Simple Theory

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Application Note AN # 58

Analysis of the gas phase spectrum of hydrogen chloride measured with the ALPHA FT-IR spectrometer

An experiment commonly performed in the physical chemistry teaching laboratory.

Introduction

Infrared spectroscopy is a classical technique, which depends upon the interaction of infrared radiation with the vibrating dipole moments of molecules. In the vapor phase, with the exception of homonuclear diatomics and noble gases, a characteristic spectrum for each substance is obtained. This individual spectrum is based on the unique physical properties of each investigated molecule. Infrared spectroscopy serves as an excellent tool for gaining the values of these physical properties, in particular the molecular structure and force constants of the chemical bonds. The vapor phase spectrum of the heteronuclear diatomic molecule hydrogen chloride (HCl) is an ideal example to illustrate the principles.

When infrared radiation absorbed by a liquid or solid is measured, well-defined regions of absorption can be attributed to the vibrational transitions. The IR spectra of molecules in the gas phase, assuming the resolution of the instrument is adequate, no longer show such smooth and structureless absorption bands but rather absorption regions of considerable complexity. The fine structure of these absorption bands can be correlated to changes in the rotational energy of the molecule accompanied by a vibrational transition.

FT-IR spectrum of hydrogen chloride in the gas phase. Insert: The ro-vibrational lines are split due to the chlorine 35 and chlorine 37 natural isotopic ratio.

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obtained by classical mechanics; the solution is represented by a sinusoidal motion of two masses at a frequency determined by their masses and the restoring force of the spring. During the vibration the potential and the kinetic energy of the system continually interconvert but the sum of both energies keeps constant as in a pendulum.

![Figure 1](image1.png)

**Figure 1:** Mechanical model of the vibrating diatomic molecule. k the spring constant corresponds to the molecular binding force, \(m_1\) and \(m_2\) are the atomic mass and \(r_0\) the equilibrium distance.

![Figure 2](image2.png)

**Figure 2:** The potential energy of the two mass model can be assumed to be a parabola, that is harmonic. The further the masses are displaced from their equilibrium position, the higher the potential energy of the system.

The resulting classical vibrational frequency of such an oscillator is given by:

\[
v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}
\]

being the reduced mass.

\[
\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}
\]

For the description of the vibrational motion of a heteronuclear diatomic molecule, the quantum mechanical description of the harmonic oscillator can be used. The quantized energy levels are given by:

\[
E_v = \hbar v (v + \frac{1}{2})
\]

Where \(E_v\) is the energy of the vibrational state with quantum number \(v\), \(\nu\) is the classical vibrational frequency and \(\hbar\) is Planck’s constant. \(v\) takes integer values starting from 0.

Under normal conditions, the vibrational transitions take place from the ground state (\(v=0\)) to the first excited state (\(v=1\)). This simple vibrational model predicts just one single vibrational band for a diatomic molecule. However, we can observe a series of closely spaced bands as for the spectrum of HCl shown in the figure. These lines are due to the rotational sub-structure and a further quantum number \(J\) for the rotational energy is introduced. \(J\) also takes integer values starting from 0. So each vibrational level has a stack of rotational levels and transitions occur from \(v=0\) to \(v=1\) with \(J\) changing by +1 (so called R branch lines) and \(J\) changing by –1 (so called P branch lines).

The figure for the HCl spectrum shows a few examples where lines are assigned and the number in brackets refers to the \(J\) number of the \(v=0\) level. It turns out that the Q branch line with no change in \(J\) and expected at the band centre is missing due to the operation of selection rules. This results in a gap between \(R(0)\) and \(P(1)\), see the figure.

The rotational energies are given by \(B(J+1)\) where \(B\) is known as the rotational constant. Knowledge of \(B\) leads to the molecular structure determination or in this simple case, the bond length. To a first approximation, the rotational constants \(B\) of the \(v=0\) (lower) and \(v=1\) (upper) vibrational levels are determined as follows. For each \(J\), take the differences in cm\(^{-1}\) positions of the pairs of lines shown on the left side of the two equations and divide by \((2J+1)\).

\[
R(J-1) - P(J+1) = 2B_{\text{lower}} (2J+1)
\]

\[
R(J) - P(J) = 2B_{\text{upper}} (2J+1)
\]
A plot of the previously determined 2B values versus (2J+1)^2 will result in a straight line. The slope will be \(-D\) and the intercept \((2B-3D)\).

### Calculation of the internuclear distance

Extrapolate the rotational constants to the equilibrium state when the molecule would reside hypothetically at the bottom of the potential well.
Assuming an harmonic oscillator, the band origins for HCl-35 and HCl-37 are related by:

\[ V_{0,1}^{\text{HCl-37}} = V_{0,1}^{\text{HCl-35}} \times \sqrt{\frac{\text{reduced mass HCl-35}}{\text{reduced mass HCl-37}}} \]

Using values of the reduced mass for HCl-35 and HCl-37 from the table, the prediction for HCl-37 is 2883.78 cm\(^{-1}\) compared with the experimental value of 2883.84 cm\(^{-1}\).

### Conclusions

The ALPHA is a compact and affordable FT-IR spectrometer that makes it ideal for teaching applications as well as QA/QC. With the high resolution option for the ALPHA, excellent spectra of HCl vapor measured in a gas cell can be obtained. Analysis of the HCl spectrum, making full use of the OPUS peak pick software installed on the ALPHA PC or Laptop, yields molecular constants entirely consistent with values published in the spectroscopic research literature. These excellent experimental results are possible because of the good line shape, signal to noise and precise frequency registration of the ALPHA FT-IR spectrometer line.