

Computed solvatochromic effects in mesityl oxide UV spectra

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Abstract

Solvochromatic shifts were investigated by calculating UV excitation energies for mesityl oxide (4-Methyl-3-pentene-2-one), in various solvents. π to π^* transitions are responsible for many absorption peaks in the UV spectrum with compounds containing sp^2 and sp^1 hybridized bonds. By computing excitation energies in the mesityl oxide molecule using ab initio quantum chemical methods, the UV spectra of the compound can be predicted. These absorptions for mesityl oxide in polar and non-polar solvents demonstrated a bathochromic shift in its strongly absorbing near-UV peak correlating with an increasing solvent dielectric constant and were generally in agreement with reported results. Two solvent-related hypsochromic shifted peaks were also investigated, one associated with an n to π^* transition reported. This modeling did not account well for variations of solvent index of refraction, perhaps contributing to a computed vs physical disparity. The understanding of the contributions to absorption shift by solvation is challenging due to the two conformations of this molecule and their differing relative stability in the various solvents. I try to explore this by accounting for the shifts in ratios between the two conformers, in the set of solvents chosen, and comparisons to reported results. The results demonstrate the effect of solvent polarity, molecular conformation, and highlight shortcomings in methods failing to account for solvent interactions in liquid systems.

Introduction

Solvent polarity and its effects are of significant importance for understanding reaction thermodynamics and kinetics, transition state stability, conformational stability, and absorption spectra. While this study focuses on solvatochromic shifts in mesityl oxide (MOx) UV spectra, it underscores solvation effects by illustrating shifts in excited state energies with changing solvent polarity.

Mesityl oxide is a colorless, volatile liquid with a slightly minty, honey-like odor and one of the simpler α,β -unsaturated ketones. It's typically produced via an aldol self-condensation of acetone. It is of interest to this research because of the polar nature of the α,β -unsaturated ketone resonance structure and how this polarity is affected by solvents of various polarities. It contains little in the way of other groups that would complicate the investigation. The resonance between the ketone carbonyl and the double bond, combined with the polar aspect introduced by the ketone group allows for interesting solvent effects on its excitation energies.

This investigation was computational, with the syn and anti conformer structures of MOx forming the focal point of the computational models, in a range of solvents. These models were submitted for computational processing to determine the highest strength excitation energies expected for the MOx conformers, in solvents with different dielectric constants. Commonly these are seen in a lab setting as dominant UV peaks. A 1988 study[1] of the spectral shifts of MOx with changing solvents was used as a real-world reference to the computed peaks, with the non-solvated reference coming from the NIST[3].

Solvents were chosen based on their dielectric constant to investigate the effects of a wide range of solvent polarities on the MOx excitation energies. The solvents investigated were none [gas phase], heptane, ether, tetrahydrofuran, acetone, methanol, acetonitrile, dimethyl sulfoxide, propylene carbonate, and water, listed here in order of increasing dielectric constant.

Methodology

The computational software used was IQMol, ver 2.15.2, as the front end/extended user interface, and Q-Chem 5.3.1 for running the quantum mechanical computations on the data submitted. The processing was performed on the Expanse server through Georgia State University, under the supervision and advice of Dr. Samer Gozem. The Expanse server is an x86-64 multi-blade server, running CentOS Linux 8, with Linux Kernel 4.18.0-147.el8.x86_64, using a BASH shell.

Each of the primary computational submissions was composed of three jobs. The first job, Geometry, was used to compute an optimal geometry using the Becke, 3 parameter, Lee-Yang-Parr exchange-correlation functional (B3LYP) and a basis set of 6-31G*. 6-31G* basis set was sufficient for this molecule and it's very fast. The second, Frequencies, builds on the previous job results to compute frequencies the molecule absorbs/vibrates at in the IR range. This used the B3LYP method and a basis of 6-31G*. The third job, Energy, was to compute excitation energies of the molecule using the Time-dependent density functional theory (TD-DFT) method and a basis of 6-31G*, with the number of states requesting being 8 and no triplets. The last job is most pertinent to absorption and excitation in the ultraviolet region.

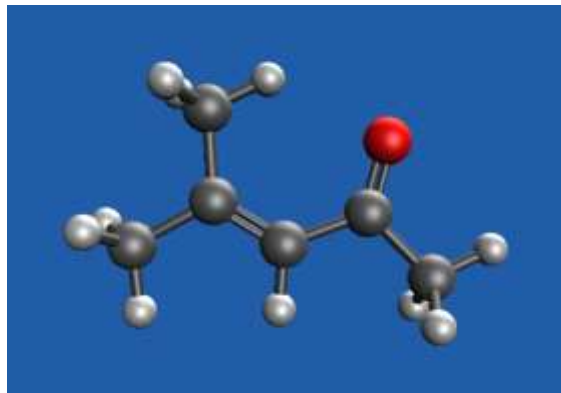
In the following, the grouping of jobs into sets to be run together is referred to as job sets.

Initially, a molecule was constructed in IQMol and its energy was minimized. The job was run to optimize the geometry. Once geometry optimizations were done, the newly obtained geometry data replaced the initial geometry data in the input file. Next, a second job, Frequencies, was added to the run set to check the frequency calculations. The results were reviewed and any imaginary frequencies found were used to manually alter the model in IQMol. This was an iterative process, repeated until all imaginary frequencies were eliminated. Then a third job, Energy, was added to the job set, including a solvent model. The solvent method used was PCM, with a CPCM calculation model, the boundary

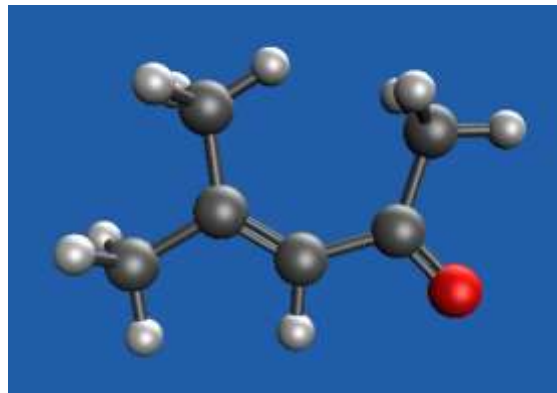
set to SWIG, and Radii set to BONDI. Each solvent's dielectric constant was used for their respective run set. The entire preceding procedure was performed for both syn and anti conformers. For each conformer, a run set was completed for each solvent, then executed. There were a total of 20 job sets created. The solvents investigated were none [gas phase], heptane, ether, tetrahydrofuran, acetone, methanol, acetonitrile, dimethyl sulfoxide, propylene carbonate, and water. Once run, the pertinent data for each run was extracted from the job output and reviewed. The excited state energies corresponding to the first two highest strengths, along with one corresponding to an $n - \pi^*$ peak reported in the literature, were considered of interest, extracted, and collated. Generally, energies with strengths below 0.2 were excluded, with the exception of the $n - \pi^*$ peak.

Data and Analysis

The data demonstrated a linear plot of inverse dielectric constant versus excitation energy or wavelength. This correlation, having a high R^2 value, was considered a good linear fit. It revealed the degree of solvatochromic shift, a gauge of deviation from reported values, and the energy/wavelength shift between the two conformers. The output data was used, with IQMol, to produce Gaussian plots corresponding to expected UV absorption spectra. Predicted IR spectra were produced, but not considered relevant to this research.



MOx Syn conformer



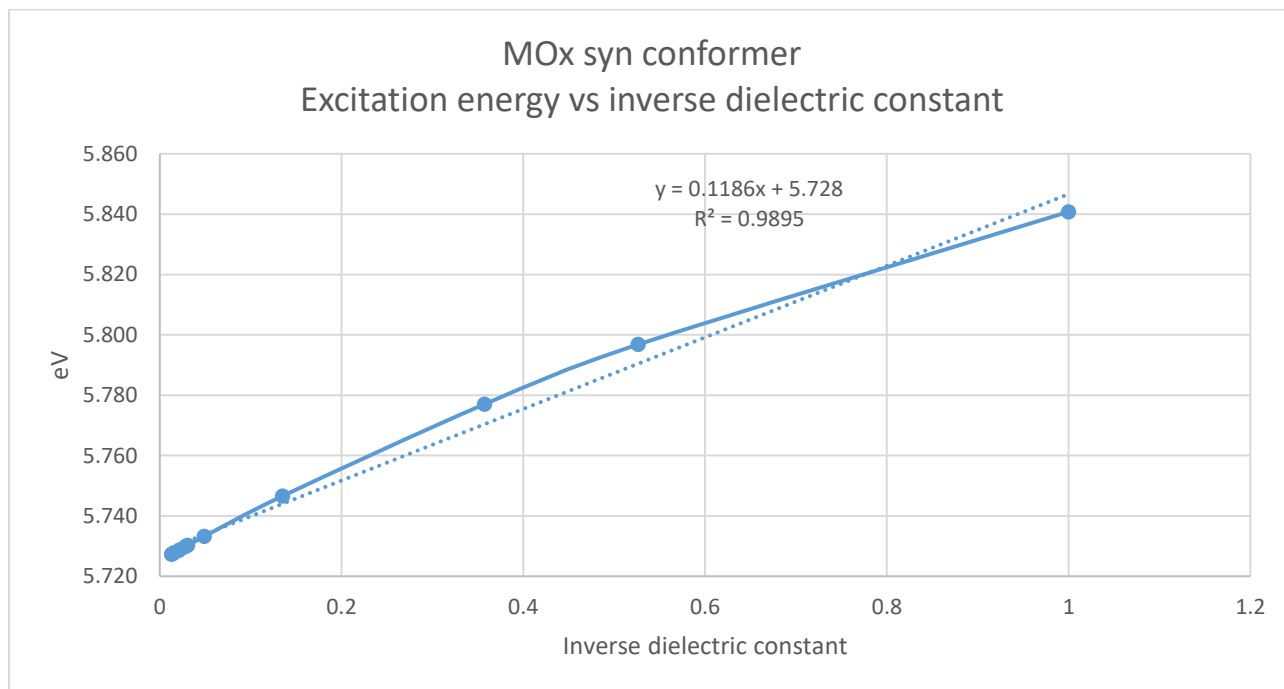
MOx Anti conformer

MOx syn Conformer Excitation energies and wavelengths

Solvent	Dielectric constant	eV	Strength	λ (nm)
gas phase	1	5.841	0.59386	212.27
heptane	1.9	5.797	0.60003	213.88
ether	2.8	5.777	0.60290	214.61
THF	7.4	5.747	0.60739	215.74
acetone	20.5	5.733	0.60943	216.25
methanol	32.6	5.730	0.60988	216.36
acetonitrile	35.7	5.730	0.60995	216.38
DMSO	46.68	5.729	0.61012	216.42
propylene CO ₃	64.90	5.728	0.61028	216.46
water	78.39	5.727	0.61035	216.47

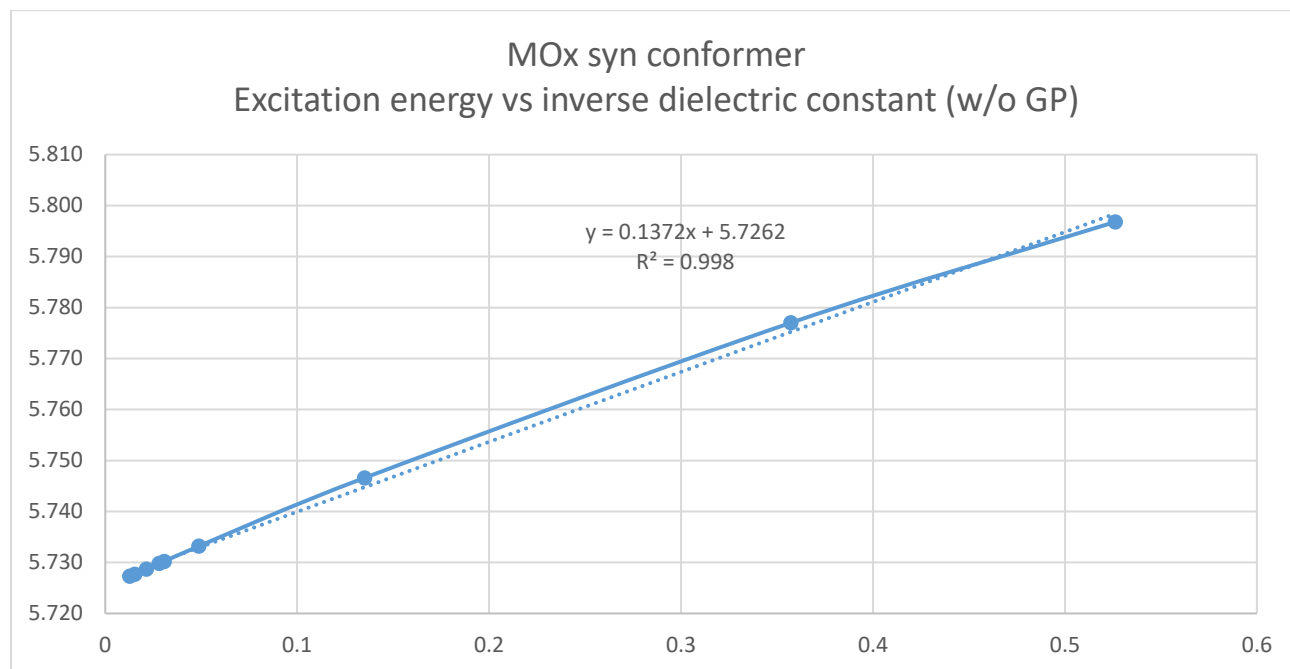
Table 1

When the energies or the wavelengths are plotted against the inverse of the dielectric constant, it is linear, with a good fit. The R^2 value is very close to 0.99.



Graph 1

Without the gas phase entry, the data has a better linear fit, having an R^2 of 0.998.



Graph 2

MOx anti conformer excitation energies and wavelengths

Solvent	Dielectric	eV	Strength	λ
gas phase	1	5.979	0.68196	207.345
heptane	1.9	5.918	0.68487	209.496
ether	2.8	5.891	0.68650	210.460
THF	7.4	5.850	0.68958	211.942
acetone	20.5	5.832	0.69152	212.593
methanol	32.6	5.828	0.69149	212.717
acetonitrile	35.7	5.828	0.69155	212.739
DMSO	46.68	5.826	0.69171	212.794
propylene CO ₃	64.90	5.825	0.69185	212.841
water	78.39	5.824	0.69191	212.863

Table 2

The linear plots of the anti conformer were an even better linear match, having R²s of 0.9915 and 0.9985 (with and without gas phase, respectively). This shows a close association with excitation energy and solvent dielectric constant. There is a much poorer, apparent relationship seen when comparing wavelength and solvent dipole moment (Table 5, Graph 8).

Solvent	Dielectric constant	syn $\Delta\lambda$	anti $\Delta\lambda$
gas phase	1	0.00	0.00
heptane	1.9	1.61	2.15
ether	2.8	2.34	3.11
THF	7.4	3.48	4.60
acetone	20.5	3.98	5.25
methanol	32.6	4.10	5.37
acetonitrile	35.7	4.11	5.39
DMSO	46.68	4.15	5.45
propylene CO ₃	64.90	4.19	5.50
water	78.39	4.21	5.52

Table 3

The following tables, 3 and 4, reveal the red shift induced by the solvent used. The table is ordered by ascending solvent polarity.

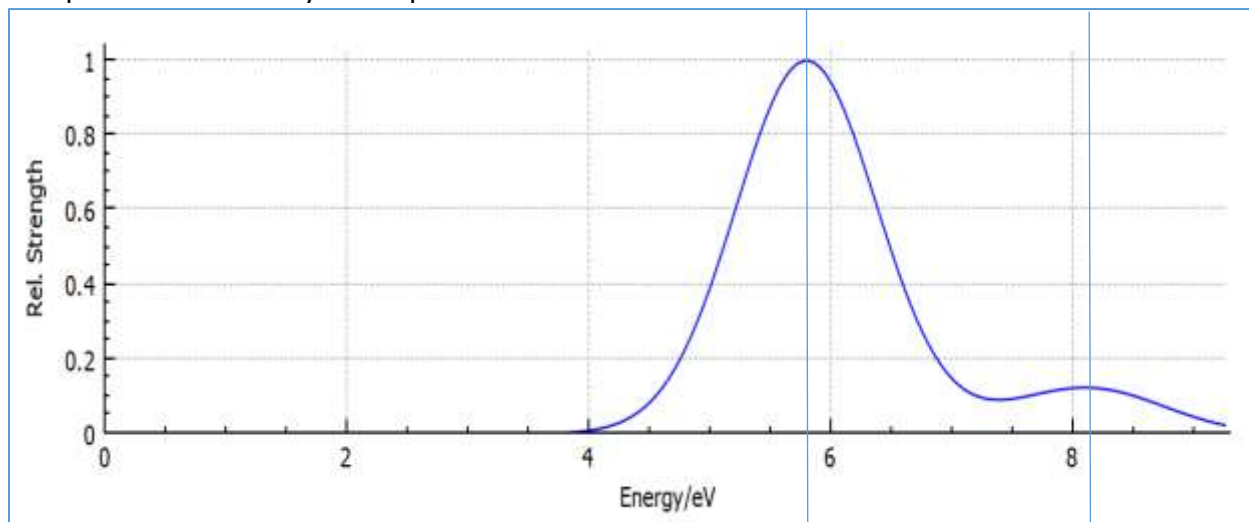
The difference between the lowest and highest wavelength is 4.21 nm for the syn conformer and 5.52 nm for the anti conformer. This is significantly lower than the red shift seen by Bhat and Gupta [1], which was around 13 nm.

Solvent	Bhat[1] λ	Syn λ	Anti λ
heptane	230	213.88	209.50
ether	231	214.61	210.46
methanol	238	216.36	212.72
acetonitrile	234	216.38	212.74
water	243	216.47	212.86

Table 4

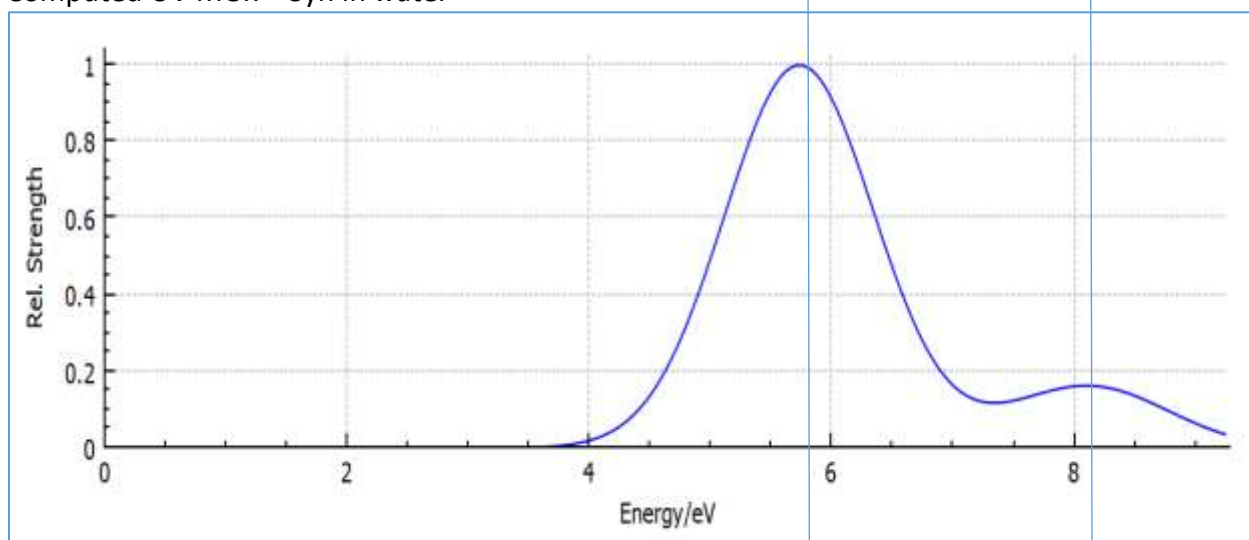
Table 4 demonstrates both the negative displacement of predicted values from actual and the relatively diminished red shift in the computed batches. The red shift seen by Bhat and Gupta was close to three times that computed in this study for the syn conformer and even higher disparity to compared to the anti conformer shift.

Computed UV MOx – Syn in Heptane



Graph 3

Computed UV MOx – Syn in water

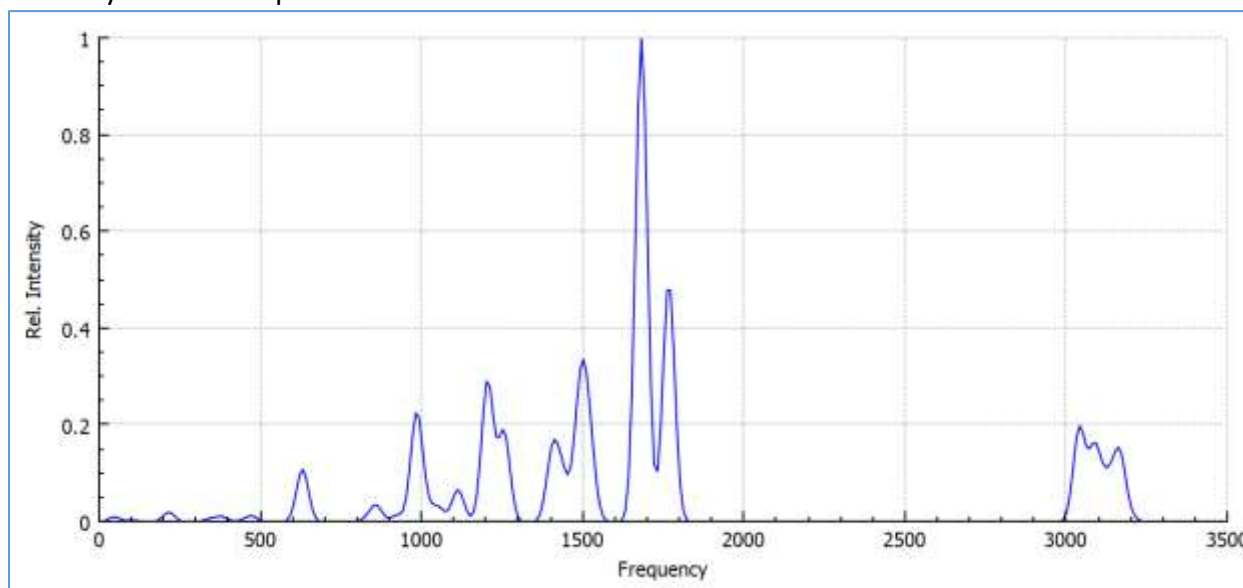


Graph 4

The red shift, due to solvent polarity, is apparent comparing graphs 3 and 4. A similar shift was observed in the anti-conformation runs, just at higher excitation energies. The blue shift in the minor peak is small and not easily apparent from the plots.

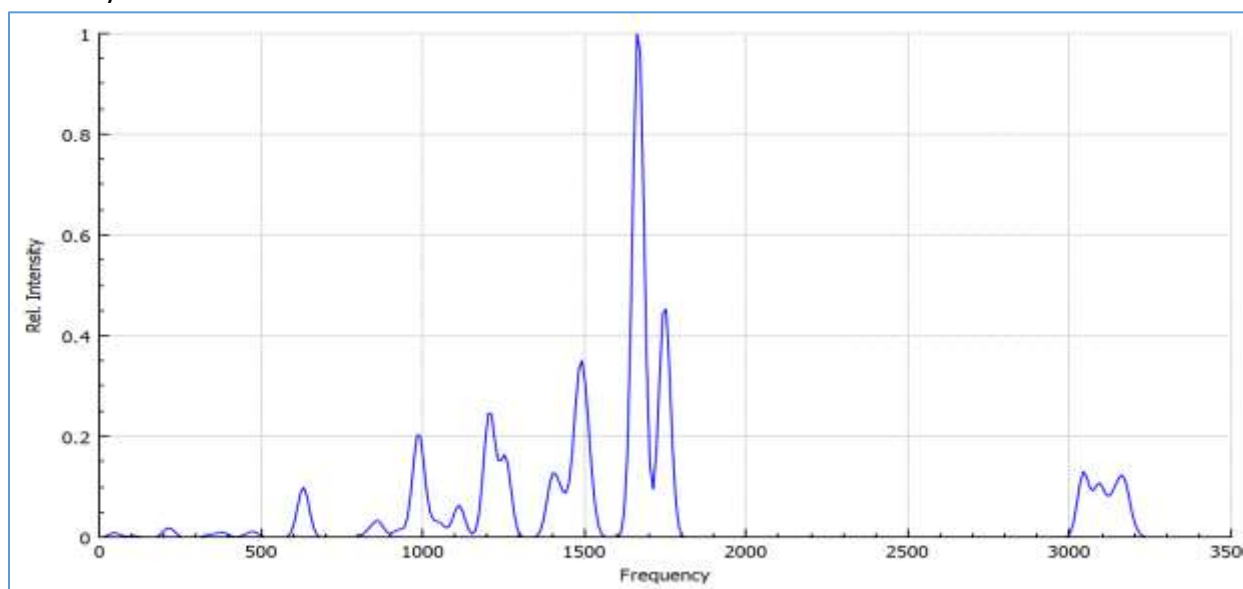
By comparison, the predicted IR spectra show little or no shift due to solvent polarity

Mesityl oxide in heptane



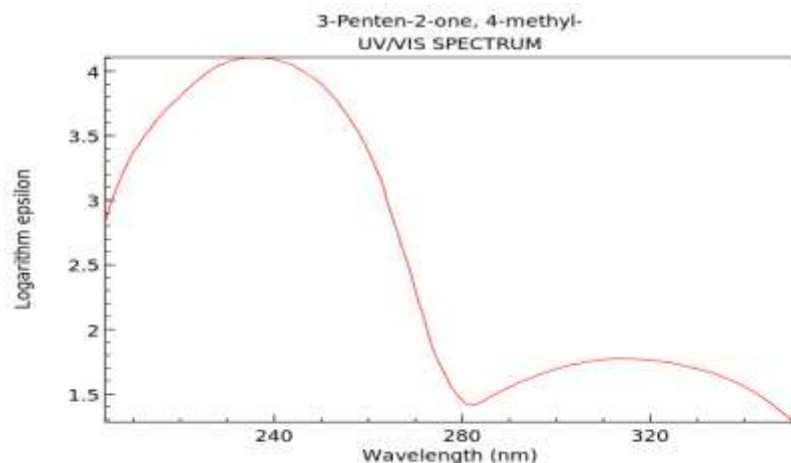
Graph 5

Mesityl oxide in water



Graph 6

The NIST UV spectra of mesityl oxide



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

Graph 7

Solvent	K	μ	λ
gas phase	1	0	212.27
heptane	1.9	0	213.88
ether	2.8	1.098	214.61
THF	7.4	1.75	215.74
acetone	20.5	2.88	216.25
methanol	32.6	1.7	216.36
acetonitrile	35.7	3.93	216.38
DMSO	46.68	3.96	216.42
propylene CO ₃	64.9	4.9	216.46
water	78.39	1.85	216.47

Comparing a shift in wavelength to a change in solvent dipole moment, there is no clear relationship apparent. In the table below, K represents dielectric constant, μ - dipole moment (sources [4,5,6,7,8]), and λ - wavelength. Comparing excitation energy shifts to dipole moment fared no better. This appears to be related to differing dipole moments, depending on if it is gas phase or bulk. The effect of a dipole in bulk can enhance the dipole

Table 5

moment of a molecule[10].

Plotting the solvent dipole moment against the wavelength gives nothing of value.

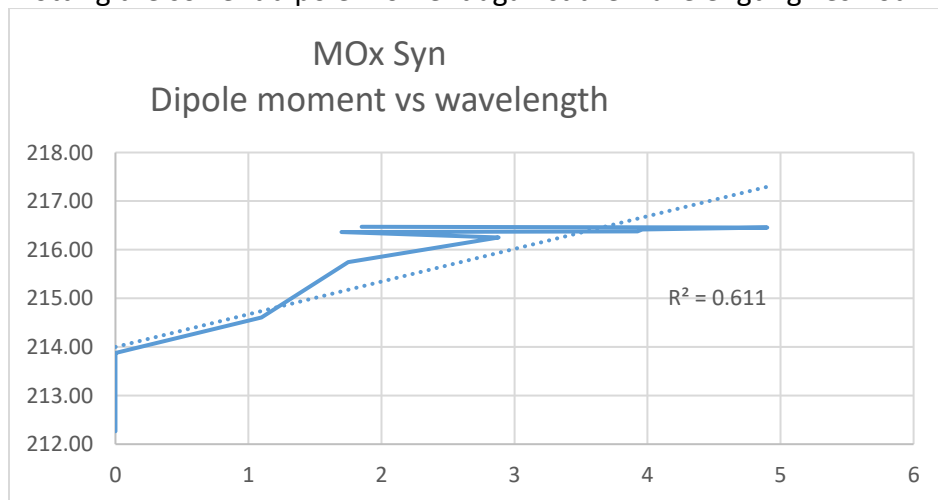


Chart 8

I found nothing in the literature for the minor peak, at 8 eV. It is in the far UV range which is why it's not reported. The minor peak, seen below (Table 6), shows a hypsochromic shift. It didn't have as strong a fit, with respect to inverse dielectric constant and shift in wavelength, but did have an R^2 above 0.98. The data for the gas phase was excluded due to its very low excitation energy strength.

Solvent	κ	eV	Strength	λ
heptane	1.9	7.9914	0.180544	155.1
ether	2.8	8.0049	0.201422	154.9
THF	7.4	8.0168	0.221047	154.7
acetone	20.5	8.0183	0.227011	154.6
methanol	32.6	8.0205	0.062219	154.6
acetonitrile	35.7	8.0206	0.228468	154.6
DMSO	46.68	8.0206	0.228888	154.6
propylene CO ₃	64.9	8.0207	0.22927	154.6
water	78.39	8.0207	0.229438	154.6

Table 6

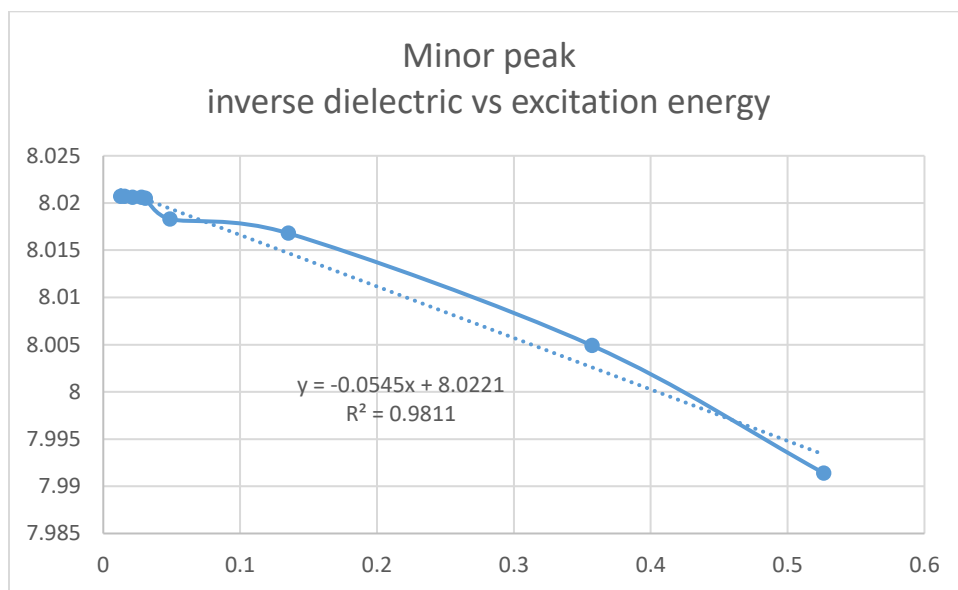


Chart 9

I could find no external data for a MOx peak lower than ~230 nm.

$n-\pi^*$ transition peak

Solvent	Dielectric	$1/\kappa^{-1}$	eV	λ
gas phase	1	1	3.64	340.60
heptane	1.9	0.526316	3.6877	336.20
ether	2.8	0.357143	3.7081	334.35
THF	7.4	0.135135	3.7382	331.76
acetone	20.5	0.048780	3.7512	330.51
methanol	32.6	0.030675	3.7540	330.26
acetonitrile	35.7	0.028011	3.7544	330.23
DMSO	46.68	0.021422	3.7554	330.14
propylene CO ₃	64.9	0.015408	3.7564	330.05
water	78.39	0.012757	3.7568	330.01

Table 7

A very small peak was found corresponding to an $n-\pi^*$ transition, with a pronounced hypsochromic shift, as described in the literature [1,2] and matching the NIST UV data [3], located in the 330 to 340 range. Unlike the major peak, it was shifted higher, about 20 nm, than seen in the NIST data[3].

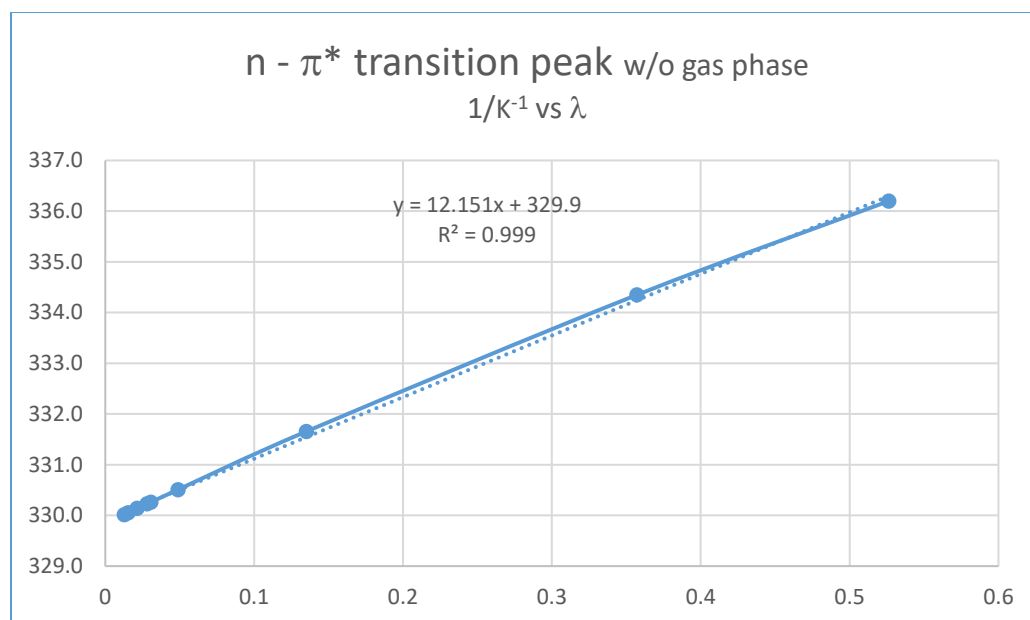


Chart 10

The $n - \pi^*$ solvatochromic blue shift had a very good linear fit, with an R^2 of greater than 0.99 for all data points and greater than 0.999 excluding the gas phase. This peak was approximately 128 nanometers higher than the major peak, with a very low strength.

Results from syn and anti conformer solvent runs were plotted showing a striking correlation between major peaks excited state energy/absorption wavelength and dielectric constant. A linear fit, when plotted against the inverse of the dielectric constant yielded an R^2 value of between 0.9895 and 0.9985, for the different data sets. See tables 1 and 2, graphs 1 and 2.

For this study, the solvatochromic shift maximum deltas are a little over 4 nm for the syn conformer and a little over 5 nm for the anti conformer. Comparing this with over a 13 nm spread for the Bhat/Gupta[1] data, the $\frac{\delta\lambda}{\delta(\kappa^{-1})}$ seen here is $\frac{1}{3}$ of what's reported. In other words, the absorption wavelength shifts were proportionally smaller in my computed results, compared to reported values[1]. This actual-to-computed difference was exacerbated by the fact the actual MOx anti/syn ratio increases with increasing solvent dielectric constant [2]. Given the anti conformer has a higher excitation energy/lower UV peak absorption this should narrow the deviation from actuals rather than increase them. These deviations indicate changing the solvent model could improve the match to reality.

When looking at the smaller of the two major peaks, the one yielding excitation energy strengths of about 0.2, it shows up at higher excitation energies compared to the primary peak. This peak isn't mentioned in the Bhat and Gupta[1] data and is below the range shown by NIST. This peak has a hypsochromic shift with increasing solvent polarity located in the 150-155 nm range (see Table 6). There was still a good correlation to solvatochromic shift with wavelength, having an R^2 of 0.9811.

There was a much poorer correlation of solvent dipole moment to excitation energy than would be expected considering the excellent fit of dielectric constant to excitation energy (chart 8, table 5). It had an R^2 value of around 0.6, which was poor

considering the small sample size. Given often conflicting reported dipole moment of solvents, the explanation for this mystery may lie in if the dipole measurement was for gas phase or bulk. The effect of a dipole in bulk can enhance the dipole moment of a molecule[10].

I knew of no way to account for a solvent index of refraction. The solvent index of refraction can affect the UV spectra of a compound so may contribute to deviation from the physical UV spectra of MOx.

Further research is required to determine if a better computational model would produce results more closely aligned with the physical world and solve some of the mysteries which have arisen.

Summary

The computed results saw solvatochromic shift due to changing solvent polarity in the three peaks, and a blue shift from syn to anti conformers, consistent with results seen previously by Bhat and Gupta [1] and Cezar, Canuto, and Coutinho [2]. The major peak solvatochromic shift ($\frac{\delta\lambda}{\delta(K^{-1})}$) in this study, were considerably smaller, on the order of about one-third of that seen in other studies [1,2], with no known reason for the discrepancy. The $n - \pi^*$ peak blue shift ($\frac{\delta\lambda}{\delta(K^{-1})}$) was closer to those reported. Something not taken into account here was the change in the ratio of the two conformers with increasing solvent polarity but which cannot account for this difference.

Previous studies [2,9] demonstrated anti to syn conformational ratios increased with solvent polarity and reached a high percentage of anti conformer in highly polar solvents, like water, but was virtually all syn conformer in non-polar solvents such as hexane or heptane. This implies the blue shift of the anti conformer, by dampening expected differences in bathochromic shift induced by higher polarity solvents as the ratio of anti to syn conformers increases, should narrow the actual to computed difference with my results. I did not observe this in the data.

Another point of curiosity is why there wasn't a good, clean relationship between solvent dipole moment and absorption peak/excitation energy found in the data. I would assume they should track analogous to dielectric constant. In future research, I intend to get bulk dipole data for the comparisons.

The discrepancy between the location of the NIST $n-\pi^*$ transition peak and that of my data is puzzling, in that there wasn't a consistent offset. Put another way, my major peak was lower than NIST, and my $n-\pi^*$ transition peak was higher. This is most likely due to the way B3LYP localized and delocalized transitions differently. It treats $\pi-\pi^*$ transitions as delocalized and $n-\pi^*$ transitions as localized.

Further research is necessary to determine the causes of three things: why the results here for the major peak deviated by 15 to 20 nms for these results versus actuals, why the deviation for

the $n - \pi^*$ transition peak is in the opposite direction of the major peak, and why the slope of the bathochromic shift seen in this study data was about a third of that seen in other studies [1,2].

With more time, it would be very interesting to examine the shifts in wavelength/excitation energy in the context of linear solvation energy relationships (LSER) [9] and perhaps get more insight into the solvation effects on the MOx molecule.

Summary PostScript

In consultation with Dr. Samer Gozem, further investigations were performed using a more advanced model*, including each solvent's optical dielectric[11]. This did improve the reported[1] wavelength offset from previously reported but not the narrow solvatochromic spread.

Upon further reflection, Dr. Gozem was able to lay the mystery of the narrow solvent-induced wavelength spread to rest. The model used were "implicit" solvent models. "This means we are treating the solvent as simply a dielectric 'swimming pool' in which we embed the molecule. These models only account for electrostatic interactions between the molecule you build and the solvent, but they miss all other effects, some of which are likely quite important (e.g., hydrogen bonding, dispersion, etc.)" [Dr. Gozem].

	eV	λ (nm)	ϵ^{-1}	DE
heptane	5.6444	219.65	0.523204	1.9113
ether	5.6189	220.65	0.235849	4.24
THF	5.5809	222.15	0.132878	7.5257
acetone	5.5702	222.58	0.048797	20.493
methanol	5.5712	222.54	0.030663	32.613
acetonitrile	5.5676	222.68	0.028021	35.688
DMSO	5.5416	223.73	0.021356	46.826
water	5.5652	222.78	0.012762	78.355

Table 8

* Basis set 6-311G++, Solvent method PCM, Theory IEFPCM, non-equilibrium

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