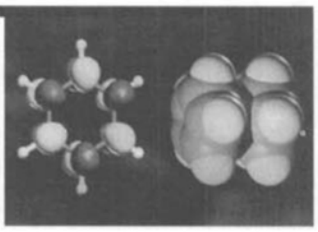
CHIMIA 49 (1995) Nr. 5 (Mai)

COMPUTATIONAL CHEMISTRY COLUMN

Column Editors:
Prof. Dr. J. Weber, University of Geneva
Prof. Dr. H. Huber, University of Basel
Dr. H. P. Weber, Sandoz AG, Basel



Chimia 49 (1995) 153–159
© Neue Schweizerische Chemische Gesellschaft
ISSN 0009–4293

Vibrating Molecules on Your Computer Screen

Daniel Huber*

A program that allows visualization and animation of molecular normal vibrations: Available for *MacIntosh*, PowerMac, and PC computers as public domain software, see [1–3].

IR spectroscopy is one of the major tools of organic analysis. Nevertheless, its base, molecular vibration, is often shrouded in mystery. We will discuss a tool that gives you some hands-on experience and lets you experiment with molecular vibrations without the burden of intricate mathematics.

Have you ever had difficulties visualizing a particular vibrational normal mode of a molecule? Have you ever had to explain the equivalence of degenerate normal vibrations? Or would you just like to play around with the vibrations of a molecule? See how it looks if you superimpose several normal modes? Investigate what group vibrations are, without which vibrational spectroscopy would hardly be such a valuable tool?

Well, we cannot solve all of your problems, but we may offer some help. We will first try to explain how such information may be calculated. Subsequently, with the help of a computer program called 'Molvib' we will discuss some examples. We hope that we will whet your appetite for more and encourage you to do some experiments of your own.

Motivation for a Classical Approach

To calculate the internal motion of a molecule is a formidable task. Fortunately, many of the observed phenomena, which are due to electron motion, nuclei motion and rotation of the whole molecule, can be separated on the basis of their energies into distinct groups. Remembering that electrons are involved in phenomena like emitting or absorbing UV or visible light, vibrations of molecules are associated with IR radiation and rotations with microwave radiation, we realize that the energies involved differ by orders of magnitudes. Classically, the higher the energies, the faster the corresponding motion. If we have two superimposed motions with widely differing velocities, the faster one has time to equilibrate. We can calculate the fast motion to a good approximation assuming that the slow motion is frozen. This is the basis of the so-called adiabatic approximation, which allows separation, that means 'to calculate separately', of the different motions. Unfortunately, we have to perform the calculation of the fast motion for every fixed position of the slow motion, but this is a small price to pay for the reduction of complexity achieved.

In many applications, this trick of separation works well, but there are cases where this approximation breaks down. We then speak of 'coupling', *e.g.* vibronic (vibrational-electronic) coupling in floppy molecules like NH_3 (the 'umbrella' vibration splits electronic energies), or vibration-rotation coupling in linear molecules like H_2, where centrifugal forces change the vibrations. Expressed in 'classical' language, the two 'separated' motions influence each other. In terms of quantum mechanics, the combined eigenstate can no longer be expressed as a product of two independent eigenstates.

Having dealt with the separation we now assume that the motion of the electrons is already known. There are many different quantum chemical methods, differing wildly in accuracy and computational effort, to obtain this information, *e.g.* HF-SCF,MCSCF,CI.... These calculations give the equilibrium geometry as well as the forces on the nuclei if we deform the molecule away from the equilibrium position. For the calculation of the vibration, we neglect the rotation altogether.

Normal mode analysis is a classical approach. Knowing that the atomic world is governed by quantum mechanics, it may well be asked if it is reasonable to adopt a classical model. Electrons in a molecule hardly exhibit any classical features (*e.g.* well defined position and velocity) and, if they do, only in very particular circumstances (*e.g.* in extremely high excited *Rydberg* states, a certain localization of the electron has been observed). Why should it be different for nuclei? The answer is twofold. First, the mass m of a nucleus is four orders of magnitude larger than that of an electron and second, in most molecules, the electrons push the nuclei rather strongly towards the equilibrium position. To determine the quantum mechanical ground state one searches for a state with as low an energy as possible. To minimize the energy in the ground state, a compromise between small potential energy and small kinetic energy must be reached. To minimize the potential energy we must try to squeeze the wave function near the potential minimum. However, because of the *Heisenberg* uncertainty principle, localizing the wave functions leads to high momentum p. As the kinetic energy is equal to: $p^2/(2\ m)$, the contribution of the momentum to the energy depends on the mass of the particle. We may therefore localize a nucleus with less energy than an electron. Nuclei in the ground and low energy states are therefore

---

**Correspondence*: Dr. D. Huber
Metrohm Ltd.
CH-9100 Herisau

much more localized than lighter particles. That is why the nuclei in a molecule are more amenable to classical treatment than electrons.

To calculate any possible motion of all the nuclei belonging to a molecule using classical mechanics and the approximations to be discussed later on, is still a formidable task (by nucleus we mean the nucleus and the nonbinding core electrons). To solve it, we try the time honored principle of divide and conquer. We do not ask, 'what is the most general motion', but 'what are the most simple motions'. Having found some simple solutions we can build up more complicated motions by running several simple ones at the same time, we say we 'superpose' them (for the math enthusiast: this is allowed because all the equations are linear). If you think about this, a question will come to your mind: 'Can any possible motion be obtained this way?'. That this is indeed the case was already shown 200 years ago by the French mathematician *Fourier* (provided the simple solutions fulfill a number of requirements). In our case, the simple solutions are called 'normal modes' or normal vibrations. The more general term '*Eigen*' mode or vibration is also used. It turns out (see separate box) that normal vibrations associated with low energies can be described to a good approximation by a synchronous motion of all the atoms that is sinusoidal as a function of time. Every single atom moves as if it were a point mass connected to a spring, all atoms move with the same frequency and all pass the equilibrium position at the same time.

One question still remains: 'What can be inferred from the classical treatment about the quantum properties of the molecule?' The quantum mechanical energies of a harmonic oscillator are given by $(n+{}^1/_2)\ h\nu$, where ν is the classical frequency. We may therefore obtain the energy levels from the classical calculation. On the other hand, we do not get any information about the wave function and the probability to find the nuclei somewhere (probability density). Note that the classical amplitude has nothing to do with the amplitude of the wave function. The former is related to energy, the latter to position probability. We also note that only for very high quantum states does the smoothed out probability density begins to approach its classical counterpart.

Approximations

Vibrational normal mode analysis is based on two approximations that have proved useful in many applications.

The first one consists of replacing the quantum treatment by a classical model of point masses. The second one in restricting our discussion to 'small' vibrations. This leads to a model of point masses moving under the effect of spring forces, *i.e.*, the classical model we already talked about.

The justification for the springs follows from the assumption of 'small' vibrations and the existence of an equilibrium position. Small vibrations means that the nuclei only deviate slightly from their equilibrium position. Assuming an equilibrium geometry is equivalent to stating that the potential energy surface has a minimum. In the vicinity of a minimum, the potential can always be approximated by a quadratic function, a parabola (*e.g.* $f(x) = c_0 + c_1x + c_2x^2$). As the total force acting on each nucleus is zero in the equilibrium position ($c_0 = 0$, $c_1 = 0$), we get forces F (the negative derivatives of the potential) that are proportional to the deviation x from the equilibrium. Or expressed in a formula:

$$F = -k\,x$$

This is the formula for a spring (*Hooke*'s law); k, termed the force constant, determines how stiff the spring is. The minus sign indicates that the force opposes the deviation, it pushes the nuclei back to the equilibrium position.

The assumption of 'small' vibrations also allows replacement of all bent movements like bending or torsion by the tangent in the equilibrium position. Therefore, the nuclei will move along straight lines.

By the same reasoning we neglect all changes of distance and force that are not proportional to x (because, provided x is small enough, x^2 or any higher power of x is much smaller than x). Considering, *e.g.*, a bond between atom A and B and moving B in a direction perpendicular to the A–B axis, we may neglect the change in distance and force due to this move because they are proportional to x^2.

Applications

You may learn to drive a car without knowing how the engine works. However, normal mode analysis is not such a reliable tool as a car. If you are simply using it without any knowledge about its working, you may draw wrong conclusions. You should at least be familiar with the approximations involved.

On the other hand, a car should be easy to operate, so that the driver can concentrate on the traffic. To make normal mode analysis easy to understand we developed a computer program that allows you to concentrate on the chemical problems and frees your mind from the intricate calculations involved. The program is available for the *MacIntosh* and PC computer. Version 2 for the *MacIntosh* can be obtained from the American Chemical Society [1] and version 3 for the *MacIntosh* directly from the author [2]. There is also an adaptation for the PC available that can be obtained from [3]. This program makes it possible to examine normal vibrations graphically, with and without animation, as well as numerically. We hope that such a tool may help to obtain a deeper understanding of normal vibrations. As an example, *Fig. 1* shows a screen shot of an animation of NH_3. Different representa-

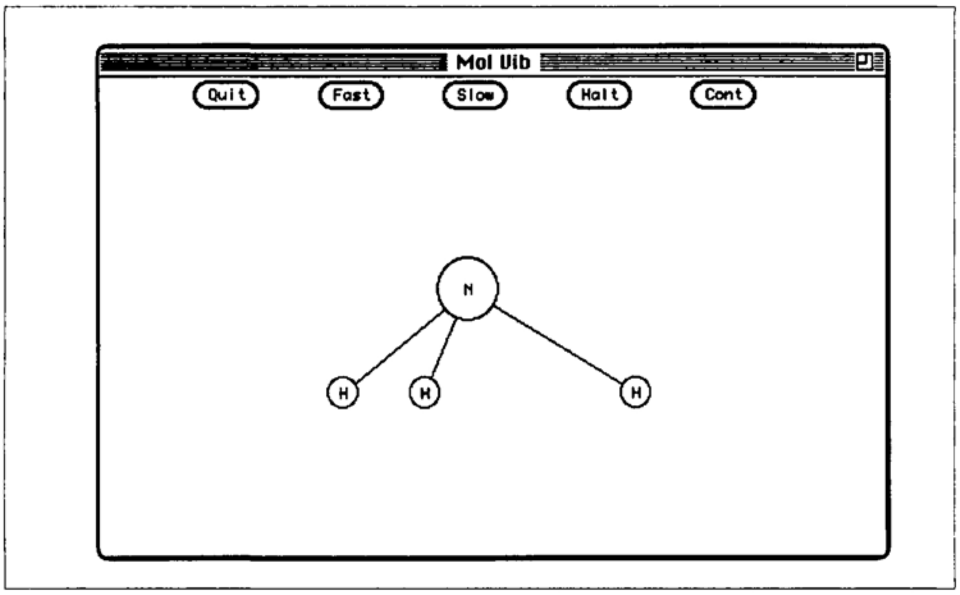


Fig. 1. *Animation window with* NH_3

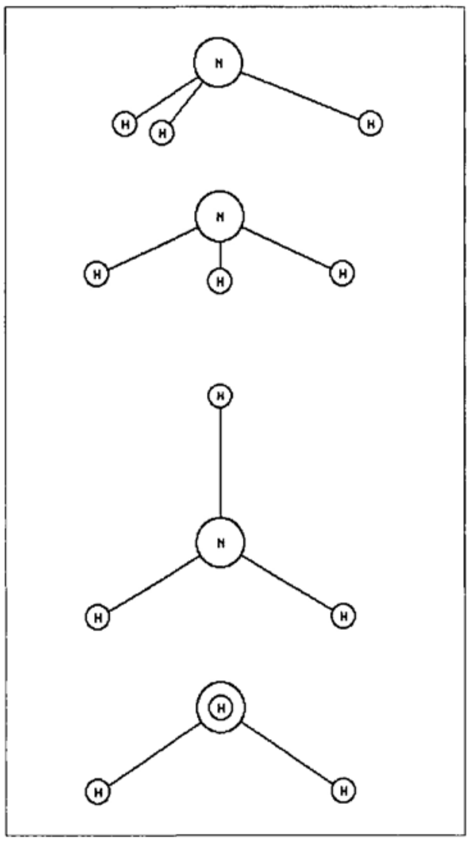


Fig. 2. *Equilibrium geometry of NH_3 seen from different view points*

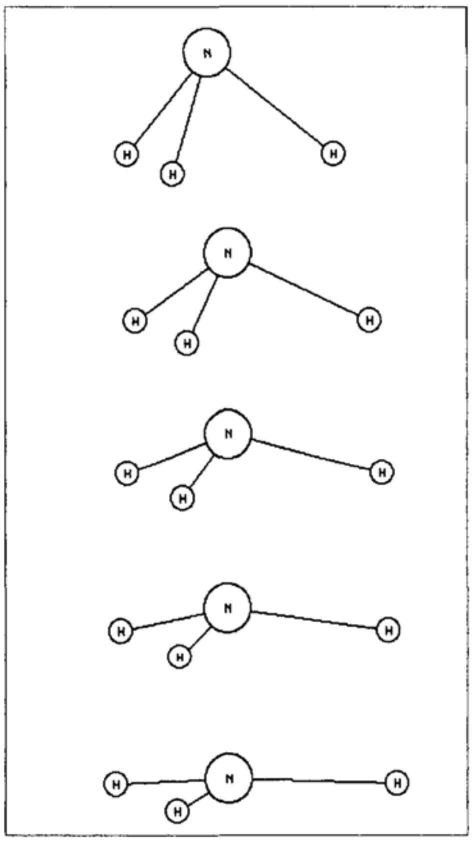


Fig. 3. *Five snap shots of the NH_3 'umbrella' mode*

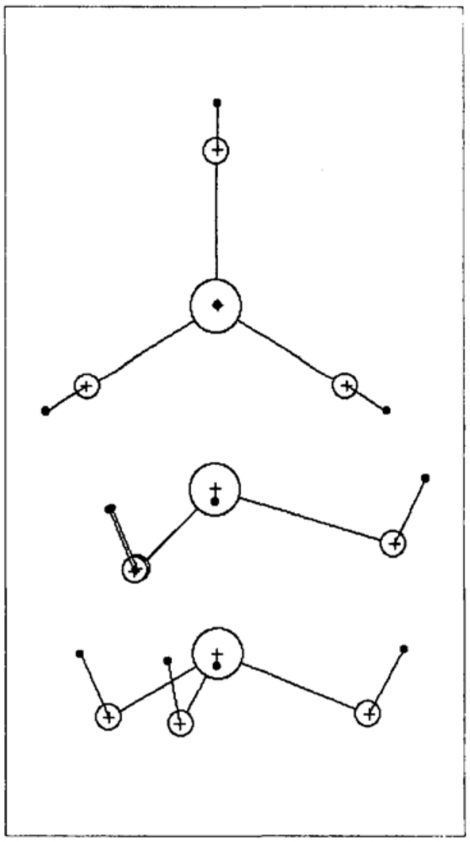


Fig. 4. *Static representation of the NH_3 'umbrella' mode*

tions of a molecule may be choosen depending on the feature we want to stress. *Fig. 2* shows different representations of NH_3. *Fig. 3* depicts five snapshots of the animated umbrella vibration of NH_3. *Fig. 4* provides a static picture of the same vibration in three different representations. The line drawn from the center of an atom to a small circle indicates the relative size of the amplitude. *Fig. 5* demonstrates how you can use (or misuse) perspective.

To untertain you further in this field, we describe below some simple applications.

Simple Observations

First we consider some simple molecules such as H_2O, CH_4, *etc.* Try to verify that, due to the simplifications made, all the atoms move on straight lines. Convince yourself that this is also true for 'bend' vibrations. Try to see how all the atoms pass the equilibrium position at the same time with maximum velocity and how they slow down near the turning points, exactly like a point mass connected to a spring. Take into account the masses and verify that the center of mass stays at the same place (note however, that the graphical representation is only accurate to plus or minus one pixel; you may therefore see spurious motion of this size). Note also, but this is harder to see, that there is no angular momentum in a (non degenerate) normal vibration. Also, try to verify that lighter atoms often have larger amplitudes.

Isotope Effect (Mass Effect)

From elementary courses you may remember that the frequency of a point mass m connected to a spring with force constant k is proportional to $\sqrt{k/m}$, that is, inversely proportional to the square root of m. Further, because in a normal mode motion several point masses are moving synchronously, you may try to replace the different masses by one single effective mass m_{eff}. This is like pulling the string of a jumping jack: the arms move, the hands move, but you only feel one single inertia. But how do we calculate an effective mass? The effect of the mass consists in opposing acceleration, that is inertia. As all the atoms move synchronously, the acceleration is the larger, the larger the amplitude. To take this into account, we have to weight the mass m of the atoms with their amplitude a to get an average mass and to multiply by the number n of nuclei:

$$m_{eff} = n\frac{\sum_i a_i m_i}{\sum_i a_i}$$

where i runs over all atoms. Consider now a molecule and a given normal vibration with effective mass m_1. How will the fre-

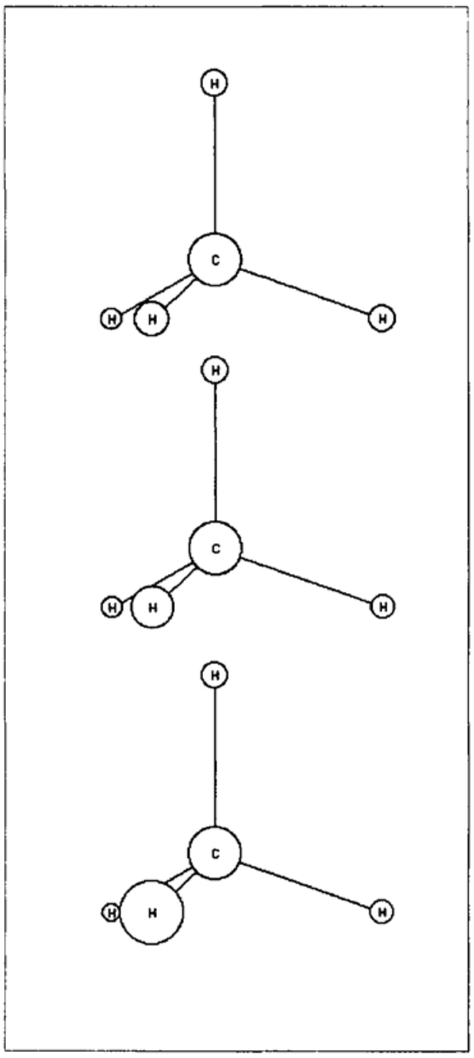


Fig. 5. *Three different settings for perspective*

quency change if we replace an atom by another isotope (that is a chemically equivalent atom with the same number of protons but a different number of neutrons). As the new atom is chemically equivalent, the force constants do not change. If we know (or can guess) the amplitudes, we can make a guess at the frequency change. If we do not know the new amplitudes, needed to obtain the effetive mass, we may approximate them by the old ones. Assuming we estimated (or calculated) the old and new effective masses m_1 and m_2, the frequency changes proportionally to the inverse of the square root of the effective mass. We may therefore make an estimation (or calculate the accurate value if we know all the amplitudes accurately) of the new frequency ω_2 from the old one ω_1 using the expression:

$$\omega_2 = \omega_1 \sqrt{\frac{m_1}{m_2}}$$

Let us look at the example of H_2: The amplitude must be the same for both H-atoms (center of mass system) and we obtain a measure for the effective mass of 2 amu (atomic mass unit). If we now change one of the H-atoms to deuterium (2 amu) and use the old amplitudes, we obtain an effective mass of 3 amu. Our estimation gives a ratio of $\omega_2/\omega_1 = 0.816$.

Let us now test our prediction by a normal mode calculation:

The equilibrium distance is 0.74 Å, the force constant 1.625 10^5 dyn/cm and the mass of H: 1 amu. The program gives a frequency of 2349 cm^{-1}. Changing one of the H to deuterium we obtain a frequency of 2035 cm^{-1}. The ratio is $\omega_2/\omega_1 = 0.866$. Well, the accuracy of our prediction is not overwhelming. Can you imagine where the error comes from? Sure, we did not account for the change in amplitudes. Often it is possible to obtain some useful information without too much calculation. But do not expect too much accuracy from a coarse guess.

Group Vibrations

It may be a long time since you played with swings. However, you may have observed that two swings of approximately the same length, mounted on the same support do exert an influence on each other. If you excite one swing the other will start to move on its own, a phenomenon known as resonance. Not so if the two swings differ appreciably in length. A similar thing happens in a molecule. If some fragment of a molecule on its own has an *Eigen* frequency that is largely different from all the other frequencies in the rest of the molecule, then this *Eigen* mode survives even in the whole molecule. This phenomena is heavily exploited in IR spectroscopy where specific groups are identified by their characteristic frequencies that survive in the composite molecule. As a simple example we take CH_4 and replace three of the hydrogens by the heavier tritium to get CT_3H:

- mass C: 12.012 amu, H: 1.008 amu, T: 3.015 amu

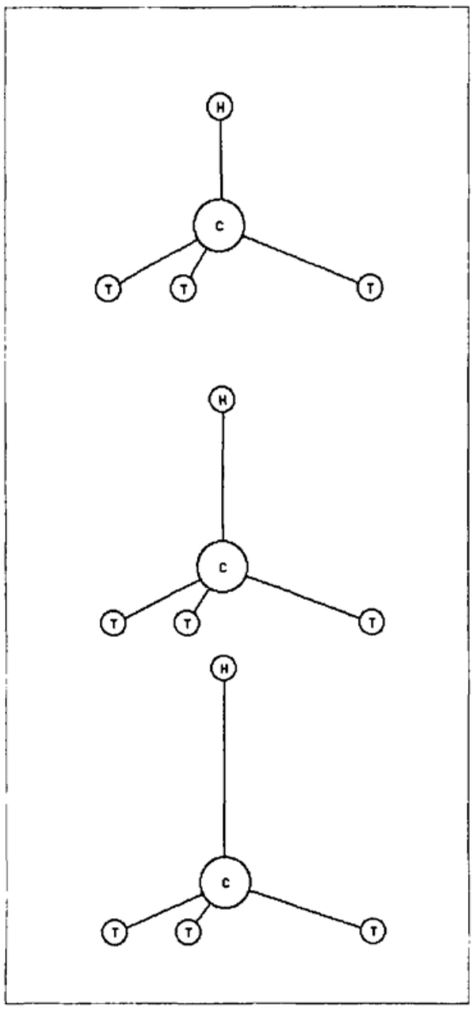


Fig. 6. *Decoupled CH stretch vibration in CT_3H.* Mainly the CH stretch vibration is active, the rest of the molecule does scarcely move. The pure CH stretch vibration has a much higher frequency than all the other bonds and therefore couples poorly to the rest of the molecule.

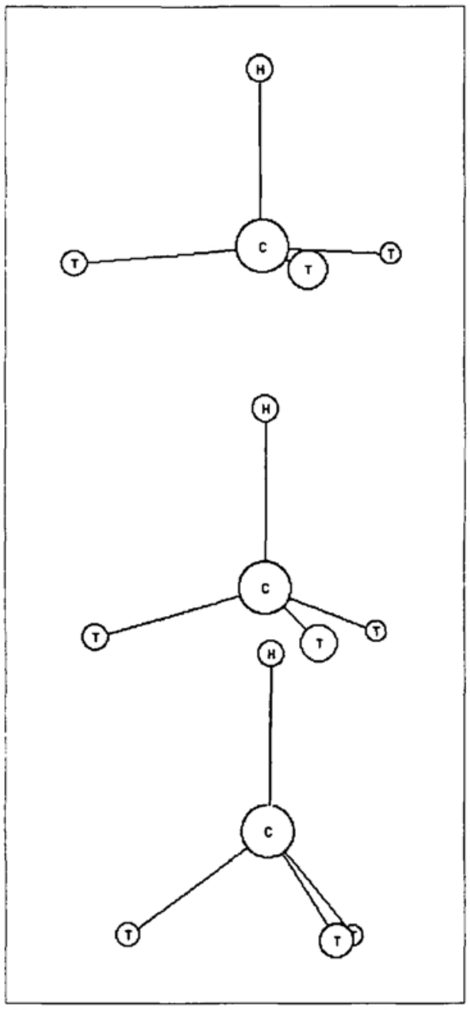


Fig. 7. *Decoupled CH stretch vibration in CT_3H.* Here the CH stretch is scarcely active whereas the rest of the molecule moves strongly.

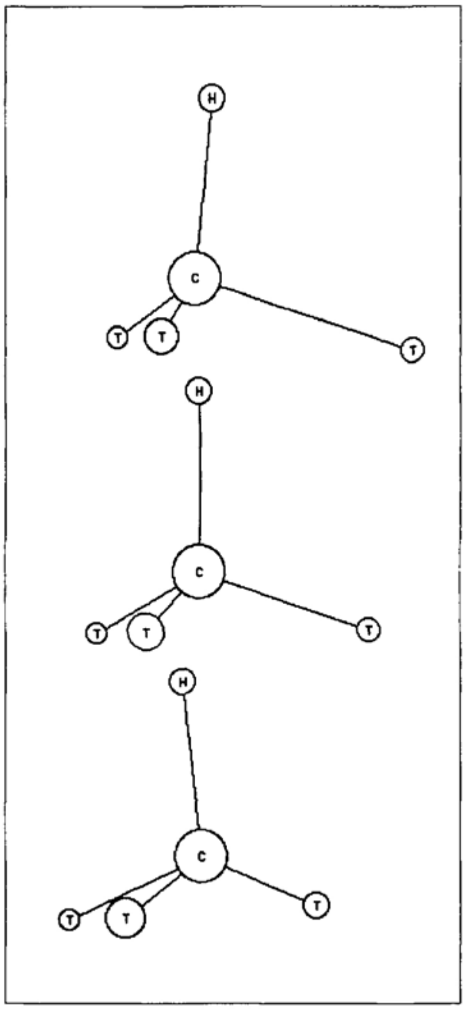


Fig. 8. *The bending frequency of (T_3C)H is much lower than the CH stretch frequency and couples well to the rest of the molecule*

- distance C–T and C–H: 1.0929 Å
- force constant stretch: 5.04 10^5 dyn/cm, bend: 0.703 10^5 dyn/cm
- all the other force constants are assumed to be zero

All the frequencies observed in the CT_3 fragment are much lower than the CH stretch one. Therefore, we may expect to observe a normal mode that consists mainly of a CH stretch motion. This is the highest frequency mode (3045 cm^{-1}) and it is depicted in *Fig. 6*. In all the other modes, the CH stretch is only very little excited, either the H simply 'rides' on the C (frequencies: 1758, 1098, 446 cm^{-1}) or the CH bend vibration is active (frequencies: 2011, 1995, 1510, 1508, 1076 cm^{-1}) in which case the distance C–H does not change neither. *Fig. 7* gives a mode, where the H is 'riding'. This is in contrast to CH_4, where no isolated mode CH stretch exists, because the different CH stretch will couple to each other. Convince yourself by running all the modes of CH_4. On the other hand, the bending motion of the CH bond in CT_3H has a much lower frequency and is therefore well able to couple to the rest of the molecule. An example is given in *Fig. 8*.

Degenerate Normal Vibrations

If two normal vibrations have the same frequency, that is they are degenerate, they will in general exhibit some symmetry. Actually, the symmetry is the origin of degeneracy (there are some rare exceptions, called accidental degeneracy). If there is symmetry, there are several equivalent vibrations. However, a normal vibration calculation does not usually yield all of the equivalent vibrations. One may well ask, why the calculation does distinguish several of them.

We mentioned above that if we superpose (running at the same time) two normal vibrations, we obtain a possible motion of the molecule. If the frequencies of the vibrations are different, the result is no more an normal motion (if the frequencies have an irrational ratio the atoms do not even come back to their original position). On the other hand, if we superpose two normal vibrations with the same frequency, we obtain a new normal vibration. By changing the relative phase and amplitude (the starting configuration) of the two motions we may create an infinite number of them. They are all equivalent to each other. We may pick some of them to create the others by superposition. The calculation we did was guided by our choice of the *x*, *y*, *z* coordinate system. If we would have chosen the axis along different directions in the molecule, we would have got some different, but equivalent vibrations. Note that you cannot try that with 'MolVib', because the program chooses the axes along the principal axes of inertia by default.

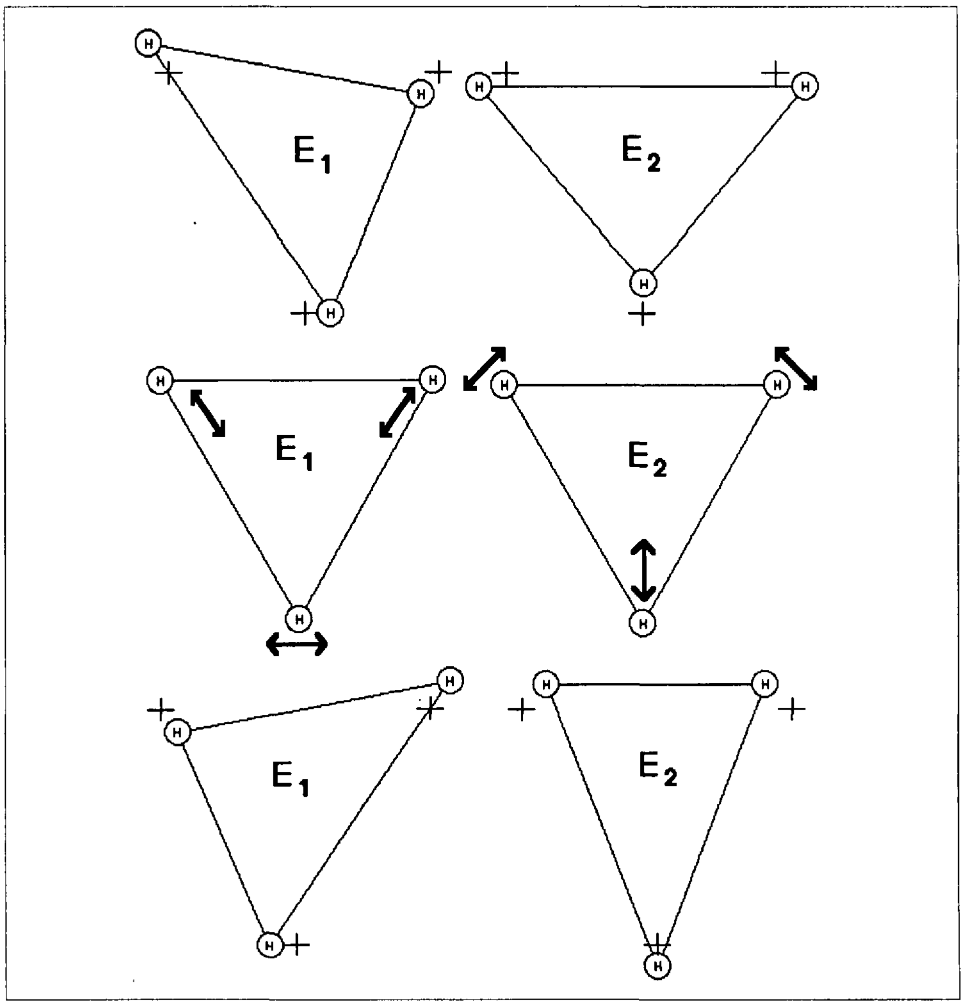


Fig. 9. *Two degenerate normal vibrations, E_1 and E_2, of H_3*

Let us look at a fake molecule H_3 whose equilibrium geometry is choosen as an equal sided triangle:

- mass H: 1 amu
- distance H–H: 1 Å
- force constant stretch: 7.7 10^5 dyn/cm, all other force constants are zero.

Due to the symmetrical equilibrium configuration we obtain from our program two degenerate normal vibrations, technically called E_1 and E_2 (due to their symmetry). They are depicted in *Fig. 9*. To demonstrate that we can generate a different equivalent normal vibration, we will superpose these two vibrations. To run these two normal vibrations at the same time, we choose for the amplitude of E_1 a value of 0.5 arbitrary units (the amplitude of the second vibration is chosen by the program: $a_2 = \sqrt{1-a_1^2}$) and a phase shift of zero. We then obtain the vibration depicted in *Fig. 10*. This is the vibration E_1 from *Fig. 9*, but rotated by 120 degrees counter clockwise. Therefore, we have obtained an equivalent, but different nor-

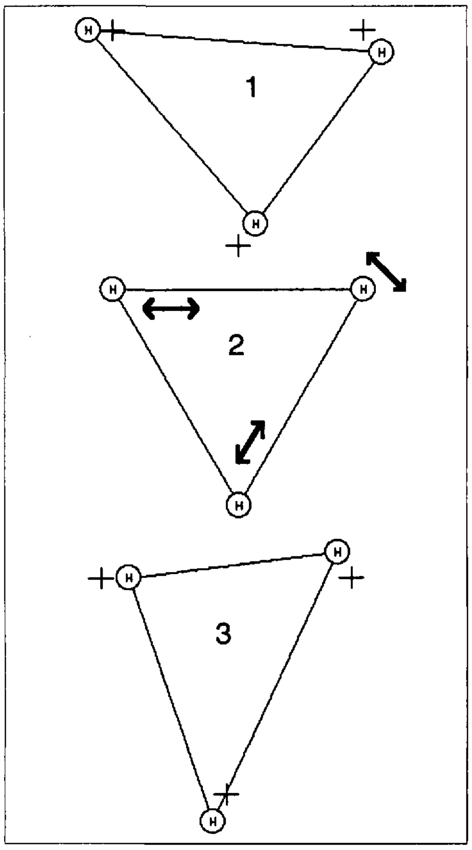


Fig. 10. *Same vibration as E_1 from* Fig. 9 *but rotated by 120 °.* This vibration is obtained by superposition of E_1 and E_2 from *Fig. 9*.

mal vibration by combining the two vibrations calculated by the program. By changing the phase shift and amplitudes we can generate all of the other equivalent vibrations.

Vibrational Normal Mode Analysis

We will solve this problem in *Cartesian* coordinates using the good old *Newton* formula: Force equals mass times acceleration.

As preparatory work, we first look at a simple point mass with mass m connected to a spring with force constant k. By x we denote the deviation of m from the equilibrium position, that is the elongation of the spring. *Newton*'s formula leads to:

$$x'' = -(k/m)\,x$$

where x" denotes the second derivative relative to time, that is the acceleration. This means, that the acceleration is proportional to the negative elongation. A possible solution to this equation is given by the sine function:

$$x = x_0 \sin(\omega t)$$

where ω is the angular frequency and x_0 the amplitude. By inserting the solution back into the equation, we find:

$$\omega = \sqrt{k/m}$$

With this we are ready to tackle normal vibrations.

In the equilibrium configuration, the total force on an atom is zero; we only obtain forces different from zero if we change distances between atoms. For instance, if we move atom i by an amount of x_i along the x direction, the force on atom j along the y direction f_{yj} will be proportional to x_i:

$$f_{yj} = -k_{yj;xi}\ xi$$

the proportionality constant $k_{yj,xi}$ is called 'force constant'. Collecting all the forces into a column vector $\boldsymbol{F} = (f_{x1}, f_{y1}, f_{z1}, f_{x2}, \ldots)$ and similarly all the displacements into a vector $\boldsymbol{X} = (x_1, y_1, z_1, x_2 \ldots)$ and finally all the force constants into a matrix $\boldsymbol{K}$ with first raw $(k_{x1;x1}, k_{x1;y1}, k_{x1;z1}, k_{x1;x2}, \ldots)$, second row $(k_{y1;x1}, k_{y1;y1}, \ldots)$ *etc.* allows us to write

$$\boldsymbol{F} = -\boldsymbol{K}\,\boldsymbol{X}$$

which looks exactly like the formula for a spring. If we also collect the masses into a matrix $\boldsymbol{M}$ that contains 0 in all positions except on the diagonal, where we have $(m_1, m_1, m_1, m_2, m_2, m_2, m_3, \ldots)$, we may write *Newton*'s formulae: for m_l along direction x: $f_{x1} = m_1\, x_1''$, for m_1 along direction y: $fy_1 = m_1\, y_1''$ *etc.*, very compact as:

$$\boldsymbol{F} = \boldsymbol{M}\,\boldsymbol{X}''$$

or if we replace **F** by $-\boldsymbol{K}\,\boldsymbol{X}$:

$$-\boldsymbol{K}\,\boldsymbol{X} = \boldsymbol{M}\,\boldsymbol{X}''$$

We may rewrite that to:

$$\boldsymbol{X}'' = -(\boldsymbol{M}^{-1}\boldsymbol{K})\,\boldsymbol{X}$$

and read it as: The second derivative of $\boldsymbol{X}$ is proportional to $-\boldsymbol{X}$. Here $\boldsymbol{M}^{-1}$ is similar to $\boldsymbol{M}$ but m replaced by $1/m$. This looks like the 'point mass and spring' example above, does it? No? You object that we do not have numbers like above but vectors and a matrix. Now you have a chance to get a glimpse of the beauty of mathematics. If you hate mathematics, please skip the rest of this paragraph. For the proof of the sine differential equation the only assumption made is that we have an 'object' y that changes with a continuous parameter t, in our example the time. That two such objects y (*e.g.* y for two different t) can be 'subtracted' to give an object of the same type y. And that a second type of object p exists (*e.g.* the proportionality factor) that can 'multiply' y to give an object of type y. And finally that t has an inverse. If y, p, and t are numbers as above or if y is a vector and p a matrix or anything else does not matter at all, the proof is always true. Mathematics tries to focus on the essential. And a lot of problems from many different fields, stripped from unimportant details, are essentially identical! Therefore, by the same reasoning as above, a possible solution for $\boldsymbol{X}$ consists in a motion that varies sinusoidally with time:

$$\boldsymbol{X} = \boldsymbol{X}_0 \sin(\omega t)$$

where $\boldsymbol{X}_0$ is a now a vector of amplitudes. Therefore, all the atoms move in unison. They all pass through the equilibrium position at the same time, they all move with the same frequency. Only the amplitudes and directions are different.

Our treatment has one shortcoming. By using plain *Cartesian* coordinates we included rotation and translation as well and we will get six normal vibrations with zero frequency corresponding to these motions (no restoring force). There is nothing wrong in principle, but we have more work to do. Therefore, usually internal coordinates like stretching and bending are used. This choice makes the calculation more complicated to understand, but does add nothing to the principle. We therefore will abstain from discussing it here.

Vibrational Angular Momentum

Separate treatment of vibration and rotation quite often gives an excellent approximation. However, in general it is not possible to completely separate rotation and vibration. Angular momentum, that is 'rotation', can be created by the motion we consider as vibration. Only the total angular momentum of the nuclei motion (neglecting coupling to electrons) is constant. It is given by the addition of the rotational and vibrational angular momenta. Or in simpler terms, the rotational energies depend slightly on the vibrational state and *vice versa.*

We mentioned above that nondegenerate normal vibrations of a molecule can never have an average angular momentum. Classically, this can be understood by noting that all the atoms make a concerted sinusoidal motion along straight lines. Every configuration occurs twice, once with forward and once with backward momentum. Therefore, as the angular momentum is constant (no external torque), the average angular momentum must be zero. If we have more than one normal mode with different frequencies, the phase relation changes continuously, and the average probability for left and right angular momentum is the same. Therefore, no average angular momentum can result neither. This is different for a degenerate normal vibration. Here it is possible that two independent degenerate modes have a fixed phase relation. If you ever played with *Lissajous* figures and realized that one may generate a circular motion out of two straight motions, you will easily understand that an average angular momentum can result. If you do not know what *Lissajou* figures are, imagine a circular motion and choose two perpendicular axes. Projecting the circular motion onto the axes you will get two linear motions with a relative phase shift of 90° that are sinusoidal with time. If you now reverse the process and superpose the linear motions you regenerate the circular motion. By changing the phase shift you can even generate elliptical motions. In *Fig. 9* two degenerate normal modes of the H_3 from the above examples, E_1 and E_2, are shown. If we let these two modes run at the same time, it is possible to generate an average angular momentum whose magnitude and direction depend on the phase between the two independent motions and

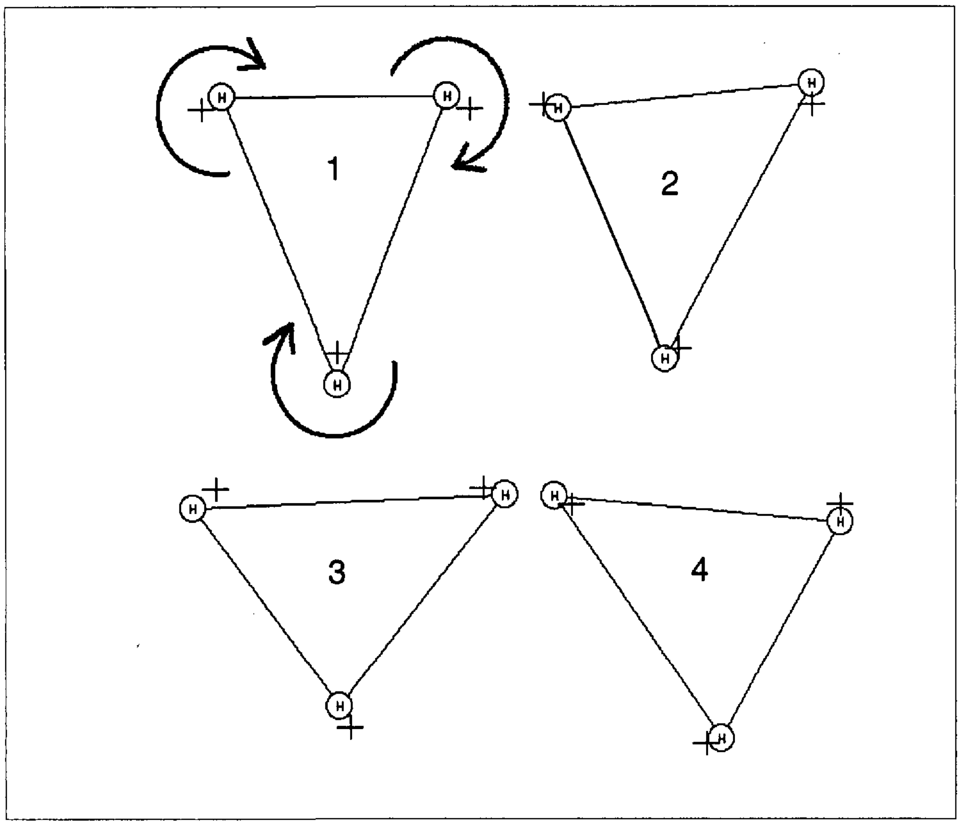


Fig. 11. *Vibration with angular momentum obtained by superposition of E_1 and E_2 from* Fig. 9

their amplitudes. In *Fig. 11* we chose for the first mode an amplitude of 0.707 arb. units (= $1/\sqrt{2}$, both vibrations have equal amplitudes) and a phase shift of 90°. Obviously, we obtain an average angular momentum. On the other hand, if we choose a phase shift of 0 or 180 ° we obtain vibrations similar to *Fig. 9* E_2, but rotated by 120 and 240 °. In both cases the average angular momentum is zero. The conclusion is, that by running several degenerate normal vibrations simultaneously we can create angular momentum (that is 'rotation') by pure vibrational motion. The value of the angular momentum generated depends on the relative amplitudes and phases.

Requirements to Run the Program

The Mac version of Molvib has been tested an the following *MacIntosh* computers: MacPlus, MacII, and the PowerMac. It needs at least 512 kB of RAM. On the MacPlus the animation is a bit slow but still usable. It has been tested with version 6.07 and 7.0 as well as 7.5 of the MacOS. The PC version runs under MS DOS version 3.1 or higher. It needs at least 256 kB of free RAM and a numeric coprocessor is recommended.

Included in 'Molvib' are several sample input files as well as documentation about the handling of the program and a TEX file about the underlying theory.

---

[1] Daniel Huber, *J. Chem. Educ.*, Software, Vol. III, Number 1, Feb. 1991.

[2] To obtain the program directly from the author, please send an addressed envelope together with a formatted floppy disc for the *MacIntosh* (low density, sorry I only have an old floppy drive) and either the stamps or the necessary amount to cover the postage to the reader.

[3] To obtain the PC version, please send a formatted PC disc to Prof. *E. Schumacher*, Kalchackerstr. 69, CH–3047 Bremgarten, Switzerland. Please include either the stamps or the necessary amount to cover the postage to the reader.

Announcement

Summer School (3rd Cycle out-of-town Seminar of Physical Chemistry) on *'Advances and Challenges in Computational Chemistry'*

Organized by Profs. *J. Weber* (Department of Physical Chemistry, University of Geneva) and *M. Grätzel* (Institute of Physical Chemistry, EPF-Lausanne). This summer school is intended for graduate students, post-docs and researchers (chemists, physicists, biochemists, crystallographers, *etc.*), working in both academia and industry, and intersted in a review of the basic tools which are now popular in computational chemistry:

- force field methods, classical molecular dynamics, free-energy perturbation methods
- semi-empirical quantum chemical methods
- *ab initio* methods at various levels of theory (SCF, *Moller Plesset*, Coupled Cluster, *etc.*)
- density functional theory, local and nonlocal exchange-correlation functionals
- first-principles (*Car-Parnnello*)

For all the methods, the main features of the theoretical aspects will be presented, followed by selected applications. The emphasis will be placed in this School on recent *advances* in the field and on some topics which are considered as *challenges* for modellers.

For further information and registration, contact:
Prof. *J. Weber*, Département de Chimie Physique, Université de Genève, 30 quai Ernest-Ansermet, CH–1211 Genève 4
(Tél. 022/702 65 30;
Fax: 022/702 65 18;
E-Mail: weber@sc2a.unige.ch).