CALCULATING INFRARED SPECTRA

The infrared spectrum of a molecule arises because of transitions between vibrational energy levels. Each line in an infrared spectrum is characterized by a frequency (energy) and an intensity. In one dimension (a diatomic molecule), it is common practice to assume that the frequency is proportional to the square root of the ratio of the second-derivative of the energy with respect to the internuclear distance, r, and the reduced mass (the product of the masses of the two atoms divided by their sum).

$$\text{vibrational frequency} \propto \sqrt{[(d^2E(r)/dr^2/)\text{reduced mass}]}$$

This is referred to as the ***harmonic approximation***, the origin of which can be seen by expanding the energy in a Taylor series.

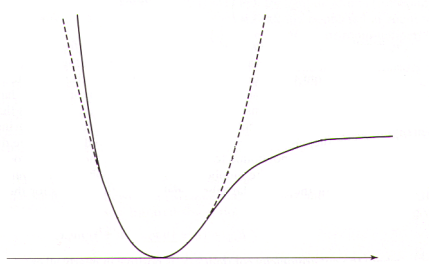
$$E(r) = E(r_0) + (dE(r)/dr)\, r + (d^2E(r)/dr^2)\, r^2 + \text{higher-order terms}$$

$E(r_0)$ is a constant and dE(r)/dr (the gradient) is assumed to be zero. The latter implies that the underlying structure corresponds precisely to a minimum (or a maximum) on the potential energy curve. Were this not the case, the first derivative would be non zero and the calculated frequency would be meaningless. Nearly all practical calculations ignore cubic and higher-order terms (***anharmonic*** terms), leaving only the second derivative term (the ***force constant***). This said, the frequency may be interpreted as the relative ease or difficulty of stretching the bond away from its equilibrium position, that is, the curvature of the energy surface at the minimum. Where distortion away from the equilibrium position is easy, the result is a low frequency; where it is difficult the result is a high frequency. High (reduced) mass leads to a low frequency while low mass leads to high frequency.

The expression for vibrational frequency qualitatively accounts for mass effects on reaction energies (***equilibrium isotope effects***). Even at 0K molecules vibrate, giving rise to the so-called zero-point vibrational energy (or simply ***zero-point energy***). Zero-point energy is directly proportional to the sum of the vibrational frequencies and decreases with increasing mass. For example, the zero-point energy of HCl is lowered upon replacement of hydrogen by deuterium. Thus, the measured energy

(enthalpy) decreases with increasing mass and the energy of DCl is smaller (more negative) than that for HCl.

Because the potential energy has been approximated by a quadratic function, calculated frequencies will almost always be larger than measured frequencies. This is because a quadratic function goes to infinity with increase in distance rather than going asymptotically to a constant (separated atoms), meaning that the potential curve will be too steep.



It is possible to extract the harmonic frequency from an experimental spectrum by measuring the spacing of the energy levels associated with the ground and excited states of a particular vibration. (The lines would be evenly spaced were the potential quadratic.) However, such an analysis is impractical for any but diatomic and very simple polyatomic molecules.

Generalization from a diatomic to a polyatomic molecule is straightforward. The energy of displacement away from the equilibrium position is expanded in the same way as before, the only difference being that a vector quantity, **x**, replaces a scalar quantity, x.

$$E(\mathbf{x}) = E(\mathbf{x_0}) + \Sigma_i(\partial E(\mathbf{x})/\partial x_i)x_i + \tfrac{1}{2}\Sigma_{ij}(\partial^2 E(\mathbf{x})/\partial x_i \partial x_j)x_i x_j + \text{higher-order terms}$$

As with the expression for a diatomic molecule, the leading term is a constant, the first derivative term is zero and cubic and higher-order terms are ignored. For a molecule with N atoms, the dimension of **x** is 3N (x,y,z Cartesian coordinates for each atom), although there

are only 3N-6 (3N-5 for a linear molecule) vibrational frequencies. Six dimensions (five for a linear molecule) correspond to translation away from and rotation around the center of mass.

The first (and only computationally expensive) step involved in calculating the vibrational spectrum of a polyatomic molecule is evaluation of the full set of second energy derivatives in Cartesian coordinates. These then need to be mass weighted. Diagonal terms ($\partial^2 E(\mathbf{x})/\partial x_i^2$) are divided by the mass of the atom associated with x_i, and off-diagonal terms ($\partial^2 E(\mathbf{x})/\partial x_i \partial x_j$) are divided by the product of the square root of the masses of the atoms associated with x_i and x_j. These expressions reduce to that already provided for the one-dimensional case.

The second step involves replacing the Cartesian coordinates by a new set of coordinates $\boldsymbol{\zeta}$, such that the matrix of mass-weighted second derivatives is diagonal. δ_{ij} is the so-called Kronecker delta function which is 1 if i=j and 0 otherwise.

$$[\partial^2 E(\zeta)/\partial \zeta_i \partial \zeta_j]/(\sqrt{M_i}\sqrt{M_j}) = \delta_{ij}\,[\partial^2 E(\zeta)/\partial \zeta_i^2]/M_i$$

These new coordinates are referred to as ***normal coordinates***. While the normal coordinates for some vibrations may be described in terms of stretching of one bond or bending of one angle, more commonly they will be made up of mixtures of several bond stretches, angle bends and other motions.

The third step involves removing the six coordinates corresponding to the three translations and three rotations, leaving 3N-6 vibrational coordinates.

The intensity of a line in the infrared spectrum is proportional to the change in the dipole moment along the vibrational coordinate. It follows that where there is no change in dipole moment, for example, in a homonuclear diatomic molecule, the infrared intensity is zero.

The two major components of the earth's atmosphere, N_2 and O_2, are homonuclear diatomics and do not absorb in the infrared, that is, the intensity is zero. However, two of the four vibrational motions of CO_2, the third most common but very minor molecular component in the

atmosphere, have non-zero infrared intensities. As a result, carbon dioxide absorbs radiation reflected from the earth's surface thereby trapping heat and leading to an increase in temperature (the so-called ***greenhouse effect***).

Lack of a line in the infrared spectrum does not mean that the molecule does not vibrate or that the vibrational energy for this line does not contribute to the zero-point energy. Rather, it means that absorption of radiation does not occur leading to a change in vibrational energy state. It should also be noted that a particular line that is infrared inactive might be visible in the Raman spectrum (an alternative form of vibrational spectroscopy based on reflectance rather than absorption). Here the intensity is related to the change in the polarizability rather than the change in dipole moment.

The application of quantum chemical models to infrared spectroscopy requires calculation of the second energy derivatives and first dipole moment derivatives with regard to changes in geometrical coordinate. The former completely dominates and scales as the fifth power of the size (number of basis functions). Infrared spectra may be calculated using semi-empirical molecular orbital models, for example, the PM3 models available in ***Spartan***, Hartree-Fock molecular orbital models, density functional models and MP2 models. Of the theoretical models available in ***Spartan***, semi-empirical models provide a poor account, Hartree-Fock models provide a reasonable account but density functional and MP2 models with polarization or larger basis sets perform best. Density functional models are the obvious choice for infrared spectra calculations, offering better results than Hartree-Fock models at comparable cost, and comparable results at much lower cost than MP2 models.

For two reasons, we recommend EDF2/6-31G* over the ωB97X-D/6-31G* model for infrared spectra calculations. First, EDF2/6-31G* was specifically formulated to reproduce measured infrared frequencies. Second, it is significantly (factor of two) less costly than ωB97X-D for frequency calculation and is easily applicable to the calculation of infrared spectra of organic molecules of moderate size (up to 400-500 amu). There are two major deficiencies with infrared

spectra obtained directly from the EDF2/6-31G* model. The first is that calculated frequencies are almost always too large, typically by 3-5%. This can be directly traced to the harmonic approximation and to a potential energy curve that is too steep.

> Other density functional models and the MP2 model show similar behavior. Vibrational frequencies obtained from Hartree-Fock models show an even larger systematic error in the same direction (frequencies too large), typically by 12-14%. Here two factors contribute. The first is the insistence on a quadratic potential, the same problem associated with density functional and MP2 models. The second is due to the fact that bond dissociation is improperly described by Hartree-Fock models, as evidenced by the fact that Hartree-Fock bond lengths are uniformly shorter than experimental distances. This suggests that the potential energy surface will be too steep and the frequency will be too large.

The second and more conspicuous deficiency is due to the fact that the lines in an infrared spectrum measured at finite temperature are broadened due primarily to rotational structure, whereas the lines in a calculated spectrum correspond to an isolated molecule at 0K and are sharp. There may be other differences, such as the absence of overtones, that is, vibrational transitions originating from excited vibrational states and, more importantly, lack of solvent. Although these are more difficult to quantify.

It is straightforward to correct the calculated spectrum to account for both deficiencies. First the spectrum may be uniformly scaled (multiplied by a parameter in the range of 0.95-0.97 for density functional models). Second, the calculated frequencies and intensities may be fit to a Lorentzian function with peak width and half peak height being treated as a second parameter.

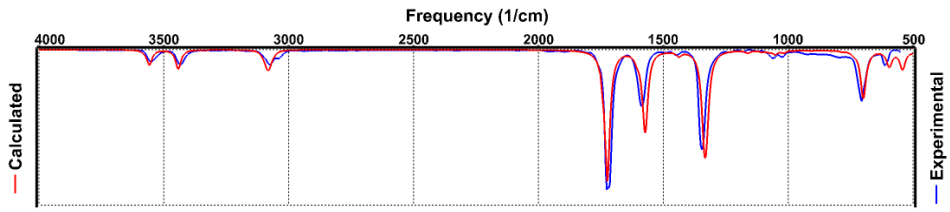
Quality of Calculated Infrared Spectra

An infrared spectrometer records frequencies in the range 500-4500 cm^{-1}. Frequencies below this range (which may require special instrumentation to measure) typically correspond to torsional motions and may depend strongly on conformation. It should be noted that the spectral region beyond ~2800 cm^{-1} is dominated by

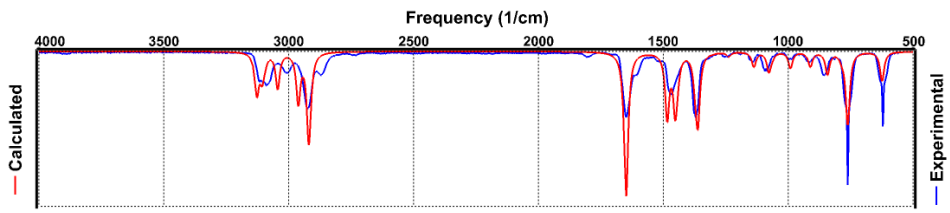
CH stretching vibrations and may be too crowded to be of value.

Calculated infrared spectra from the EDF2/6-31G* model that have been scaled to account for the systematic error in frequency and broadened to account for finite temperature are visually quite similar to the corresponding experimental spectra (taken from the NIST database). The four examples that follow, benzamide, (dimethylmethylidene) cyclopentadiene, 1,2-epoxy-*cis*-4-vinylcyclohexane and camphor are typical of the ~1000 comparisons that have been made.

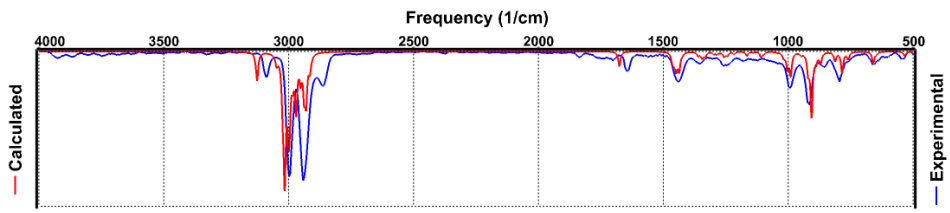
benzamide



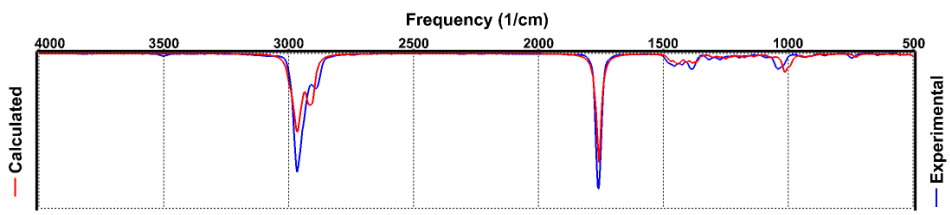
(dimethylmethylidene)cyclopentadiene



1,2-epoxy-cis-4-vinylcyclohexane



camphor



Even though scale and line-broadening parameters have been individually adjusted for these four examples, the values of the parameters are quite similar. Default parameters could have been substituted with little change.

Database of Infrared Spectra

More than 300,000 infrared spectra from the EDF2/6-31G* model are available in the Spartan Spectra and Properties Database (SSPD). ωB97X-D entries in SSPD presently do not include infrared spectra.

Raman Spectra

Spartan is also able to calculate Raman spectra. The frequencies are identical to infrared frequencies but the intensities depend on the charge in polarizability rather than the change in dipole moment.