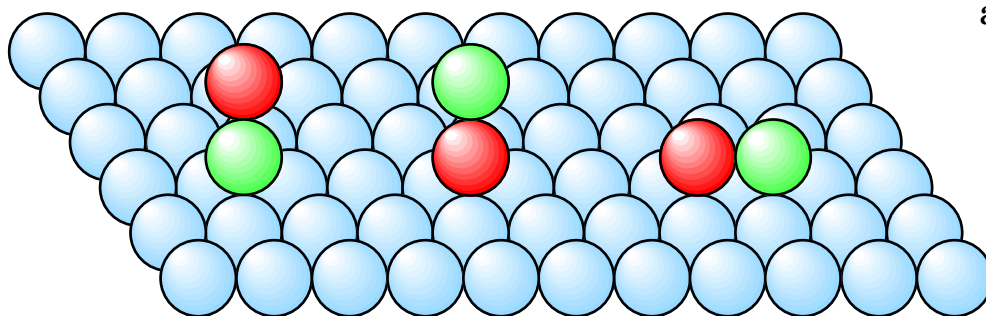


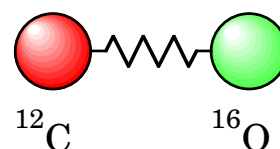
Vibrational Spectroscopy

Using simple harmonic motion

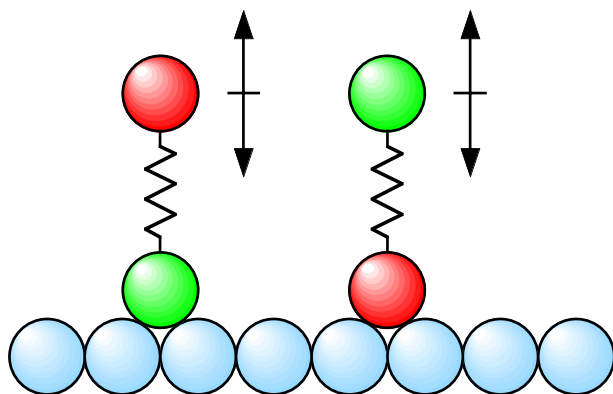
When a molecule lands on a surface, which way up does it prefer to sit? This is an important question to answer, as it is fundamental to the process of catalysis. For instance, how does a CO molecule sit on a Pt surface inside a car exhaust catalytic convertor?



Imagine the CO molecule as two different masses attached by a spring. In the gas phase, both atoms are free to move.



However, if one of the atoms is bonded to the atoms in a surface, then its movement will be greatly restricted. If the molecule sits on a surface with the O atom bonded to the surface, then the C atom will be free to oscillate up and down and so will undergo simple harmonic motion. Similarly for the case if the C atom is bonded to the surface, but because the masses of the O and C atoms are different, the resonant frequency of vibration will be different for these two geometries.



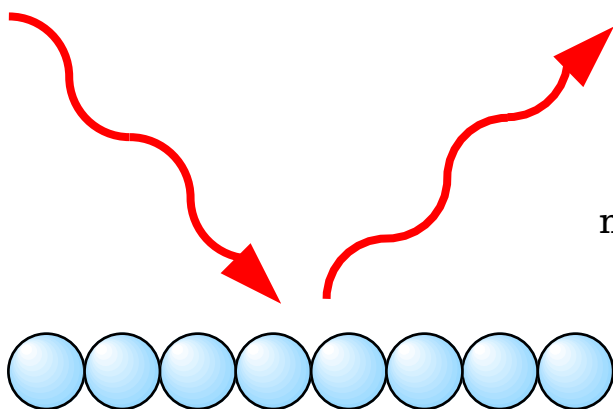
Thus, if the resonant frequency of a molecular vibration can be measured, then the orientation of the molecule can be determined.



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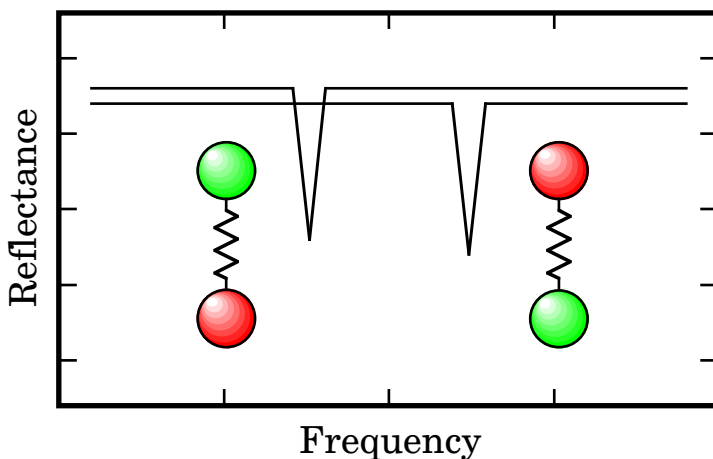
Vibrational Spectroscopy

Using simple harmonic motion



Shine light onto a surface and see how much gets reflected, scanning through a range of wavelengths (or frequencies). When the frequency matches the resonant frequency of a molecule sitting on the surface, some light will be absorbed – some of the photons will be absorbed by the molecule, increasing the amplitude of its vibration.

Plotting reflectance as a function of frequency will show a dip, the position of which is characteristic of the identity and orientation of the molecule sitting on the surface.



Typical 'spring constants' for simple molecules are $k \sim 10^4 \text{ N m}^{-1}$, and thus resonant vibrational frequencies are $\sim 10^{13} \text{ Hz}$. Light of this frequency is in the infrared region of the spectrum.

In practice, vibrational spectra show more features than indicated above. Even the simplest diatomic molecule will show reflectance dips due to the vibration of the components of the molecule and the vibration of the molecule as a whole relative to the surface (the latter usually occur at much lower frequencies than the former).

For large molecules containing many atoms, the number of modes of vibration and hence the number of resonant frequencies can lead to very complex vibrational spectra.

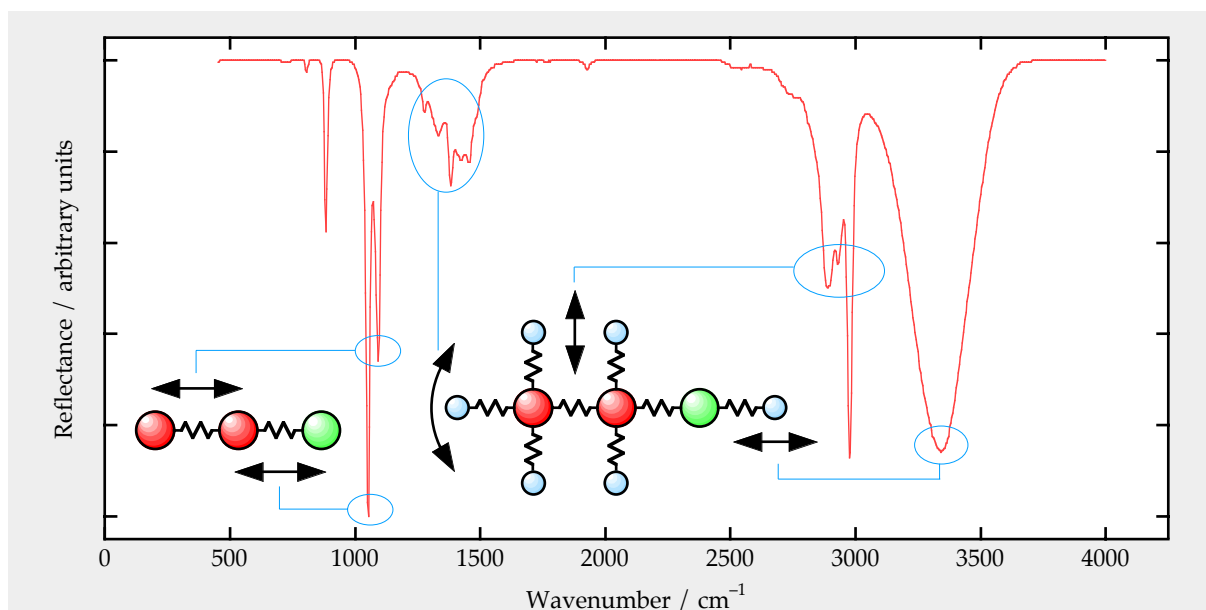
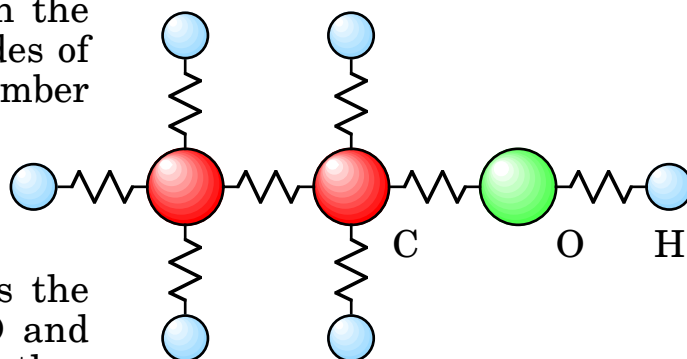


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Vibrational Spectroscopy

Using simple harmonic motion

A molecule of ethanol, shown on the right, has a large number of modes of vibration, and a corresponding number of dips are seen in the reflectance spectrum (below). The longitudinal vibration (called a *stretch*) of the H atom bonded to the O atom has the highest frequency, and the C–O and C–C stretches are seen close together at the lower end of the spectrum. The five H atoms attached to the C atoms do not vibrate at quite the same frequency because they each have a slightly different atomic environment (the molecule is not actually flat) and hence the forces acting on them are not the same.



Other dips in the spectrum correspond to various other modes of vibration, such as bending modes (*rocking, wagging* or *twisting*) in which the atoms move in directions that are not aligned with the bonds.

To study complex organic molecules, the highest possible resolution is required to distinguish modes of vibration that have similar frequencies.



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