

Lecture 35, April 26, 2006

(Some material in this lecture has been adapted from Cramer, C. J. *Essentials of Computational Chemistry*, Wiley, Chichester: 2002; pp. 301-303; 314-315.)

Solved Homework

From

$$K_{i/j} = \frac{[A]}{[B]} = \frac{\%_o(E_A)}{\%_o(E_B)} = \frac{e^{-E_A/k_B T}}{e^{-E_B/k_B T}} = e^{-(E_A - E_B)/k_B T}$$

Let us assume $K = 1$, in which case $E_A - E_B$ is zero. An error of a factor of 10 means $K = 10$ (or 0.1, the only difference will be in the sign of $E_A - E_B$ and not its magnitude). So, we simply need solve

$$10 = e^{-(E_A - E_B)/k_B T}$$

for $\Delta E = E_A - E_B$, which is, at 25 °C (298 K)

$$\begin{aligned}\Delta E &= -k_B T \ln 10 \\ &= -(1.3806 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})(2.3026) \\ &= 9.4733 \times 10^{-21} \text{ J}\end{aligned}$$

At 500 °C (773 K), we have

$$\begin{aligned}\Delta E &= -k_B T \ln 10 \\ &= -(1.3806 \times 10^{-23} \text{ J K}^{-1})(773 \text{ K})(2.3026) \\ &= 2.4573 \times 10^{-20} \text{ J}\end{aligned}$$

The numbers above correspond to the errors in the predicted energy difference that would lead to an error of an order of magnitude in the equilibrium constant (the numbers are, of course, independent of what the equilibrium constant really is).

A quick glance at the form of the equation for the rate constant

$$k = \frac{k_B T}{h} e^{-(G_{TS} - G_A)/k_B T}$$

should make clear that the energy errors will be the same for the rate constant as for the equilibrium constant (prove this to yourself if you don't see it! Note that the prefactor of $k_B T/h$ makes no difference because an error that is a "factor" of ten implies that the *ratio* of the wrong and right rate constants is 10, so the prefactor disappears as it is present in both the numerator and denominator of the ratio).

These are, of course, tiny energy differences, but that is because we really in this case need to think in terms of large collections of molecules, not single molecules (how can there be an equilibrium constant for one molecule?) So, if we multiply by Avogadro's number ($6.02 \times 10^{23} \text{ mol}^{-1}$) and divide by 1,000 (so we have kJ instead of J), we get the more typical molar quantities 5.7 kJ mol^{-1} (298 K) and 14.8 kJ mol^{-1} (773 K) [or, $1.4 \text{ kcal mol}^{-1}$ (298 K) and $3.5 \text{ kcal mol}^{-1}$ (773 K)]. So, not much room for error, particularly at low temperatures... (drat interesting chemical quantities always depending *exponentially* on energy differences!)

The final question was what fraction is this energy difference at 298 K of the total energy of HF/STO-3G water. Noting 1 a.u. of energy ($1 E_h$) is $4.36 \times 10^{-18} \text{ J}$, the total energy of water, at $-74.9659012170 \text{ a.u.}$ is $3.27 \times 10^{-16} \text{ J}$. The energy error $9.47 \times 10^{-21} \text{ J}$ is a mere 0.003% of that energy. So, an error of 0.003% in a calculation of water could throw off an equilibrium constant or a rate constant by an order of magnitude. Imagine how tight the requirements are for a *really* big molecule!

Vibrational Spectroscopy Revisited

Last lecture, we considered the solution of the 1-dimensional vibrational Schrödinger equation for an arbitrary potential to compute accurate vibrational wave functions and transition energies. While this approach is quite accurate for select instances, it is too demanding for a molecule with many degrees of freedom. Given the importance of vibrational (infrared) spectroscopy for identification of molecular structure, it would be nice to have a quicker, approximate method to obtain *all* of the vibrational frequencies for a molecule from quantum mechanics.

You will recall that, in the 1-dimensional case, a dramatic simplification occurs when the potential is assumed to be harmonic. In that case, one has a Schrödinger equation for which there are analytical solutions (the quantum mechanical harmonic oscillator wave functions). These eigenfunctions are products of Hermite polynomials and gaussian functions, and their eigenvalues are

$$E = \left(n + \frac{1}{2} \right) h\omega \quad (35-1)$$

where n is the vibrational quantum number beginning at 0 and

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (35-2)$$

where μ is the reduced mass and k is the bond force constant, i.e., the second derivative of the energy with respect to bond stretching evaluated at the equilibrium bond length (see eq. 9-3).

So, what about the polyatomic case? In that case, we must carry out a multidimensional Taylor expansion analogous to the 1-dimensional eq. 9-2. This leads to the multidimensional analog

$$\left[-\sum_i^{3N} \frac{1}{2m_i} \frac{\partial^2}{\partial q_i^2} + \frac{1}{2} (\mathbf{q} - \mathbf{q}_{eq})^t \mathbf{H} (\mathbf{q} - \mathbf{q}_{eq}) \right] \Xi(\mathbf{q}) = E \Xi(\mathbf{q}) \quad (35-3)$$

where \mathbf{q} is the vector of atomic cartesian coordinates, \mathbf{q}_{eq} defines the equilibrium structure, and \mathbf{H} is the Hessian matrix defined by eq. 32-6. (Remember, no gradient terms appear in *this* Taylor expansion because we're expanding about a minimum, so all gradients are zero. Thus, to use this approach, one *must* have an optimized geometry from which \mathbf{q} is taken and for which \mathbf{H} is computed.)

While eq. 35-3 has a well defined potential energy function, it is *quite* difficult to solve in the indicated coordinates. However, by a clever transformation into a unique set of mass-dependent spatial coordinates \mathbf{q}' , it is possible to separate the $3N$ -dimensional eq. 35-3 into $3N$ *one*-dimensional Schrödinger equations. These equations are identical to eq. 9-4 in form, that is they appear as

$$\left[-\frac{1}{2\mu} \frac{d^2}{dq'^2} + \frac{1}{2} kq'^2 \right] \xi(q') = E \xi(q') \quad (35-4)$$

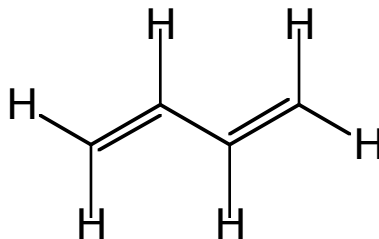
but they have force constants and reduced masses that are defined by the action of the transformation process on the original coordinates. Each component of \mathbf{q}' corresponding to a molecular vibration is referred to as a “normal mode” for the system, and with each component there is an associated set of harmonic oscillator wave functions and eigenvalues that can be written entirely in terms of square roots of the force constants found in the Hessian matrix and the atomic masses.

Note that because eq. 35-3 is over the full $3N$ coordinates, the transformed coordinate system \mathbf{q}' includes 3 translational and 3 rotational (2 for linear molecules) “modes”. The eigenvalues associated with these modes are typically very close to zero, and indeed, the degree to which they *are* close to zero can be regarded as a diagnostic of how well optimized the structure is in terms of being at the local minimum geometry.

A separate interesting point is that the form of eq. 35-3 is valid for *all* stationary points, *not* just minima on the PES. However, for non-minima there will be one or more normal mode force constants that will be negative, corresponding to motion along modes that lead to energy lowering. Insofar as the frequencies are computed from the square roots of the force constants, this leads to an imaginary frequency. *Frequency calculations thus are diagnostic as to the nature of stationary points:* All positive frequencies implies a (local) minimum, one imaginary frequency implies a transition state structure, and two or more imaginary frequencies refer to stationary points characterized by additional negative force constants. Such structures are sometimes useful in searching for TS structures by following the various energy-lowering modes, but they have no chemical significance. Thus, since there is no guarantee that a geometry minimization that leads to a structure with zero gradients will produce a minimum (or a transition-state, if that is what one is looking for), a frequency calculation is useful to verify what has happened.

So, how good is theory for IR spectral prediction? In the table below are listed experimental and computed vibrational frequencies (cm^{-1}) at the Hartree-Fock level using a basis set called 3-21G (it's about twice the size of STO-3G, so more flexible) for *s-trans* 1,3-butadiene (*s-trans* means the two double bonds are *trans* about the single bond). There are 10 atoms, so there are $3N-6 = 24$ degrees of freedom.

Experiment	Computed	Unsigned Error	Scaled Comput.	Unsigned Error
162	165	3	149	14
301	333	32	300	1
512	578	66	520	8
522	588	66	529	7
770	869	99	782	12
894	950	56	855	39
908	1112	204	1001	93
912	1097	185	987	75
976	1159	183	1043	67
990	1135	145	1022	32
1013	1180	167	1062	49
1196	1339	143	1205	9
1280	1461	181	1315	35
1294	1474	180	1327	33
1381	1576	195	1418	37
1438	1636	198	1472	34
1596	1809	213	1628	32
1630	1873	243	1686	56
2984	3316	332	2984	0
2992	3310	318	2979	13
3003	3324	321	2992	11
3055	3329	274	2996	59
3087	3396	309	3056	31
3101	3397	296	3057	44
Mean error:		183.7		33.0



s-trans 1,3-butadiene

Notice that the performance of the raw HF level is not particularly impressive. There is a mean unsigned error of almost 184 cm^{-1} , which is quite a bit in an IR spectrum. However, if we simply multiply each frequency by 0.9 (i.e., we apply a “scale factor”) we can improve the mean unsigned error to only 33 cm^{-1} . This is really quite good! Indeed, the predictive quality is sufficient to be useful in identifying unknown molecules, as we will see in a moment. However, before doing that, it is instructive to consider, why do we need to apply a scale factor to get better accuracy?

To answer that question, first notice the sense of the error in the unscaled predictions. Every single frequency is predicted to be too large compared to experiment. Since the frequency depends only on the force constant and the reduced mass, and since there is no quantum chemistry in the reduced mass (it just comes from coordinate transformation), it must be that HF theory predicts the force constants all to be too large. Put differently, HF bonds are too strong. So, why might HF bonds be too strong?

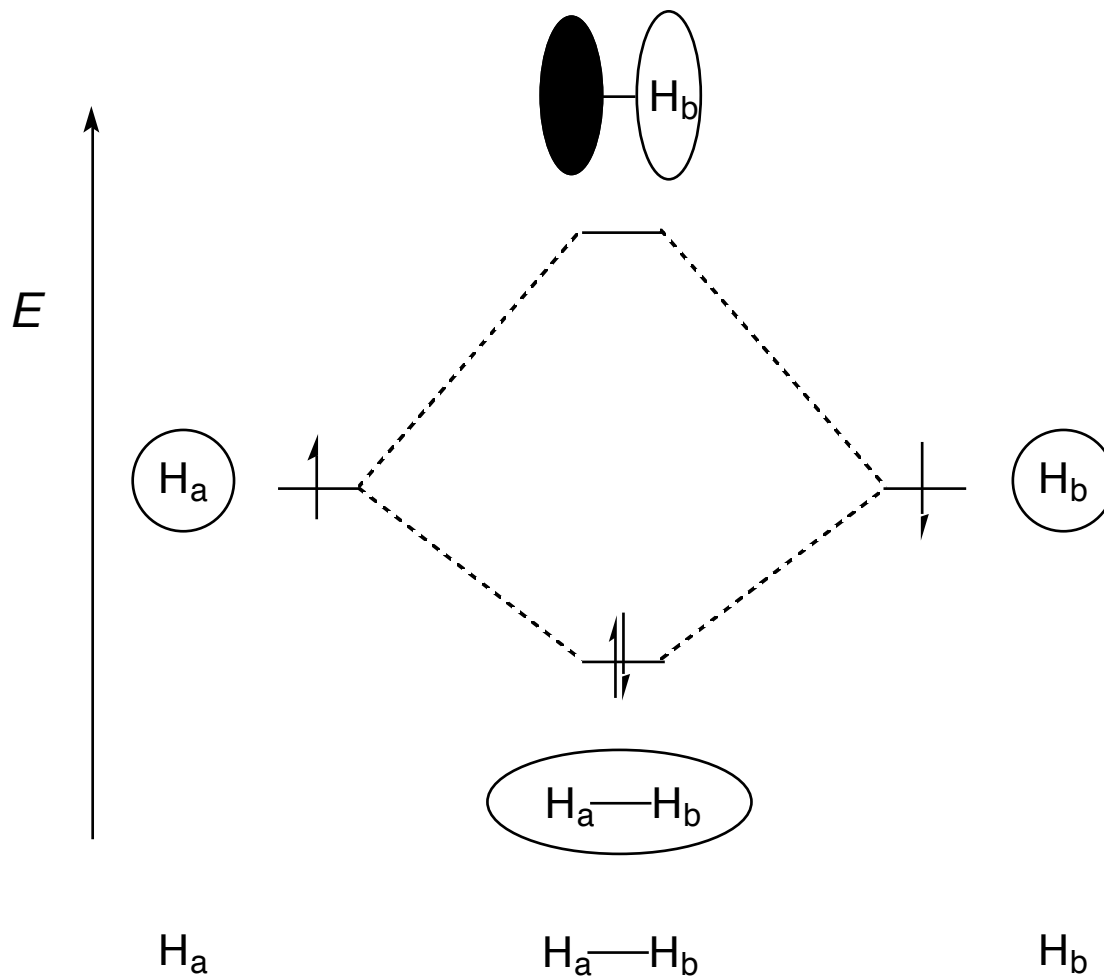
In this case, it is helpful to think about a *very* simple molecule, H_2 . If we were to do an HF calculation on molecular hydrogen, taking as our basis set a $1s$ function on each H (label the two H atoms “a” and “b”), we would find that our two MOs (one occupied with 2 electrons, one empty) would be an in-phase combination of equally weighted $1s$ basis functions (the occupied MO) and an out-of-phase such combination (the empty one). These are the classic σ bonding and σ^* antibonding orbitals of H_2 . So, the many electron determinant is just

$$\Psi = |\sigma^2\rangle \quad (35-5)$$

But, let’s actually write this simple Slater determinant out in more detail, noting that

$$\sigma = \frac{1}{\sqrt{2}}(1s_a + 1s_b) \quad (35-6)$$

Then we have



$$\begin{aligned}
 \Psi &= \frac{1}{\sqrt{2}} [\sigma(1)\alpha(1)\sigma(2)\beta(2) - \sigma(2)\alpha(2)\sigma(1)\beta(1)] \\
 &= \frac{1}{\sqrt{2}} \sigma(1)\sigma(2) [\alpha(1)\beta(2) - \alpha(2)\beta(1)]
 \end{aligned}
 \tag{35-7}$$

which is the usual result for the closed-shell singlet. Let's consider only the spatial part of the wave function. If we expand that using eq. 35-6 we have

$$\begin{aligned}
 \Psi &= \frac{1}{\sqrt{2}} \sigma(1)\sigma(2) \\
 &= \frac{1}{\sqrt{2}} \left\{ \frac{1}{\sqrt{2}} [1s_a(1) + 1s_b(1)] \right\} \left\{ \frac{1}{\sqrt{2}} [1s_a(2) + 1s_b(2)] \right\} \\
 &= \frac{1}{2\sqrt{2}} \left[1s_a(1)1s_a(2) + 1s_a(1)1s_b(2) \right. \\
 &\quad \left. + 1s_b(1)1s_a(2) + 1s_b(1)1s_b(2) \right]
 \end{aligned}
 \tag{35-8}$$

Qualitatively, what does eq. 35-8 mean? It says that we should think of the spatial part of the wave function as being one part both electrons around H_a (the first term in brackets), two parts one electron around H_a while the other is around H_b (the next two terms), and one part where both electrons are around H_b . This is evidently perfectly fine when the two H atoms are separated by their equilibrium bond length (about 0.7 Å).

But, what happens if we pull the two hydrogen atoms far away from one another? In that case, the parts of the wave functions with one electron around each H atom seem quite reasonable—that's how H_2 separates. But, the two components where both electrons are around a single H atom correspond to the situation where one H is H^+ and the other H^- . This is a *very* high energy situation since the ionization potential of H (to make H^+) is 13.6 eV (remember that we know this from *exact* one-electron quantum mechanics), and the electron affinity of H (to make H^-) is very, very small.

So, those so-called ionic terms make the energy very high. We know that the *reasonable* long-distance wave function should include only the one-electron-on-each-H terms, i.e.,

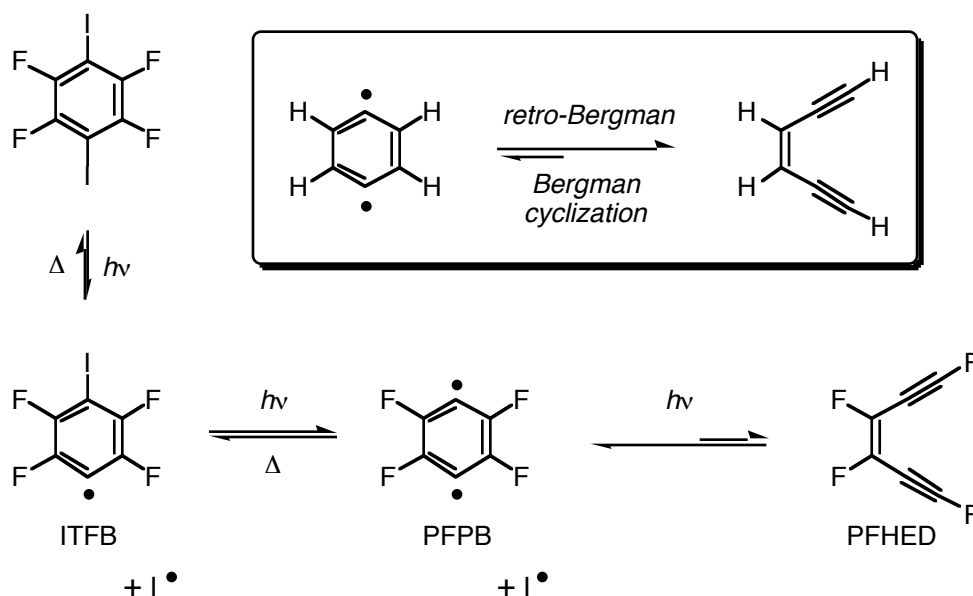
$$\Phi = \frac{1}{2} [1s_a(1)1s_b(2) + 1s_b(1)1s_a(2)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (35-9)$$

where we've put the singlet spin function back in explicitly. But, notice that *this* is our old friend the open-shell singlet (cf. eq. 22-5), which we know is not a single determinant but is instead a linear combination of two determinants. Since restricted Hartree-Fock theory *requires* a single determinant, it can't ever "make" this better wave function, so when bonds stretch the energy goes too high too fast.

That's why RHF force constants are too large, because the single determinant formalism of RHF forces dissociation to be unrealistically high in energy by inclusion of ionic terms in the wave function. What is fascinating is that the same scale factor that improved our computed frequencies for 1,3-butadiene works equally well for just about any HF/3-21G frequency calculation. That is, the scale factor is universal, not molecule-specific. So, the HF method, after scaling, is still an excellent way to predict IR spectra.

Matrix Isolation Spectroscopy (A Case Study)

The class of antitumor-antibiotics known as enediynes undergo *in vivo* Bergman cyclization of the enediyne functionality to generate *p*-benzyne reactive intermediates that damage genetic material (see figure below). Because the damage results in double-stranded DNA cleavage, they are extraordinarily cytotoxic, and this has sparked interest in better understanding *p*-benzynes in general. One issue associated with the parent *p*-benzyne is that it is thermochemically unstable relative to its enediyne precursor, making its isolation quite challenging. In work reported in Wenk, H. H.; Balster, A.; Sander, W.; Hrovat, D. A.; Borden, W. T. "Matrix Isolation of Perfluorinated *p*-Benzyne"



Angew. Chem., Int. Ed. Engl. **2001**, *40*, 2295, Wenk et al. sought to identify a precursor not suffering from this problem, and determined from computational quantum chemistry that perfluorinated *p*-benzyne was roughly 8 kcal mol⁻¹ more stable than the enediyne that would be produced from retro-Bergman ring opening, and moreover that the barrier to that ring opening was nearly 38 kcal mol⁻¹, this being nearly double the barrier in the unfluorinated case. Girded with this thermochemical armor, they set out to synthesize the diradical by UV photolysis of 1,4-diiodo-2,3,5,6-tetrafluorobenzene.

When this precursor is photolyzed at 3 K (brrr) in a neon matrix, IR spectroscopy indicates rapid formation of a new species **A** (at 3 K in a matrix made of frozen neon, individual molecules can't bump into other molecules, and it is too cold to do any reaction chemistry unless a photon brings in new energy). Prolonged photolysis (i.e., more photons) creates a second product **B** whose IR bands are distinct from the first. And, if the matrix containing the second product is irradiated with UV light of somewhat longer wavelength, IR analysis indicates that a third product **C** is generated. All of the IR bands observed for **A**, **B**, and **C** are listed in the below table. These bands are compared to frequencies computed by quantum chemistry (to be perfectly honest, it's a level of quantum theory better than HF theory, but the point of this case study is to show how predictive IR spectroscopy is useful, not to show off HF theory).

The generally excellent agreement between the experimental and computed spectra permits the secure assignment of the bands for **A** to the ITFP, the bands for **B** to PFPB, and the bands for **C** to PFHED as would be suggested by the synthetic scheme in the figure above. The "missing" bands in the experimental IR spectra are all predicted to be very low in intensity in the computed spectra (we haven't talked about how to compute intensity, but as always it depends on the transition dipole moment since it is a measure of "allowedness"). In the absence of IR spectroscopy and theoretical confirmation, it is difficult to imagine what experiments one would do in a 3 K neon

Table. Experimental and computed IR spectra (cm^{-1}) for A, B, and C, and ITFP, PFPB, and PFHED, respectively.

A	ITFP	B	PFPB	C	PFHED
693	693		677		576
834	834		690		591
942/956	954	925	911		680
1138	1145		1148	912	918
1188	1195	1117	1151	1072	1067
1259	1298		1154		1151
1352	1400		1360		1363
1428	1441	1407	1421	1398	1414
1472	1487	1502/1516	1499	1678	1707
1574	1585		1560	2337	2419
			1610		2426

matrix to prove that the various reactive intermediates had been created. This represents, then, an excellent example of how theory can aid experiment in the identification of short-lived reactive species.

Homework

To be solved in class:

What is the Coulomb integral for the interelectronic repulsion for the closed-shell wave function of H_2 in eq. 35-8? (Don't try to come up with a number, just express it in some useful shorthand notation, like Dirac notation.) Now, compute the same thing for the open-shell wave function of eq. 35-9. Which wave function has the greater Coulomb repulsion, and how might that depend on interatomic distance? Why do you think H_2 forms a stable, closed-shell singlet bond?

To be turned in for possible grading Apr. 28:

Use the virial theorem (described in the solved homework of Lecture 16) to prove that since H_2 is bound (i.e., is lower in energy than two separated H atoms) then the kinetic energy of the electrons in H_2 must be greater than it is in two separated H atoms.