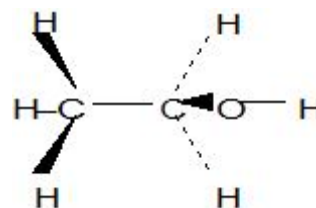


DATABASE OF QUANTITATIVE INFRARED SPECTRA OF GASES

QASoft is the Infrared Analysis, Inc. automatic quantitative analysis program for the measurement of gases.

The foundation of QASoft is the database of quantitative reference spectra. When the development of QASoft was begun some 10 years ago there were no available quantitative gas phase spectra. The available gas spectra such as those in the collections from Sadtler, Aldrich or EPA were recorded only for purposes of molecule detection and identification, not for measurement. In almost all cases the absorbances in the strong bands were too high for any quantification. It was therefore necessary for Infrared Analysis, Inc. to create its own collection of reference spectra.

It is the strongest spectral features that will most often be used for measurement, and these should be in the absorbance region of linearity--where absorbance is proportional to the concentration-pathlength product. The extent of this linear region depends on sample pressure, instrumental spectral resolution, and the nature of the spectrum. Large and unsymmetrical molecules usually have a large range of absorbance linearity. Small molecules with individual spectral lines will have a much narrower linear range. At one atmosphere total pressure and half wavenumber resolution, the linearity region for any molecule will range from zero to approximately 0.1 absorbance units. Therefore the database spectra usually show maximum absorbance values no higher than 0.1 absorbance units (log to the base 10).



The QASoft database currently covers 386 gases, including most of those normally encountered in the environment and in industry. The spectra of these gases are supplied at spectral resolutions of 0.5, and 1.0 cm⁻¹. They are organized by chemical type into 21 chapters, listed on page 5..

Discussion of Database

GASES AND VAPORS The database presents infrared absorption spectra of substances in the gaseous state--gases and vapors. By gases we mean those compounds that at room temperature have a vapor pressure higher than one atmosphere. Examples are CO₂, CO, NO₂, NO, methane, dimethyl ether and arsine. By vapors we mean the gaseous phases of compounds that normally are liquids or solids (room temperature vapor pressure less than one atmosphere). Examples here are water, methanol, pentane, and diethyl ether. Present equipment allows the detection limit for many trace gases to be extended down to a partial pressure of 10⁻⁹ atmospheres, or less. However, most polymers, metals, salts, sugars and other crystalline materials do not have sufficient vapor pressure for detection as gases. Most organic molecules that are part of living systems will never be detectable as gases because they will decompose before they are vaporized.

INFRARED SIGNATURES All polyatomic molecules and hetero-nuclear diatomic molecules absorb infrared radiation. The absorption causes changes in the molecular rotation and vibration. The pattern of absorption is determined by the physical properties of the molecule--such as the number and type of atoms, the bond angles and bond strengths. This

means that each spectrum differs from all others and may be considered the molecular "signature". Diatomic molecules such as NO, CO, HCl, and HF have a single major band that is an array of individual lines. At atmospheric pressure each line has a width of about 0.2 cm^{-1} . Linear polyatomic molecules like CO_2 , N_2O and C_2H_2 also show arrays of individual lines. Non-linear polyatomic molecules like O_3 , SO_2 , NH_3 , H_2CO , CH_4 , and H_2O have many apparent "lines" that are in fact small bundles of lines, with the widths of the bundles varying from 0.2 cm^{-1} to many cm^{-1} . For larger polyatomic molecules at atmospheric pressure there are so many lines overlapping each other that the spectral features are broad and smooth, except for occasional "spikes". In general, the great detail in the infrared spectra of the gases allows every molecule in this database to be readily distinguished from all the others. Homo-nuclear diatomic molecules such as O_2 , N_2 , H_2 and Cl_2 and monatomic gases such as helium, and radon do not have infrared bands and therefore must be measured by non-infrared means.

SPECTRAL REGION The infrared spectra of the database extend across the spectral region 3700 cm^{-1} to 500 cm^{-1} (except for HF). This is the fundamental infrared region where the rotation and vibrations of the molecules give rise to the infrared absorption. It has been fashionable lately to call this region mid-infrared, to distinguish it from near infrared and far infrared. For the measurement of gases, however, mid-infrared is a mis-leading expression. For gases there is nothing of any value on either side of the fundamental region. Only HF has a strong band at frequencies higher than 3700 cm^{-1} . At higher frequencies there are only very weak overtones. At lower frequencies there may be good strong rotation lines, but strong absorption by water vapor makes them quite inaccessible. For these reasons we choose to retain the traditional name The Fundamental Infrared Region.

RESOLUTION CONSIDERATIONS Inaccuracies of absorption coefficient arise when there is unresolved fine structure in the spectrum. When a spectral line is narrower in wavenumbers than the resolution bandwidth of the spectrometer, a line will appear wider and shorter than it actually is. For lines that have small maximum absorbance, the area under the unresolved line will be the same as the area under the line when fully resolved. For lines that have large maximum absorbance, however, the nature of the absorption process makes the area under the unresolved line smaller than it should be. The absorption function is $\log I_0/I = a \cdot c \cdot l$, where I_0/I is the ratio of the incident and transmitted intensities at a single frequency, a is the absorption coefficient at that frequency, c is the concentration of the absorber, and l is the optical pathlength. Measurements with varying concentrations of an absorber whose lines are distorted by incomplete resolution will show a deviation from this absorption law. In such cases the absorption law is not obeyed at high absorbance values, but it is nearly always obeyed at low absorbance values. Thus, the main way to avoid error in quantitative analysis of gases is to work with low absorbances, 0.1 absorbance units or lower. If the lines being used for measurement absorb strongly, the sample should be diluted, or the path should be shortened.

SPECTROMETERS Most of the spectra in the database were recorded on an Analect RFX-65 Fourier transform spectrometer equipped with a mercury-cadmium-telluride detector. This instrument had a resolution bandwidth of approximately 0.125 cm^{-1} . The spectra were smoothed by computer program to the lesser resolution values of 0.5 and 1.0 cm^{-1} . The computer smoothing closely reproduces the smoothing that results from instrumental band-pass. Some of the spectra were recorded directly at half wavenumber on a Digilab or a MIDAC spectrometer. Those spectra marked "from EPA" were smoothed from originals recorded on an Analect spectrometer at 0.25 wavenumber resolution.

ZERO FILLING HAS BEEN USED Normally, a half wavenumber spectrum has four data points per wavenumber and a one wavenumber spectrum has 2 data points per wavenumber. In both cases the data points are not close enough together to yield a good line shape with the

expected line width. If the number of data points is doubled, a better line definition is obtained. Point doubling is obtained in the calculation of the spectrum by adding a straight line to double the length of the interferogram. This is called zero filling and it is a function included in almost all FT-IR software. Point doubling may also be obtained by using the software to interpolate the extra points into an existing spectrum.

The spectra in this database all have the doubled number of data points. In recording sample spectra to be analyzed by QASoft, the operator should use a zero-filling factor of two.

PRESSURE AND TEMPERATURE CONSIDERATIONS Spectral line widths vary with pressure. If the sample pressure is lowered, the absorption lines get taller and narrower. There is then an increase in the deviations from the logarithmic absorption law because of incomplete resolution. A set of quantitative calibration spectra created at one atmosphere total pressure will not apply to a sample at one-half an atmosphere. Temperature changes in a gas sample affect the distribution of intensities among the rotational lines. This causes changes in the size and shapes of spectral features. Calibration spectra recorded at normal temperature may be difficult to apply to samples at other temperatures. The present database mainly applies to samples at ordinary temperature and pressure; that is, a temperature near 70 degrees F. and pressure near one atmosphere. Temperature changes within the range in which people live will not invalidate the quantitative nature of the spectra. Likewise, pressure changes within the normal living range will not invalidate the spectra. Some corrections to the absorption coefficients might be considered for samples at especially high altitudes, such as at Denver or Mexico City. Some EPA spectra apply to samples at 100 degrees C. If these are used for measurement of samples at room temperature, the absorbances should be raised by the factor $373/298$ ($= 1.25$) to correct for the density difference.

THE CONCENTRATION-PATHLENGTH PRODUCT In the study of a gas, the intensity of infrared absorption depends on the total number of molecules in the path of the radiation. At a fixed total pressure, trace gas concentration and optical pathlength are interchangeable. Thus a 10 cm. cell with air and a trace gas at a partial pressure of 10^{-4} Atm. will give the same spectrum as a 10 meter cell with air and the trace gas at a partial pressure of 10^{-6} Atm. Most of the spectra in the database have absorbance scales adjusted to a concentration of 100 micro-atmospheres with a one meter path. At one atmosphere total pressure a micro-atmosphere is equivalent to a volume mixing ratio of one part-per-million (PPM). We therefore use the expression 100 ppm-meters. A few of the spectra with very strong bands have been adjusted to 10 ppm-meters, and a few with weak bands have been adjusted to 1000 ppm-meters.

COMPUTER NAMES

Following is the key to the computer names of the spectra:

1st letter.....Chapter (A to T)

2nd letter.....Spectrum position within the chapter (A to Z)

3rd letter.....Spectral resolution--H = 0.5 cm⁻¹; N = 1.0 cm⁻¹

4th letter.....Concentration-path product--X = 10 ppm-meters; Z = 100 ppm-m.; K = 1000 ppm-m

5th through 8th letters....Compound designation by formula or mnemonic

GAS HANDLING TECHNIQUE The gaseous samples were handled in a glass vacuum line. Some gases were obtained from lecture bottles, but in most cases, vapors were obtained from pure liquids or solids. Some of the gases were generated in chemical reactions conducted in an attachment to the vacuum line. In these cases, a purification step was put in by trapping the gas

at liquid nitrogen temperature and re-vaporizing it. In making these reference spectra, several possible sources of error were anticipated.

- (1) If the gas is placed in the absorption cell at a very low partial pressure, wall interactions can cause the actual pressure to be different from the measured pressure. Adsorption can cause the measured absorption coefficients to come out too low. Desorption of previously adsorbed gas can cause the measured absorption coefficients to come out too high. Acidic vapors tend to adsorb on metal walls; basic gases tend to adsorb on glass walls.
- (2) It is difficult to obtain and maintain a reliable calibration of an electronic pressure gauge that operates in the range below one Torr. It is better to use a manometer.
- (3) When vaporizing a solid or liquid compound of low vapor pressure, a volatile impurity can release as much vapor as the principal component.

In order to minimize the envisioned errors, the following techniques were adopted.

- (1) In most cases, the gases were metered into a glass single-pass absorption cell, 11 centimeters long.
- (2) Gas pressures were measured on a manometer containing silicone oil, with the height difference between the two arms of the manometer being in the range 5 to 20 centimeters (about 4 to 15 Torr.)
- (3) Nitrogen or air was added to the sample to bring the total pressure to one atmosphere.
- (4) Gases that dimerize, such as the aliphatic acids, were measured at parts-per-million mixing ratios in a long path cell, usually set for 11 meters path.
- (5) When a gas could only be seen in a mixture with other infrared absorbing gases (such as HNO_2 in equilibrium with NO , NO_2 and H_2O), the unwanted bands of the other gases were subtracted from the spectrum before it was plotted.

The above technique of error avoidance was initiated 10 years ago and adhered to ever since. Recently, there have been discussions and publication on anticipated difficulties in preparing quantitative gas phase spectra, but these discussions did not raise any points that were not considered by us when we initiated the preparation of our database.

IDENTIFICATION OF GASEOUS MOLECULES In gas analysis, identification of the absorbing species is not usually the main problem. Most of the spectra are easily recognized. If an unknown spectrum is encountered, the number of possible absorbing species is not great. This database will in most cases contain the unknown. Some consideration of functional group frequencies will often assist in finding the molecule. For example, a strong band in the region 1800 cm^{-1} to 1700 cm^{-1} will indicate a compound with a carbonyl group, and a band near 3000 cm^{-1} will say that there are C-H groups in the molecule. Also, for example, nitrate groups and halogen atoms have characteristic strong bands. The amount of fine structure in a spectrum is an indication of molecular size and symmetry. If there are resolvable lines, the molecule is small. If there are regular arrays of lines, the molecule is linear. If the lines are bunched in a regular way, the molecule is probably a symmetric top. If the bands are smooth and structureless, the molecule is large and non-symmetrical.

To assist in identifying unknown bands, QASoft includes a browse program that allows all the spectra in the database to be superimposed on an unknown spectrum, one at a time. This may be done using either the full spectrum or a selected portion. A browse through the full database takes only a few minutes.

The Infrared Spectra

Presented here are the spectra that are in the Infrared Analysis, Inc. digitized database of quantitative gas-phase reference spectra. An alphabetical listing is given, with chapter letters, spectrum letters and molecular weights. The spectra are displayed by chemical categories, A through T. This is the way they are called up from the database. Molecular weights are given so that the user may convert his concentration values from parts-per-million to micrograms per cubic meter. At normal conditions of temperature and pressure, the conversion relationship is:

Micrograms per cubic meter = molecular weight x PPM x 41.31.

The spectra are presented in absorbance form with the x-axis in wavenumbers. Spectral resolution of the printed spectra is half wavenumber, although the database also includes them at one wavenumber.

Spectra from PNNL (Pacific Northwest National Laboratory) are included in the database. These are all marked from PNNL. The originals of these spectra were taken from the PNNL website: <http://NWIR.PNL.GOV>. These spectra were re-processed to QASoft format, and the necessary integration parameters were written into their headers. These spectra are public property and may be taken from the website at no cost. In accordance with the government's requirements, there has been no additional charge for inclusion of the PNNL spectra in the database. The price of the QASoft programs remains the same as it was before the inclusion of the PNNL spectra.

Here are the chapters:

- | | |
|---|------------------------------------|
| A - Hydrocarbons, C1 through C4 | O - Sulfur-containing compounds |
| B - Hydrocarbons, C5 and C6 | P - Halogenated methanes |
| C - Hydrocarbons, C7 and up, non-aromatic | Q - Halogenated ethanes |
| D - Hydrocarbons, Aromatic | R - Halogenated ethenes and others |
| E - Hydrides | S - Halogenated benzenes |
| F - Oxides and Peroxides | T - Miscellaneous |
| G - Organic Acids and Aldehydes | U - Add-Ons |
| H - Amines and Amides | |
| I - Ketones | |
| J - Alcohols | |
| K - Esters | |
| L - Ethers | |
| M - Nitrogen compounds, inorganic | |
| N - Nitrogen-containing organics | |