Experiment S2 INFRARED SPECTROSCOPY Chemistry 114

Analyzing Rotational and Vibrational Structure in the Spectra of Linear Molecules

Analysis of the rotational and vibrational spectra of molecules in the gas phase can give very accurate values for internuclear distances, force constants, and other molecular parameters.

This experiment is divided into three parts:

1 Vibrational-Rotational Spectra of HCl and DCl

You will download the HCl and DCl FTIR spectra from the VOH. These data will be analyzed following the approach taken by Garland, Nibler, and Shoemaker[1] (Experiment 37, p 403-1,1 7th Ed.; ignore Experimental Section)

Your report should include the following results: υ_0, B_e, α_e, D_e and r_e for *all four isotopes ($H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$, $D^{37}Cl$).* Also calculate υ_e, $\upsilon_e x_e$, k, and C_v for $H^{35}Cl$, and include a comment on the anharmonicity of HCl based on a comparison of the ratio υ_0^*/υ_0 with $(\mu/\mu^*)^{1/2}$

A mathematical approach is presented below, with a derivation for the dissociation energy based on a Morse Potential. You should calculate the dissociation energy, D_e, of HCl using this method and compare it with the accepted literature value.

The Morse Potential

According to Herzberg,[2] the vibrational energy levels, G(v), can be represented by a power series:

$$G(v) = \upsilon_e(v + {}^1/_2) - \upsilon_e x_e(v + {}^1/_2)^2 + \upsilon_e y_e(v + {}^1/_2)^3 + \ldots \qquad (1)$$

where $\upsilon_e \gg \upsilon_e x_e \gg \upsilon_e y_e$. Since you are dealing with low vibrational levels, only the first two terms on the right hand side of Equation 1 are necessary.

The most popular potential function for real diatomic molecules is the Morse potential:[2]

$$V(r) = D_e\{1 - \exp[-\beta(r - r_e)]\}^2 \qquad (2)$$

where D_e is the dissociation energy, measured from the minimum , and β is a parameter related to the force constant of the bond. Note, $V(r = r_e) = 0$ and $V(r = \infty) = D_e$. If this Morse potential is inserted into the one-dimensional Schrödinger equation, the resulting differential equation can be solved exactly to give quantized energy levels (Note that D_e has the same units as υ_e) :

$$G(v) = \beta[D_e\, h\, (2\pi^2 c\mu)^{-1}]^{1/2} (v + {}^1/_2) - \beta^2 h\, (8\pi^2 c\mu)^{-1} (v + {}^1/_2)^2 \qquad (3)$$

Equation (3) has the same form as the first two terms of the empirical Equation (1). That is to say, the Morse potential has the correct shape to fit the observed lower vibrational levels in real molecules, at least to a good approximation. For larger values of the vibrational quantum number, when the higher order terms in Equation (1) become significant, Equation (3), and thus the Morse potential, become poorer approximations for real molecules.

If you equate the coefficients of $(v + {}^{1}/_{2})$ in Equations (1) and (3), you can relate the parameters of the Morse potential to the experimental values of υ_e and $\upsilon_e x_e$. By manipulating the resulting expressions, it is possible to derive an expression for D_e. This is known as the linear Birge-Sponer extrapolation; it is frequently used to get an estimate for the dissociation energy of a diatomic molecule. (Warning, the Birge-Sponer method usually overestimates the bond energy by 5 to 20%)

2 Vibrational-Rotational Spectra of the CO_2 asymmetric stretch

An interesting alternative to the linear diatomic HCl molecule is the linear polyatomic Carbon Dioxide case, that can be treated in a fairly simple way, since both bonds are identical.

The CO_2 asymmetric stretch fundamental band, around 2350 cm^{-1}, can be easily seen and resolved in a background signal. (Which also shows the sensitivity of this analytical technique, considering that the atmospheric concentration of carbon dioxide is only on the order of 350 ppm). You will follow the experimental procedure bellow to acquire an IR transmission spectrum of carbon dioxide. This procedure, which is slightly more involved than just collecting an atmospheric background signal, will give you the opportunity to work with a vacuum line.

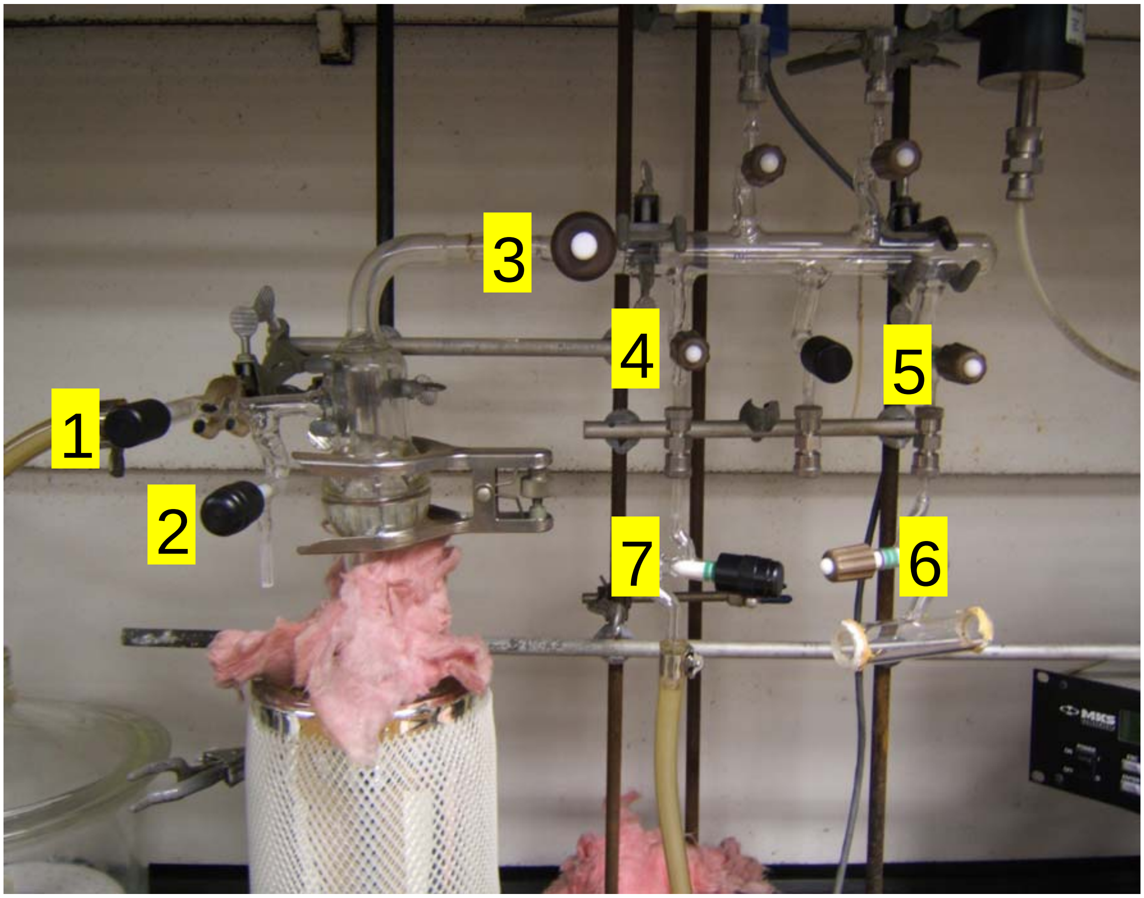
2.1 Experimental procedure

PLEASE, be **EXTREMELLY CAREFUL** with the vacuum line:

Use both hands to handle valves! Wear goggles!

- Turn the FTIR instrument on.
- Find the IR cell inside the dessicator in the hood and attach it to the vacuum line (position 6, picture below), make sure the o-ring is in place (it might be stuck inside the female connector).
- Turn the vacuum pump on. Make sure valve 2 is closed. Open vacuum valves (1 & 3) and cell valves (5 & 6).
- Turn on digital pressure meter (PR4000) and wait until pressure is lower than ~0.5 Torr (or reaches a pressure of < 1Torr that is constant for a few minutes)
- At the computer, open the EZ OMNIC software (if you get an error message, just close the software, wait a couple of minutes and open it again). Measure a Background spectrum (remember to use 0.5 cm^{-1} resolution, selected under "collect/Experimental Setup"), you will see Carbon Dioxide lines from the air inside the instrument.
- Open the Nitrogen purge cylinder main valve. Do not touch the pressure adjustment handle and make sure the needle valve (small black rotating knob at the output of the regulator) is completely opened. Record the time.

- Back to the vacuum line close cell valves (5 & 6) and take the cell out.
- Insert the cell in the FTIR, and check with a business card (in drawer underneath) that the red laser light goes through the cell (Have the top instrument port opened as little as possible).
- After flushing the instrument for 10 minutes (since you opened the nitrogen valve), close the nitrogen purge (main cylinder valve only), and take another background spectrum. You should see that the CO_2 lines are now much weaker. Save this background as a CSV file. (CSV stands for comma separated values, that can be opened in Excel)
- Take the cell out, and open the vacuum valve to let air inside the cell. Put the cell back into the instrument, measure a Sample spectrum and save it (as CSV).
- Turn the pressure meter off, and vacuum pump off in the hood and proceed to do part 3 of this experiment.
- Please put the gas cell back in the dessicator after completing your measurements.



Analysis and Results

Only the asymmetric stretch of the $^{16}O^{12}C^{16}O$ isotopic species will be considered in the following analysis.

Similar to the diatomic molecule case, the energy levels of a vibration–rotation stretching mode of a linear molecule can be express as follows (in wavenumber units):

$$E(\mathrm{v}_1, \mathrm{v}_2, \ldots, J) = \sum w_i \left(\mathrm{v}_i + \frac{d_i}{2}\right) + \sum_i \sum_{j \geq i} x_{ij} \left(\mathrm{v}_i + \frac{d_i}{2}\right)\left(\mathrm{v}_j + \frac{d_j}{2}\right) + \sum B_e J(J+1) - \sum D_v J^2 (J+1)^2 \quad - \sum \alpha_\mathrm{i} \left(\mathrm{v}_i + \frac{d_i}{2}\right) J(J+1) \qquad (4)$$

where the different terms represent the harmonic oscillator, the anharmonic correction, the rigid rotor rotational contribution, the centrifugal distortion term, and the vibration-rotation interaction respectively. The only new variable with respect to HCl is d_i, the degeneracy of the different normal modes. For the case of v_2, the bend mode with fundamental transition at 667 cm^{-1} and responsible for the greenhouse property of CO_2, $d_i = 2$, for the other two modes d_i=1.

Thus, the central frequency of the transition studied in this experiment: the asymmetric stretch fundamental $\Delta \mathrm{v}_3$ (001 ← 000), , can be expressed as $\widetilde{v_3} = w_3 + 2x_{33} + {}^1\!/_2\, x_{13} + x_{23}$; which accounts for the first two terms in Eq 4.

The "equilibrium" rotational constant B_e, is the rotational constant for the hypothetical rigid molecule with no vibrational energy, and is related to the rotational constant of the molecule in its lowest vibrational state, $B_{[0]}$ ($\mathrm{v}_1 = \mathrm{v}_2 = \mathrm{v}_3 = 0$), by the expression:

$$B_{[0]} = B_e - \sum \alpha_i \frac{d_i}{2}$$

$B_{[0]}$ will be determined from the experimental data and then will be used to determine $r_{\mathrm{C=O}}$, using

$$B_{[0]} = \frac{h}{8\pi^2 I_0\ c} \qquad \text{where } I_\mathrm{o} = r^2 2m_{oxygen} \qquad (5)$$

The rotational selection rules follow the familiar $\Delta J = \pm 1$, so that $\Delta \mathrm{v}_3$ presents the expected R and P branches with energies:

R branch: $J + 1 \leftarrow J$: $v_3 = \widetilde{v_3} + 2B_{[0]}(J + 1) - \alpha_3 (J + 1)(J + 2) - 4D_\mathrm{e}(J + 1)^3$ (6)

P branch: $J - 1 \leftarrow J$:$v_3 = \widetilde{v_3} + 2B_{[0]}(-J) - \alpha_3 (J - 1) J - 4D_\mathrm{e}(-J)^3$ (7)

where we have approximated D_v by D_e, a good approximation for polyatomic linear systems.

Repeating the same change of variables as for the HCl experiment: $m = J+1$ for the R branch and $m = -J$ for the P branch, equations 6 and 7 can be combined into a single expression, which will then be used for the data analysis:

$$\tilde{\nu}(m) = \tilde{\nu}_3 + 2B_{[0]}(m) + \alpha_3(-m - m^2) + D_e(-4m^3) \qquad (8)$$

A careful inspection of the symmetry of the CO_2 wavefunction reveals that only half of the rotational lines predicted by equation 8 will be observed for this transition.

CO_2 has totally symmetric ground electronic and vibrational states. The rotational wavefunction, on the hand, will depend on the quantum number J according to $(-1)^J$. Therefore, the sign on the overall wavefunction that results from the exchange of the chemically equivalent ^{16}O bosons via rotation can be written as:

$$\Psi = \Psi_{\text{electronic}}\,\Psi_{\text{vibrational}}\,\Psi_{\text{rotational}}\,\Psi_{\text{nuclear}} \Rightarrow (+1)\,(+1)\,(-1)^J\,(+1)$$

Rotational states in the ground vibrational state of $C^{16}O_2$ labeled by odd J will violate the Pauli exclusion principle and therefore do not exist.

On the other hand, the vibrationally excited CO_2, with one quanta in the asymmetric stretch, is anti-symmetric with respect to molecular rotation around the carbon atom:

$$\Psi = \Psi_{\text{electronic}}\,\Psi_{\text{vibrational}}\,\Psi_{\text{rotational}}\,\Psi_{\text{nuclear}} \Rightarrow (+1)\,(-1)\,(-1)^J\,(+1)$$

therefore, rotational states with even J violate the Pauli exclusion principle for the exchange of the chemically equivalent ^{16}O bosons via rotation and thus do not exist.

Since the overall symmetry is preserved after photon absorption; then, the observed rotational transitions that correspond to R branch are ΔJ: 1←0, 3←2, 5←4 etc. and to the P branch are ΔJ: 1←2, 3←4, 5←6 etc. Therefore, the m dummy variable in Eq *8* will have values 1, 3, 5, 7, … for the R branch and values -2, -4, -6, … for the P branch.

3 Averaging effects on noise

Measure five background signals with 8, 16, 32, 64 and 128 scans (N). Calculate the noise level of these scans and verify that it decreases with $\sqrt{N}$

One way of determining the noise is by fitting a line to a linear part of the background (2450-2500 cm^{-1} for example), subtracting out the fit and computing the standard deviation of the residuals.

References

1. C. W. Garland and J. W. Nibler, D. P. Shoemaker, "Experiments in Physical Chemistry", 7th Ed., McGraw-Hill, New York (2003), Experiment 37, p. 403.

2. G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules", 2nd Ed., Van Nostrand, Princeton (1950).