Molecular Modeling Problems

Part A. Structure and Vibrational Spectra

1. Using Vibrational Frequencies to Verify an Equilibrium Structure. Each of the frequencies that make up the vibrational (infrared/Raman) spectrum of a molecule is proportional to the square root of the ratio of the curvature of the potential surface in the vicinity of the structure (the second derivative of the energy) and a mass. As mass is positive, this means that the resulting frequency will be a real number only if the surface curves upward (the second derivative is positive). Therefore, the presence of one or more imaginary frequencies in a calculated spectrum indicates that the structure is not an energy minimum.

Use the HF/6-31G* model to obtain equilibrium geometries and vibrational spectra for the chair and boat forms of cyclohexane. Are all frequencies real for both molecules? Which if either molecule is not a minima on the energy surface? Elaborate.

2. Equilibrium Geometry of Disilylene ($H_2Si{=}SiH_2$). As discussed in the previous problem, a structure that gives rise to a vibrational spectrum with an imaginary frequency is not an energy minimum. However, a minimum energy structure can be located from such a structure by “walking along” the geometrical coordinate associated with the imaginary frequency.

Use the B3LYP/6-31G* model to obtain the equilibrium geometry of planar (like ethylene) disilylene, the simplest molecule with a silicon-silicon double bond, and calculate the vibrational spectrum. Are all frequencies real numbers? If they are not, perform the following operations: First, animate any imaginary frequencies to see how disilylene wants to distort to move it toward an energy minimum. Next, distort your structure accordingly. Finally, reoptimize the geometry (of the distorted molecule) and again calculate vibrational frequencies. Is it now an energy minimum? If not, repeat the process until you get a minimum energy structure. Describe the equilibrium geometry of disilylene.

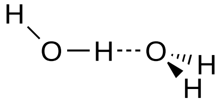
3. Limiting Hartree-Fock Bond Lengths. The Hartree-Fock model almost always yields bond lengths that are shorter than experimental distances. This may be explained by noting that improvements to the Hartree-Fock model involve promotion of electrons from molecular orbitals that are occupied to orbitals that are unoccupied. Occupied orbitals are typically either bonding or non-bonding whereas unoccupied orbitals are typically antibonding. Therefore, electron promotion not only leads to a better description but also presumably to bond lengthening. This in turn suggests that Hartree-Fock bond distances are too short.

Compare the experimental bond length for hydrogen fluoride (0.917Å) with that obtained from the Hartree-Fock model using the cc-pVTZ basis set. This is a sufficiently large basis set to approximate the limit of the Hartree-Fock model for equilibrium geometries. Is the calculated distance shorter than the experimental value?

Repeat your calculations for lithium hydride (the experimental bond length is 1.596Å). Is the Hartree-Fock distance shorter than the experimental length? If it is not, provide an explanation why not. Hint: examine both highest-occupied and lowest-unoccupied molecular orbitals.

4. Bond Lengths in Cyclopropane and Cyclobutane. Use the Hartree-Fock model with the 6-31G* basis set to obtain equilibrium geometries for propane and cyclobutane. Are the carbon-carbon bond lengths in the cycloalkane shorter, longer or about the same as those in propane (the "standard)? Is what you find consistent with the fact that CH bonds on adjacent CH_2 groups nearly eclipse each other leading to an increase in non-bonded repulsion? Elaborate. Given your result for cyclobutane, what you expect the carbon-carbon bond lengths in cyclopropane to be? Is your expectation supported by the calculated equilibrium structrure? If it is not, provide a plausible explanation as to why not.

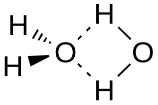
5. Water Dimer. The water dimer exhibits a structure with a single hydrogen bond. While the H --- O distance is not known experimentally, the distance between the two oxygen atoms has been measured as 2.98Å.



The Hartree-Fock model with the very large cc-pVQZ basis set shows a similar overall geometry but with an OO distance that is 0.05Å longer than the experimental value. This suggests that electron correlation shortens the hydrogen bond, the opposite of what is normally observed for covalent bonds. To model the effect of correlation on the geometry of water dimer, consider the consequences of promoting electrons from filled to empty molecular orbitals, most simply from the highest-occupied to the lowest-unoccupied molecular orbital.

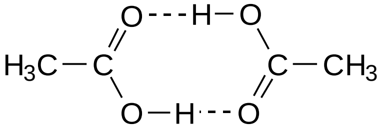
Obtain the geometry of water dimer using the Hartree-Fock/6-31G* model, and display the highest-occupied and lowest-unoccupied molecular orbitals. Is the HOMO bonding, antibonding or non-bonding with respect to the H --- O hydrogen bond? Would loss of an electron lead to shortening or lengthening of the hydrogen bond or would it be expected to have little effect? Is the LUMO bonding, antibonding or non-bonding with respect to the H --- O hydrogen bond? Would gain of an electron lead to shortening or lengthening of the hydrogen bond or would it be expected to have little effect? Overall, would you expect the limiting Hartree-Fock hydrogen bond distance in water dimer to be shorter or longer than or unchanged from the experimental value?

6. Alternative Structure of the Water Dimer. As detailed in the previous problem, water forms a dimer with a single hydrogen bond. However, because water incorporates two electron pairs that may act as hydrogen bond acceptors and two OH bonds that may act as hydrogen-bond donors, it should be possible to construct an alternative dimer with two hydrogen bonds. Does such a structure actually exist?



Attempt to obtain an equilibrium geometry for the doubly hydrogen-bonded structure of water dimer. Use the B3LYP/6-31G* model. If you find such a structure, confirm that it is or is not an energy minimum. If it is an energy minimum, calculate the room-temperature Boltzmann distribution of the two different forms of water dimer.

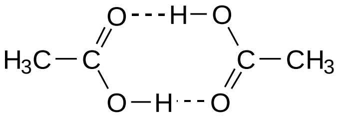
7. Acetic Acid Dimer. Acetic acid forms a dimer with two equivalent hydrogen-bonds. Has the geometry of acetic acid remained largely unaffected by hydrogen bonding (as suggested in the drawing below), or have significant structural changes occurred?



Use the B3LYP/6-31G* model to calculate equilibrium structures for acetic acid and its dimer. Point out any significant changes in bond lengths between the two. Does the dimer incorporate distinct CO single and double bonds? Have the hydrogen atoms involved in the hydrogen bonds moved to positions halfway between the oxygen atoms, or has each hydrogen atom remained with a single oxygen atom? Do the structural changes (or lack of structural changes) suggest that hydrogen bonds are comparable in strength to normal (covalent) bonds or that they are weaker? Elaborate.

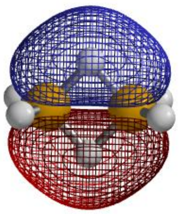
Repeat your calculations for trifluoroacetic acid and its dimer. Are geometry changes smaller, larger or about the same as those seen for acetic acid? Is the dimerization energy for trifluoroacetic acid smaller, larger or about the same as that for acetic acid? If the two are different, is the acid with the larger dimerization energy also that with exhibits the larger changes in structure?

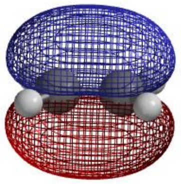
8. Infrared Spectrum of Acetic Acid Dimer. Use the B3LYP/6-31G* model to calculate infrared spectra for acetic acid and its dimer. (You already have equilibrium structures if you completed the previous problem.)



Point out and rationalize any significant differences between the frequencies and/or intensities associated with the (two) OH stretching motions in the dimer and the OH stretching frequency in acetic acid.

9. Radical Cation of Diborane. One of the valence molecular orbitals of diborane closely resembles the π orbital in ethylene.

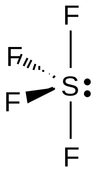




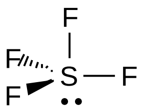
Removal of an electron from this orbital should increase the separation of the boron atoms, just as removal of an electron from the π orbital in ethylene should lengthen the CC bond.

Use the B3LYP/6-31G* model to obtain geometries for diborane and its radical cation. Make certain that you start with a distorted (C_1 summetry) structure for the radical cation. Also, obtain vibrational frequencies (infrared spectrum) for the radical cation to be certain that it is an energy minimum. Does ionization lead to the “anticipated” increase in distance between the two boron atoms? If it does not, then explain why not. Hint: Is the molecular orbital in diborane that resembles the π orbital in ethylene the HOMO?

10. Limitations of VSEPR Theory. VSEPR (**V**alence **S**tate **E**lectron **P**air **R**epulsion) theory uses two simple rules to assign geometry. First, the geometry about an atom follows by insisting that electron pairs (bonds or lone pairs) are as far apart as possible. Second, it is more important to separate two lone pairs than it is to separate a lone pair from a bond than it is to separate two bonds. Taken together, these two rules properly account for the observed "see-saw" structure of sulfur tetrafluoride, SF_4. Sulfur atom surrounded by five electron pairs (four bonds and a lone pair) assumes a trigonal bipyramidal geometry, and the lone pair prefers an *equatorial* position. What VSEPR theory does not tell us is whether this is the only structure of SF_4, in particular, whether a trigonal pyramid structure (which obeys the first rule but violates the second) might also be an energy minimum.



"see saw"



trigonal pyramid

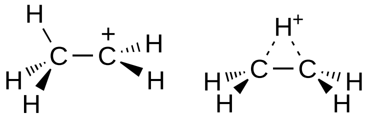
Use the HF/6-31G* model to obtain geometries for both forms of SF_4. Start with C_{2v} symmetry for the see-saw structure and C_{3v} symmetry for the trigonal pyramid structure. Are both structures energy minima or is there only one structure? Detail your reasoning. If there is only one structure, is it the observed structure? If there are two structures, is the observed structure favored? Is the higher-energy structure likely to be observed at room temperature? (Assume that it must make up at least 5% of the mixture to be detected.)

11. Failures of VSEPR Theory. The crystal structure of CaF_2 shows that the molecule is bent, at odds with the prediction of VSEPR theory which assigns a linear geometry. Is this a failure of VSEPR theory or is it due to crystal packing? Use the B3LYP/6-31G* model to obtain the equilibrium geometry of CaF_2. Start with a bent structure, Does this collapse to linear geometry or does the molecule remain bent?

If "free" CaF_2 is linear, calculate the geometry for a molecule with a FCaF bond angle constrained to 140^o, and compare its energy to that of linear CaF_2. What does the energy difference tell you about the magnitude of the crystal packing energy? If on the other hand, "free" CaF_2 is bent, calculate the geometry of "linear" CaF_2 and compare its energy to that of the bent molecule.

12. Geometry Changes with Change in the Number of Electrons. The geometry of a molecule depends not only on the constituent atoms, but also on the total number of electrons. Use the HF/6-31G* model to obtain equilibrium geometry for 2-methyl-2-propyl cation (*tert*-butyl cation), as well as those for the corresponding radical (with one additional electron) and the anion (with two additional electrons). Describe any changes to the geometry of the central carbon with increasing number of valence electrons, and speculate on the origin of these changes. Hint: examine the lowest-unoccupied molecular orbital (the next orbital to be occupied) in *tert*-butyl cation.

13. Protonated Ethylene. What is the geometry of protonated ethylene? Is the proton primarily associated with a single carbon does it "bridge" both carbons?



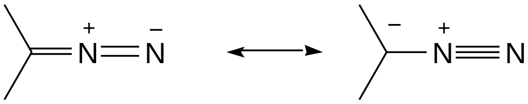
Use the B3LYP/6-31G* model to calculate equilibrium geometries for both open and bridged forms of protonated ethylene. Do both structures appear to be minima on the $C_2H_5^+$ potential surface or does one of the structures "collapse" to the other? Elaborate. If there is only one energy minimum, is it open or bridged?

14. Protonated Methane. The structure of the ion resulting from protonation of a molecule with a non-bonded electron pair should be similar to the structure of the corresponding isoelectronic neutral molecule, that is, the neutral molecule with the same number of electrons. For example, protonated ammonia should be tetrahedral by analogy with methane. There are, however, no known (characterized) neutral analogues of ions resulting from protonation of alkanes. Here, all the valence electrons are already tied up in σ bonds, and any new bonds must be made at the expense of these existing bonds. Nevertheless, protonated alkanes are observed by mass spectrometry. What do they look like?

Use the B3LYP/6-31G* model to explore possible structures for protonated methane (CH_5^+). Calculate vibrational frequencies for whatever you uncover to verify it is actually and energy minimum. Describe the bonding in terms of a weak complex or a molecule with a pentavalent carbon. If it is a complex, identify the components and calculate the binding energy. The gas-phase proton affinity of methane is 544 kJ/mol, which is significantly less than the proton affinity of water (691 kJ/mol), but larger than the proton affinity of N_2 (494 kJ/mol). What is the calculated proton affinity? (Note that the energy of a proton is 0.)

Repeat you calculations and analysis for protonated ethane ($C_2H_7^+$).

15. Structure of Diazomethane. Is there a single Lewis structure for diazomethane or is a composite of two structures required for proper description?



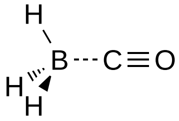
To decide, compare the geometry of diazomethane obtained from the HF/6-31G* model with those of methylamine, CH_3NH_2, and methyleneimine, $H_2C{=}NH$, molecules incorporating normal CN single and double bonds, respectively, and those of *trans* diimide, HN=NH, and nitrogen, N≡N, molecules incorporating normal NN double and triple bonds, respectively. If two Lewis structures are required, which appears to be the more important?

16. Structure of Ozone. Ozone, O_3, leads a proverbial double life. In the upper atmosphere, it protects the earth and its inhabitants from harmful UV radiation, while nearer to the surface it is a serious pollutant contributing to respiratory problems. Draw two different Lewis structures for ozone, one or both of which may require non-zero formal charges. Attempt to obtain equilibrium geometries corresponding to both structures using the B3LYP/6-31G* model. Verify your results by obtaining infrared spectra. If you do obtain two different structures, identify which structure is lower in energy. Is it in accord with the experimentally known equilibrium geometry? If the preferred structure has more than one distinct oxygen atom, which is most positively charged? Most negatively charged? Is your result based on electrostatic charges consistent with that based on formal charges (in the Lewis structure)?

17. Hydrated Hydronuim Cation. Use the B3LYP/6-31G* model to calculate the equilibrium geometry of hydronium cation, H_3O^+. Next, calculate the structure of a complex between H_3O^+ and four water molecules. Point out any significant changes that have occurred to the cation a result of interaction with water. In particular, is there evidence for "sharing" the proton? Has the positive charge remained localized on the hydronium cation or has it spread out to the surrounding water molecules?

18. Hydrated Chloride Anion. Use the B3LYP/6-31G* model to calculate the equilibrium geometry for chloride anion surrounded by four water molecules. Has the negative charge remained on the chlorine or has it spread out to the water molecules?

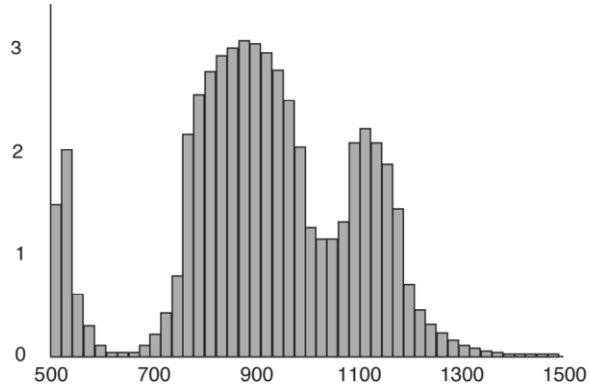
19. Borane Carbonyl. Borane carbonyl, BH_3CO, results from interaction of the non-bonded electron pair (on carbon) in carbon monoxide and an empty p-type orbital in borane.



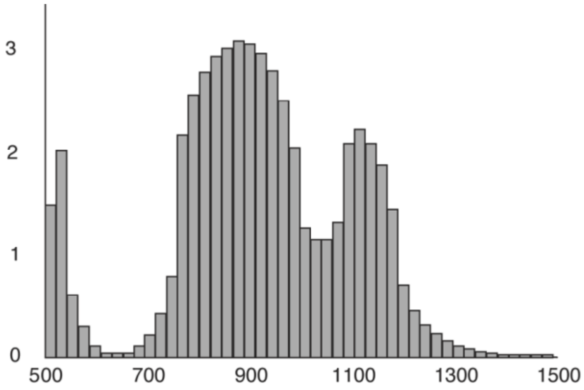
Unlike transition-metal carbonyl complexes (see following problem), there is little possibility for significant back bonding, that is, interaction of a high-energy filled molecular orbital on borane with an empty π^* orbital on carbon monoxide. This suggests that neither the CO bond length nor the vibrational frequency of carbon monoxide is likely to change significantly as a result of complexion.

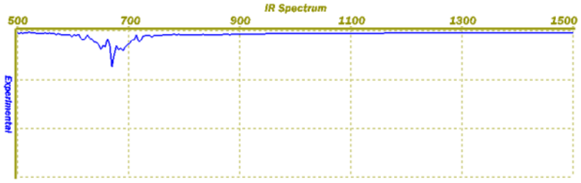
Use the B3LYP/6-31G* model to obtain equilibrium geometries and infrared spectra for both carbon monoxide and borane carbonyl. Is there a significant change in CO bond length? Identify the frequency in borane carbonyl corresponding to the CO stretch. Is it smaller, larger or about the same as that in free carbon monoxide?

20. Greenhouse Gases. In order to dissipate the energy that falls on it due to the sun, the earth "radiates" as a so-called "blackbody" into the universe. The "theoretical curve" is a smooth distribution peaking around 900 cm^{-1} and decaying to nearly zero around 1500 cm^{-1}. This is in the infrared, meaning that some of the radiation will be intercepted by molecules in the earth's gaseous atmosphere. This in turn means that the earth is actually warmer than it would be were it not to have an atmosphere. This warming is known as the ***greenhouse effect***, to make the analogy between the earth's atmosphere and the glass of a greenhouse. Both allow energy in and both impede its release. The actual distribution of radiated energy as measured from outside the earth's atmosphere in the range of 500-1500 cm^{-1} is given below. The overall profile matches that for a blackbody, but the curve is peppered with holes.



Neither nitrogen nor oxygen, which together comprise 99% of the earth's atmosphere absorbs in the infrared and causes the "holes". However, several "minor" atmospheric components, carbon dioxide most important among them, absorb in the infrared and contribute directly to greenhouse warming. Its infrared spectrum shows a strong absorption in the region centering 670 cm^{-1}, the location of the most conspicuous hole in the blackbody radiation profile.





Identify three of the top ten chemicals manufactured worldwide. Use the B3LYP/6-31G* model to calculate the infrared spectra for each and comment whether or not you would expect it to be a significant greenhouse gas.

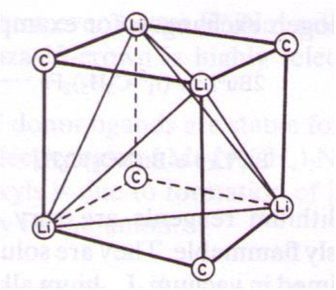
21. Comparison of Measured and Calculated Frequencies. Frequencies routinely obtained from quantum chemical calculations assume that the potential in the vicinity of the minimum is a quadratic function. This means that they are generally larger than measured frequencies. (The correct potential for say a bond stretching motion goes to zero whereas a quadratic potential goes to ∞. It is possible to correct calculated frequencies for cubic and higher-order terms, but this is generally prohibitive in terms of computer time. It is also possible to correct measured frequencies for anharmonic behavior, leading so-called "harmonic frequencies". These exist only for diatomic and very small polyatomic molecules, and include: LiF, 914; CO, 2170; N_2, 2360 and F_2, 923 (all in cm^{-1}).

Use the HF/6-311+G** model to calculate equilibrium geometries and vibrational frequencies for LiF (914), CO (2170), N_2 (2360) and F_2 (923). (Harmonic frequencies in cm^{-1} are given in parentheses.) What is the average percentage error between calculated and measured (harmonic) frequencies? Are calculated frequencies uniformly too small or too large?

Repeat your calculations using the B3LYP/6-311+G** model. What is the average percentage error between calculated and measured (harmonic) frequencies? Is this smaller than the average error for Hartree-Fock calculations? Are calculated frequencies uniformly too small or too large?

22. Methyl Lithium: The structure of methyl lithium appears to be "normal" insofar as it incorporates a carbon with a roughly tetrahedral geometry. This could either mean that the C-Li bond is covalent, or that lithium cation is loosely associated with methyl anion (which also incorporates a tetrahedral carbon). Which of these descriptions is more consistent with atomic charges obtained from the HF/6-31G* model? Elaborate.

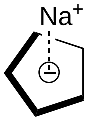
Experimentally, methyl lithium exists most simply as a tetramer with the four lithium atoms and four methyl groups at the corners of a cube.



Use the HF/6-31G* model to calculate the geometry of methyl lithium tetramer. Does the conclusion you reached about the nature of the bonding in methyl lithium maintain?

23. Lithium Aluminum Hydride. Lithium aluminum hydride ($LiAlH_4$) is among the most important reducing agents, that is, source of "hydride". Is it best described as an ion pair between lithium cation and aluminum hydride anion (AlH_4^-), a weak complex between lithium hydride (LiH) and aluminum hydride (AlH_3), or are one or more hydrogen atoms "shared" by the two metals? To decide, obtain the equilibrium geometry using the B3LYP/6-31G* model. Are the calculated atomic charges consistent with your geometry? Elaborate. Is there more than one stable structure for lithium aluminum hydride? Start from one or more structures that are different from what you have found and see if you get a different result.

24. Sodium Cyclopentadienide: Is sodium cyclopentadienide accurately represnted in terms of a structure in which sodium cation associates with cyclopentadienyl anion?



Obtain the equilibrium geometry of sodium cyclopentadienide using the B3LYP/6-31G* model. Is the charge on sodium close to unity? Calculate the equilibrium geometry of cyclopentadienyl anion and compare it with the cyclopentadienyl fragment in sodium cyclopentadide. Is what you find indicative of a weak complex? Elaborate. Calculate the energy of dissociation to cyclopentadienyl anion and sodium cation (you need to obtain the energy for sodium cation). Is the binding energy weak (< 100 kJ/mol), comparable to that of a normal covalent bond (~400 kJ/mol) or somewhere in between? Is your result consistent with the calculated charges and geometries?

25. Proton NMR Spectrum of Cyclohexane. At very low temperatures, the proton NMR spectrum of cyclohexane shows two equal intensity lines at 1.12 and 1.60 ppm. Use the HF/6-31G* model to obtain the equilibrium geometry and the proton chemical shifts. Which line corresponds to the *equatorial* protons and which corresponds to the *axial* protons?