CHE502 Chemical and Statistical Thermodynamics

Homework 1

URL: http://theo.ism.u-bordeaux.fr/PBopp/vistec.2020.2021

A few (out of many possible) answers

Remember the GAUSSIAN/GaussView lab

What can we know about a molecule? And how?

Property	method	comment
molecular geometry (distances, angles)	X-ray and neutron scattering	difficult, usually one has to use a crystal which may change the geometry. With the usual X-ray wavelengths and neutron energies these techniques are better suited to intermolecular structures. Note: IR and Raman spectroscopy contain information about the molecular symmetry (via the ”selection rules”)
`https://courses.lumenlearning.com/introchem/chapter/determining-atomic-structures-by-x-ray-crystallography/`		
molecular geometry	quantum chemistry	This is the most frequent application of quantum chemistry. The Schrödinger equation (S.eq.)for the electrons is solved and the energy levels are found. The electronic wave functions ψ are also found Most codes (eg GAUSSIAN) can ’move’ the nuclei (which are kept fixed when the S.eq. is solved) until the lowest possible electronic energy is found. This is then (usually) the equilibrium geometry of the molecule
”size”	X-ray indirect	usually from measurements in condensed phases (molecular radius = 1/2 distance between two atoms
electronic energies	visible, UV-vis, X-ray spectroscopies	The oldest types of spectroscopy, energies around 1 eV (10,000 cm^{-1} or so) and up also from quantum chemistry as differences between energy levels Energies, see `http://halas.rice.edu/conversions`
vibrational energies ,	IR (FTIR) variation of dipole moment μ when the molecule vibrates Raman variation of polarizability	IR and Raman both ’see’ the molecular vibrations can be measured very precisely in gases (± less than a cm^{-1} (also the intermolecular ones in condensed phases) but differently (different selection rules) Vibrational energies can also be obtained from GAUSSIAN calculation by taking the 2nd derivatives of the energies + a few (usually quite reasonable) assumptions
rotational energies	similar to vibrations, but much smaller energies	can be measured quite precisely in gases Easy to calculate from the geometry (neglecting ro-vib couplings)
nuclear spin	NMR chemical shift NMR relaxation	Chemical shift: measure changes in the energy levels of the nuclear spin of one atom as a function of the neighboring atoms Gaussian: yes, since we have ψ and thus ψ^2 at the location of the nucleus of interest. Same for ’NMR coupling constants’ Gaussian NO, since this involves movements of the nuclei and GAUSSIAN knows nothing about movement (thus the trick needed for IR/Raman ie vibrations)
thermochemistry U, H, G miscibility, boiling point, melting point, phase transition enthalpy	 calorimetry macroscopic measure statistical mechanics	 macroscopic property, say not much about the molecule itself GAUSSIAN produces these numbers with many assumption, see built-in module ’quantum-thermochemical extrapolation methods’ → chi501

Electrostatic properties		
Dipole moment μ, higher multipoles	can be measured	can be calculated from ψ
static and dynamic polarizabilities	with specialized instruments	often useful just to compare with experiment
Electrostatic potential (ESP)	(ie not so easy)	
Ionization potential, electron affinity	ESP cannot be measured	
in condensed phases		
dielectric constants $\epsilon(0), \epsilon(\omega)$	stat. mech	
permittivity		→ chi501

In all cases, measurements <u>and</u> calculations, one must always be aware of the uncertainties (error bars).
Certain quantities can be measured (and/or computed) with a high precision (uncertainties in the range of 1 in 1000 or so), others may have, for many reasons, much larger uncertainties
→ always report your results with a number of decimal places in keeping with your uncertainty, and with the uncertainty:
eg 9.57±0.02 not 9.57321456±0.0234... (specially for calculations, the computer will of course give you many decimal places, they probably mean nothing)