DETERMINATION OF TORSIONAL ANGLES OF BIPHENYL MOLECULES ON Al₂O₃

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Abstract

Dihedral angles for biphenvyl containing molecules were plotted as functions of fluorescence wavelengths of these molecules on Al₂O₃. The equation for the best fit line gave an estimate of the dihedral angle from the fluorescence wavelength of any other biphenvyl molecule. Since biphenvyl becomes more planar on naphthalene than when it had been directly deposited on Al₂O₃ due to epitaxy, this equation was used to determine whether sterically hindered 2-methyl and 2,2'-dimethylbiphenvyl would compete epitaxially when similarly deposited onto naphthalene. A change of 26º and 29º towards planarity were observed for these molecules on naphthalene, respectively. In addition, they formed van der Waals complexes, or exciplexes, with naphthalene for which the change in dihedral angles of 36º and 56º were observed, respectively. Other biphenvyl molecules such as 4-methylbiphenvyl exhibited three distinct fluorescence peaks with λmax of 321, 352 and 372 nm. A variety of methods were used to characterize the nature of these three molecular types during the temperature programmed desorption (TPD). The analyses show that the 4-methylbiphenvyl that has the λmax of 321 nm with a dihedral angle of 37º is associated with the amorphously deposited molecules, while the dominant species in the ordered adlayer has a λmax of 352 with a dihedral angle of 0º. The species with the λmax of 372 nm fluorescence is the excimer of 4-methylbiphenvyl. The dihedral angle of 31º did not change epitaxially when 4,4'-dimethylbiphenvyl was deposited on naphthalene, but did form an exciplex with naphthalene. 3-Methylbiphenvyl, with a dihedral angle of 53º became slightly more planar when deposited on planar biphenvyl.

Introduction

The two phenyl groups in biphenvyl can have varying dihedral angles. In the gas phase, biphenvyl is in the twisted conformer, whereas in the solid crystal, biphenvyl has a more planar conformer. Previous studies have shown that these conformers gave rise to different fluorescence spectra, so that these spectral signatures can be used to assign biphenvyl’s conformer when it is vapor deposited on a surface. When biphenvyl is vapor deposited on Al₂O₃ at 110 K, the fluorescence is from the twisted conformer and has a λmax = 320 nm. When the surface temperature is ramped in a temperature programmed desorption (TPD) experiment subsequent to deposition, biphenvyl undergoes changes in the conformer from twisted to a more planar conformer with λmax = 331 nm during the disorder-to-order transition at 160 K with a concomitant reduction in intensity. Finally, if biphenvyl is deposited on top of a planar molecule such as naphthalene, it will deposit epitaxially in the planar conformer.

The dihedral angles of other molecules that have the biphenvyl moiety within the structure, such as 9,10-dihydrophanthrene, fluorene, 2-methylbiphenvyl, 2,2'-dimethylbiphenvyl, 4-methylbiphenvyl and 4,4'-dimethylbiphenvyl have been reported. In Figure 1, these dihedral angles are plotted as a function of the observed fluorescence λmax of these molecules. From the trend line equation, the torsional angle can be estimated from the observed fluorescence λmax for any biphenvyl containing molecule.

This plot was then applied to an interesting question related to the facility with which biphenvyl accommodates an epitaxial underlayer’s geometry by overcoming the rotational energy barrier. Just as naphthalene caused biphenvyl to become more planar, would it cause the sterically hindered 2-methylbiphenvyl and 2,2'-dimethylbiphenvyl to also become more planar, or would the rotational energy barrier be too large to overcome when epitaxially deposited on naphthalene. In addition, the λmax’s of the conformers of 3-methylbiphenvyl, 4-methylbiphenvyl, 4-ethylbiphenvyl and 4,4'-dimethylbiphenvyl are interpreted and the surface dynamics on Al₂O₃ during the TPD are reported.

Experimental

Naphthalene, 2-methylbiphenvyl, 2,2'-dimethylbiphenvyl, 3-methylbiphenvyl, 4-methylbiphenvyl, 4,4'-dimethylbiphenvyl and 4-ethylbiphenvyl were of the highest purity that was commercially available. (Sigma-Aldrich, St. Louis, MO; TCI, Pittsburgh, PA; Santa Cruz Biotechnology, Santa Cruz, CA). These compounds were placed in separate sample holders and outgassed by freeze-pump-thaw cycles. Since the Al₂O₃ crystal was mounted on a differentially-pumped rotatable high-vacuum adapter, deposition was accomplished by orienting the crystal perpendicularly to tubes attached to high-precision leak valves. These valves were used to quantitatively leak in the vapor from the sample holders into the facility with which biphenvyl accommodates an epitaxial underlayer’s geometry by overcoming the rotational energy barrier. Just as naphthalene caused biphenvyl to become more planar, would it cause the sterically hindered 2-methylbiphenvyl and 2,2'-dimethylbiphenvyl to also become more planar, or would the rotational energy barrier be too large to overcome when epitaxially deposited on naphthalene. In addition, the λmax’s of the conformers of 3-methylbiphenvyl, 4-methylbiphenvyl, 4-ethylbiphenvyl and 4,4'-dimethylbiphenvyl are interpreted and the surface dynamics on Al₂O₃ during the TPD are reported.

Figure 1. Dihedral angles of biphenvyl and related molecules with biphenvyl moiety as a function of fluorescence wavelength. The trend line equation is shown.
The temperature programmed desorption experiment was done by ramping the surface temperature by passing current through a tantalum foil that was in thermal contact with the Al$_2$O$_3$. A chromel-alumel thermocouple was mounted directly onto the crystal in order to continuously monitor the surface temperature and provide the necessary feedback to generate the linear temperature ramp in the TPD experiment. To ensure a clean surface, the Al$_2$O$_3$ was heated to 300 K after each run.

Optical pumping was accomplished by filtering the light from a super high-pressure mercury lamp through a 0.25 m monochromator centered on 250 ± 10 nm. The image of the Al$_2$O$_3$ crystal upon which the fluorophore had been deposited was focused by a quartz lens onto the tip of a fiber optic cable that had been placed inside the vacuum chamber. The fiber cable was fed through a port and the signal was collected by a computer interfaced Ocean Optics spectrometer (Dunedin, FL) that viewed the spectrum every 300 ms. During the TPD, a LabVIEW (National Instruments, Austin, TX) program that had been written in-house took the fluorescence spectra from an Ocean Optics USB4000 spectrometer (Ocean Optics, Dunedin, FL) in real time. The program simultaneously monitored the surface temperature of the Al$_2$O$_3$ crystal, and through a PID (proportional-integral-derivative) feedback algorithm, linearly ramped the temperature of the Al$_2$O$_3$ crystal at 2 K s$^{-1}$. The program also scanned the residual gas analyzer for the masses of the compounds that had been deposited on the Al$_2$O$_3$. The spreadsheet that comprised the spectra as a function of temperature was transferred to Matlab (MathWorks, Natick, MA) from which the wavelength-resolved TPD figures were made.

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 was based on the mass spectral peak desorption temperature, $T_p$. The uncertainties in the desorption temperatures and the propagated error in the activation energies were ±3%.

The adlayer coverages were determined as follows: the beam from a diode laser was directed at the surface during deposition. As the adlayer thickness increased, an optical interference occurred in the laser beam between the reflected beam at the vacuum-adlayer interface and the adlayer-Al$_2$O$_3$ interface. The integrated mass spectral peaks were calibrated to the optical interference experiment and the coverages, $\Theta$, are reported in monolayers (ML) with an error of ±25%. For three molecules, 4-ethylbiphenyl, 3-methylbiphenyl, and 3,3’-dimethylbiphenyl interference experiment failed to yield sufficient intensity and only an approximate conversion factor was used to obtain the coverages; estimates of the error is about ±50%.

Transmittance experiment was performed by sending part of the excitation light that had passed through the sample to a photomultiplier that was interfaced to an analog-to-digital converter. In this way, the transmitted light intensity was logged during the TPD.

Once deposited, annealed samples were prepared by passing current through the tantalum foil to ramp the temperature to a target value, and then maintaining it for about 5 seconds to anneal the adlayer. The crystal was allowed to cool back down to the deposition temperature, following which the TPD experiment was done.

Vapor deposition at different temperatures from that of the usual 115 K as shown in Figures 14 was performed by ramping to a set temperature and maintained (±1 K) during the deposition. After deposition was completed, the current to the Ta foil was turned off and the sample allowed to cool back to 115 K before the TPD experiment was done.

In the plot shown in Figure 1, the error in the torsional angle was determined from the uncertainty in the $\lambda_{max}$, which is about 1 nm. This uncertainty resulted in an error of ±2º in the angle and should be noted when the uncertainty is not explicitly stated. If a negative dihedral angle was determined by the trend line equation, 0º was reported.

For the epitaxial experiments, the underlayer was deposited first, followed by the substituted biphenyl. Naphthalene underlayer was deposited at 115 K. For biphenyl, the underlayer was either deposited at 138 K to form the biphenyl excimer which was nearly planar, 3º, or it was annealed at 170 K, which was past the disorder-to-order transition, in which case the dihedral angle was 25º.

Results and Discussion

Naphthalene and 2-methylbiphenyl multilayers and naphthalene/2-methylbiphenyl bilayer:

The wavelength-resolved TPD of naphthalene multilayer (neat) that had been vapor deposited with a coverage of $\Theta_{naphthalene}$ of 65 ML is shown in Figure 2. Upon deposition, the excimer fluorescence origin was observed at $\lambda_{max}$ ~ 398 nm. The mass spectrometer was used to determine the peak desorption temperature, $T_p$, which was 216 K. First-order desorption was assumed and the activation energy for desorption, $E_a$, was calculated to be 54.9 kJ/mol.11-13

Figure 2. Wavelength resolved TPD of multilayer naphthalene. $\Theta_{naphthalene}$ = 65 ML. The fluorescence at $\lambda_{max}$ ~ 398 nm is due to the excimer as seen in the inset which is the top view.
The wavelength-resolved TPD of 2-methylbiphenyl multilayer at \( \Theta_{2\text{-methylbiphenyl}} \) of 99 ML is shown in Figure 3. Upon deposition, the fluorescence was observed at \( \lambda_{\text{max}} \sim 310 \text{ nm} \). As can be seen from the inset to Figure 3, the fluorescence \( \lambda_{\text{max}} \) remained fixed through the TPD. The trend line from Figure 1 gave a dihedral angle of 63º at this wavelength. The peak desorption temperature, \( T_{\text{p}} \), was 227 K. First-order desorption was assumed and the activation energy for desorption, \( E_a \), was calculated to be 58.7 kJ/mol.\(^{11-13}\)

As shown in Figure 4, when 2-methylbiphenyl was deposited on naphthalene, a new fluorescence peak was observed at \( \lambda_{\text{max}} \sim 321 \text{ nm} \) the dihedral angle of which was calculated to be 37º. This angle was 26º more planar than in the multilayer 2-methylbiphenyl. A plot of the fluorescence intensity at 321 nm as a function of the ratio of \( \Theta_{2\text{-methylbiphenyl}} \) to \( \Theta_{\text{naphthalene}} \) is shown in Figure 5. Here, \( \Theta_{\text{naphthalene}} \) was kept constant at \( 74 \pm 14 \text{ ML} \) while \( \Theta_{2\text{-methylbiphenyl}} \) was varied. The intensity of 2-methylbiphenyl fluorescence increased with coverage of 2-methylbiphenyl and continued to do so past that which is shown in the figure. The ever increasing intensity of the peak at 321 nm was evidence that epitaxy was driving the growth of this more planar 2-methylbiphenyl species and if deposition were continued, so will this peak’s intensity.

As also seen in Figure 4, the most intense peak appeared at 204 K. It begins at 190 K and disappeared at desorption. Since this was present only in the bilayer (Cf. Figures 2 and 3) this fluorescence was tentatively attributed to a weakly held van der Waals complex composed of the two components in the excited state complex or exciplex. This was composed of two peaks at \( \lambda_{\text{max}} \sim 326 \) and 336 nm. Since the intensities of these two peaks increased proportionately with coverage, the longer wavelength peak was assigned as a vibration built on the 326 nm peak. Based on the \( \lambda_{\text{max}} \) values, the dihedral angle for the complex is 27º which is 10º more planar than when it was epitaxially on naphthalene. The ratio of fluorescence intensities of the 326 nm to 310 nm was plotted as a function of the ratio of \( \Theta_{2\text{-methylbiphenyl}} \) over \( \Theta_{\text{naphthalene}} \) and is shown in Figure 5. Instead of just the fluorescent intensities of the 326 nm peak, the ratios were used to normalize the intensities due to the run-to-run variation in the coverages. The leveling in the plot shows that the exciplex composed of naphthalene and 2-methylbiphenyl interacted with a molecular ratio of roughly 1:1.

As also seen in Figure 4, when 2-methylbiphenyl was deposited on naphthalene, a new fluorescence peak was observed at \( \lambda_{\text{max}} \sim 310 \text{ nm} \). As can be seen from the inset to Figure 3, the fluorescence \( \lambda_{\text{max}} \) was varied. This shows the stiochiometry of exciplex composition. 2,2’-Dimethylbiphenyl adlayer and naphthalene/2,2’-dimethylbiphenyl bilayer:

The wavelength-resolved TPD of 2,2’-dimethylbiphenyl multilayer (neat) at \( \Theta_{2,2'\text{-dimethylbiphenyl}} = 36 \text{ ML} \) is shown in Figure 6. The peak desorption temperature, \( T_{\text{p}} \), was 228 K. First-order desorption was assumed and the activation energy for desorption, \( E_a \), was calculated to be 58.9 kJ/mol.\(^{11-13}\) Upon deposition, the fluorescence origin was at \( \lambda_{\text{max}} \sim 301 \text{ nm} \) and remained fixed throughout the TPD experiment. The dihedral angle from the trend line equation is 87º.

Shown in Figure 7 is the wavelength resolved TPD of the naphthalene and 2,2’-dimethylbiphenyl bilayer. As can be observed from both the angled view and the inset, there are two peaks in the initial spectra: \( \lambda_{\text{max}} \) at 301 and 312 nm. The first of these is also observed in the neat spectrum and therefore is assigned to the molecules that are not bound to the underlayer naphthalene.

The wavelength-resolved TPD of 2-methylbiphenyl multilayer at \( \Theta_{2\text{-methylbiphenyl}} \) of 99 ML is shown in Figure 3. Upon deposition, the fluorescence was observed at \( \lambda_{\text{max}} \sim 310 \text{ nm} \). As can be seen from the inset to Figure 3, the fluorescence \( \lambda_{\text{max}} \) remained fixed through the TPD. The trend line from Figure 1 gave a dihedral angle of 63º at this wavelength. The peak desorption temperature, \( T_{\text{p}} \), was 227 K. First-order desorption was assumed and the activation energy for desorption, \( E_a \), was calculated to be 58.7 kJ/mol.\(^{11-13}\)

As shown in Figure 4, when 2-methylbiphenyl was deposited on naphthalene, a new fluorescence peak was observed at \( \lambda_{\text{max}} \sim 321 \text{ nm} \) the dihedral angle of which was calculated to be 37º. This angle was 26º more planar than in the multilayer 2-methylbiphenyl. A plot of the fluorescence intensity at 321 nm as a function of the ratio of \( \Theta_{2\text{-methylbiphenyl}} \) to \( \Theta_{\text{naphthalene}} \) is shown in Figure 5. Here, \( \Theta_{\text{naphthalene}} \) was kept constant at \( 74 \pm 14 \text{ ML} \) while \( \Theta_{2\text{-methylbiphenyl}} \) was varied. The intensity of 2-methylbiphenyl fluorescence increased with coverage of 2-methylbiphenyl and continued to do so past that which is shown in the figure. The ever increasing intensity of the peak at 321 nm was evidence that epitaxy was driving the growth of this more planar 2-methylbiphenyl species and if deposition were continued, so will this peak’s intensity.

As also seen in Figure 4, the most intense peak appeared at 204 K. It begins at 190 K and disappeared at desorption. Since this was present only in the bilayer (Cf. Figures 2 and 3) this fluorescence was tentatively attributed to a weakly held van der Waals complex composed of the two components in the excited state complex or exciplex. This was composed of two peaks at \( \lambda_{\text{max}} \sim 326 \) and 336 nm. Since the intensities of these two peaks increased proportionately with coverage, the longer wavelength peak was assigned as a vibration built on the 326 nm peak. Based on the \( \lambda_{\text{max}} \) values, the dihedral angle for the complex is 27º which is 10º more planar than when it was epitaxially on naphthalene. The ratio of fluorescence intensities of the 326 nm to 310 nm was plotted as a function of the ratio of \( \Theta_{2\text{-methylbiphenyl}} \) over \( \Theta_{\text{naphthalene}} \) and is shown in Figure 5. Instead of just the fluorescent intensities of the 326 nm peak, the ratios were used to normalize the intensities due to the run-to-run variation in the coverages. The leveling in the plot shows that the exciplex composed of naphthalene and 2-methylbiphenyl interacted with a molecular ratio of roughly 1:1.

Shown in Figure 7 is the wavelength resolved TPD of the naphthalene and 2,2’-dimethylbiphenyl bilayer. As can be observed from both the angled view and the inset, there are two peaks in the initial spectra: \( \lambda_{\text{max}} \) at 301 and 312 nm. The first of these is also observed in the neat spectrum and therefore is assigned to the molecules that are not bound to the underlayer naphthalene.
The second peak is assigned to those molecules that are epitaxially bound to the naphthalene underlayer. The resolvable $\lambda_{\text{max}}$'s infers that the conformer of 2,2'-dimethylbiphenyl on naphthalene is discrete, rather than distributed over a range of dihedral angles. From the trend line in Figure 1, the torsional angles for 2,2'-dimethylbiphenyl were determined to be 87º and 58º for the 301 and 312 nm peaks, respectively.

A plot of the ratio of 312 nm / 301 nm intensities as a function of $\Theta_{\text{naphthalene}} / \Theta_{2,2'-\text{dimethylbiphenyl}}$ is shown in Figure 8. The relative intensities leveled as the ratio of naphthalene to 2,2'-dimethylbiphenyl coverage was increased to about 1.0-1.5 ML/ML. The inference is that the interaction between naphthalene and 2,2'-dimethylbiphenyl occurred with this molecular composition.

During the TPD, two intense peaks with $\lambda_{\text{max}}$= 324 and 334 nm appeared at 210 K as seen in Figure 7. As with 2-methylbiphenyl, the 334 nm peak that is separated by 10 nm from the 324 nm peak was assigned to a molecular vibration. From the trend line equation, the dihedral angle of the peak at 324 nm was 31º. The 2,2'-dimethylbiphenyl in the exciplex was more planar than the epitaxial conformer by 27º. This could mean that the complex was very tightly bound with a small intermolecular distance. A plot of the ratio of intensities of the 324 nm to 301 nm as a function of the ratio of 2,2'-dimethylbiphenyl to naphthalene coverages, $\Theta_{\text{naphthalene}} / \Theta_{2,2'-\text{dimethylbiphenyl}}$ is shown in Figure 8. The leveling off occurred at about coverage ratio of 1.5-2 ML/ML and most likely represents the stoichiometric composition of the exciplex.

It should be noted that neither 2,2'-dimethylbiphenyl nor 2-methylbiphenyl exhibited the distinct disorder-to-order transition exhibited by other substituted biphenyl molecules. This was due to the steric hindrance at the ortho positions.

3-Methylbiphenyl multilayer:

The wavelength-resolved TPD of 3-methylbiphenyl is shown in Figure 9. The coverage of $\Theta_{3\text{-methylbiphenyl}}$ was 108 ML. The fluorescence had a $\lambda_{\text{max}}$ of 314 nm that correlated to a dihedral angle of 53º from Figure 1. At about 200 K, 3-methylbiphenyl underwent a weak disorder-to-order transition, where the transition in which the intensity change was not as distinct compared to biphenyl. The desorption temperature, $T_p$, was 223 K and the calculated activation energy for desorption was 57.6 kJ mol$^{-1}$.

In the bilayer study with naphthalene as the underlayer, the fluorescence had a $\lambda_{\text{max}}$ of 320 nm with a corresponding dihedral angle of 39º for 3-methylbiphenyl. This showed that 3-methylbiphenyl has the tendency to deviate from the initial dihedral angle by 14º. This was comparable to the behavior of biphenyl. In addition, when deposited on biphenyl that had been annealed at 170 K...
which was past the disorder-to-order transition, the fluorescence $\lambda_{\text{max}}$ red-shifted from ~314 nm in the neat to 321 nm in the bilayer. The same wavelength shift was also observed when deposited on biphenyl that had been deposited at 138 K.

3,3'-Dimethylbiphenyl multilayer:
The wavelength-resolved TPD of 3,3'-dimethylbiphenyl with a coverage of approximately 200 ML is shown in Figure 10. The $T_d$ was 238 K and the activation energy for desorption was calculated to be 61.7 kJ mol$^{-1}$. Upon deposition, a $\lambda_{\text{max}}$ of of 307.7 nm was observed, along with a more intense vibrational peak with a $\lambda_{\text{max}}$ of 318 nm. The disorder-to-order transition was observed at 200 K, with a red-shift of the $\lambda_{\text{max}}$ to 345 nm (black arrow in Figure 10). At approximately 226 K, a broad, featureless peak with a $\lambda_{\text{max}}$ of 370 nm was detected, which has been assigned as the excimer of 3,3'-dimethylbiphenyl (green arrow in Figure 10).

An epitaxial study was done with naphthalene as the underlayer and no shift in the $\lambda_{\text{max}}$ of was detected. A complex appeared to form at about 202 K, with a $\lambda_{\text{max}}$ of of 324 nm, along with the vibrational $\lambda_{\text{max}}$ at 333 nm. Here again, the 333 nm peak was more intense than the 324 nm fluorescence. When biphenyl that had been deposited at 138 K or annealed to 170 K as underlayers, 3,3-dimethylbiphenyl did not show evidence of epitaxial growth on these two planar forms of biphenyl.

4-Methylbiphenyl multilayer:
The wavelength-resolved TPD of 4-methylbiphenyl that had been vapor deposited with a coverage of $\Theta_{4\text{-methylbiphenyl}}$ of 188 ML is shown in Figure 11. The peak desorption temperature was 236 K. First-order desorption was assumed and the activation energy for desorption, $E_a$, was calculated to be 61.3 kJ mol$^{-1}$. As can be seen from Figure 11, the $\lambda_{\text{max}}$ of the fluorescence which is at 321 nm upon deposition remains constant through the TPD. Theoretically calculated angle$^\circ$ of 42$^\circ$ agree well with the dihedral angle of 37$^\circ$ as determined from the trend line given in Figure 1. A narrowing of the peak width was observed at 150 K, presumably from the reorganization of the molecules as the thermal energy was increased and the adlayer underwent an annealing process.

During a 10 K interval beginning at 172 K the adlayer underwent a disorder-to-order process that was analogous to the behavior of biphenyl. The process was associated with the almost complete quenching of the fluorescence. Although not shown here, the intensity of the transmitted excitation light was plotted as a function of temperature. The plot showed that the transmittance increased subsequent to the disorder-to-order transition. This would be the result expected of a more transparent adlayer when the transition to an ordered adlayer occurred and was consistent with a disorder-to-order transition.

Figure 12 shows the effect of annealing to 170 K, which is just short of the disorder-to-order transition. This caused the fluorescence intensity to fall linearly with increasing temperature due to thermally induced relaxation processes. In addition, annealing had the effect of narrowing the width of the peak at 321 nm while still exhibiting a disorder-to-order transition at the same temperature as without the anneal as shown in Figure 11.

When the deposition was performed at 130 K instead of 115 K as in Figure 11, a very different wavelength-resolved TPD was observed and is shown in Figure 13. Here two peaks were measured: one at a $\lambda_{\text{max}}$ of 352 nm and another at 372 nm. From the trend line...
equation in Figure 1, the 352 nm peak corresponded to a 0° dihedral angle, and represented 4-methylbiphenyl molecules that were planar on Al₂O₃. The conclusion was that sufficient thermal energy existed at this surface temperature to cause the 4-methylbiphenyl to become ordered immediately upon deposition. This peak at 352 nm is qualitatively more narrow than the peak at 321 nm that was observed at deposition at 115 K.

Indicated by an arrow in Figure 13, the second peak at 372 nm is tentatively attributed to the excimer of 4-methylbiphenyl. Three reasons support this assignment. First, the λ_{max} of 372 nm for 4-methylbiphenyl was close to the λ_{max} of 370 nm of the excimer of biphenyl. Second, the broad spectrum that was observed here is characteristic of excimers. Third, from Figure 1, the dihedral angle with this λ_{max} exceeded that of the planar molecule, 9,10-dihydrophenanthrene. We believe this is the first reported excimer of 4-methylbiphenyl. When the 352 nm spectrum was subtracted from the complete wavelength-resolved TPD as shown in Figure 14, what remains was the wavelength-resolved TPD of the 4-methylbiphenyl excimer. In the inset, the spectrally broad feature that is characteristic of excimer fluorescence is clearly evident.

Since the deposition temperature determined the species of 4-methylbiphenyl that form on Al₂O₃, in Figure 15, the fluorescence intensities at 321 nm (blue plot, y-axis to the left), 352 nm (green plot, y-axis to the right), and 372 nm (purple plot, y-axis to the right) were plotted as a function of the deposition temperature. When the intensity of the 321 nm peak (4-methylbiphenyl with a dihedral angle of 37°) decreased to almost zero at a deposition temperature of 130 K, the 352 nm (planar) and 372 nm (excimer) peaks increased to maximum at ~140 K as seen in the figure. These plots show that the presence of the planar conformer allowed for the formation of the excimer. Both intensities decrease after the disorder-to-order transition at 175 K (See Figure 15) until desorption at 236 K when they decreased to zero.

Three bilayer studies were done to understand the behavior of 4-methylbiphenyl when it was deposited on other molecules, such as naphthalene and biphenyl. These are described next.

**Bilayers of naphthalene/4-methylbiphenyl and biphenyl/4-methylbiphenyl:**

In previous epitaxy studies, the conformer of biphenyl was found to be fairly sensitive to the nature of the underlayer molecule. For example when naphthalene was the underlayer, biphenyl readily became planar upon deposition on it. When 4-methylbiphenyl was deposited on naphthalene, however, it did not deposit in the planar conformer, and rather it remained twisted as evidenced by the 321 nm fluorescence as seen in Figure 16. Furthermore, intermolecular interaction is presumed to be relatively weak in this case because naphthalene was found to desorb
Biphenyl undergoes the disorder-to-order transition at about 160 K, whereupon it becomes more planar with the dihedral angle decreasing from 41° to 25°. When 4-methylbiphenyl was deposited on biphenyl that had been annealed at 170 K, so that the biphenyl underlayer was more planar, then 4-methylbiphenyl deposited in the most planar conformation (λ<sub>max</sub> = 352 nm) (See Figure 17). In addition, the excimer was also present.

When biphenyl was deposited at 138 K, it was mostly in the planar conformer, but sufficiently amorphous that allowed for the formation of excimers. When 4-methylbiphenyl was then deposited upon this underlayer of biphenyl, it also formed excimers with λ<sub>max</sub> of 372 nm, along with the planar conformer with λ<sub>max</sub> of 352 nm as shown in Figure 18. Noteworthy was that in both Figures 17 and 18, biphenyl, that normally desorbed at 227 K, desorbed with the 4-methylbiphenyl. This was indicative of the high degree of van der Waals association for these two molecules.

4,4'-Dimethylbiphenyl multilayer:
The wavelength-resolved TPD of 4,4'-dimethylbiphenyl that had been vapor deposited with a coverage of Θ<sub>4,4'-dimethylbiphenyl</sub> of 117 ML is shown in Figure 19. The peak desorption temperature was 255 K. First-order desorption was assumed and the activation energy for desorption, E<sub>a</sub>, was calculated to be 65.4 kJ mol<sup>-1</sup>. As can be seen from the inset to the figure, the λ<sub>max</sub> of the fluorescence which was at 324 nm upon deposition remained constant throughout the TPD. The trendline equation in Figure 1 gave a dihedral angle of 31° for this molecule. Possible disorder-to-order transition occurred at 200 K, but without change in the λ<sub>max</sub>.

Attempts were made to epitaxially cause 4,4'-dimethylbiphenyl to become more planar by deposition on the more planar conformer of biphenyl. The more planar conformers of biphenyl were formed by deposition at 138 K and 170 K that favored the formation of planar excimer and ordered biphenyl, respectively. In both cases, the λ<sub>max</sub> of 4,4'-dimethylbiphenyl did not change from 324 nm.

When 4,4'-dimethylbiphenyl was deposited on naphthalene, an intense peak occurred at 220 K, with λ<sub>max</sub> of 324 nm, as shown in Figure 20. A plot of the intensity of this peak (blue arrow), normalized against the intensity of this peak at deposition temperature of 120 K (green arrow) as a function of the ratio of coverages of naphthalene and 4,4'dimethylbiphenyl, Θ<sub>naphthalene</sub>/Θ<sub>4,4'-dimethylbiphenyl</sub> ML, is shown in Figure 21. The leveling of the plot
at a coverage ratio of 2:1 naphthalene/4,4’-dimethylbiphenyl gave the approximate stoichiometry of the van der Waals complex. It should be noted that 4,4’-dimethylbiphenyl did not epitaxially form on naphthalene as indicated by the $\lambda_{\text{max}}$ that did not change when deposited on naphthalene underlayer.

4-Ethylbiphenyl multilayer:

The wavelength-resolved TPD of vapor deposited 4-ethylbiphenyl on Al$_2$O$_3$ with a $\Theta_{4$-ethylbiphenyl} of 107 ML is shown in Figure 22. The peak desorption temperature, T$_p$, for lower coverages was 240 K, and the E$_a$ was calculated to be 61.4 kJ mol$^{-1}$. Three $\lambda_{\text{max}}$’s at 322, 349 and 369 nm were observed. The peak at 322 nm was 4-ethylbiphenyl with a dihedral angle of 35º as determined from the equation in Figure 1. This would be the twisted conformer of the amorphous adlayer molecules. The second peak at 349 nm was observed after the disorder-to-order transition which was at 180 K and was due to the planar conformer with a dihedral angle of 0º. The third peak at 369 nm was most likely due to the excimer fluorescence, analogously to biphenyl and 4-methylbiphenyl. The intensities of these peaks as a function of deposition temperatures are plotted in Figure 23. The intensity of the 322 nm peak decreased at 130 K with a concomitant increase in intensities of the 349 and 369 nm peaks. The optimum temperature for the formation of the 4-ethylbiphenyl excimer was determined to be 150 K.

The wavelength-resolved TPD for 4-ethylbiphenyl that had been deposited at 150 K is shown in Figure 24. As can be clearly seen in the inset, the 349 nm peak was present, along with the broader fluorescence at 369 nm. Both of these fluorescence emissions are from the planar conformers of 4-ethylbiphenyl, with the latter being attributed to the excimer.

In the bilayer experiments, 4-ethylbiphenyl did not complex with naphthalene, nor did it epitaxially become more planar when deposited on naphthalene. In addition, when 4-ethylbiphenyl was deposited on the planar conformers of biphenyl by depositing at...
138 K to form the excimer or by annealing to 170 beyond the disorder-to-order transition, its fluorescence did not red-shift from the 322 nm. The conclusion was that the extra floppiness due to the added methylene group did not allow for it to interact as strongly as 4-methylbiphenyl did with either biphenyl or naphthalene.

In summary:

The results are summarized in Table 1. From these changes in the biphenyl group’s torsional angle when epitaxially deposited on naphthalene and when complexed with naphthalene, the rotational energy barrier appears low. Van der Waals energies are of the order of a few kJ/mol. Since calculations show that the rotational barriers are about 7 kJ mol\(^{-1}\) for biphenyl, 50 kJ mol\(^{-1}\) for 2-methylbiphenyl and > 100 kJ mol\(^{-1}\) for 2,2′-dimethylbiphenyl,\(^6,10\) perhaps the rotational barriers are steeply inclined when closer to 0º, but flatter otherwise. Some rotational barrier calculation seem to indicate this,\(^6,10\) and this study appears to provide experimental evidence to support these calculations.

Although actual structures of the complexes must await further studies by computation and/or experiment, it is encouraging that additional insight as to the dihedral angles that these biphenyl molecules have in different environments can be obtained by this method. The hope is to add other biphenyl molecules to this list to increase the precision of the torsional angles in relation to their spectra.

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**References**

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