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EXCIMER OF BIPHENYL ON Al_2O_3

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Abstract

A molecular adlayer of biphenyl was vapor deposited onto a single crystal of cryogenically cooled Al_2O_3 that was held at 135 K. Vapor deposition at this temperature creates an amorphous biphenyl adlayer in which biphenyl imolecules are in the planar conformation. Under these conditions, the excimer of biphenyl was formed that is characterized by a broad and featureless spectrum that is red-shifted relative to the monomer.

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Introduction

Some years ago, while observing the violet fluorescence of pyrene in dilute solutions, Stevens *et al*. reported concentration dependent self quenching that was accompanied by the appearance of a red-shifted broad structureless fluorescence (1). Self quenching occurs when the concentration of the emitting species is sufficiently high to mimic a disordered array of molecules, so that a complex with a proximate molecule forms when a molecule is electronically excited (2). The term excimer was used to describe this excited dimer that dissociated in the ground state. The name distinguishes it from a normal dimer that exists in both the excited and ground states (1). Since then the list of molecules that have been found to form excimers has grown extensively with aromatic molecules such as benzenes, naphthalenes, anthracenes, even including pyrenes (2). As large as this list is, the excimer of biphenyl has never been reported. Biphenyl is structurally unique because of the steric hindrance of the proximal ortho-hydrogens that result in the stability of a non-planar conformer such as that observed in the gas phase where the dihedral angle is 45^o (3). The torsional angle has been the subject of many theoretical studies as well, with dihedral angles reported to be in the range of 35.5° – 41.1° (4,5). The crystallographic structure of biphenyl was first reported by Trotter wherein the crystal was found to be monoclinic with 2 molecules per unit cell and the biphenyl molecules in planar conformation (6). Furthermore in the solid crystal, ordered molecules are too far apart to form excimers.

In a previous paper, the existence of both planar and non-planar conformers of biphenyl were identified during the temperature programmed desorption experiment (TPD) of vapor deposited biphenyl on Al_2O_3 (7). Vapor deposition prepares the biphenyl amorphously in the twisted conformer (8). As the amorphous adlayer of biphenyl is heated, it undergoes a disorder-to-order transition at 161 K, after which the biphenyl is ordered and in a planar conformation (8). In a related paper, the biphenyl was deposited on the Al_2O_3 at a sufficiently high temperature to overcome the torsional energy barrier, but low enough for the adlayer to remain amorphous. In this way the biphenyl excimer was formed (9). Laser induced fluorescence lifetime of 84 ± 5 ns was reported for the excimer (9).

This report is a continuation of the study of vapor deposited biphenyl on the surface of Al_2O_3. The aim is to unravel the morphology of the molecular adlayer of biphenyl and to better understand how to control the growth of molecular crystals in which varying conformers are possible.

Experimental

Biphenyl was purchased from a commercial source (Sigma-Aldrich, St. Louis, MO), and was placed in a sample holder and outgassed. Deposition was accomplished from the vapor through adjustable leak valves. The lowest crystal temperature that can be achieved in the system is 110 K which is the normal deposition temperature. In order to heat the Al_2O_3 and to maintain the temperature so that deposition at elevated temperatures can be accomplished, a LabVIEW program (National Instruments, Austin, TX) was written to hold a set temperature to within ± 0.5 K while an adlayer was deposited. Then the surface was allowed to cool to 110 K, and the usual wavelength resolved TPD was performed.

Details of the experimental set up have been previously published (7-9) and a brief summary is given here. A LabVIEW program was written in-house that takes the complete spectrum from the Ocean Optics USB4000 spectrometer (Ocean Optics, Dunedin, FL) every 300 ms. The program simultaneously monitors the surface temperature of the Al_2O_3 crystal, and via a PID (proportional-integral-derivative) feedback algorithm, linearly increments the temperature of the Al_2O_3 crystal in the TPD experiments. 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.

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 and based on the mass spectral peak desorption temperature, T_p (10-12). 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 to an optical interference experiment. The interference experiment yielded accurate rate of deposition, and is described in detail elsewhere (13).

Results and Discussion

From the peak desorption temperature of biphenyl, T_p of 227 K, the activation energy for desorption, E_a, was calculated to be 58.9 kJ mole^{-1}. In Figure 1 the spectral profile for biphenyl as a function of temperature is shown with $\Theta_{biphenyl}$ = 384 ML. During the TPD experiment that begins at 110K, the intense fluorescence at λ_{max} ~ 320 is due to the amorphous biphenyl in the twisted (non-planar) conformer. (Cf. Figure 1). The disorder-to-order transition occurs at 161 ± 1 K and the intensity decreases to 20 ± 5% of the original, and there is a spectral red-shift to λ_{max} of 345 nm. Compared to the amorphous phase, the ordered phase was previously reported to be the more thermally stable phase(8). This was shown by annealing the adlayer at a temperature higher than the transition temperature, followed by cooling to 110 K and then conducting the TPD experiment. For $\Theta_{biphenyl}$ = 91 ± 16 ML, the post-anneal wavelength-resolved TPD showed a λ_{max} of 345 nm indicating the presence of only the ordered biphenyl with the molecules in the planar conformation (Cf. Figure 2).

When the deposition temperature was lowered to 135 K, the wavelength-resolved TPD was as shown in Figure 3. A new fluorescent species with λ_{max} at 370 nm was observed. When the fluorescence of the ordered planar biphenyl (spectrum at 220 K) was subtracted from Figure 3, the fluorescence of the biphenyl excimer was isolated in the wavelength-resolved TPD that is shown in Figure 4. This spectral profile is consistent with that of an excimer, which is red-shifted relative to the monomer, and one that is spectrally broad and featureless.

In the wavelength-resolved TPD, the range of temperatures during which the ordered planar biphenyl is present can be revealed by subtracting the spectrum that was obtained initially at

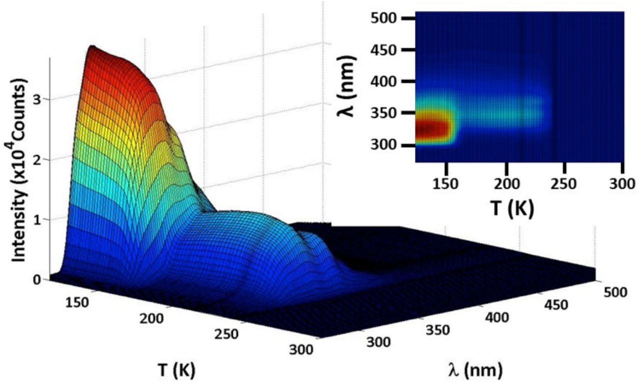

Figure 1. Wavelength-resolved TPD of multilayer biphenyl with $\Theta_{biphenyl}$ ~384 ML. Initially the amorphous twisted conformer is observed with λ_{max} ~ 320. At the transition temperature at 161 ± 1K the intensity decreases to ~20% and the λ_{max} red shifts to ~ 345 nm which is the ordered planar conformer. Inset is the top view.

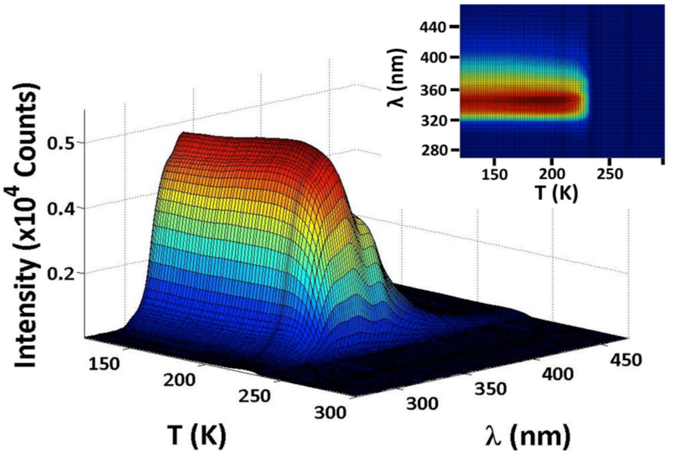

Figure 2. Wavelength-resolved TPD of multilayer biphenyl with $\Theta_{biphenyl}$ ~91 ML. Deposition temperature = 165 K. Only the ordered planar conformer of biphenyl is observed. Inset is the top view.

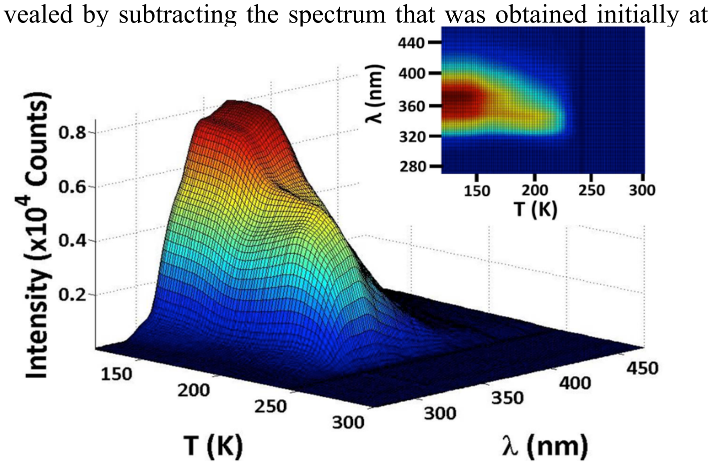

Figure 3. Wavelength resolved TPD of multilayer biphenyl with $\Theta_{biphenyl}$ ~116 ML. Deposition temperature = 135 K. The intensity of the excimer with λ_{max} at 370 nm dominate. The planar ordered biphenyl at 345 nm is also visible. Inset is the top view.

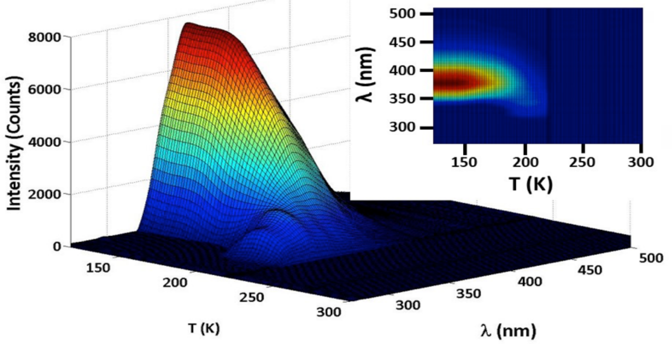

Figure 4. Wavelength resolved TPD of multilayer biphenyl with $\Theta_{biphenyl}$ ~250 ML but spectrum at 220 K subtracted from Figure 3 so that only the excimer is apparent. Inset is the top view.

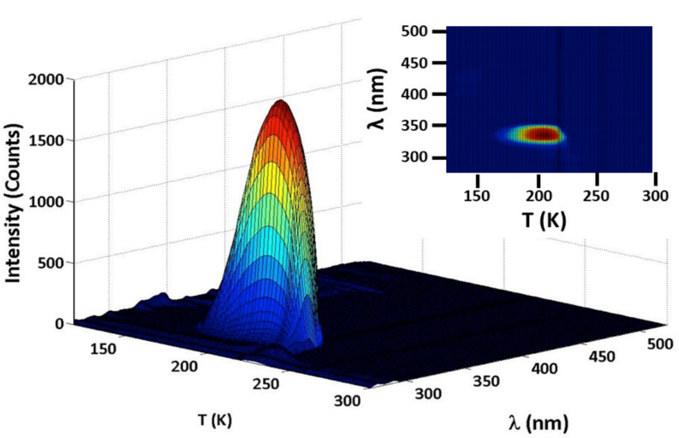

Figure 5. Wavelength resolved TPD of multilayer biphenyl with $\Theta_{biphenyl}$ ~167 ML but spectrum at 110 K subtracted from Figure 3 so that only the ordered planar conformer of biphenyl is observed. Inset is the top view.

110 K in Figure 3 from the rest of the wavelength-resolved TPD in the same figure. What remained after the subtraction is shown in Figure 5. Since the initial spectrum is rich in excimer fluorescence, the residual wavelength-resolved TPD is that of the ordered biphenyl with the molecules in the planar conformation. This is identical to that portion of the spectrum > 161 K that is shown in Figure 1. Therefore when the biphenyl adlayer is annealed at 135 K, the two forms of biphenyl in the planar conformations are present: the excimer (amorphous planar biphenyl) and the ordered planar biphenyl. It should be noted that when the biphenyl was deposited at 110 K, then annealed at 135 K, cooled back down to 110 K and the TPD experiment was done, what was observed was as shown in Figure 1. This indicates that once the amorphous biphenyl matrix is formed, biphenyl cannot overcome the torsional energy barrier.

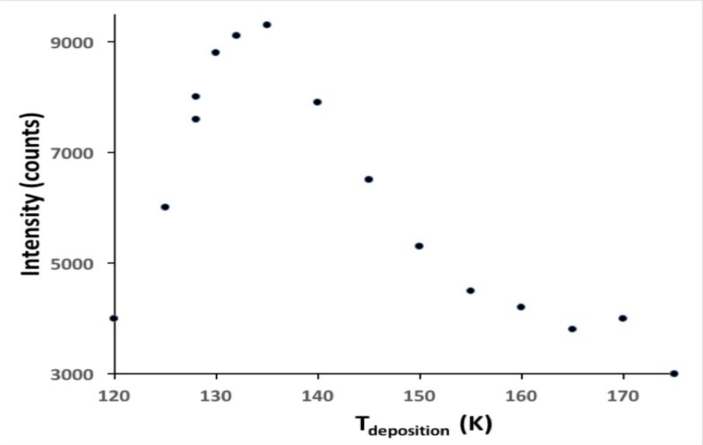

Figure 6. Plot of the intensity of the excimer at 370 nm as a function of deposition temperature. $\Theta_{biphenyl}$ was held at 120 ± 20 ML.

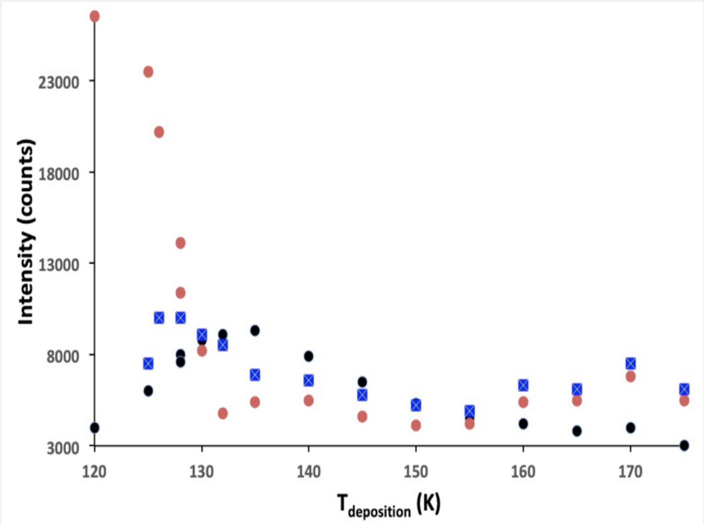

Figure 7. Plots of the intensities as a function of deposition temperature of the amorphous twisted conformer with λ_{max} ~ 320 in red, the ordered planar conformer with λ_{max} ~ 345 nm in blue and the excimer with λ_{max} at 370 nm in black. $\Theta_{biphenyl}$ was held at 120 ± 20 ML

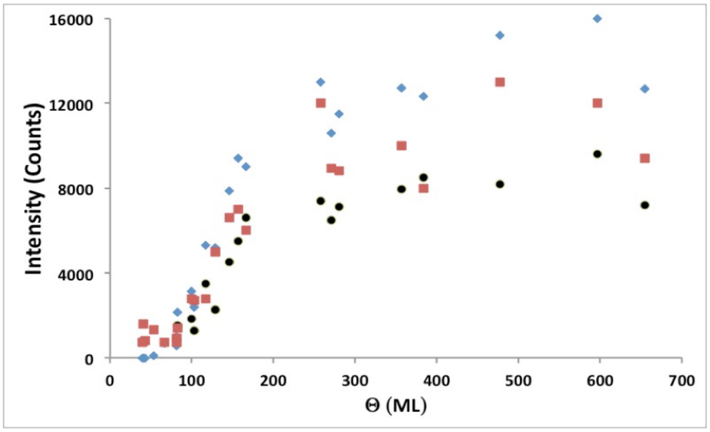

Figure 8. Plots of the intensities as a function of biphenyl coverage of the when the biphenyl at the deposition temperature of 140 K of the overlapped excimer (in blue) and ordered planar biphenyl (in red) and with the ordered planar biphenyl spectrum subtracted from the total spectrum (in black). Hence the black plot represents the excimer only intensity as a function of biphenyl coverage.

The intensity of the biphenyl excimer with λ_{max} at 370 nm as a function of deposition temperature is shown in Figure 6. Here $\Theta_{biphenyl}$ was held at 120 ± 20 ML. As the plot shows, excimers were formed by deposition onto the Al_2O_3 in the temperature interval of 125-155 K. Lower deposition temperatures yielded spectra such as that shown in Figure 1 and at higher temperatures, the spectra were similar to that shown in Figure 2. Arrhenius-like plots of the rising and falling edges as a function of inverse of the temperature revealed that the slope of the rising edge was about 10 times that of the falling edge. The falling edge is the result of the adlayer undergoing an ordering transition. Activation energy of crystallization for biphenyl was reported to be about 72 kJ mol^{-1} (14). Theoretical calculations have shown the planar and perpendicular torsional energy barriers in biphenyl to be about 8.0-9.1 and 8.3-13.7 kJ mol^{-1} (15,16). Although the torsional barrier reported here is much higher, it is consistent with our current experimental findings.

In Figure 7, the intensity versus deposition temperature plots of the various conformers of biphenyl with $\Theta_{biphenyl}$ = 120 ± 20 ML are shown. The plot in red is the intensity of the λ_{max} ~ 320 nm that has been identified as the amorphous twisted conformer. The black data points correspond to the excimer at λ_{max} ~ 370 nm and the blue, to the planar ordered form of biphenyl with λ_{max} at 345 nm. The intensities in the plots are uncorrected for the apparent overlap due to the low resolution of the spectrometer as is evident from Figure 3 in which both peaks at 345 and 370 nm have comparable intensities. Nevertheless the deposition temperature clearly has an effect on the relative amounts of the three species that are formed. When the deposition temperature reaches the torsional energy barrier, the formation of the planar excimer quenches the fluorescence of the twisted biphenyl. Quenching occurs because the quantum yield of the excimer is not as favorable as that of the amorphous twisted conformer of biphenyl. One noteworthy feature in the plot is that the intensities decrease to minima at about 5 K lower than the disorder-to-order transition at 161 K, the cause of which is being investigated.

The relative fluorescence intensities immediately after deposition at 110 K of the two amorphous species as a function of biphenyl coverage are shown in Figure 8. The intensities of the initial excimer intensity at 370 nm is shown as blue diamonds and the intensity of the planar ordered biphenyl at λ_{max} of 345 nm is shown as red squares. The plot in black is the intensity of the excimer when the spectrum at 220 K (spectrum that was rich in the ordered planar biphenyl) was subtracted from the entire wavelength resolved TPD. The resulting spectrum that result is almost entirely due to the biphenyl excimer as shown in Figure 4. Although the data are somewhat scattered at the higher coverages, it appears that the intensity levels at a deposition of roughly 300 ML. The interpretation is that at coverages higher than ~300 ML, the system has reached the limit in the available photons to excite the fluorophores in the adlayer has been reached. Since this leveling occurs at a high coverage, the adlayer appears to be relatively transparent to the excitation light which is a feature that is not often encountered in these aromatic molecular adlayers.

Of interest is what was observed at coverages lower than $\Theta_{biphenyl}$ of about 80 ML. Figure 9 shows the wavelength resolved TPD of an ~ 50 ML adlayer when the deposition was done at 140 K. The absence of the excimer fluorescence intensity is thought to occur because of one or more of these factors: non-uniformity in the deposition, required minimum surface coverage of biphenyl for the formation of the excimer, and when excimer do form, relative to the intensity of the monomer, the intensity of the excimer is quenched due the twice required number of biphenyl molecules to form the excimer. This effect was observed in a previous study in which the homoepitaxy of biphenyl was investigated (7). In order to effect homoepitaxy, biphenyl-d10 in which $\Theta_{biphenyl\text{-}d10}$ ~ 40 ML was deposited and annealed to 165 K to effect ordering prior to the deposition of biphenyl as an overlayer (7). Lower coverages of biphenyl-d10 showed wavelength-resolved TPD of biphenyl similar to that of Figure 1, whereas coverages of biphenyl-d10 that were greater exhibited wavelength-resolved TPD similar to Figure 2 where the adlayer ordering was complete (7). Hence $\Theta_{biphenyl\text{-}d10}$, ~ 40 ML was the lower limit of annealed biphenyl that exhibited homoepitaxy (7). It is not surprising then that the excimer is not observed in the low coverage regime. Excimers can form within the islands as long as the activation energy to overcome the torsional angle barrier is thermally available.

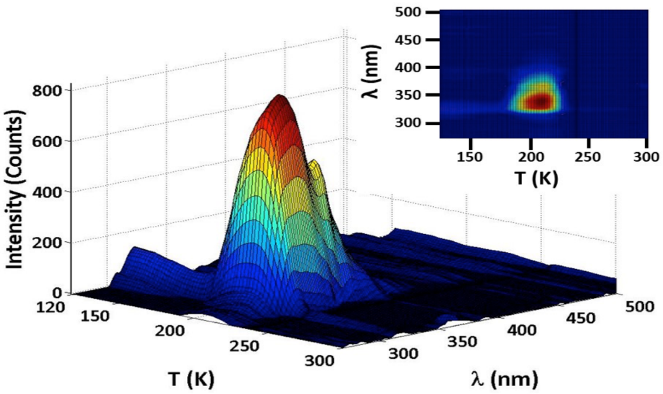

Figure 9. Wavelength resolved TPD of multilayer biphenyl with $\Theta_{biphenyl}$ ~50 ML with the absence of the excimer fluorescence intensity.

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