

ADSORBATE-ADSORBATE INTERACTION IN DIMETHYLNAPHTHALENE-BIPHENYL VAN DER WAALS COMPLEXES ON Al_2O_3

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Abstract

In an ultra-high vacuum chamber, 1,4-dimethylnaphthalene was deposited from the vapor phase onto a cryogenically cooled Al_2O_3 surface. A bilayer was formed with the deposition of a second layer consisting of biphenyl. Then the crystal with the bilayer was subjected to temperature programmed desorption during which the adlayer was illuminated by ultraviolet light which optically pumped the molecular adlayers. The bilayer exhibited a novel spectrum that was quite different from either biphenyl or 1,4-dimethylnaphthalene alone, and this new spectrum was attributed to a van der Waals complex that formed as the two layers mixed during the temperature programmed desorption. Examination of the plots of the fluorescence intensities of the bilayer spectrum as a function of the molecular composition of the bilayer showed that the composition of the complex was one molecule of biphenyl to one molecule of the dimethylnaphthalene. Bilayers of 1,5-dimethylnaphthalene and biphenyl were also deposited on the Al_2O_3 crystal. The results showed that the composition of the complex was 4:1 biphenyl to 1,5-dimethylnaphthalene.

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Introduction

The two phenyl groups in biphenyl can be in planar or twisted conformers.¹⁻² In the gas phase, biphenyl is in the twisted conformer, whereas in the solid crystal, biphenyl is in the planar conformer.¹⁻² Previous studies showed that these conformers gave rise to different fluorescence spectra, so that these spectral signatures can be used to assign the conformer that biphenyl is in when it is vapor deposited on a surface.¹⁻² When biphenyl is vapor deposited at 110 K, the fluorescence is from the twisted conformer and has a $\lambda_{\text{max}} \sim 320 \text{ nm}$.³⁻⁵ When the surface is temperature ramped in a temperature programmed desorption (TPD) experiment subsequent to deposition, biphenyl undergoes changes in the conformer from twisted to planar with $\lambda_{\text{max}} \sim 340 \text{ nm}$ during the disorder-to-order transition at 160 K with a concomitant reduction in the intensity.³⁻⁵ The excimer of biphenyl forms when deposited onto a surface such as Al_2O_3 at $138 \pm 5 \text{ K}$.³⁻⁵ Finally, if biphenyl is deposited on top of a planar molecule such as naphthalene, it will deposit epitaxially in the planar conformer.³⁻⁵ In this paper, these spectral signatures of biphenyl were used to study the formation of van der Waals complex between 1,4-dimethylnaphthalene and biphenyl. The complex between 1,5-dimethylnaphthalene and biphenyl was also studied.

Dimethylnaphthalene form excimers when optically pumped. It was also known that if the surface is heated, dimethylnaphthalene undergo a disorder-to-order transition that is accompanied by a blue-shift in the molecular spectrum. The molecular symmetry of 1,4-dimethylnaphthalene is such that it has a two-fold rotation axis that is *in-plane* that allow the eclipsed form of the excimer to lower its energy by reducing the steric hindrance caused by the methyl groups by a simple 180° rotation about the out-of-plane axis. However same energy lowering of the excimer is not possible for 1,5-dimethylnaphthalene which has a two-fold rotation axis that is *out-of-plane*. If another molecule such as biphenyl in this study with which the dimethylnaphthalene can form a complex, would such a complex prevent this postulated molecular rotation when the disorder-to-order transition occurs? In other words, which complex is energetically more stable, the excimer or the heteromolecular exciplex. We hoped to answer these questions with this

study.

Experimental

Biphenyl, 1,5- and 1,4-dimethylnaphthalene were of the highest purity that was commercially available. (Sigma-Aldrich, St. Louis, MO). These compounds were placed in separate sample holders and outgassed by freeze-pump-thaw cycles. Since the Al_2O_3 crystal was mounted on a differentially-pumped rotatable high-vacuum adapter, deposition was accomplished by orienting the crystal perpendicularly to tubes that are connected to high-precision valves. These valves were used to leak in the vapor from the samples into the chamber.

The TPD experiment was done by linearly ramping the surface temperature by passing current through a tantalum foil that was in thermal contact with the Al_2O_3 . A chromel-alumel thermocouple was mounted directly onto the crystal in order to continuously monitor the surface temperature and provided the necessary feedback to generate the linear temperature ramp in the TPD experiment.

Optical pumping was accomplished by filtering the light from a super high-pressure mercury lamp through a 0.25 m monochromator centered on $250 \pm 10 \text{ nm}$. The image of the Al_2O_3 crystal upon which the fluorophore had been deposited was focused onto a quartz lens that was attached to a fiber optic cable that had been placed inside the vacuum chamber. The fiber cable was fed through a port and into Ocean Optics spectrometer (Dunedin, FL) that was interfaced to a computer so that the spectrum could be viewed every 300 ms. The spreadsheet that comprised the spectra as a function of temperature was transferred to Matlab (MathWorks, Natick, MA) from which the 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 .⁶⁻⁸ The uncertainties in the desorption temperatures and the propagated error in the activation ener-

gies were $\pm 3\%$.

The adlayer coverages were determined in the following way: 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-Al₂O₃ interface. The integrated mass spectral peaks were calibrated to the optical interference experiment and the coverages (Θ) are reported in monolayers (ML) with an error of $\pm 25\%$.^{9,10}

Results and Discussion

biphenyl multilayer

Shown in Figure 1 is the wavelength-resolved TPD of multilayer (neat) biphenyl. The peak desorption temperature, T_p , was 234 K. First-order desorption was assumed and the activation energy for desorption, E_a , was calculated to be 60.8 kJ/mol.⁶⁻⁸ Upon deposition, excitation of biphenyl on Al₂O₃ exhibited fluorescence with a λ_{\max} of 320 nm that has been previously assigned to the twisted conformer.³⁻⁵ The adlayer underwent a disorder-to-order transition at 160 K, where λ_{\max} red-shifted to 340 nm and has been assigned to the planar conformer of biphenyl.³⁻⁵

1,4-dimethylnaphthalene multilayer

The wavelength-resolved TPD of 1,4-dimethylnaphthalene

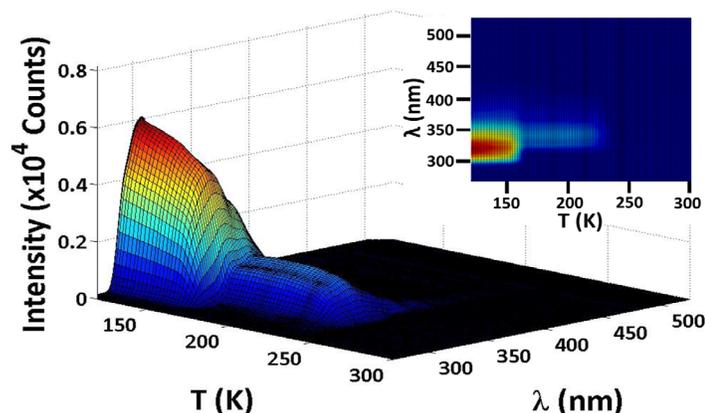


Figure 1. Wavelength-resolved TPD of multilayer biphenyl. Θ_{biphenyl} was 75 ML. At deposition, $\lambda_{\max} \sim 320$ nm. Disorder-to-order transition is at 160 K when λ_{\max} shifts to ~ 340 nm. Inset: top view reveals the disorder-to-order red-shift.

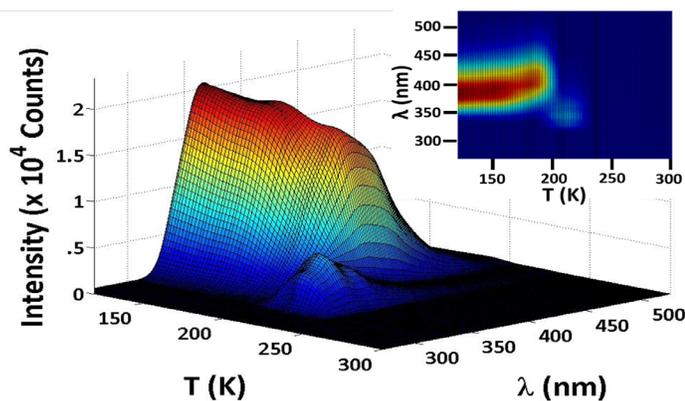


Figure 2. Wavelength-resolved TPD of multilayer 1,4-dimethylnaphthalene with $\Theta_{\text{1,4-dimethylnaphthalene}}$ was 102 ML. At deposition, $\lambda_{\max} \sim 395$ nm. Excimer red-shift ~ 402 nm. Disorder-to-order transition is at 200 K when $\lambda_{\max} \sim 340$ nm. Inset: top view clearly shows the red-shift.

multilayer at $\Theta_{\text{1,4-dimethylnaphthalene}}$ of 102 ML is shown in Figure 2. Upon deposition, the excimer fluorescence origin was at $\lambda_{\max} \sim 395$ nm. As the surface was heated, the spectrum red-shifted to $\lambda_{\max} \sim 402$ nm which has tentatively postulated to be due to the in-plane rotation. Then at about 200 K, the disorder-to-order transition caused the spectrum to blue-shift to ~ 340 nm from molecular fluorescence. The peak desorption temperature for 1,4-dimethylnaphthalene was 220 K. A first-order desorption kinetics was assumed and E_a was calculated to be 57 kJ/mol.⁶⁻⁸

1,4-dimethylnaphthalene/biphenyl bilayer

Upon deposition of the bilayer, biphenyl fluorescence showed two peaks at 327 and 341 nm that corresponded to the twisted and planar conformers (See Figure 3). The reason that both conformers of biphenyl were observed in the bilayer was that the underlayer (1,4-dimethylnaphthalene in this case) was amorphous at deposition. Hence the overlayer of biphenyl would be conformationally randomized as it deposited, although as indicated by the relative intensities, the planar conformer was slightly favored epitaxially, since the underlayer was also planar. Throughout the TPD, the fluorescence due to the planar conformer remained relatively more intense than from the twisted conformer. At 160 K, the 1,4-dimethylnaphthalene excimer intensity increased due to the disorder-to-order transition of the biphenyl. The red-shift of the excimer to 400 nm occurred due hypothetically to the energetic relaxation caused by the relief of steric hindrance upon 180° in-plane rotation. Another possible explanation of this excimeric red-shift is that the change in the crystal arrangement from the transition of the overlayer. The relaxation of the *underlayer* (1,4-dimethylnaphthalene) that accompanied the disorder-to-order transition of the *overlayer* (biphenyl) was indicative of strong adsorbate-adsorbate interaction. At about 175 K, the percolation of the dimethylnaphthalene into the biphenyl caused the intense 327 and 341 nm peaks as a result of energy transfer from 1,4-dimethylnaphthalene to biphenyl. These two peaks were assigned to the twisted and planar conformers of biphenyl, respectively. Since the two molecules desorbed separately, the van der Waals complex was relatively weak.

Shown in Figure 4 is a plot of the of the intensity of the 327 nm peak at 215 K (indicated by an arrow in Figure 3) as a function

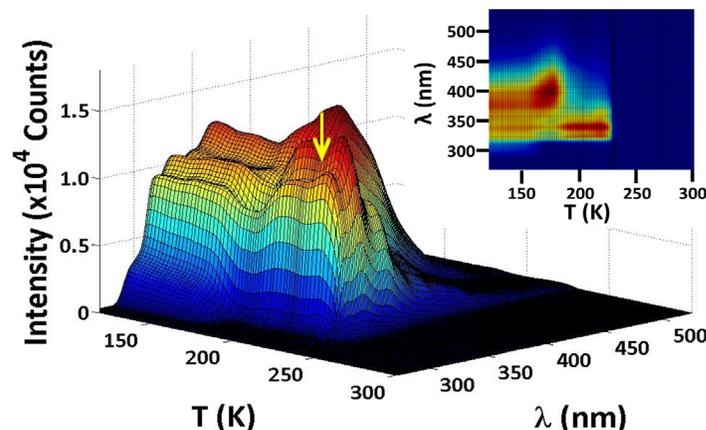


Figure 3. Wavelength-resolved TPD of bilayer of 1,4-dimethylnaphthalene (deposited first) with $\Theta_{\text{1,4-dimethylnaphthalene}}$ was 43 ML and biphenyl with Θ_{biphenyl} was 42 ML. Red-shift of 1,4-dimethylnaphthalene excimer occur at \sim biphenyl's disorder-to-order transition temperature. The enhanced fluorescence of biphenyl is attributed to the formation of the van der Waals complex (arrow). Inset: top view shows the excimeric red-shift.

of the ratio of coverages of 1,4-dimethylnaphthalene to biphenyl, for which the biphenyl was held constant at 45 ± 15 ML. In this plot, multiple data were averaged for each point in the plot. The plot showed a leveling of the fluorescence intensity due to the biphenyl at a ratio of coverage of about 1:1. This can be interpreted to mean that the composition of the van der Waals complex is approximately 1 molecule of 1,4-dimethylnaphthalene to 1 molecule of biphenyl.

1,5-dimethylnaphthalene multilayer

The wavelength-resolved TPD of 1,5-dimethylnaphthalene multilayer at $\Theta_{1,5\text{-dimethylnaphthalene}}$ of 106 ML is shown in Figure 5. Upon deposition, the fluorescence origin was at $\lambda_{\text{max}} \sim 395$ nm which was comparable to 1,4-dimethylnaphthalene. As the surface was heated, the spectral peak at $\lambda_{\text{max}} \sim 395$ nm remained relatively constant which appeared to confirm that the stabilization due to any in-plane rotation did not occur to the same extent as with the 1,4-dimethylnaphthalene isomer. However, close examination of the inset indicated that there was a very slight red-shift that gradually occurred from 190 K to about 210 K with $\lambda_{\text{max}} \sim 398$. Then at

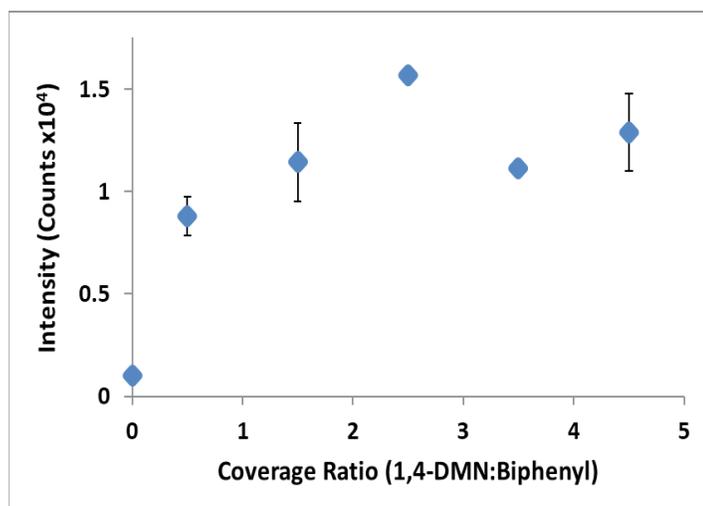


Figure 4. Enhanced fluorescence of biphenyl for the van der Waals complex as a function of the ratio of 1,4-dimethylnaphthalene:biphenyl coverages ($\Theta_{1,4\text{-dimethylnaphthalene}}/\Theta_{\text{biphenyl}}$). Θ_{biphenyl} was kept at 45 ± 15 ML. The intensities were taken at ~ 215 K and $\lambda_{\text{max}} \sim 327$ nm (arrow in Fig 3). The intensity of the $\lambda_{\text{max}} \sim 341$ nm peak correlated with the 327 nm peak.

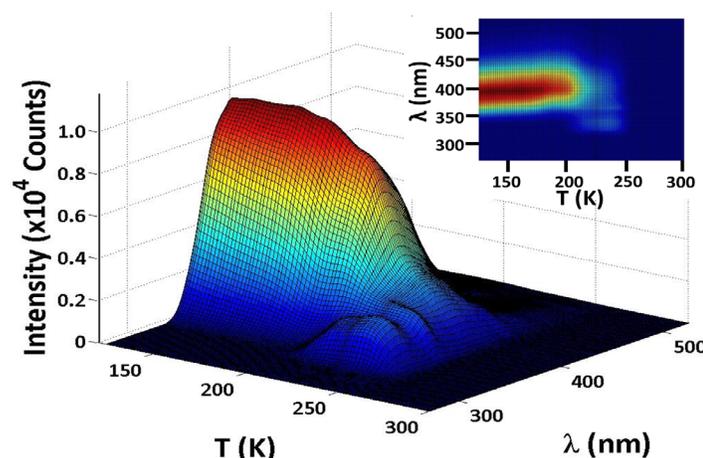


Figure 5. Wavelength-resolved TPD of multilayer 1,5-dimethylnaphthalene with $\Theta_{1,5\text{-dimethylnaphthalene}}$ was 106 ML. At deposition, $\lambda_{\text{max}} \sim 395$ nm. Excimer red-shift $\lambda_{\text{max}} \sim 400$ nm. Disorder-to-order transition is at 200 K when $\lambda_{\text{max}} \sim 340$ nm. Inset: top view.

about 210 K, the disorder-to-order transition caused the blue-shift in the spectrum to $\lambda_{\text{max}} \sim 340$ nm. This is due to molecular fluorescence in the ordered crystal. The peak desorption temperature for 1,5-dimethylnaphthalene was 231 K. A first-order desorption kinetics was assumed and E_a was calculated to be 60. kJ/mol.⁶⁻⁸

1,5-dimethylnaphthalene/biphenyl bilayer

Shown in Figure 6 is the total fluorescence spectra as a function of temperature for the 1,5-dimethylnaphthalene/biphenyl bilayer. Interestingly, the excimer fluorescence of 1,5-dimethylnaphthalene showed a distinct red shift to 402 nm, similar to 1,4-dimethylnaphthalene, although the multilayer exhibited a lower intensity of the red-shifted peak. The observation of this red-shift for 1,5-dimethylnaphthalene/biphenyl bilayer might indicate that this more stable excimer might not be the result of the 2-fold rotation, but rather to a more subtle relaxation of the excimer caused by the aforementioned adsorbate-adsorbate interaction during disorder-to-order transition of biphenyl. When the adsorbate-adsorbate interaction is stronger than the adsorbate-surface interaction, such as in these molecules, deposition models indicated that the adlayers grew as isolated islands as would be the case for the first layer on the Al_2O_3 .¹¹ The results are: a) biphenyl is expected to deposit more evenly over the entire surface, since the surface now appeared to be covered with dimethylnaphthalene and b) during the TPD, since biphenyl underwent a disorder-to-order transition at a lower temperature than the dimethylnaphthalene, the biphenyl controlled the relaxation of the dimethylnaphthalene underlayer. Hence 1,5-dimethylnaphthalene in the bilayer relaxed to a more stable excimer than in the neat multilayer.

The total intensity at 327 nm at 215 K (arrow in Fig. 6) is plotted in Figure 7 as a function of the ratio of coverages of 1,5-dimethylnaphthalene to biphenyl, for biphenyl coverages of 48 ± 40 ML. As in Figure 4, each point is the average of multiple trials. Since the enhancement in the biphenyl fluorescence intensity was considerably less, the error was a bit more pronounced. However, the leveling of the intensity appeared to occur at ~ 0.25 for the coverage ratio of 1,5-dimethylnaphthalene to biphenyl, or about 1 molecule of dimethylnaphthalene to 4 biphenyl molecules. This may be due to the steric hindrance caused by the methyl groups on

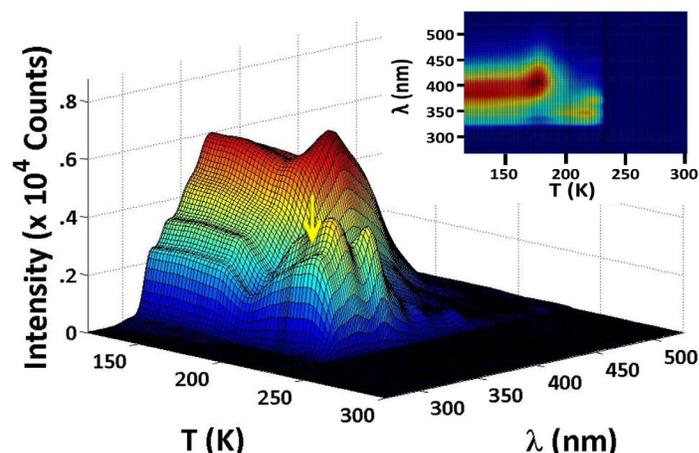


Figure 6. Wavelength-resolved TPD of bilayer of 1,5-dimethylnaphthalene (deposited first) with $\Theta_{1,5\text{-dimethylnaphthalene}}$ was 71 ML and biphenyl with Θ_{biphenyl} was 61 ML. Red-shift of 1,5-dimethylnaphthalene excimer occur \sim biphenyl's disorder-to-order transition with $\lambda_{\text{max}} \sim 400$ nm. The enhanced fluorescence of biphenyl is attributed to the formation of the van der Waals complex (arrow). Inset: top view.

each ring that would make the complex more difficult to form and therefore, required more biphenyls to cluster around the dimethylnaphthalene.

In summary:

a. As with other naphthalene and methylnaphthalene:biphenyl complexes,³⁻⁵ heteromolecular van der Waals complexes formed between 1,4-dimethylnaphthalene and biphenyl, and between 1,5-dimethylnaphthalene and biphenyl. These complexes have a molecular composition that vary from 1:1 (i.e. one molecule of 1,4-dimethylnaphthalene to one molecule of biphenyl) and 1:4 (i.e. one molecule of 1,5-dimethylnaphthalene to 4 molecules of biphenyl).

b. For bilayers in which the adsorbate-adsorbate interaction is stronger than the adsorbate-surface interaction, the stress that originates with the adlayer of the underlayer can be relaxed by the movement of molecules in the biphenyl overlayer. This would be *reverse* epitaxy and might have uses in controlling crystal growth.

7. F.M. Lord, J.S. Kittelberger. *Surf. Sci.*, **1974**, 43, 173-182.
8. D.A. King. *Surf. Sci.*, **1975**, 47, 384-402.
9. B.D. Fonda, M.K. Condi, Z.E. Moreau, Z.I. Shih, B. Dionisio, A. Fitts, L. Foltz, K. Nili and A.M. Nishimura. *J. Phys. Chem. C.*, **2019**, 123, 26185-26190.
10. M.K. Condie, B.D. Fonda, Z.E. Moreau and A.M. Nishimura. *Thin Solid Films*, **2020**, 697, 137823.
11. J.A. Floro, E. Chason, R.C. Cammarata and D.J. Srolovitz, *MRS Bulletin*, **2002**, 27, 19-25.

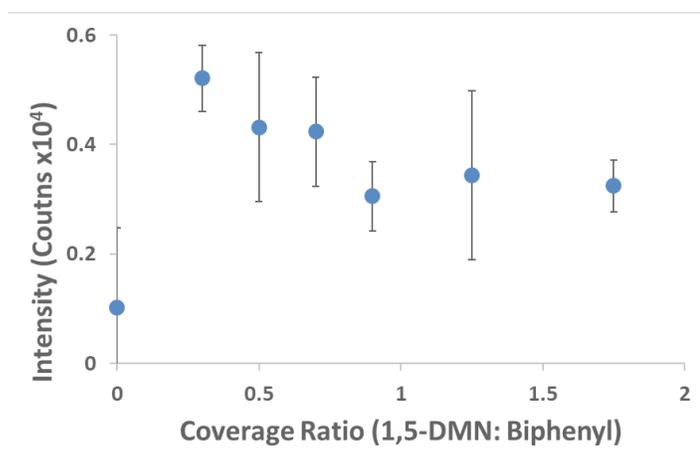


Figure 7. Enhanced fluorescence of biphenyl for the van der Waals complex as a function of the ratio of 1,5-dimethylnaphthalene:biphenyl coverages ($\Theta_{1,5\text{-dimethylnaphthalene}}/\Theta_{\text{biphenyl}}$). Θ_{biphenyl} was 48 ± 40 ML. The intensities were taken at ~ 215 K and $\lambda_{\text{max}} \sim 327$ nm (arrow in Fig. 6). The intensity of the $\lambda_{\text{max}} \sim 341$ nm peak correlated with the 327 nm peak.

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References

1. A. Almenningen, O. Bastiansen, L. Fernholt, B.N. Cyvin, S.J. Cyvin and S. Samdal. *J. Mol. Struct.*, **1985**, 128, 59-76.
2. G.P. Charbonneau and Y. Delugeard. *Acta Crystallographica B*, **1976**, 32, 1420-1423.
3. M.K. Condie, Z.E. Moreau and A.M. Nishimura. *J. Undergrad. Chem. Res.*, **2019**, 18, 15-18.
4. B.D. Fonda, M.K. Condi, Z.E. Moreau, Z.I. Shih, B. Dionisio, A. Fitts, L. Foltz, K. Nili and A.M. Nishimura. *J. Phys. Chem. C.*, **2019**, 123, 26185-26190.
5. M.K. Condie, C. Kim, Z.E. Moreau, B. Dionisio, K. Nili, J. Francis, C. Tran, S. Nakaoka and A.M. Nishimura. *J. Undergrad. Chem. Res.*, **2020**, 19, 14-17
6. P.A. Redhead. *Vacuum*, **1962**, 12, 203-211.