EFFECT OF CYCLOHEXANE AND BENZENE ON THE DISORDER-TO-ORDER TRANSITION OF BIPHENYL ON Al$_2$O$_3$

Samie T. Watanabe*, Isaac Z. Song*, Nicole K. Bond*, John Baker*, Mariyan Popov* and A.M. Nishimura†

Department of Chemistry, Westmont College, Santa Barbara, CA 93108

Abstract

The spectral signature of biphenyl is sensitive to the molecular environment. In addition, the disorder-to-order transition that biphenyl undergoes when vapor deposited on Al$_2$O$_3$ can vary with the environment. This study compares the effect that benzene and cyclohexane, two molecules of similar molecular masses but different structurally, have on biphenyl. With these to molecules as underlayers in a bilayer system, the enhanced fluorescence intensities is attributed to the molecular volume that caused the formation of defect sites in the biphenyl adlayer. Hence for cyclohexane under biphenyl, the density of defect sites manifest in a higher fluorescence intensity than for benzene.

†Corresponding author: nishimu@westmont.edu   *Undergraute co-authors and researchers

Introduction

In previous studies of the fluorescence of biphenyl on Al$_2$O$_3$, the density of defects sites were found to be created in the biphenyl adlayer when an underlayer substrate with a lower desorption temperature was made to percolate through the fluorescent overlayer of biphenyl.[1-3] Percolation is achieved by choosing an underlayer that has a lower desorption temperature.[1-3] Increase in the density of defect sites was manifested by an increase in the fluorescence intensity due to the trapping of the excitation in the ordering transition that occur in biphenyl crystals.[1-3] The optical pumping of the adlayer would be expected to excite most of the molecules in the adlayer, limited only by the penetration depth of light. Since vapor deposition prepares the adlayer in an amorphous arrangement, the highest fluorescence intensity is expected to to be observed at deposition. Vapor deposited biphenyl on Al$_2$O$_3$ is known to undergo disorder-to-order transition at 157 K.[1-3] In this paper, the result of two molecules, cyclohexane and benzene, which have similar footprint sizes but differing in molecular volume are used as underlayers to see which would would cause the greater disruption in the ordering in vapor deposited biphenyl.

Experimental

Biphenyl, cyclohexane and benzene were of the highest purity that were commercially available, typically > 99% (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 published previously (10-13) and a brief summary is given here. The ultra-high vacuum chamber had a background hydrogen base pressure of 1 x 10^{-9} Torr. A single crystal of Al$_2$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 Al$_2$O$_3$ with a sapphire spacer for electrical and thermal isolation. Resistive heating of the Al$_2$O$_3$ was done by sending current through a thin tantalum foil that was in thermal contact with the substrate. A type-K (chromel/alumel) thermocouple (Omega, Norwalk, CT) that was also in thermal contact with the Al$_2$O$_3$ monitored the temperature. Process control during the temperature programmed desorption (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 increments the temperature of the Al$_2$O$_3$ crystal.[1-3]

During the TPD, the program also took the fluorescence spectra from an Ocean Optics USB4000 spectrometer (Ocean Optics, Dunedin, FL) in real time every 300 ms. Finally, the program scanned the residual gas analyzer for the masses of the compounds that were deposited onto the Al$_2$O$_3$. Manipulation of the array of spectra as a function of temperature by a MATLAB (Mathworks, Natick, MA) template yielded the wavelength resolved TPD that are shown in the figures. To ensure a clean surface, the Al$_2$O$_3$ was heated to 300 K after each run. Temperature ramps to higher temperatures did not indicate any other adsorbates.

The activation energy for desorption, E$_a$, was calculated by Redhead analysis in which a first-order desorption kinetics as described by King was assumed. The analysis was based on the mass spectral peak desorption temperature, T$_P$.[4-6] The uncertainties in the desorption temperatures and the propagated error in the activation energies were ± 2%.

The surface coverages, Θ, in monolayers (ML) were calculated by calibrating the integrated mass spectral peaks using an optical interference experiment. The interference experiment as described in detail elsewhere[7] yielded accurate rate of deposition with coverage error of ± 30%.

Results and Discussion

The peak desorption temperature, T$_P$, of neat biphenyl at low coverages (~ 20 ML) was 227 K. First-order desorption was assumed and the activation energy for desorption, E$_a$, was calculated to be 58.9 kJ/mol.[4-6] Upon deposition, excitation of neat biphenyl on the Al$_2$O$_3$ surface with a high-pressure Hg lamp caused the amorphous biphenyl to fluoresce with a λ$_{max}$ of 320 nm. As can be seen from Figure 1, when the surface temperature was linearly ramped in a TPD experiment, the adlayer underwent a disorder-to-order transition at 157 K as evidenced by the red shift of the λ$_{max}$ to 340 nm and the overall intensity decreased due to the emergence of nonradiative pathways that are available for relaxation (Inset to Figure 1). The reduction in intensity arose partly from the ordered molecules that became energy carriers for the trap sites

from which fluorescence occurred.[1]

In a previous study, the dihedral angle of biphenyl was correlated to the fluorescence λ_{max}.[3] If the trendline from that study is used, biphenyl's dihedral angle is 44° at deposition and the dihedral angle become more planar to 10° after the disorder-to-order transition.

The peak desorption temperatures of benzene and cyclohexane are 137 and 151 K, respectively. If first order desorption kinetics are assumed, then the activation energies for desorption of benzene and cyclohexane can be calculated and were determined to be 34.9 and 38.6 kJ/mole, respectively.[4-6] Note that the desorption temperatures for these two underlayers are lower than that of biphenyl. In this way, disruption in the biphenyl overlayer in the bilayer experiments would be evident as the temperature is increased in the TPD dexperiment.

Bilayer: benzene underlayer with biphenyl overlayer
The wavelength resolved TPD for the bilayer with benzene as the underlayer and biphenyl as the overlayer is shown in Figure 2. Notice the enhanced fluorescence intensity at about 210 K. The increase in intensity is tentatively postulated to occur as a result of
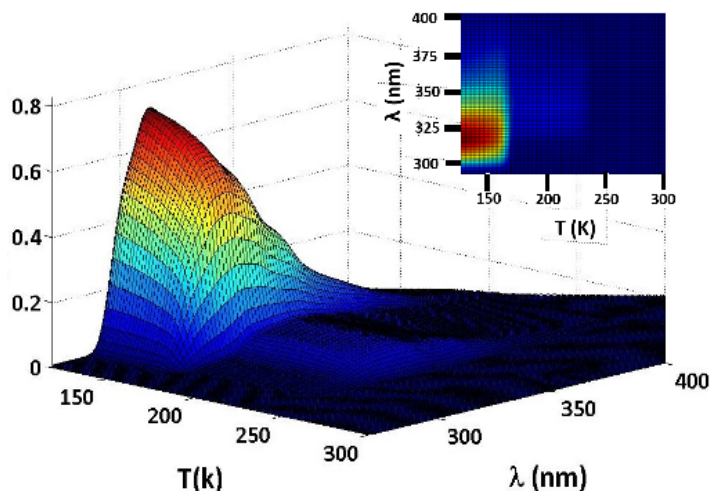

Figure 1. Wavelength-resolved TPD of biphenyl neat sample. $\Theta_{biphenyl}$ was 108 ML. Inset: top view. Note the disorder-to-order transition at 157 K with an accompanying red-shift in λ_{max} to 340 nm.
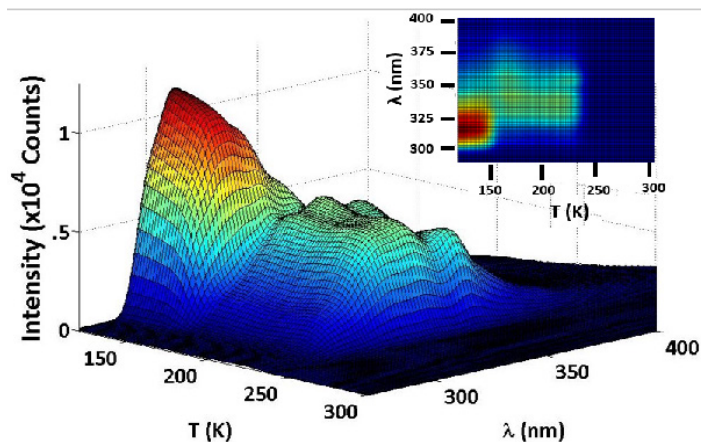

Figure 2. Wavelength-resolved TPD of biphenyl in which $\Theta_{benzene}$ was 238 ML and $\Theta_{biphenyl}$ was 140 ML. Inset is the top view. The two relevant wavelengths that are observed after the disorder-to-order transitions are 331 and 345 nm. These correspond to distinct sites created by the benzene. Inset: top view.

an increase in the density of defect sites during the disorder-to-order transition. Note that subsequent to the disorder-to-order transition, several peaks can be resolved: 331, 345 and 364 nm. The latter is attributed to an atomic Hg line from the excitation lamp. The other two wavelengths represent biphenyl in discrete molecular sites and correlate to dihedral angles of 22° and 6°, respectively.

In order to more quantitatively determine the effect that the underlayer has in causing an increase in the biphenyl's density of defect sites as it is undergoing the disorder-to-order transition, a series of experiments was conducted. The results are reported in Figure 3. On the vertical axis is the intensity of the biphenyl fluorescence at ~ 210 K and λ_{max} at 345 nm where the maximum intensity is observed. The biphenyl coverage was held constant at 110 ± 37 ML when the underlayer was benzene. In order to account for the variation in coverage, the intensity at 210 K was normalized using the fluorescence intensity at deposition. Note that the intensity at 210 K increases until about 100 ML of benzene, and then the intensity levels off. The tentative explanation is that the formation of defects within the biphenyl adlayer is efficiently accomplished by approximately one molecule of benzene to one of biphenyl, and that this density of sites has a maximum value, so that additional benzene molecules that percolate through the biphenyl layer are not effective, once that maximum is reached. In addition, a variation of 20.3 ± 0.7 K in T_p for benzene was observed when it as deposited under biphenyl. These findings lend support to the hypothesis that scomplexation due to aromatic π-π interaction occurred to some degree between benzene and biphenyl.

Bilayer: cyclohexane underlayer with biphenyl overlayer
Shown in Figure 4 is the wavelength-resolved TPD of cyclohexane and biphenyl bilayer that had been vapor deposited as distinct layers. The coverages of the bilayer shown were similar to those shown in Figure 2 for benzene and biphenyl bilayer. What is immediately apparent is the larger enhanced fluorescence intensity. The postulated mechanism for the increase in fluorescence intensity is the increase in the density of defect sites. It makes sense if the larger molecular volume cyclohexane compared to benzene is the cause of the enhanced fluorescence. It should be noted that the scatter in the data was due to the formation of defect sites that
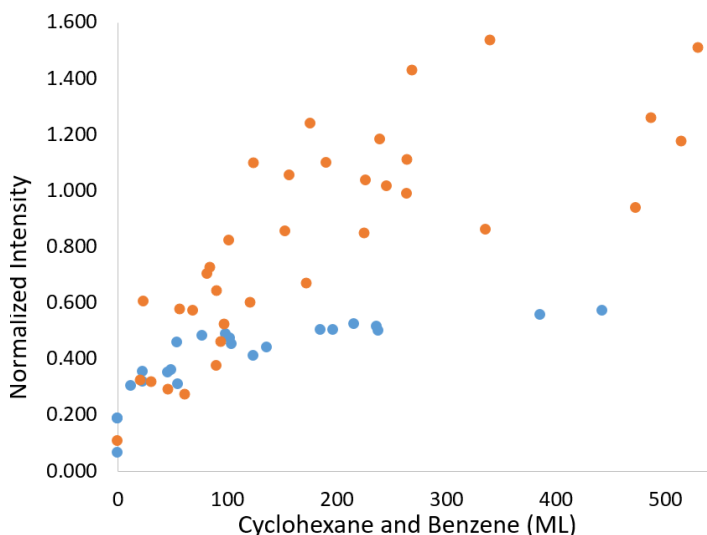

Figure 3. Plot of the ratio of the fluorescence intensity at 210 K and at 115 K as a function of the coverages of underlayer, benzene (in blue) and cyclohexane (in orange), respectively. The coverages of biphenyl were kept constant at 120 ±40 ML.

is probabilisticly random.

Shown also in Figure 3 is the normalized intensity of the enhanced fluorescence caused by the formation of defects by cyclohexane underlayer. Here again, biphenyl coverage was held constant at 120 ± 40 ML and the temperature at which the maximum was observed was about 190 K with λ_{max} of 346 nm although some variation in the temperature of about ± 18 K was detected. The fluorescence spectra showed two peaks after the disorder-to-order transition, with λ_{max} of 334 and 347 nm. These corresponded to dihedral angles of 18° and 5°, respectively. Here again, the fluorescence intensity rose rapidly with cyclohexane coverage and reached a maximum at about one molecule of cyclohexane to one of biphenyl. The intensity of the fluorescence when the underlayer is cyclohexane is much larger by about 2.5 times greater compared to benzene. This observation might be explained by noticing the larger molecular volume that cyclohexane occupies compared to benzene. Another possible cause for the enhancement in the fluorescence intensities as indicated in Figure 3, the contrasting scatter in the normlized intensities for cyclohexane-biphenyl versus benzene-biphenyl would suggest that aromatic π-π interaction between benzene-biphenyl might remove some of the randomness to the interaction.

One final observation is that the trap sites caused by the percolation of cyclohexane through the biphenyl layer was irreversible. This was determined by ramping the temperature of the bilayer to 190 K, where the maximum in the fluorescence intensity is observed. Then cooling the crystal back to 115 K, followed by a normal TPD experiment, that is, another ramp in temperature through the desorption temperature of biphenyl. The wavelength-resolved TPD of the final TPD experiment is shown in Figure 5. Note that once the traps are formed, the adlayer did not revert back to the amorphous molecular arrangement.

Acknowledgement

References

1. Marissa K. Condie, Blake D. Fonda, Zackery E. Moreau and A.M. Nishimura, *Thin Solid Films*, **2020**, 697, 137823-137828.
2. Samantha C. Rosenhagen, Cassidy C. Tran and A.M. Nishimura, *JUCR*, **2021**, 20, 34-37.
3. Nicole M. Bond and A.M. Nishimura, *JUCR*, **2022**, 21, 84-92.
4. P.A. Redhead. *Vacuum*, **1962**, 12, 203-211.
5. F.M. Lord and J.S. Kittelberger. *Surf. Sci.*, **1974**, 43, 173-182.
6. D.A. King. *Surf. Sci.,* **1975***, 47, 384-402.
7. C.L. Binkley, T.C. Judkins, N.C. Freyschalg, K.AMartin, and A.M. Nishimura. *Surf. Sci.,* **2009**, 603, 2207-2209.
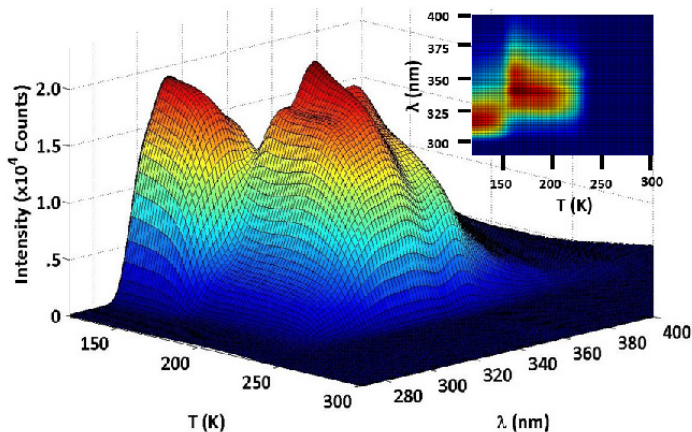
Figure 4. Wavelength-resolved TPD of biphenyl in which $\Theta_{cyclohexane}$ was 240 ML and $\Theta_{biphenyl}$ was 98 ML. The two relevant wavelengths that are observed after the disorder-to-order transitions are 334 and 347 nm that are distinct sites of biphenyl with different dihedral angles that were created by the cyclohexane. Inset: top view.
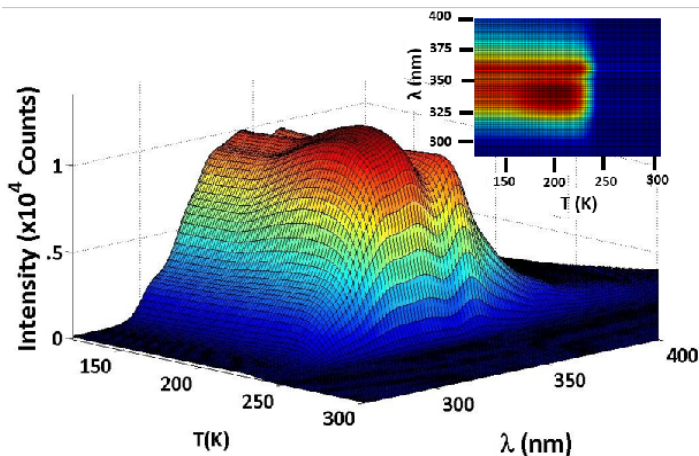

Figure 5. Wavelength-resolved TPD of biphenyl in which $\Theta_{cyclohexane}$ was 31 ML and $\Theta_{biphenyl}$ was 148 ML. The temperature of the Al_2O_3 on which the bilayer had been deposited was ramped to 190 K to desorb the cyclohexane and allowed to cool to the deposition temperature. Then this TPD experiment was done. Inset: top view.