



DYNAMENT

TAKING INVENTIVE STEPS IN INFRARED...

Application Note AN4

MINIATURE INFRARED GAS SENSORS GOLD SERIES

UK Patent App. No. 2372099A
USA Patent App. No. 09/783,711
World Patents Pending

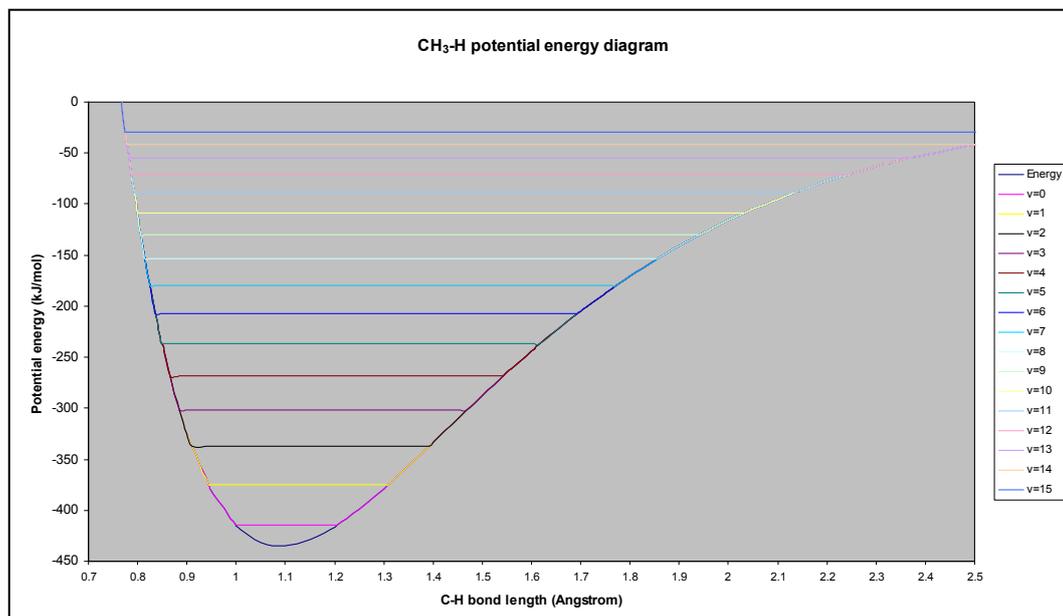
INFRARED SPECTROSCOPY



Infrared spectroscopy is the study of how molecules absorb infrared radiation and how the infrared spectra of molecules can be interpreted to give information on molecular structure. Infrared radiation interacts with the vibration of certain chemical bonds within a molecule and the wavelength of the absorbed infrared radiation is dependent on the nature of those chemical bonds.

Potential Energy

As two isolated atoms move towards each other from a great distance the overall potential energy of the pair drops. Since energy must be conserved the corresponding kinetic energy increases and the two atoms accelerate towards each other. As the atoms become extremely close the potential energy rises due to inter-atomic repulsion by the two positive nuclei and to prevent collision they then start to move apart again. Unless some energy is subsequently removed from the system, the two atoms will fly apart and fully separate. Collisions of this system with a third body will remove energy, typically in the form of heat, and result in the atoms being effectively trapped in a potential energy well and therefore bonded together. The bonded atoms retain some kinetic energy and therefore are free to move within the potential energy well but there is insufficient kinetic energy to allow the atoms to fly apart. As more collisions with third bodies occur, more energy is removed from the system until it ultimately reaches its lowest energy condition, known as the ground state. This potential energy surface is illustrated below for the carbon-hydrogen bond in methane, where a hydrogen atom is considered in relation to the associated methyl group:



Vibrational levels

The inter-nuclear separation distance will vary within limits governed by the available kinetic energy and since this movement constitutes a stretching or compression of the inter-nuclear distance it is usually described as a vibration. The above diagram shows the discrete vibrational energy levels for the carbon-hydrogen bond in methane with the ground state denoted by the $v=0$ level. Vibrational energy is quantised and the energy levels are defined by the expression $E_v = h\nu_0[(v+\frac{1}{2}) - \chi_e(v+\frac{1}{2})^2]$. The carbon-hydrogen bond therefore has a minimum vibrational energy (when $v=0$) and the frequency of this vibration is related to the strength of the chemical bond and the masses attached to that bond. Absorption spectra arise from transitions from each of these levels to the next and appear in the infrared region of the electromagnetic spectrum.

Rotational levels

The bond can not only vibrate but also rotate and to a good approximation the rotational energy can be treated as independent of vibrations, which is particularly relevant for linear molecules (including all diatomic molecules). So for each vibrational energy state there is a series of rotational energy states. Considering the rotations to be those of a rigid rotor, the rotational energy levels are also quantised according to the expression $E_r = BhcJ(J+1)$ where B , the rotational constant, is related to the moment of inertia of the bond. The spacing between rotational energy levels increases linearly with J such that absorption spectra arising from transitions to the next rotational level consist of a series of lines with equidistant frequency spacing. These rotational lines appear in the microwave region of the electromagnetic spectrum and can also provide fine structure to vibrational spectra.

Vibration-rotation spectra

In order to observe vibration-rotation spectra the molecule must have certain properties:

A vibrational spectrum can be observed when the vibration produces a *changing* dipole moment. Diatomic molecules must therefore possess a permanent dipole moment to have a vibrational spectrum but polyatomic molecules need not, a typical example being the case of the asymmetric stretch in carbon dioxide.

A rotational spectrum can be observed when the rotor has a permanent dipole moment, for example HCl displays a rotational absorption spectrum in the far infrared but N_2 (which is also not infrared active) does not.

A molecule will not absorb vibrational energy in a continuous fashion but will do so only in discrete steps corresponding to the difference in energy between two vibration-rotation states. As the energy of incident infrared photons approaches the energy difference between two vibration-rotation states the chemical bond can absorb the radiation and the vibrational quantum number v then increases by 1.

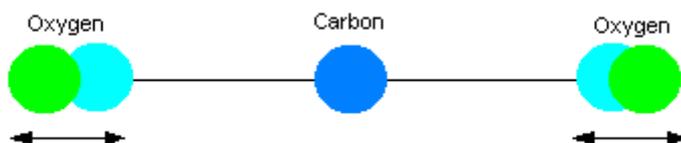
Molecular rotation is not usually resolved in most infrared spectra of large organic molecules (which show a broad absorption band) but is resolved in diatomic and simple polyatomic molecules (which show a "comb" like absorption spectrum corresponding to different rotational transitions). In this case the rotational quantum number J can change by ± 1 , although in the exceptional case that a diatomic molecule has an angular momentum about the internuclear axis (e.g. NO) there is also allowed a zero change in rotational level. A resolved vibration-rotation band can therefore display three branches corresponding to three cases:

- $\Delta J = -1$; P branch (lower energy lines)
- $\Delta J = 0$; Q branch (centre energy line)
- $\Delta J = +1$; R branch (higher energy lines)

The infrared spectrum of Carbon Dioxide

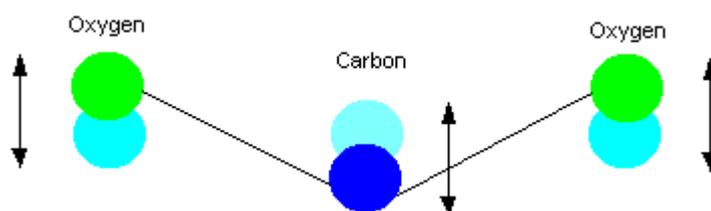
Carbon dioxide is a linear symmetric triatomic molecule with no permanent dipole moment. Since the molecule is linear there are $3n - 5 = 4$ normal modes of vibration as follows:

a) Symmetric stretch:



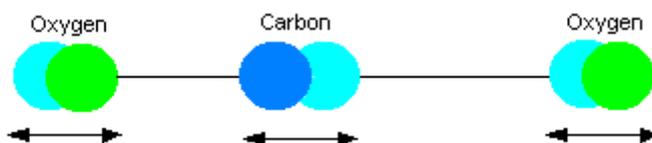
The atoms vibrate along the internuclear axis in a symmetric manner. Since this does not produce a changing dipole moment this vibration is said to be inactive in the infrared.

b) Bending mode:



The vibration of the atoms is perpendicular to the internuclear axis, creating a changing dipole moment. This mode is doubly degenerate and there is a similar bending vibration normal to the page. The fundamental absorption for this vibration occurs at 14.986 microns.

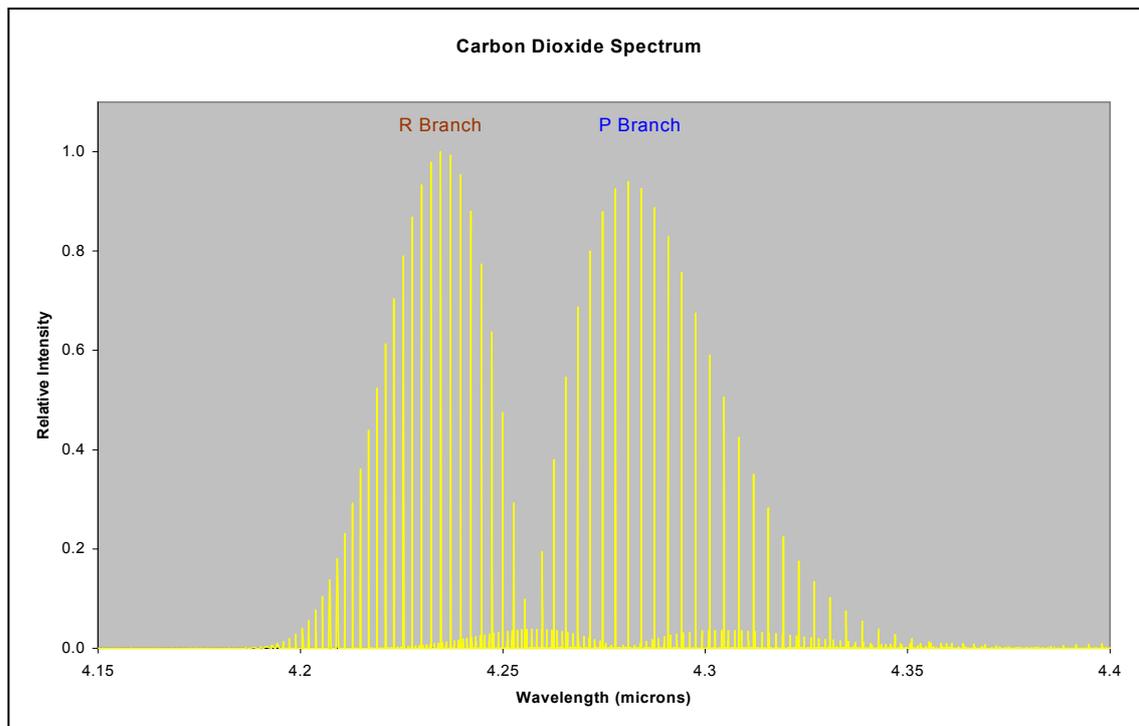
c) Asymmetric stretch:



The atoms vibrate along the internuclear axis in an asymmetric manner, creating a changing dipole moment. The fundamental absorption for this vibration occurs at 4.25 microns and is the target absorption band for the carbon dioxide sensors. Note that the stretch wavelength is much shorter than the bending wavelength; this is because it is easier to distort a molecule by bending than by stretching and the force constant and subsequent energy requirement for the bending mode is much lower.

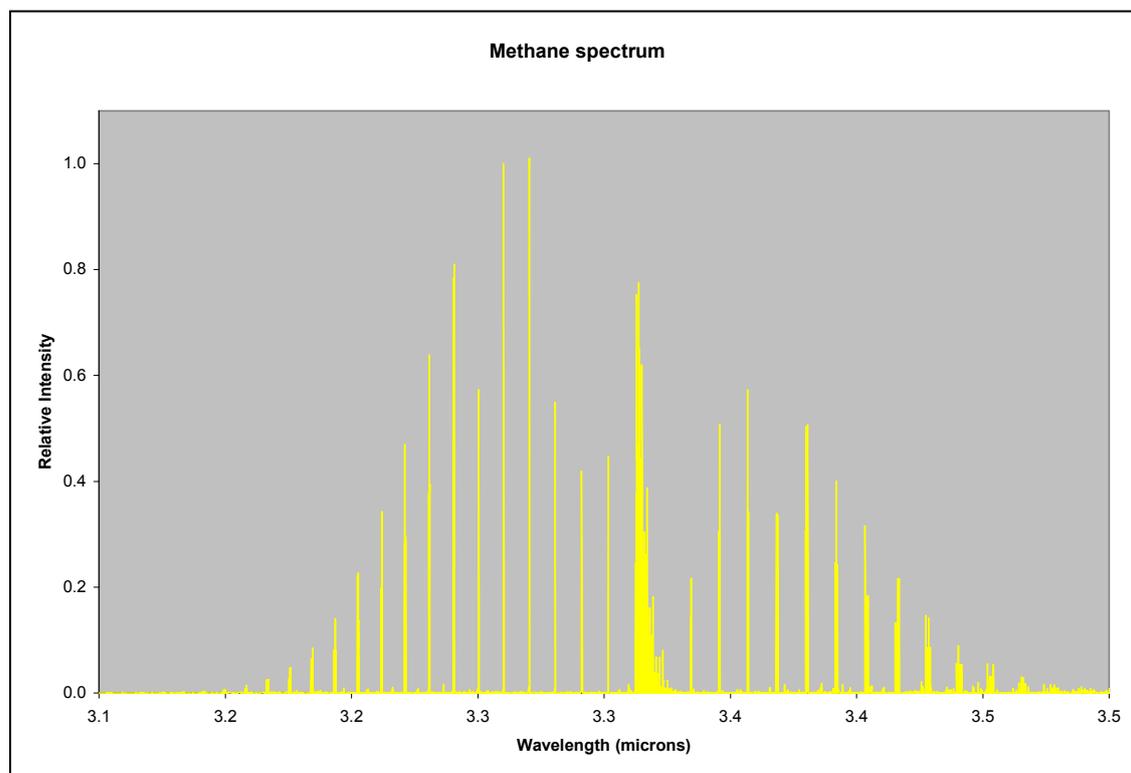
In addition to the fundamental absorption bands described above, there are several combination and overtone bands at various wavelengths but these are of much lower intensity than the fundamentals.

The presence of P and R branches caused by rotational level changes is clearly illustrated in the asymmetric stretch region of the infrared spectrum of carbon dioxide:



The infrared spectrum of Methane

Methane is a pyramidal molecule with no permanent dipole moment. Since the molecule is nonlinear there are $3n - 6 = 9$ normal modes of vibration, made up of C-H stretches and H-C-H bends. The fundamental absorption for the C-H stretch occurs in the region of 3.2 microns to 3.5 microns and is the target band for the hydrocarbon sensors. Although there is only one type of C-H bond there are symmetric and non-symmetric, degenerate and non-degenerate stretch combinations. The C-H stretch region of the methane spectrum therefore shows some complex structure but also illustrates P and R branches due to rotational level changes:



Infrared spectra of functional groups containing C-H bonds

The fundamental absorptions for various functional groups within molecules generally occur within certain bands of wavelengths. For instance, by assuming all C-H stretching force constants are similar it is reasonable to expect the C-H stretching wavelengths to be similar. This is based on the assumption that the mass of the carbon atom and whatever else it is bonded to is much greater than the mass of the hydrogen atom. Therefore the reduced mass for vibration of the C-H bond would be similar to the mass of the hydrogen atom alone. As a result, all aliphatic C-H stretches absorb in the region of 3.3 microns to 3.5 microns, methane being a basic example. Other bonding types equally absorb in specific wavelength bands that are dependent on the stiffness of the bond, the nature of the bond and the presence of any substituted atoms.

Aliphatic C-H bonds:

These generally absorb between 3.3 microns and 3.5 microns. Molecules that have local symmetry will show symmetric and asymmetric stretches in the same region resulting in overlapping peaks, which in many cases cannot be resolved. Absorption peaks are usually intense and broad.

Vinyllic and aromatic C-H bonds:

These generally absorb between 3.1 microns and 3.3 microns, which represents a higher energy than for aliphatic C-H bonds due to increased stiffness of the C-H bond. Absorption peaks are usually sharp and of low to medium intensity.

Acetylinic C-H bonds:

These generally absorb in the 3.0 micron region, illustrating the increased stiffness of the bond due to the adjacent C≡C triple bond. Absorption peaks are usually sharp and of medium to strong intensity.

Aldehyde C-H bonds:

The C-H stretching absorption appears as a doublet at approximately 3.5 microns and 3.64 microns, this being the effect of the associated C=O bond on the C-H stretches.

Additional C-H bonds and exceptions:

High ring strain, such as in cyclopropane and its derivatives, causes the aliphatic C-H stretch to move towards shorter wavelengths, often below 3.3 microns. Halogen substitution also tends to shift aliphatic C-H stretches to shorter wavelengths, again below 3.3 microns. Other factors that can cause a shift in the absorption wavelength include steric hindrance, where C-H bond stretching leads to increased crowding, and hydrogen bonding, which can cause peak broadening. However, in general, the C-H stretch areas are as outlined above.

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