

Rotation Vibration Spectrum of the HCl Molecule

Experiment IRS

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Objective

The infrared absorption spectrum of the HCl molecule is measured using a Fourier-transform infrared (FTIR) spectrometer. The spectra from several isotopes of HCl are analyzed for common information about the molecular bond and for variations arising from the differing nuclear masses.

References

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Introduction

One might expect that quantum mechanical calculations capable of predicting the structure of even the simplest molecules would be quite complex. Indeed, solving the

Schrödinger equation for the nuclei and all electrons would be a formidable task. Fortunately, this is not always necessary. Because of their large mass difference, accurate results can be obtained while treating the electron and nuclear motion in separate steps. This is called the Born-Oppenheimer approximation. The rapid changes that occur in the electronic wavefunction as the nuclei slowly move relative to one another gives rise to effective interatomic forces that can then be used in determining the nuclear motion. The forces need not even be well determined ahead of time. Instead, they can be treated as unknowns to be determined by experiments such as this one.

Here, we will only consider the diatomic HCl molecule, which is modeled as two nuclei connected by a “spring” representing the interatomic force. The system is called a *non-rigid rotator* and the nuclear motion consists of simultaneous rotations and vibrations. The quantum mechanics of rotational and vibrational motion is only one step beyond the harmonic oscillator and rigid rotator systems, both of which are paradigms of the subject. The non-rigid rotator (in the case of the HCl molecule) has nearly independent harmonic oscillations and rigid rotations, with additional effects arising from the interaction between these two motions. The vibrational energy levels can be predicted based on the molecular bonding strength (spring force con-

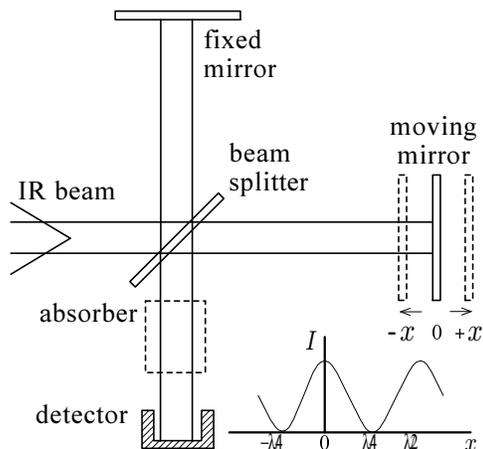


Figure 1: Simplified schematic of a Fourier-transform spectrometer. The harmonic variations of I vs. x (a portion of which is illustrated in the figure) would be the interferogram for a monochromatic source.

stant) and the rotational energy levels can be predicted based on the bond length (equilibrium spring length). Quantum mechanics also predicts the selection rules giving the allowed transitions between energy levels.

In this experiment, a Fourier-transform infrared (FTIR) spectrometer will be used to measure the transmission of an infrared light beam passing through a cell containing HCl vapor. The absorption spectrum will show distinct absorption peaks whose frequencies and strengths will be compared with predictions.

FTIR Spectrometer

Fourier-transform spectroscopy is a beautiful application of a scanning Michelson interferometer. As illustrated in Fig. 1, an IR beam (from an incandescent source in the spectrometer) is split into two beams by a beam splitter. One beam travels to a fixed mirror and one to a movable mirror. The reflected beams are recombined at the beam splitter after which

they continue to the detector.

With a monochromatic source of wavelength λ and frequency $\nu = c/\lambda$, the recombined beams will interfere constructively or destructively at the detector depending on the path length difference between the arms. With the movable mirror at its central position—called the *center burst* position—the path length is effectively the same for both arms (for any λ). At the center burst position the two beams will be in phase at the detector (interfere constructively) and the measured intensity will be a maximum. If the movable mirror translates a distance $x = \lambda/4$ along the beam direction, the path length difference would then be $\lambda/2$. Now the two beams would be 180° out of phase (interfere destructively) and the detected intensity would be a minimum. Typically the movable mirror translational range is several centimeters whereas the wavelength is tens of micrometers so that the intensity would show many maxima and minima. The time varying part of the intensity at the detector can be represented as

$$\mathcal{I}(x) = I(\nu) \cos\left(\frac{4\pi}{c}\nu x\right) \quad (1)$$

where $\mathcal{I}(x)$ is the detected intensity with x the displacement of the mirror from the zero position and $I(\nu)$ is the source spectral intensity at the frequency ν .

In an FTIR spectrometer the IR beam is not monochromatic. The radiation source is typically a high-temperature lamp having a continuous range of frequencies. With such a broadband source the detected intensity will be an integral of contributions from each source frequency present.

$$\mathcal{I}(x) = \int I(\nu) \cos\left(\frac{4\pi}{c}\nu x\right) d\nu \quad (2)$$

These intensity variations are called an interferogram. The conversion of the interferogram

$\mathcal{I}(x)$ to a source spectrum $I(\nu)$ is then proportional to the Fourier transform of $\mathcal{I}(x)$

$$I(\nu) \propto \int \mathcal{I}(x) \cos\left(\frac{4\pi}{c}\nu x\right) dx \quad (3)$$

Putting an absorber in front of the detector and taking the ratio of the spectra with and without the absorber produces the transmission spectrum.

Exercise 1 Show that Eq. 3 is correct by direct substitution into Eq. 2. Take the limits of integration to be $\pm\infty$.

Electronic Motion

Because the nuclei are much heavier than the electrons, they move much more slowly. To a good approximation the nuclei can be considered as “standing still” when determining the electronic motion. Then, in principle, the Schrödinger equation for the electrons can be solved for every possible set of fixed nuclear positions. For our purposes, all that needs to be appreciated is that such calculations produce electronic eigenenergies that will depend on the relative nuclear positions. For a diatomic molecule, the relative nuclear positions are described by a single variable—the internuclear separation r .

As with atoms, there are an infinite set of solutions to the Schrödinger eigenvalue equation. In other words, for every internuclear separation there are many electronic eigenfunctions and associated eigenenergies. As the separation varies, each eigenenergy varies smoothly. A plot of the two lowest energies vs. the internuclear separation r for a diatomic molecule might appear as in Fig. 2. The repulsive Coulomb potential energy between the nuclei is also included so that these curves represent the total energy of a stationary nuclear configuration. These curves are called potential curves and are denoted by the expression

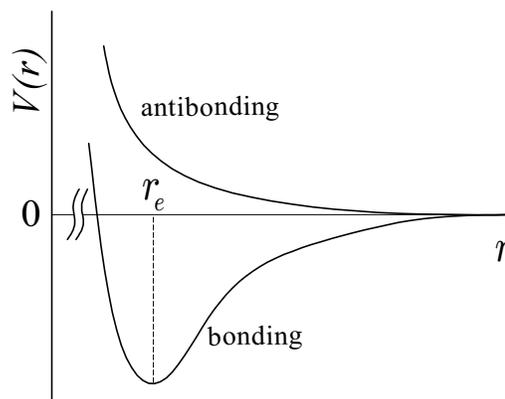


Figure 2: Potential curves for a bonding and antibonding molecular states of a diatomic molecule. The equilibrium bond length r_e for the bonding state is also shown. The zero of potential energy has been chosen to be that of two isolated atoms, $r = \infty$.

$V(r)$. Each curve is said to represent a molecular state.

The upper curve in Fig. 2 is an “antibonding” electronic configuration. For a molecule in this state, the interatomic force $-dV/dr$ is always repulsive so that the molecule would quickly dissociate. The lower curve is a “bonding” configuration because it has a minimum at some equilibrium separation r_e and thus the force is always restorative to this separation. Molecules typically have more than two electronic configurations, and each may be bonding or antibonding. For HCl, as for all stable molecules, the lowest (or ground) molecular state is bonding.

Of course, the total energy must be conserved. As the nuclei move and the internuclear separation r varies, the change in $V(r)$ must be accompanied by a corresponding change in the nuclear kinetic energy. Thus, $V(r)$ becomes the potential energy for the nuclear motion.

Nuclear Motion

The two nuclear masses are represented by m_1 and m_2 and their positions by the vectors \mathbf{r}_1 and \mathbf{r}_2 . The internuclear axis vector is then $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and the potential $V(r)$ depends only on the magnitude of \mathbf{r} . As there are two particles interacting via a potential $V(r)$, the quantum mechanical treatment begins in a manner identical to that for the hydrogen atom (without spin). In the center of mass frame, the wavefunction for both nuclei can be expressed as a function of the single internuclear axis vector \mathbf{r} . After separating out the kinetic energy of the center of mass motion, the Hamiltonian becomes an operator on this single variable.

$$H = \left[-\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \quad (4)$$

where ∇ is the gradient with respect to \mathbf{r} and the reduced mass μ is

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (5)$$

As with the hydrogen atom, the complete set of commuting observables include the Hamiltonian H , $J^2 = |\mathbf{J}|^2$ where \mathbf{J} is the total angular momentum (of the nuclei), and one component of \mathbf{J} , traditionally taken as J_z . Thus, we should be able to find simultaneous eigenfunctions of the operators H , J^2 and J_z . The solutions to the time-independent Schrödinger equation

$$H\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (6)$$

then provide the allowed energy eigenvalues E while the solutions to the angular momentum eigenvalue equations, typically written

$$J^2\psi(\mathbf{r}) = \hbar^2 J(J+1)\psi(\mathbf{r}) \quad (7)$$

and

$$J_z\psi(\mathbf{r}) = \hbar M\psi(\mathbf{r}) \quad (8)$$

provide the allowed values of J and M .

In spherical coordinates with

$$\psi(\mathbf{r}) = \frac{\chi(r)}{r} Y(\theta, \phi) \quad (9)$$

separation of variables in the Schrödinger equation proceeds as with the hydrogen atom. With the angular function $Y(\theta, \phi)$ taken to be the spherical harmonics $Y_{JM}(\theta, \phi)$, both angular momentum eigenvalue equations are satisfied. One finds values of J are restricted to non-negative integers ($J = 0, 1, 2, \dots$) and for each value of J , values of M are restricted to integers between $-J$ to J .

Vibrations

With $\psi(\mathbf{r})$ given by Eq. 9 and the Hamiltonian by Eq. 4, the radial part of Eq. 6 becomes

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2}{2\mu r^2} J(J+1) + V(r) \right] \chi(r) = E\chi(r) \quad (10)$$

The term $(\hbar^2/2\mu r^2) J(J+1)$ gives the rotational energy. Because this energy turns out to be small compared to the total energy E , the corresponding term will temporarily be neglected and treated later using perturbation theory.

For nuclear motion which is small compared to the equilibrium separation, the shape of the potential energy curve can be approximated by the first few terms of a Taylor expansion about r_e .

$$V(r) = V_0 + \frac{1}{2}k(r-r_e)^2 - g(r-r_e)^3 + \dots \quad (11)$$

The quadratic term has been written in the form of a spring of force constant k . The cubic term has been written with a negative sign so that a positive g produces the typical asymmetry of a bonding $V(r)$ shown in Fig. 2 (sharper rise on the low- r side).

Exercise 2 Prove that there can be no linear term — proportional to $(r - r_e)$ — in Eq. 11 if $V(r)$ is to have a minimum at r_e . Hint: consider the derivative of $V(r)$.

To get an approximate solution to the radial equation (without the rotational energy term), the potential for the nuclei $V(r)$ is taken to be a harmonic (quadratic) potential by neglecting the third and higher order terms in Eq. 11. The cubic and higher order terms make the system slightly anharmonic but remain small for $r \approx r_e$. For the lowest energy solutions, the eigenfunction amplitude is small for values of r far from r_e and these anharmonic terms can be neglected to first order. Their effect on the rotational energy levels will be discussed shortly. The constant V_0 in Eq. 11 offsets all energy levels by the same amount and can be eliminated by redefining the zero of potential energy. The remaining quadratic term represents a Hooke's-law force of force constant k and equilibrium length r_e .

With these approximations, the resulting Schrödinger equation for $\chi(r)$ is the harmonic oscillator equation

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{1}{2}k(r - r_e)^2 \right] \chi(r) = E_v \chi(r) \quad (12)$$

The eigenfunction solutions $\chi(r) = \chi_v(r - r_e)$ are symmetric about r_e and characterized by a vibrational quantum number $v = 0, 1, 2, \dots$. The eigenenergies are given by

$$E_v = \hbar\omega_e(v + 1/2) \quad (13)$$

where

$$\omega_e = \sqrt{\frac{k}{\mu}} \quad (14)$$

is determined by the reduced mass μ and the force constant k .

When the small anharmonic terms of $V(r)$ are included, the eigenfunctions $\chi_v(r - r_e)$

become somewhat asymmetric about $r = r_e$ compared to the symmetric harmonic oscillator eigenfunctions. Because the anharmonic $V(r)$ rises more gently on the high- r side of r_e , the nuclei spend more time there and the eigenfunctions have somewhat higher probability density on this side. The eigenenergies also change and are well represented by the expression

$$E_v = \hbar\omega_e \left[(v + 1/2) - x_e(v + 1/2)^2 \right] \quad (15)$$

where x_e is called the anharmonicity constant.

Rigid Rotator

We now turn to the rotational energy, the middle term on the left of Eq. 10. The simplest rotational system, a dumbbell or “rigid rotator” model consists of two nuclei m_1 and m_2 separated by rigid massless rod of length r_e . Separating out the center of mass motion, the wavefunction can only depend on the orientation of the dumbbell, i.e., on the polar coordinate angles (θ, ϕ) . Then, the Hamiltonian for the rigid rotator is

$$H = \frac{J^2}{2I} \quad (16)$$

where \mathbf{J} is the total angular momentum operator and I is the moment of inertia about the center of mass.

$$I = \mu r_e^2 \quad (17)$$

The solutions to the Schrödinger equation $H\psi = E_{\text{rot}}\psi$ then provide the allowed rigid rotator eigenenergies E_{rot} and the eigenfunctions $\psi(\theta, \phi)$. Taking $\psi(\theta, \phi)$ equal to the spherical harmonics $Y_{JM}(\theta, \phi)$ satisfies the requirement that the wavefunction ψ be an eigenfunction of J^2 and J_z . i.e., ψ will satisfy Eqs. 7 and 8. Furthermore, because $H = J^2/2I$, it is then

trivial to see that the $Y_{JM}(\theta, \phi)$ are also eigenfunctions of H , giving energy eigenvalues

$$E_{\text{rot}} = \frac{\hbar^2}{2I} J(J+1) \quad (18)$$

For consistency with textbook treatments of molecular rotations this is expressed

$$E_{\text{rot}} = B_e J(J+1) \quad (19)$$

where

$$B_e = \frac{\hbar^2}{2\mu r_e^2} \quad (20)$$

is called the equilibrium rotational constant (or the rotational constant for the equilibrium separation r_e).

Non-Rigid Rotator

Returning now to Eq. 10, the rotational energy term $\hbar^2 J(J+1)/2\mu r^2$ can be evaluated perturbationally for any particular eigenstate. The result can be represented

$$E_{\text{rot}} = \frac{\hbar^2 J(J+1)}{2\mu} \left\langle \frac{1}{r^2} \right\rangle_{vJ} \quad (21)$$

where $\langle 1/r^2 \rangle_{vJ}$ represents an average or expectation value of $1/r^2$ for the particular eigenfunction specified by the quantum numbers v, J . (The rotational energy is independent of M .) For low values of the quantum numbers v and J , the radial eigenfunctions are small except near r_e . Consequently, the expectation value in angle brackets above is approximately $1/r_e^2$. Taking it equal to $1/r_e^2$, the rotational energy is that of the rigid rotator as given previously (Eq. 19). However, because of the asymmetry about r_e for the anharmonic radial eigenfunctions, the average internuclear separation tends to increase with the vibrational quantum number v thereby decreasing $\langle 1/r^2 \rangle_{vJ}$. Furthermore, because of centrifugal distortion there is an increase or stretching

of the internuclear separation as the rotation rate or J increases — again, thereby decreasing $\langle 1/r^2 \rangle_{vJ}$. An excellent job of taking into account both effects is accomplished by writing Eq. 19 as

$$E_{\text{rot}} = B_{vJ} J(J+1) \quad (22)$$

with the rotational constant given by

$$B_{vJ} = \frac{\hbar^2}{2\mu r_e^2} - \alpha_e(v+1/2) - D_e J(J+1) \quad (23)$$

The second term arises from the vibrational dependence and the third from the rotational dependence.

The total rotation vibration energy thus becomes

$$\begin{aligned} E(v, J) = & \hbar\omega_e(v+1/2) \\ & - \hbar\omega_e x_e(v+1/2)^2 \\ & + B_e J(J+1) \\ & - \alpha_e(v+1/2)J(J+1) \\ & - D_e J^2(J+1)^2 \end{aligned} \quad (24)$$

The constants of the theory are $\hbar\omega_e$, $\hbar\omega_e x_e$, B_e , α_e , and D_e . However, it should be pointed out that they can all be related to the potential $V(r)$ and the nuclear masses, c.f., Eqs. 14 and 20.

Transitions

Transitions between electronic states are typically in the visible or ultraviolet spectral range and are not observed in this experiment. The infrared spectra you will observe arise from transitions between rotation-vibration states within the ground molecular state. In this section, the selection rules for these transitions are briefly discussed.

Diatomic molecules of dissimilar nuclei have a permanent electric dipole moment \mathbf{M} oriented along the internuclear axis, i.e., $\mathbf{M} =$

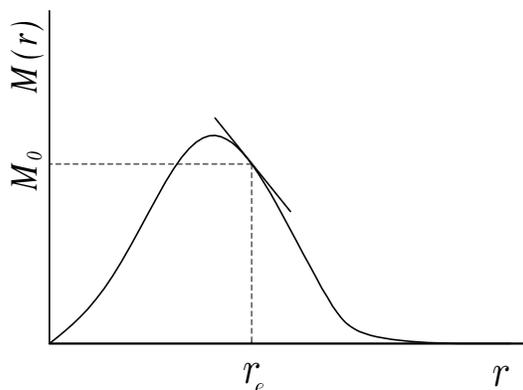


Figure 3: Typical dipole moment as a function of the internuclear separation r . In the expansion (Eq. 25) about r_e , M_0 is as shown and M_1 is the slope of the tangent line shown.

$M\hat{\mathbf{r}}$. The dipole moment arises from the arrangement of electron density in the molecule. In a totally ionic molecule, one electron from the donor atom is completely transferred to the acceptor atom giving $M = er_e$. However, even in the strongest ionic molecules the strength of the dipole moment is seldom above 50% of the fully ionic value; in the ground electronic state of HCl it is about 17 percent.

Actually, the magnitude of the dipole moment is not a constant but varies with the internuclear separation as shown qualitatively in Fig. 3. For use with eigenfunctions that stay close to r_e , it will prove useful to have a Taylor expansion for \mathbf{M} about the equilibrium separation r_e .

$$\mathbf{M} = \left[M_0 + M_1(r - r_e) + M_2(r - r_e)^2 + \dots \right] \hat{\mathbf{r}} \quad (25)$$

The probability of an electric dipole transition between two states a and b is proportional to the square of their dipole matrix element

$$\mathbf{M}_{ab} = \int \psi_a^* \mathbf{M} \psi_b d^3r \quad (26)$$

where \mathbf{M} is the dipole moment discussed above and treated as an operator with the eigenfunctions ψ_a and ψ_b . Recall that each ψ is a product of an angular and radial eigenfunction $\psi = Y_{JM}(\theta, \phi)\chi_v(r)/r$ and has three quantum numbers v, J, M associated with it. For most pairs of states, \mathbf{M}_{ab} will be very small or zero and the transition $a \rightarrow b$ will be difficult or impossible to observe. Only with certain combinations of the quantum numbers v, J, M for the two states will the dipole matrix element be appreciable and lead to transitions such as those observed in this experiment.

The angular part of the integration in Eq. 26 involves the angular eigenfunctions Y_{JM} of the ψ 's together with the factor $\hat{\mathbf{r}}$ in the dipole operator \mathbf{M} of Eq. 25. This integral is non-zero only if

$$\begin{aligned} J_b &= J_a \pm 1 \\ M_b &= M_a, M_a \pm 1 \end{aligned} \quad (27)$$

The radial part of the integration involves the radial eigenfunctions χ_v and the terms in brackets in Eq. 25. For transitions within a single vibrational state (χ_v the same for both ψ 's), a non-zero value for M_0 is enough to give a non-zero contributing factor to the integral. For transitions between different vibrational states, however, M_0 gives zero contribution due to the orthogonality of the radial eigenfunctions. The first non-vanishing contribution arises from the term including M_1 and produces the selection rule

$$v_b = v_a \pm 1 \quad (28)$$

Quadratic and higher power contributions to the dipole operator \mathbf{M} can also contribute to dipole matrix elements for $|v_b - v_a| > 1$, but the elements are small and the transitions are weak.

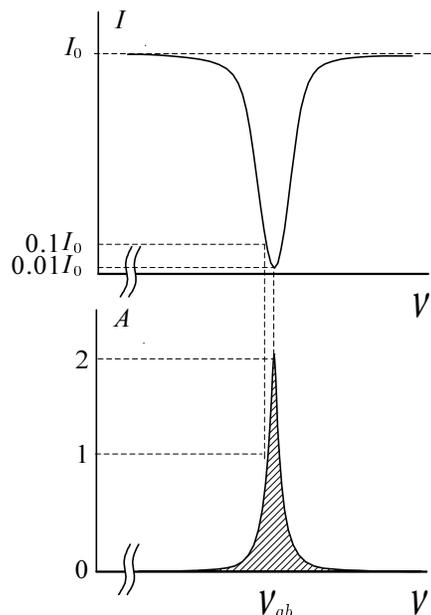


Figure 4: Isolated absorption peak. Top: The transmitted intensity I around the transition frequency ν_{ab} decreases due to sample absorption. Bottom: Same absorption peak, but the ordinate is absorbance rather than intensity.

Absorption

In this section, we would like to determine how the many possible energy levels and allowed transitions produce the absorption spectrum you will observe.

In a transition from a state of lower energy E_a to one of higher energy E_b , a photon of energy $h\nu_{ab} = E_b - E_a$ must be absorbed. The typical spectrum (transmission vs. frequency) around such an absorption frequency is as shown in Fig. 4.

Of course, to have an observable absorption peak, there must be a sufficient density of atoms in the lower energy state E_a . According to the Maxwell-Boltzmann distribution law, the number of molecules in each state of energy E is proportional to $\exp(-E/k_B T)$ where k_B is the Boltzmann constant and T is the ab-

solute temperature. This law implies that any higher energy state is less populated than any lower energy state with the population ratio given by the Boltzmann factor $\exp(-\Delta E/kT)$ where ΔE is the energy difference between the two states.

For HCl at room temperature, the first excited vibrational state lies above the ground vibrational state energy by an amount ΔE which is much greater than $k_B T$. Thus, the Boltzmann factor is quite small and there are too few vibrationally excited molecules to contribute to the absorption. Accordingly, nearly all absorption originates from the lowest $v = 0$ vibrational state and, according to the vibrational selection rule, will terminate in a $v = 1$ state.

On the other hand, the lower rotational levels lie above the ground state by an energy somewhat less than $k_B T$ and many of the lower rotational levels are thermally populated. Of course, as the J increases, the energy increases and the populations of these higher J states decreases. Within the first vibrational state, you will see that J levels up to $J = 10$ or more will be thermally populated and absorption lines like that of Fig. 4 originating from each of them will be observable in your spectrum.

The intensity of the infrared beam is low enough not to appreciably affect the populations of the molecules in the various energy levels involved in the transitions. Under these conditions, were the beam monochromatic, the change dI in the beam intensity I as it propagates through an absorber layer of thickness dx would be proportional to the intensity I , the thickness dx and the absorption coefficient α . That is

$$dI = -\alpha I dx \quad (29)$$

Exercise 3 (a) Show that Eq. 29 leads to the exponential decay of the transmitted inten-

sity with distance x traveled in the absorbing medium.

$$I = I_0 e^{-\alpha x} \quad (30)$$

The absorbance A is defined by

$$\frac{I}{I_0} = 10^{-A} \quad (31)$$

Note that for $A = 1$, $1/10$ of the intensity is transmitted, for $A = 2$ the fraction is $1/100$, etc. (b) Show that Eqs. 30 and 31 lead to

$$A = \alpha x / \log_e(10) \quad (32)$$

These results for a monochromatic beam can be extended to a source having a continuous range of frequencies by considering separately the radiation in each infinitesimal band of frequencies $d\nu$ and realizing that α will be frequency dependent.

The integrated absorbance—the shaded area in Fig. 4—is given by

$$A_{ab} = C\nu_{ab} \left(\sum_{i,j} |\mathbf{M}_{a_i b_j}|^2 \right) \rho_a \Delta x \quad (33)$$

where C is a constant, ν_{ab} is the frequency of the transition, ρ_a is the density of molecules in each of the $2J_a + 1$ degenerate eigenstates of energy E_a , Δx is the length of the absorber, $\mathbf{M}_{a_i b_j}$ is the dipole matrix element, and its sum is over degenerate states of the upper and of the lower levels.

For a given absorber and vibrational transition, Eq. 33 can be re-expressed

$$A_{ab} = C' \nu_{ab} (J_a + J_b + 1) \exp\left(\frac{-E_a}{k_B T}\right) \quad (34)$$

C' is proportional to all factors that remain constant for a given absorber such as the thickness and overall molecular density. The factor $\exp(-E_a/k_B T)$ is proportional to ρ_a and takes into account the Maxwell-Boltzmann distribution law. Finally, $J_a + J_b + 1$ is proportional to the summed term and takes into account its J -dependencies and degeneracies.

Experiment

Warnings

- **No liquids near the spectrometer.** This rule obviously applies to the lab table. The optics are sensitive to water—even high humidity—and are very expensive to replace.
- **Leave the spectrometer on at all times.** The heating provided by the source and the internal electronics help keep the insides dry. It is plugged directly into a wall outlet so you need not worry about accidentally turning it off with other electronics such as the computer.
- **Keep fingers off all window material.** This includes the windows on the absorption cell and the beam entrance and exit windows to the sample compartment.
- **Handle the HCl liquid carefully.** It is a very strong acid and can cause a serious skin burn very quickly. Wash off promptly using plenty of cold water.

Units

In the mid-infrared range of the spectrum, it is customary to give the frequency in units of cm^{-1} or wavenumbers. The frequency in wavenumbers is the frequency in Hz divided by the speed of light c in cm/s . By default, the FTIR spectrometer displays spectra in cm^{-1} with increasing frequency to the left. This need not and should not be changed. Energies are also typically expressed in wavenumbers. The energy in wavenumbers is the energy in ergs divided by hc in units of erg cm . Generally, no conversions need be applied to any reported frequencies or energies. With this convention, transition frequencies are equal

to energy level differences and constants, V_0 , $\hbar\omega_e$, $\hbar\omega_e x_e$, B_e , α_e , and D_e can all be reported and used in cm^{-1} units. One place where a conversion is needed is in the Boltzmann factor $\exp(-E_a/k_B T)$ which is only valid with E_a and $k_B T$ in common energy units ($1 \text{ cm}^{-1} \leftrightarrow 1.44 \text{ K}$). Other places where conversions are needed include the calculation of r_e from $B_e = \hbar^2/\mu r_e^2$, and the calculation of k from $\omega_e^2 = k/\mu$.

Spectrum simulation

Draw a scaled, labeled energy level diagram showing the first five rotational levels in the ground and first vibrational state. According to Eq. 24 the energy difference E_0 between the lowest rotational levels ($J = 0$) in these two vibrational states is

$$\begin{aligned} E_0 &= E(1,0) - E(0,0) \\ &= \hbar\omega_e - 2\hbar\omega_e x_e \end{aligned} \quad (35)$$

and is around 3000 cm^{-1} in HCl. For your diagram do not draw this vibrational energy separation to scale—it is too large. Simply draw the $v = 1$ levels above the $v = 0$ levels. Take $D_e = 0$, $B_e = 9.75 \text{ cm}^{-1}$ and $\alpha_e = 0.5 \text{ cm}^{-1}$; this will make the rotational spacing a bit smaller in the upper vibrational state. Next, show the eight allowed transitions among these energy levels on your diagram. Calculate the transition energies (using $E_0 = 3000 \text{ cm}^{-1}$) and make a stick spectrum showing the position of each transition on a horizontal frequency axis (in cm^{-1} with increasing frequencies to the left, as in the conventional FTIR spectrum). The set of transitions in which the upper level has the higher J is called the R branch, while the P branch has this reversed. The transitions within a branch are labeled by the J of the lower level; $R(0)$, $P(1)$ would be the labeling for the lowest J transitions. Using this notation, label the four

transitions in each branch on your stick spectrum.

Measurements

Assemble an air-filled but otherwise empty cell including its silicon windows and place it in the sample area on the cell holder. Select the **Instrument|Scan...** menu item and go into the **Scan** tab. Set the **Scan range** from 3500 cm^{-1} to 1500 cm^{-1} , **Scan type** to **Background**, and the **Scan number** (number of scans) to at least 50. Then click into the **Instrument** tab and set the **Resolution** to 0.5 cm^{-1} . Click on the **Advanced** button and change the speed to 0.5 cm/s . Also set the **Apodization** to **Medium**. Apodization tries to take care of effects associated with the finite scanning distance of the movable mirror. Now, click in the **Sample** tab and supply a file name that will distinguish it as a background scan, e.g. HClDCIBKG. Click on the **Apply** and then the **Scan** button to measure the background with these settings.

With instructor supervision, fill the gas cell with one or two drops of concentrated HCl and place it back in the spectrometer. After the background scans finish, the scan type automatically switches to **Sample** so no changes are needed before clicking on the **Scan** button again to acquire a sample spectrum using the same conditions as for the background. The program will prompt you for a new file name when the spectrum is complete.

Check and notify the instructor if the transmitted intensity at the strongest peak for the H^{35}Cl spectrum is less than 5% of the off-peak intensity. With too much absorption, there may be problems with the data analysis.

When you are satisfied with your HCl spectra, disassemble the cell, wash the cell and windows with tap water, refill the cell with two or three drops of DCl and get its spectrum. When finished, disassemble and clean the cell

and windows again and place the disassembled components back in the storage box.

Preliminary Analysis

Learn how to use the **Label Peaks** peak position finding program in the **View** menu (also on the toolbar) to determine transition frequencies for all four isotopic molecules. You may need to go to **Setup|Options** item (also accessible by right clicking on the **Label Peaks** toolbar icon) and go to the **Peak** tab to adjust the **Thresholds** for what the program will label as a peak. Thresholds are set separately depending on whether you are labeling peaks on a graph of transmission or absorbance. Before labeling peaks, you should probably adjust the graph to display only the desired region of the spectrum and then afterward click on the **File|Copy to Report** menu item to copy the spectrum and peak locations to a formatted report suitable for printing. You can highlight inappropriate peak labels and delete them manually, but it may be easier to set the threshold high enough so noise peaks are not labeled even if a few desired peaks then also go unlabeled. You can then highlight only those small peaks, lower the threshold appropriately, reselect the **Label peaks**, and then hand write the peak positions on a hard copy of the printout.

The H^{35}Cl and H^{37}Cl produce a group of double peaks around 2900 cm^{-1} ; a stronger set from H^{35}Cl and a weaker set from H^{37}Cl . D^{35}Cl and D^{37}Cl produce a similar group of peaks around 2100 cm^{-1} .

Learn how to use the **Peak Area/Height...** program in the **Process** menu to determine the areas for the peaks of the D^{35}Cl , and H^{35}Cl absorbance spectrum.

Data Analysis

Obtain an estimate of B_e and α_e from an analysis of the four transitions in the center of the

measured spectrum as follows. Use your energy level diagram to determine which pair of transitions originate from the first excited rotational state ($J = 1$) (one in each branch) and which pair of transitions are excited to the first excited rotational state of the upper vibrational state. Figure out where they are in your stick spectrum and in the actual spectrum. With D_e neglected, show that the separation between lines is predicted to be $6B_e - 9\alpha_e$ for one pair and $6B_e - 3\alpha_e$ for the other. Use the measured frequencies for these four lines from your H^{35}Cl spectrum to determine B_e and α_e for this isotope.

You can also perform a linear regression to fit the observed frequencies, and the fitting parameters can then be used to determine B_e , α_e , and D_e more accurately.

Exercise 4 *To derive the fitting formula, first write down the two formulas for the transition energies predicted by the selection rules;*

$$E_R = E(v_b = 1, J_b = J_a + 1) - E(v_a = 0, J_a) \quad (36)$$

$$E_P = E(v_b = 1, J_b = J_a - 1) - E(v_a = 0, J_a) \quad (37)$$

Next, use Eq. 24 to expand the right side of these equations in terms of $\hbar\omega_e$, $\hbar\omega_e x_e$, B_e , α_e , D_e and J_a . If you do this correctly, your formulas should become identical functions of x with the substitution $x = J_a + 1$ for the R branch of transitions and $x = -J_a$ for the P branch of transitions. Show that this substitution results in the following formula for both the R and P branch;

$$E_x = E_0 + 2(B_e - \alpha_e)x - \alpha_e x^2 - 4D_e x^3 \quad (38)$$

where $E_0 = \hbar\omega_e - 2\hbar\omega_e x_e$.

Make a spreadsheet table of the measured frequencies in cm^{-1} (E_x in cm^{-1}) vs. x and perform a polynomial regression analysis. Then, determine the molecular constants

E_0 , B_e , α_e and D_e from the fitted coefficients. Note that the constant in the fitting formula can only determine E_0 ; $\hbar\omega_e$ and $\hbar\omega_e x_e$ can not be determined separately. Compare your results with those of Table 1, a compilation from Ref. 3.

CHECKPOINT: The spreadsheet should be complete with peak frequencies for all 4 isotopes tabulated and a regression analysis should be completed for at least one isotope. Absorbance areas should be measured for $D^{35}Cl$ and tabulated in the spreadsheet.

Comprehension Questions

1. Compare the results of the quick analysis, the regression analysis and the reference values.
2. True or false? The Born-Oppenheimer approximation predicts that $V(r)$ is the same for all four isotopes. Explain. For each of the four isotopes:
 - Calculate the equilibrium separation r_e from Eq. 20.
 - Calculate the spring constant k from Eq. 14. Assume $\omega_e x_e = 0$ so that $E_0 = \hbar\omega_e$.

Explain how a comparison of these values supports or shows a lack of support with the answer to the true/false statement.

3. The equation

$$A_{ab} \approx C''(2J_a + 1) \exp[-hcB_e J_a(J_a + 1)/k_B T] \quad (39)$$

is Eq. 34 with the following approximations. The factor ν_{ab} is neglected as it varies only slightly over all absorption lines of a given isotope. Only the largest term in the dependence of E_a on J_a is used

in the exponential. The factor $2J_a + 1$ is used to approximate $J_a + J_b + 1$. In this alternate form, A_{ab} depends only on J_a . The expression can then be used to predict J_a^{\max} , the value of J_a which should produce the largest peak area. Hint: take a derivative with respect to J_a . Determine the predicted dependence of J_a^{\max} on T and B_e and compare with your spectra.

4. Determine a few ratios (peak heights or areas of absorbance graphs for transitions with the same quantum numbers but having different chlorine isotopes. Look up the natural abundance of ^{35}Cl and ^{37}Cl isotopes and compare with your measurements.
5. Add a column to your data table for the absorbance area (as determined from the Peak Areas/Height... program in the Process menu) for each peak in the $D^{35}Cl$ spectrum. You will have to learn (or ask the instructor) how to set the background level and cursors used for finding these areas. However, be sure to first apply the Equations|Scale $\times 1000$ (in the Process menu) on the absorbance spectrum (which simply multiplies the spectrum by 1000) so that the area determinations will have enough significant figures.

Analyze this data according to Eq. 34 to determine the temperature. Hint: isolate the exponential term, take a natural logarithm of both sides, then plot and fit a straight line expression with E_a as the abscissa and a predicted slope of $hc/k_B T$. It might be useful to add columns for J_a and J_b for each transition as well as a column for E_a using your fitted parameters. For the E_a column, you need only include J_a dependent terms; a constant offset in E_a will not effect the slope. Determine

Isotope	μ	$\hbar\omega_e$	$\hbar\omega_e x_e$	B_e	α_e	$D_e(\times 10^{-4})$	r_e
H ³⁵ Cl	0.97959272	2990.946	52.8186	10.59341	0.30718	5.3194	0.127455
D ³⁵ Cl	1.90441364	2145.163	27.1825	5.448794	0.113291	1.39	0.1274581

Table 1: Molecular constants for H³⁵Cl and D³⁵Cl from K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. 4. All quantities in units of cm⁻¹ except μ (in amu) and r_e (in nm).

the temperature T from the slope. Why doesn't the $\times 1000$ multiplier affect this determination?

This technique is used with astrophysical spectra to determine temperatures of interstellar gas clouds.

- Use your data to determine the classical amplitude of the vibrations in the $v = 0$ and $v = 1$ states. This is roughly the extent of the vibrational eigenfunctions. Assume $V(r) = \frac{1}{2}k(r - r_e)^2$ and $E = (v + 1/2)\hbar\omega_e$. Also express the amplitude as a fraction of r_e .
- Calculate the ratio of HCl molecules in the $v = 0, J = 0$ state to those in the $v = 1, J = 0$ state. Calculate the ratio of HCl molecules in the $v = 0, J = 0$ state to those in the $v = 0, J = 1$ state. How are these calculations relevant to this experiment?