a planar conformation and has a  $\lambda_{\text{max}} \approx 345$  nm.<sup>1,3</sup> Energy transfer within the ordered adlayer caused the fluorescence to decrease to about 15% relative to that at deposition.<sup>1,3</sup> *c.* In a separate experiment, the adlayer of biphenyl that was deposited at 138 K was amorphous and in the planar conformation, both of which are necessary requirements for the formation of excimers and the fluorescence red-shifted to  $\lambda_{\text{max}} \approx 370$  nm.<sup>1,3</sup>



**Figure 1:** Wavelength-resolved TPD of neat biphenyl on  $\text{Al}_2\text{O}_3$ .  $\Theta_{\text{biphenyl}} \approx 98$  ML deposited at 110 K. Note the loss of intensity fluorescence intensity at 160 K when the biphenyl assumes a planar conformation and has a  $\lambda_{\text{max}} \approx 345$  nm. Inset: top view.



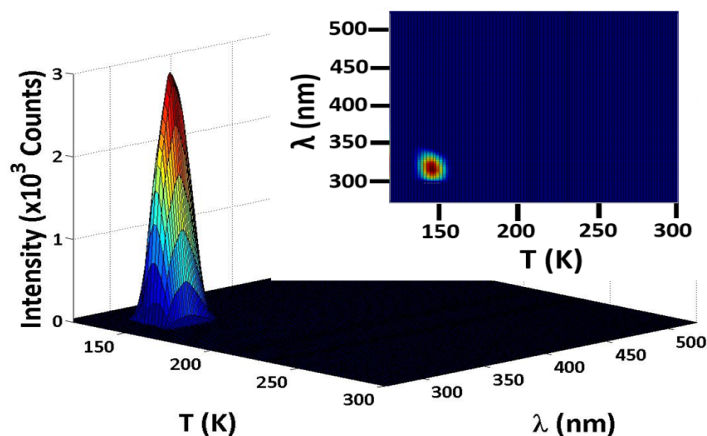
**Figure 2:** Wavelength-resolved TPD of a bilayer composed of cumene deposited directly on  $\text{Al}_2\text{O}_3$  at 110 K with  $\Theta_{\text{cumene}} \approx 38$  ML, followed by biphenyl with  $\Theta_{\text{biphenyl}} \approx 212$  ML that show the twisted and planar conformer at  $\lambda_{\text{max}} \approx 320$  and 345 nm, respectively. Inset: top view.

### Cumene multilayer

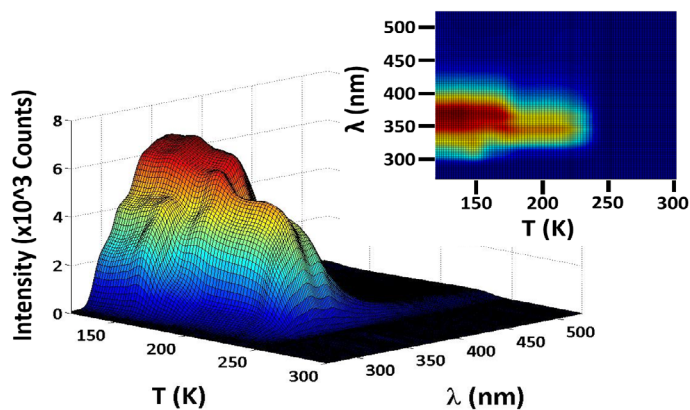
The fluorescence origin was at 294 nm and two peaks associated with the aliphatic C-H vibrational progression were observed at 304 nm and 318 nm.<sup>1,6,9</sup> The peak desorption temperature for cumene was 167 K.<sup>1,6,9</sup> A first-order desorption kinetics was assumed and  $E_a$  was calculated to be 43.0 kJ/mol.<sup>1,6,9,10-12</sup>

### Cumene complex with biphenyl in the twisted conformer

Shown in Figure 2 is the wavelength-resolved TPD of a bilayer composed of cumene that was deposited on the  $\text{Al}_2\text{O}_3$  at 110 K. Biphenyl was then deposited on top at the same temperature. Then the temperature was ramped so that the wavelength-resolved TPD could be observed. A peak that appears as a shoulder in the wavelength-resolved TPD is that of the complex. This is more clearly seen when both the spectra at 320 and 345 nm due to the twisted and planar conformers of biphenyl, respectively, are subtracted from the wavelength-resolved TPD. The result is Figure 3 that clearly shows the spectrum of the complex. This complex appears in the wavelength-resolved TPD at 147 K for about 5 K during the TPD. The fluorescence of the complex is relatively sharp and centered at 315 nm.



**Figure 3:** Wavelength-resolved TPD of a bilayer composed of cumene deposited directly on  $\text{Al}_2\text{O}_3$  at 110 K with  $\Theta_{\text{cumene}} \approx 29$  ML, followed by biphenyl with  $\Theta_{\text{biphenyl}} \approx 106$  ML in which the spectra due to the twisted conformer and the planar conformer in the ordered phase were subtracted. This is the spectrum of the biphenyl: cumene complex that appears briefly in the TPD. Inset: top view.

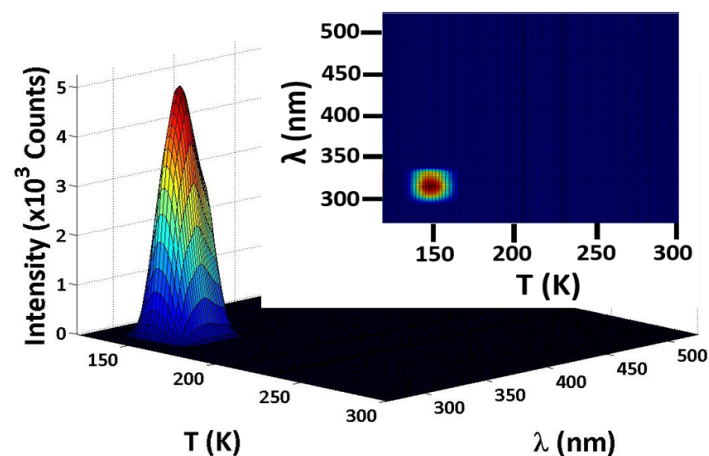


**Figure 4:** Wavelength-resolved TPD of a bilayer composed of cumene deposited on  $\text{Al}_2\text{O}_3$  at 110 K with  $\Theta_{\text{cumene}} \approx 11$  ML and biphenyl deposited on top of cumene at 138 K with  $\Theta_{\text{biphenyl}} \approx 270$  ML. Deposition at the higher temperature cause the planar conformer to form as the adlayer is deposited as seen by the  $\lambda_{\text{max}} \approx 370$  nm. Inset: top view.

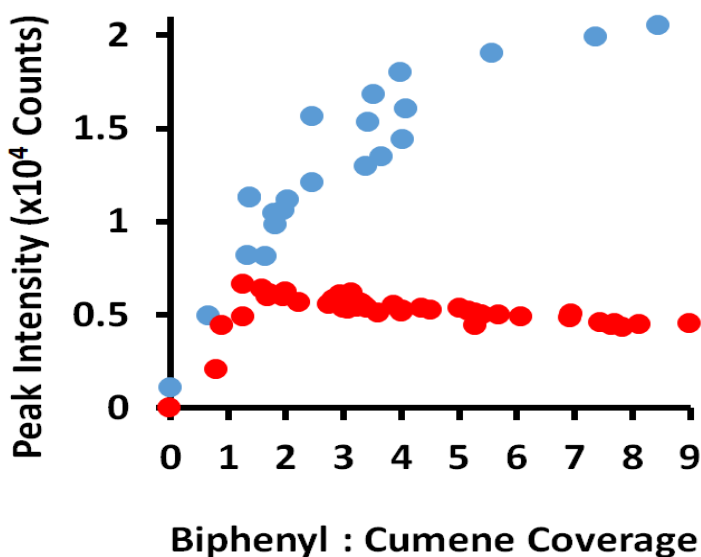
### Cumene complex with biphenyl in the planar conformer

In Figure 4, cumene was deposited directly on the  $\text{Al}_2\text{O}_3$  at 110 K. Then the crystal temperature was ramped to 138 K and held within  $\pm 1$  K while deposition of biphenyl was accomplished. Then the resulting bilayer was allowed to cool to 110 K, after which the temperature was ramped in the TPD experiment. The planar conformation of biphenyl was maintained during the cool down period after deposition as the fluorescence spectrum remained unchanged during the process.

When the fluorescence spectrum from the planar conformer of biphenyl was subtracted from the wavelength-resolved TPD, the spectrum of the complex can be observed as shown in Figure 5. Again, the spectrum of the complex with  $\lambda_{\text{max}} \approx 315$  nm at  $147 \pm 5$  K appeared during the TPD. The similarities in the complex that cumene forms with either the planar or the twisted conformer of



**Figure 5:** 3: Wavelength-resolved TPD of a bilayer composed of cumene deposited directly on  $\text{Al}_2\text{O}_3$  at 110 K with  $\Theta_{\text{cumene}} \approx 30$  ML, followed by biphenyl with  $\Theta_{\text{biphenyl}} \approx 97$  ML in which the spectra due to the planar excimer biphenyl and the biphenyl in the planar ordered phase have been subtracted. This is the spectrum of the biphenyl:cumene complex that appears briefly in the TPD. Inset: top view.



**Figure 6:** Plot of the fluorescence intensity of the  $\lambda_{\text{max}} \approx 315$  nm peak that occurs at 147 K during the TPD as a function of biphenyl to cumene bilayer coverage for biphenyl deposited in the twisted conformation (●) and for biphenyl deposited in the planar conformation (●). In these plots cumene coverage was kept constant: for the blue plot,  $\Theta_{\text{cumene}} \approx 36 \pm 8$  ML and for the red plot,  $\Theta_{\text{cumene}} \approx 31 \pm 5$  ML.

biphenyl are reflected in the nearly superimposable spectra that are shown in Figures 3 and 5.

### Cumene-Biphenyl Molecular Complex

In Figure 6 the plots of the fluorescence intensities of the complex with  $\lambda_{\text{max}} \approx 315$  nm at 147 K during the TPD as a function of biphenyl to cumene bilayer coverage for the biphenyl deposited in the twisted conformation are in blue and biphenyl deposited in the planar conformation are in red. In these plots cumene coverage was kept as constant as possible, in which the complex with the twisted biphenyl had coverages of  $\Theta_{\text{cumene}} \approx 36 \pm 8$  ML and complex with the planar biphenyl,  $\Theta_{\text{cumene}} \approx 31 \pm 5$  ML.

An examination of the blue plot indicates two slopes that intersect at biphenyl to cumene ratio of coverages at  $\sim 3 \pm 1$ . Since the fluorescence peak of the complex is a shoulder on the more intense fluorescence due to the twisted biphenyl spectrum, a contribution from the latter species contributes to the measured intensity of the complex. Although not shown here, the fluorescence intensities of the neat biphenyl precisely at 315 nm and 147 K for a series of coverages that are the same as in this plot were subtracted. The slope of the plot leveled off at biphenyl to cumene coverage ratio  $> 4:1$  biphenyl. However the point at which the two slopes intersected did not change. Hence the conclusion is that this loosely held complex is largely composed of  $\sim 3 \pm 1$  molecules of the twisted conformer of biphenyl to a single cumene molecule.

The planar biphenyl:cumene complex shown in red appears to be a very well defined ratio of biphenyl<sub>1.4±0.2</sub>:cumene and lead to a possible structure of this complex of (biphenyl)<sub>3</sub>:(cumene)<sub>2</sub>. A more likely complex might be a 1:1 complex or even a 2:1 complex where the cumene can intercalate between two biphenyl molecules that form the excimer.

### Conclusion

Molecular complexes composed of biphenyl and alkylbenzene such as cumene depend on the conformer of biphenyl. The wavelength-resolved TPD method reported here appears to give a reasonable estimate of the stoichiometric composition of such complexes. Further work is required to definitively assign the stoichiometric composition of the complex.

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