Vibrational Analysis and Spectroscopy of Li^+OH_2, $(H_2O)_2$, Edge-on Benzene Aggregates using *Gaussian*

Using Restricted Hartree-Fock (RHF), B3LYP,[1,2,3,4] and Moller-Plesset perturbation (MP2) methods in Gaussian,[5] we were able to determine the stationary structures, aggregation energies, vibrational frequencies, and infrared and Raman intensities for Li^+OH_2, $(H_2O)_2$, and point-on benzene aggregates.

Overall, we can see in Table 1 that our optimized energies were reduced as we increased our calculation level from RHF, to MP2, and finally B3LYP. Of note is the change in energy of benzene into the point-on benzene dimer. In Table 2, we can clearly see that B3LYP and RHF see the benzene molecule as having no preference to being alone or in the dimer configuration, whereas it is clear that the dimer configuration is much more energetically favorable according to MP2. This is because the MP2 method does a much better job of accounting for the van der Waals attraction between the rings.

Also included in Figure 1 are the MP2/6-311+G** optimized structures for each aggregate.[6] The MP2 basis was chosen for each as it is the highest level of computational accuracy. We also see that experimental results also compare favorably to our best method for the water and benzene dimers at -3.60±0.50 experimental kcal/mol vs -4.35 kcal/mol calculated and -3.15±.48 kcal/mol vs -3.00 kcal/mol, respectively).[7,8] Likewise, MP2/6-311+G** for Li^+OH_2 is the closest to experiment at -34.0 kcal/mol compared to our calculation of the enthalpy at -34.76 kcal/mol.[9]

It is noteworthy that B3LYP/6-311+G** overestimates the binding energy and enthalpy by ~10.0 kcal/mol when compared to MP2 and RHF methods. Because of their favorability

compared to experiment and computational level, the calculated IR and Raman spectrums for each aggregate calculated at the MP2 level have been included in Figures 2 and 3, respectively.

References

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Table 1. Calculated thermochemistry of Li^+, H_2O, benzene and their aggregates for RHF, MP2, and B3LYP methods using the 6-311+G** basis set.

Level	Molecule	Total Energy (Ha)	VZPE (kcal/mol)	Thermal Energy (kcal/mol)	Entropy (cal/molK)
RHF/6-311+G**	Li^+	-7.235840	0.00	0.89	31.80
RHF/6-311+G**	H_2O	-76.053305	14.45	16.23	44.95
RHF/6-311+G**	C_6H_6	-230.756774	66.84	69.43	68.20
RHF/6-311+G**	$Li^+(OH_2)$	-83.347146	16.60	18.76	55.00
RHF/6-311+G**	$(H_2O)_2$	-152.113658	30.64	34.09	69.15
RHF/6-311+G**	$(C_6H_6)_2$	-461.514435	133.83	140.06	114.17
MP2(full)/6-311+G**	Li^+	-7.248349	0.00	0.89	31.80
MP2(full)/6-311+G**	H_2O	-76.293723	13.62	15.40	45.08
MP2(full)/6-311+G**	C_6H_6	-231.697287	61.64	64.44	69.36
MP2(full)/6-311+G**	$Li^+(OH_2)$	-83.599392	15.61	17.84	55.44
MP2(full)/6-311+G**	$(H_2O)_2$	-152.595958	28.86	31.79	64.60
MP2(full)/6-311+G**	$(C_6H_6)_2$	-463.403534	125.22	131.52	102.74
B3LYP/6-311+G**	Li^+	-7.284918	0.00	0.89	31.80
B3LYP/6-311+G**	H_2O	-76.458463	13.36	15.14	45.09
B3LYP/6-311+G**	C_6H_6	-232.311271	62.86	65.62	69.05
B3LYP/6-311+G**	$Li^+(OH_2)$	-83.817589	15.49	17.68	55.21
B3LYP/6-311+G**	$(H_2O)_2$	-152.925161	28.41	31.30	64.27
B3LYP/6-311+G**	$(C_6H_6)_2$	-464.623077	125.86	133.01	121.89

Table 2. Calculated aggregation energies for $Li^+(OH_2)$, $(H_2O)_2$, and the benzene point-on dimer at RHF, MP2(Full), and B3LYP levels using the 6-311+G** basis set.

Level	Aggregation Reactions	ΔE (kcal/mol)	ΔH_0 (kcal/mol)	ΔH_{298} (kcal/mol)	ΔG_{298} (kcal/mol)
RHF/6-311+G**	$Li^+(OH_2)$	-36.40	-34.25	-34.76	-28.28
RHF/6-311+G**	$(H_2O)_2$	-4.42	-2.69	-2.80	3.39
RHF/6-311+G**	$(C_6H_6)_2$	-0.56	-0.40	0.66	7.28
MP2(full)/6-311+G**	$Li^+(OH_2)$	-35.97	-33.98	-34.42	-28.03
MP2(full)/6-311+G**	$(H_2O)_2$	-5.34	-3.72	-4.35	3.26
MP2(full)/6-311+G**	$(C_6H_6)_2$	-5.62	-3.68	-3.00	7.73
B3LYP/6-311+G**	$Li^+(OH_2)$	-46.57	-44.43	-44.91	-38.45
B3LYP/6-311+G**	$(H_2O)_2$	-5.17	-3.47	-4.14	3.58
B3LYP/6-311+G**	$(C_6H_6)_2$	-0.34	-0.20	1.43	6.25

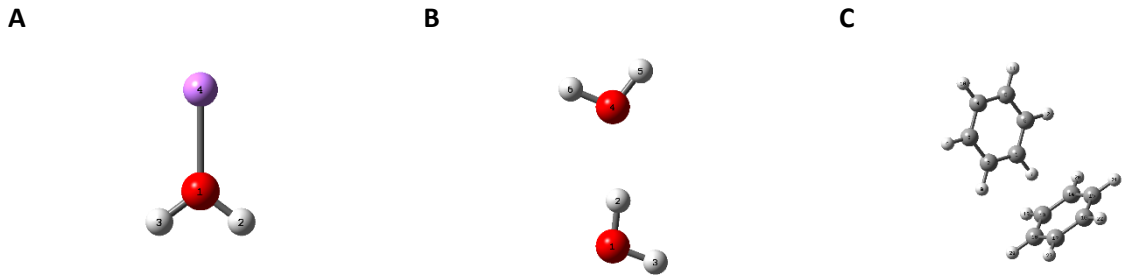

Figure 1. Optimized aggregate structures calculated at the MP2/6-311+G** level for (a) $Li^{+}OH_2$, (b) $(H_2O)_2$, and (c) the point-on benzene dimer.

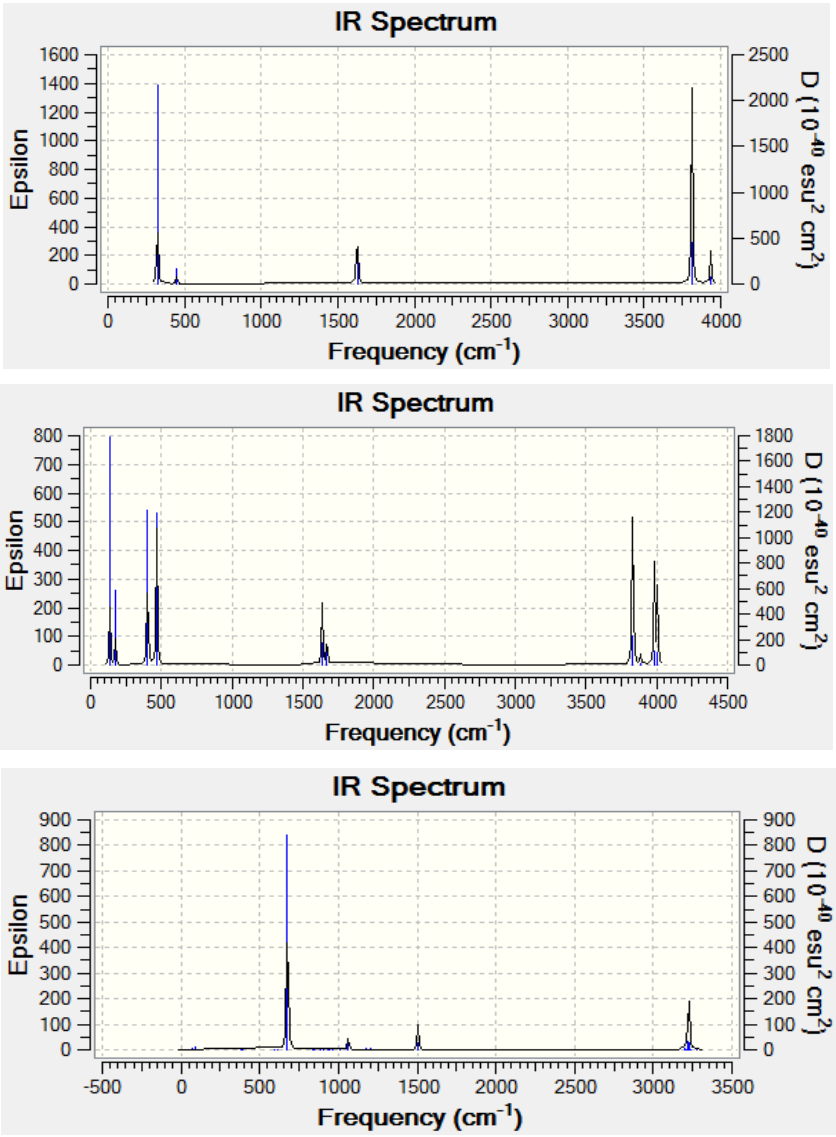

Figure 2. Arbitrary infrared intensity for (top) $Li^{+}OH_2$, (middle) $(H_2O)_2$, and (bottom) the edge-on benzene dimer in terms of cm^{-1}. All spectra were calculated at the MP2(full)/6-311+G** level.

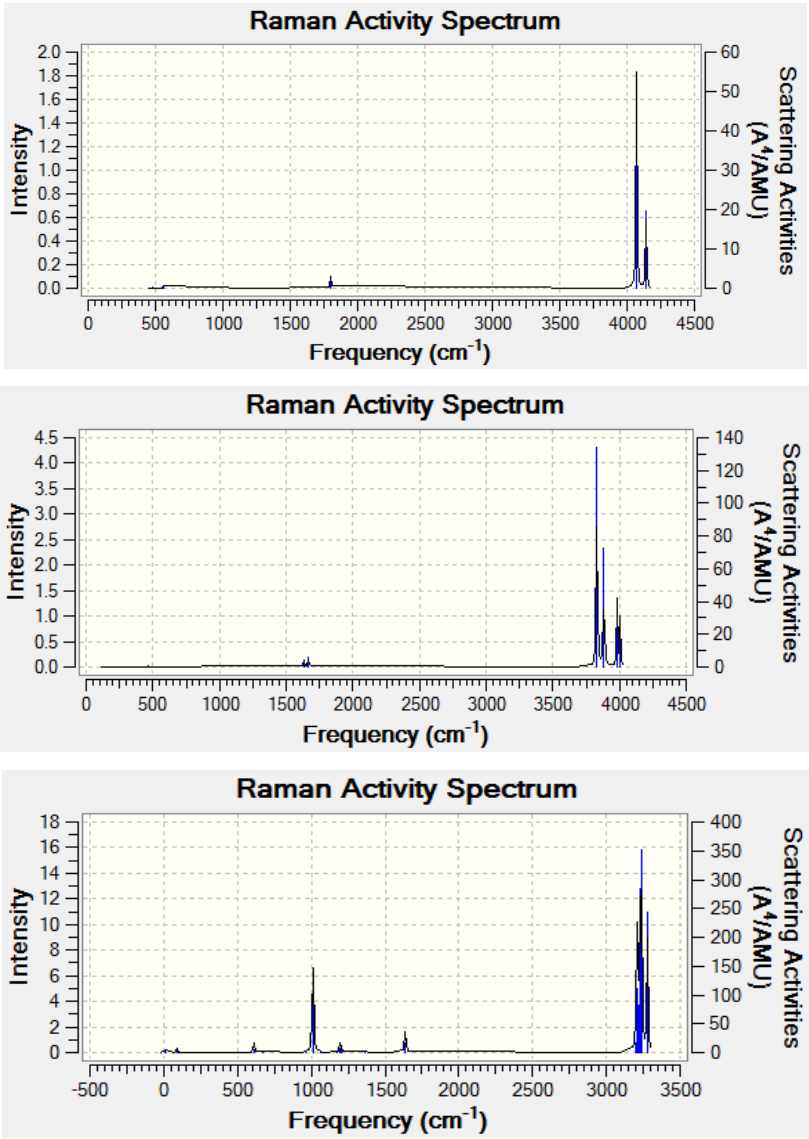

Figure 3. Arbitrary Raman scattering intensity of (top) $Li^{+}OH_2$, (middle) $(H_2O)_2$, and (bottom) the edge-on benzene dimer in terms of cm^{-1}. All spectra were calculated at the MP2(full)/6-311+G** level.