SYNTHESIS AND PHYSICAL PROPERTIES OF HYDROGEN AND DEUTERIUM HALIDES

OVERVIEW

10/9/2013 CF

Specific Objectives for This Series of Experiments on Diatomic Molecules

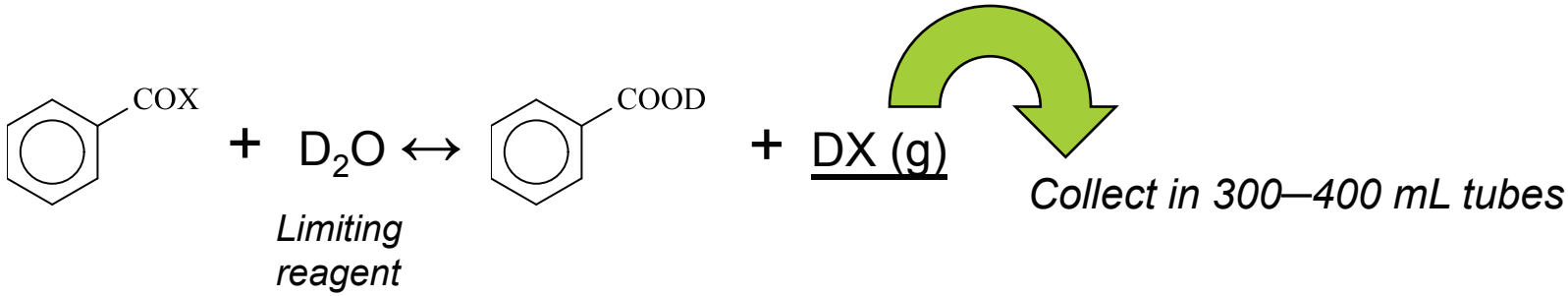
1. To obtain experimental skills in synthesizing and handling **gas** on a **vacuum** line. Use of ideal gas law.
2. To apply **interferometry** to the determination of the index of refraction and molar refractivity of HCl.
3. To determine the dipole moment of HCl from **dielectric constant** measurements.
4. To obtain familiarity with the high-resolution Mattson **FTIR** instrument and with the recording of gas phase infrared spectra. The quantitative analysis of these makes use of the harmonic oscillator and rigid rotor models of **quantum mechanics**.
5. To apply gas-phase Raman Spectroscopy to the determination of the **equilibrium constant** of an isotopic exchange reaction for comparison with a value calculated from the spectroscopic data and from statistical thermodynamics.
6. To **compare** these measured physical quantities with those calculated by quantum mechanics.

Much of the emphasis will be on making *accurate* measurements of physical quantities and on successfully analyzing these results to obtain molecular parameters of interest. Pay attention to the way that you can derive **microscopic parameters** from **macroscopic observables**.

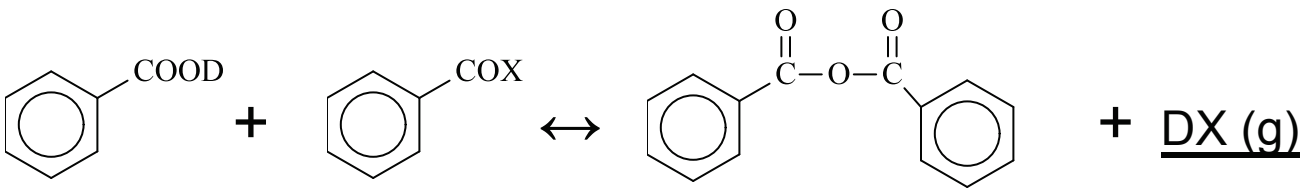
The use of spreadsheets and least-squares analysis to aid in the calculations will be stressed. An early review of the relevant theory in your physical chemistry text and one or more of references 1-9 is recommended. **Make Excel your expertise and you can benefit from it in the future!**

Synthesis of Gaseous Diatomic Molecules

Synthesis of DX (X= Cl, Br)



Side Reactions:



$$H_2O + DX \leftrightarrow HDO + HX\ (g)$$

So we are effectively getting a HX/DX mix if there is H_2O present.

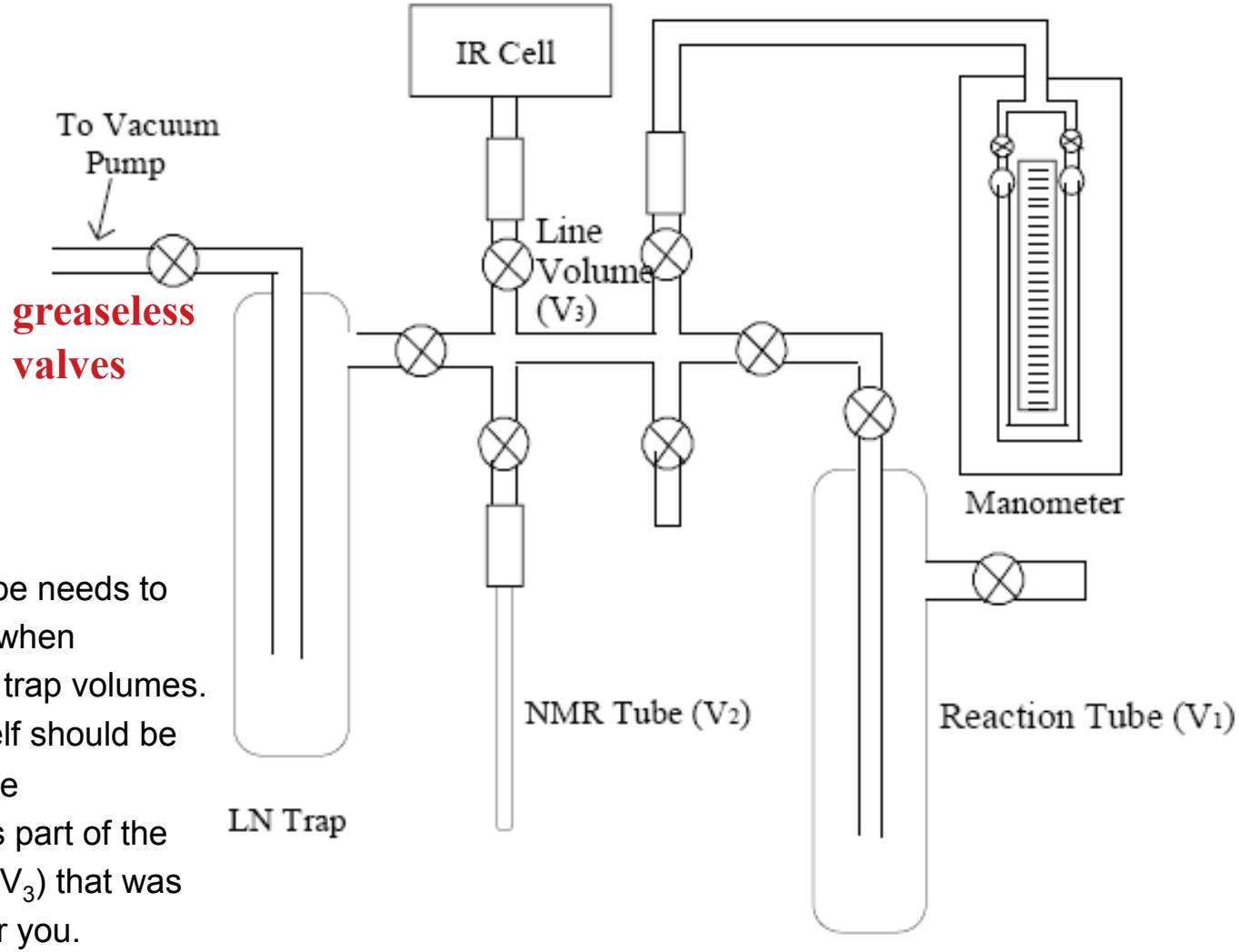
But from a quantitative point of view, if we have completely dry vacuum line system and moisture-controlled oven, we should not get HX and we can simply use our product gas pressure to deduce the yield. So if we want to estimate the reaction yield, we should determine how much deuterated gaseous molecules that we have in the sample mixture. Can we, at this point of the experiments?

Schematic of the synthesis setup for gaseous diatomic molecules

Fig. 1. Vacuum line schematic

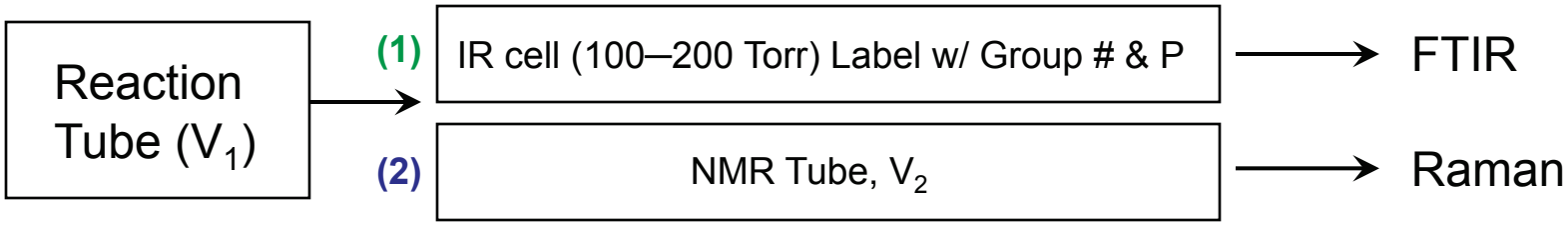
Ideal gas law: pV=nRT

Units: *p*, pressure, 1 pascal= 1 N/m^2=1 J/m^3= 10^{-5} bar.
1 atm=101,325 pascal= 1.01325 bar=760 torr.
V, volume, m^3; R, gas constant, 8.3145 J/(mol*K); T, temp in Kelvin.



The NMR tube needs to be attached when you get your trap volumes. The tube itself should be closed but the connection is part of the line volume (V_3) that was measured for you.

Vacuum Line Transfer after Reaction in the oven



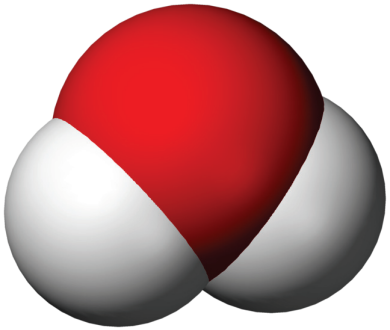
(1) Attach both NMR and IR cells to the vacuum line and evacuate them.
Attach the reaction tube (V_1) to the vacuum line and freeze your gaseous products using LN_2.
Close off vacuum and open the reaction tube to the system to check if there's any residual air.
Pump off any residual air, close off the reaction tube and warm to room temperature (~295 K).
Allow the gaseous products to fill V_1+V_3, so $P_1V_1=P_2(V_1+V_3)$, deduce P_1 and get the yield!
Close V_1, open the valve to the IR cell and note the pressure drop. The new reading is ~100 Torr.

(2) Fill the NMR tube to ~1 bar (~750 Torr) by freezing the appropriate amount of gas into the tube at 77 K.
At room temperature, $750*V_2=P_m*V_3$. So $P_m\approx750*25/250=75$ Torr. Adjust the line pressure to this value (by opening the reaction tube slowly to the line and monitoring the pressure reading).
Close V_1, open the valve to the NMR tube and freeze the gas into the NMR tube using LN_2.
Close the NMR tube when the pressure reading drops to zero. Pump on the frozen sample if needed.
Label with your group number, names, date and exact pressure. Record everything in the lab notebook.

<u>Then clean the reaction tube in the hood carefully according to lab manual instructions.</u>

Some parameters about D_2O for your calculations

D_2O is commonly referred as the “heavy water”. The isotopic substitution with deuterium alters the bond energy of the water’s H—O bond, altering the physical, chemical, and, especially, the biological properties of the pure, or highly-enriched, substance to a degree greater than is found in most isotope-substituted chemical compounds. Because there are only three atoms in water!



Its density is 1.1056 g/mL, liquid (20°C);

1.0177 g/cm^3, solid (at m.p.).

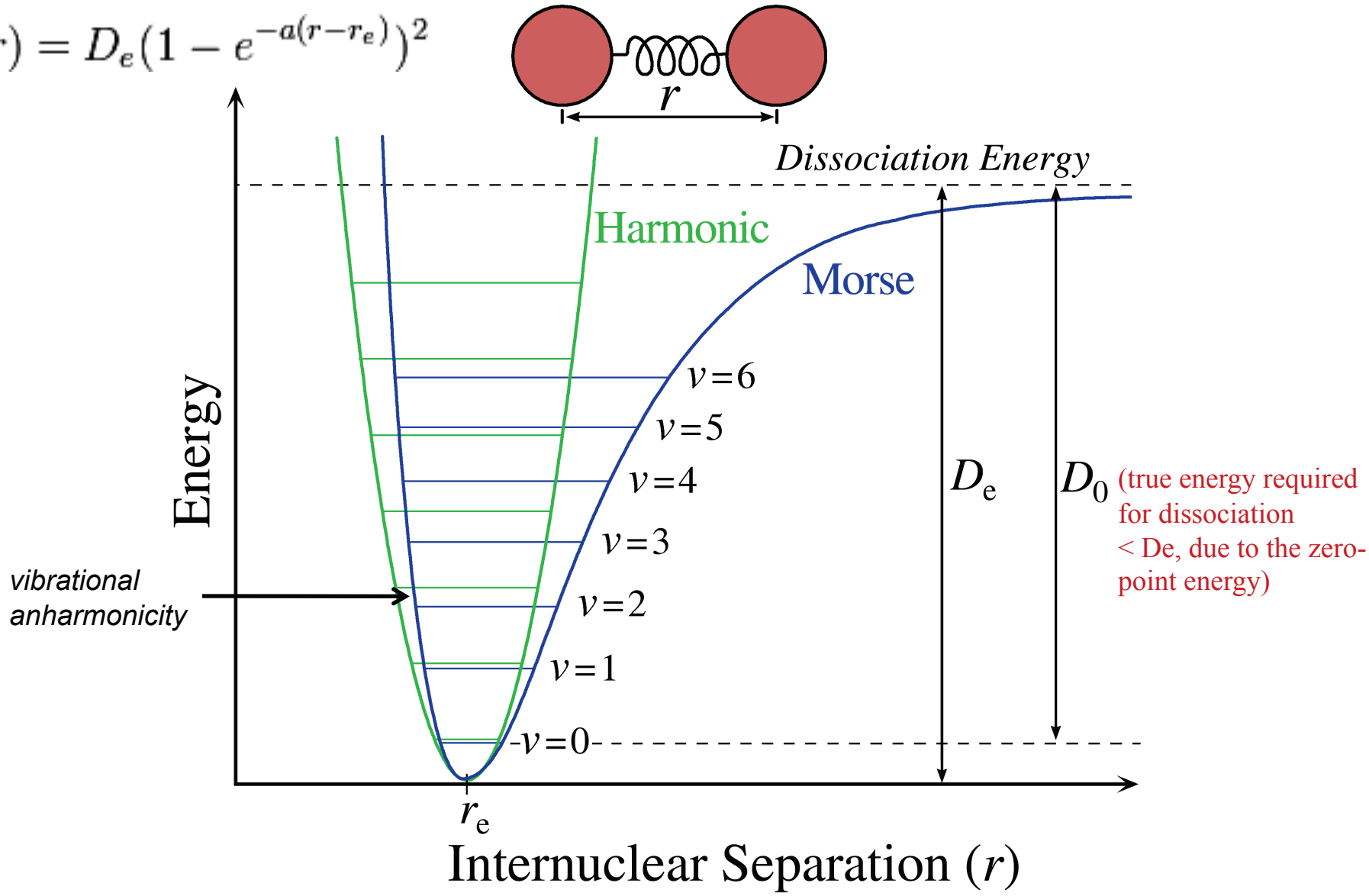
Its b.p. is 101.4 °C, 214.56 °F (374.55 K).

Its dipole moment is 1.87 D. (1.85 D for H_2O)

Fundamental Physical Chemistry Properties of Diatomic Molecules

In reference to an atom, a diatomic molecule assumes **2** new modes: **vibration** about the equilibrium distance r_e, and **rotation** about the center of mass.

$$V(r) = D_e(1 - e^{-a(r-r_e)})^2$$

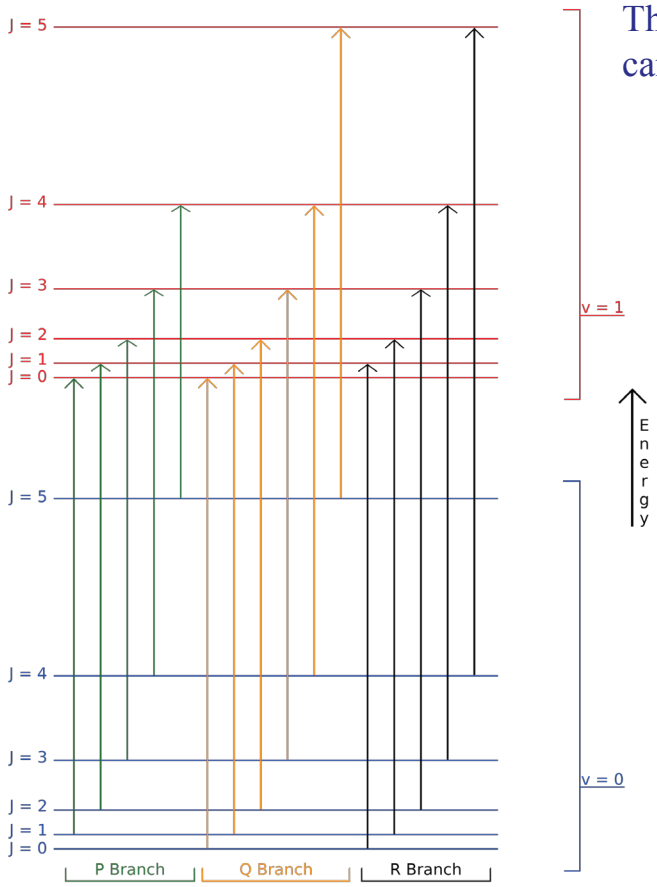


Vibrational and Rotational Levels of the Diatomic Molecules

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}+V(r)\right)\Psi(v)=E(v)\Psi(v),$$

$$E_v/hc=\omega_e(v+1/2)-\omega_e\chi_e(v+1/2)^2$$

— in which the constants ωe and $\omega e\chi e$ can be directly related to the parameters for the Morse potential.



The rotational energy levels $F(J)$ of the molecule based on rigid rotor model can be expressed as

$$F(J)=\tilde{B}_e J(J+1) \qquad J=0,1,2,...$$

where B_e is the rotational constant of the molecule and is related to the moment of inertia of the molecule (equivalent for linear molecule) as

$$\tilde{B}_e=\frac{h}{8\pi^2 c I_B}$$

$$\Delta J=J'-J''=\pm 1$$

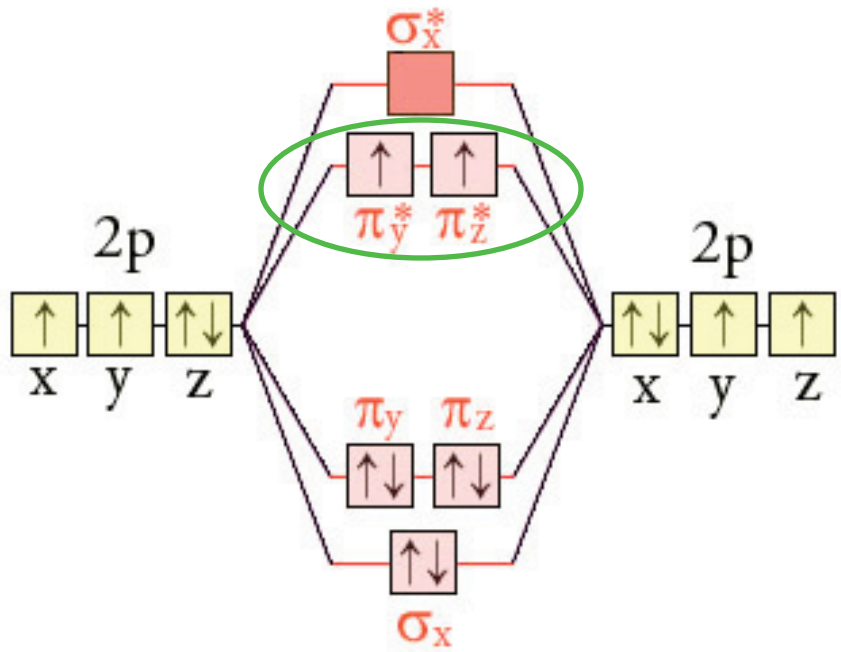
$$\tilde{\nu}_{J'\leftrightarrow J''}=F(J')-F(J'')=2\tilde{B}_e(J''+1) \qquad J''=0,1,2,...$$

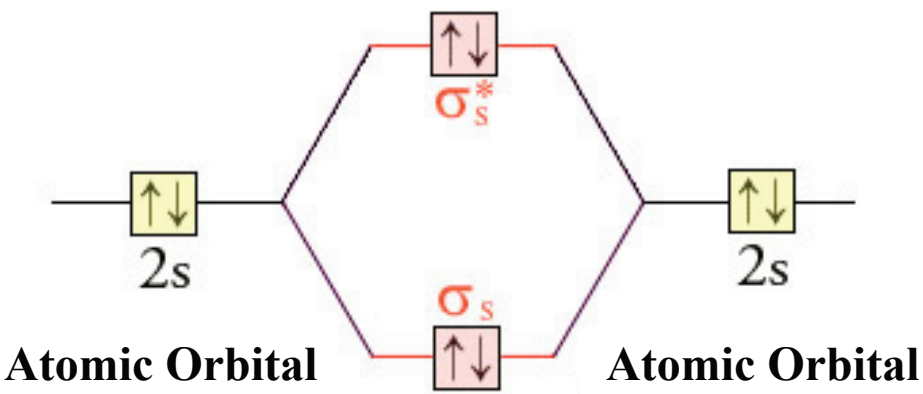
For non-rigid rotor model, we should consider changes in the moment of inertia of the molecule. Two primary reasons for this are the *centrifugal distortion* and the *effect of vibration on rotation*.

$$F(J)=\tilde{B}_e J(J+1)-\tilde{D}_e J^2(J+1)^2 \qquad J=0,1,2,...$$

$$\tilde{\nu}_{J'\leftrightarrow J''}=2\tilde{B}_e(J''+1)-4\tilde{D}_e(J''+1)^3 \qquad J''=0,1,2,...$$

Special Case: Triplet Oxygen that has the Q Branch

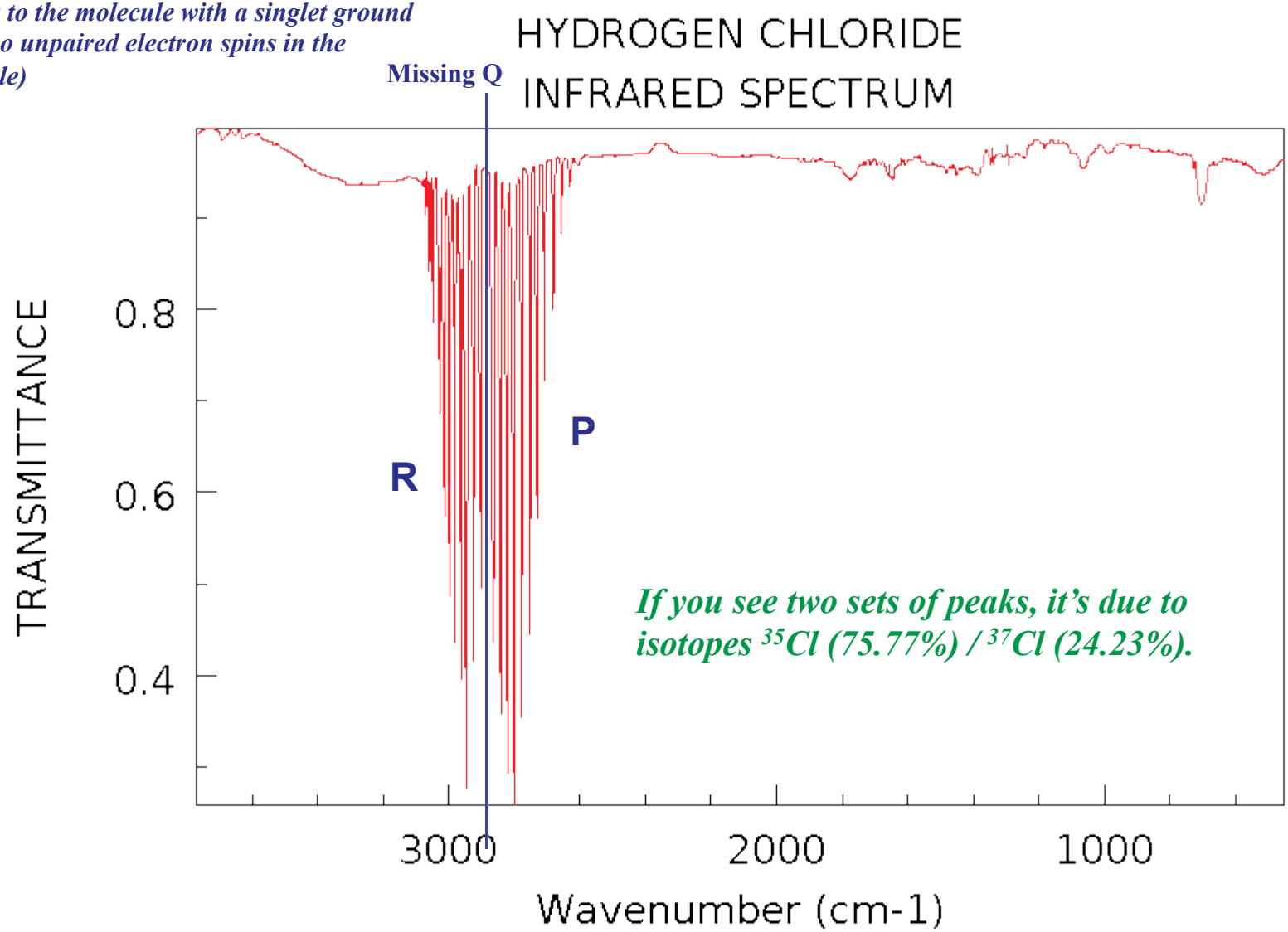




Valence Orbital

Typical Rovibrational Spectra of HCl

Applies to the molecule with a singlet ground state (no unpaired electron spins in the molecule)



If you see two sets of peaks, it's due to isotopes ^{35}Cl (75.77%) / ^{37}Cl (24.23%).

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Procedure of Taking FTIR Spectra of Gaseous Diatomic Molecules

1) Take spectra with TA's help;
2) Pick peaks and identify frequencies (cm^{-1}), obtain the m values (check for accuracy);
3) Plot the observed transitions $\nu(m)$ in cm^{-1} vs m to see if it forms a straight line. Note that you need to select multiple columns of x-input (2m, $-m^2-$2m, w/ or w.o. $-4m^3$) to do the linear regression, and find the *p*-level probability test (see manual posted online).
4) Measure the deuteration level from the peak total intensities.

Index of Refraction

Induced Dipole: $\mu_{ind} = P_m \cdot E$ where P_m is the total molar polarization, and E is the external electric field.

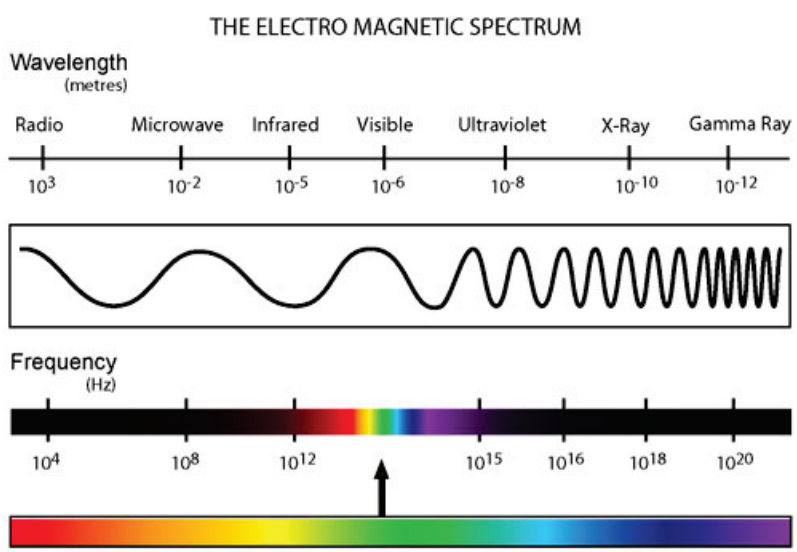
$$P_m = P_e + P_a + P_\mu$$

P_μ ← orientation polarization (Radio-Microwave)

P_e: electronic polarization (IR-VIS-UV)

P_a: atomic polarization /distortion (Microwave-IR)

The various components are excited by different fields so P_m depends on field frequency f.



If working in visible wavelength then P_a and P_μ drop out,

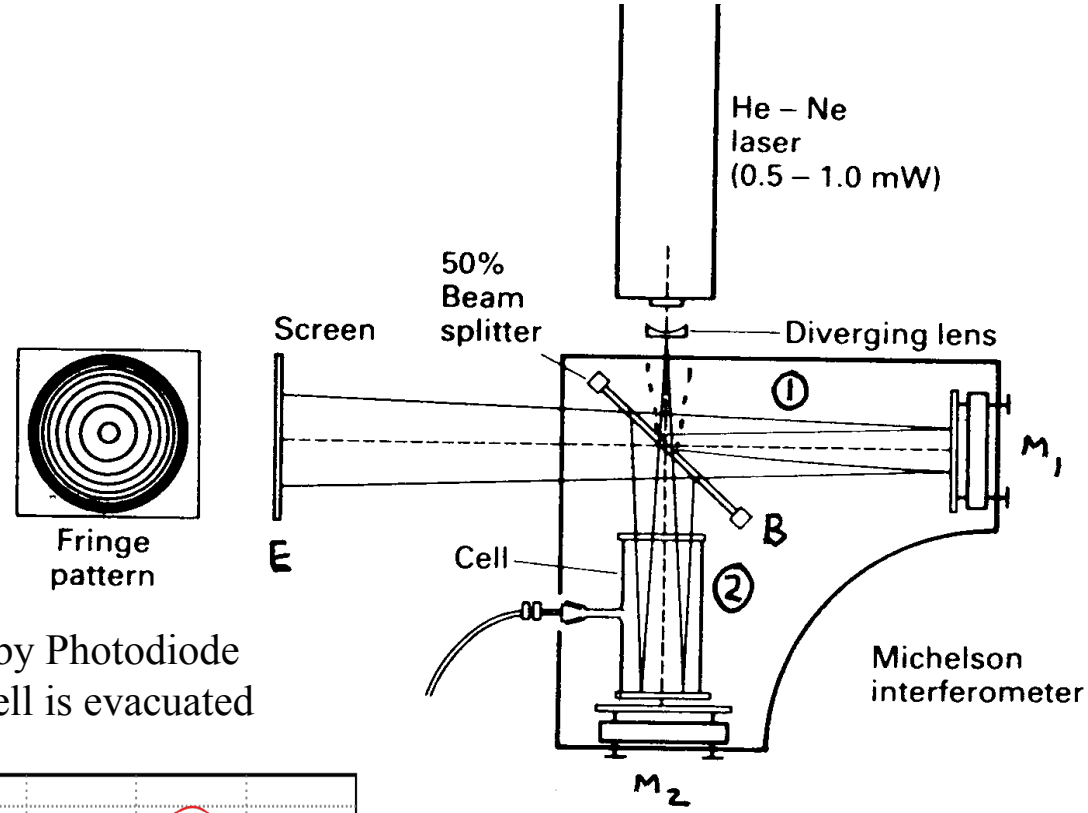
$$P_m = P_e = R_m = {4\pi N_0 \alpha_e}/{3}$$

α_e is the polarizability (unit of volume) and it plays an important role in Raman experiments later.

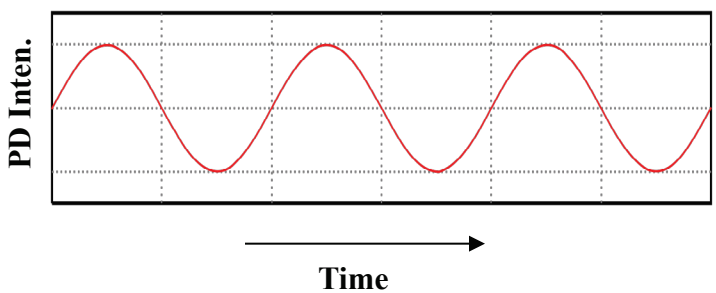
And the goal is to measure $n \rightarrow R_m \rightarrow \alpha_e \rightarrow r_e$

by interferometry, where r_e is the radius of "spherical" HCl.

Interferometry Measurement by a Michelson Interferometer



Count by Photodiode
as the cell is evacuated



You'll see the fringes appearing in the center, count them as the chamber is pumped out. Obtain n.

$$n-1 = \Delta N \cdot \lambda / 2d.$$

λ=632.8 nm, d is the length of the gas chamber.

Fill the cell with ~1 atm HCl and record the exact pressure and room temperature T(K). You need to correct the reading to STP conditions (760 Torr, 273 K) if you plan to use STP in calculation.

The van der Waals Equation of State to Account for Real Gas Behaviour

$$\left(p + a\left(\frac{n}{\tilde{V}}\right)^2\right)(\tilde{V} - nb) = nRT$$

where n is the amount of substance of the gas in question, and a and b are adjustable parameters. a is a correction for intermolecular forces and b corrects for finite atomic or molecular sizes; the value of b equals the volume of one mole of the atoms or molecules. Their values vary from gas to gas.

describes a weak attractive force among molecules (aka the van der Waals force), which increases when n increases or V decreases and molecules become more crowded together ---- effective pressure term

The molecular interaction is strongly repulsive at very short distance; thus exclusive of space as the molecules execute random motion