

Raman Spectroscopy

Once the Schroedinger equation is solved for the hydrogen atom, two paths to greater complexity are possible. The first is to retain the simplicity of the system (that is, stick to the hydrogen atom), but undertake a more sophisticated treatment. This leads to spin-orbit coupling, hyperfine structure, the Lamb shift, and so on. The other option, is to retain the simple treatment but increase the complexity of the system instead. This choice, which might be called the chemical rather than the physical approach, leads to more complicated atoms, molecules, and to the effects of vibrations and rotations that we will investigate in this laboratory.

INTRODUCTION: VIBRATIONS AND ROTATIONS, RAMAN SCATTERING

A universe made of only pure elements would be far less interesting than our own. The great variety of the physical, chemical, and most importantly biological environment, in fact, is due to the ability of different atoms to form chemical bonds. These are categorized into four main groups:

- 1) *Covalent* or *homopolar* bonds form between similar atoms (H_2 , O_2 , CO_2 , *etc.*). The electron wavefunctions (orbitals) are significantly modified to allow electron “sharing.”
- 2) *Ionic* or *heteropolar* bonds form between dissimilar atoms ($NaCl$, LiF , *etc.*). Electrons are essentially transferred from one to another, and electrostatic forces bind the resulting ions.
- 3) *Hydrogen bonds* form when two atoms are linked by a hydrogen nucleus.
- 4) Van der Waals forces form weak *molecular* bonds. There is virtually no overlap of the wavefunctions, and the strength depends upon multipole moments of the charge distribution.

The first two bond types are strong interactions (binding energies on the order of eV) in which the charge structure of the molecule is very different from that of the constituent atoms. The last two are weaker (binding energy on the order of 0.1 eV). While not relevant to this lab, such bonds are particularly important in biological systems and so are by no means uninteresting.

The Born-Oppenheimer Approximation

To describe the chemical bond in quantum mechanics we first decouple the electronic and nuclear motion via the Born-Oppenheimer approximation (Max Born, English: 1882-1970, 1954 Nobel; and J. Robert Oppenheimer, American: 1904-1967; the “Father of the Atomic Bomb”). Because nuclei are relatively slow compared to electrons, electronic states evolve *adiabatically* with nuclear motion. For small nuclear kinetic energy the molecular wavefunction is then of the form

$$\Psi_{nv}(R) = \Phi_{nv}(R) \phi_n(r,R), \quad (1)$$

where $\phi_n(r,R)$ is the n^{th} electronic wavefunction for fixed positions of the nuclei (separation R) and $\Phi_{nv}(R)$ is the nuclear wavefunction. The electronic forms are determined from the Hamiltonian

$$[T_e + V_{Ne}(r,R) + V_{ee}(r)] \phi_n(r,R) = E_n(R) \phi_n(r,R), \quad (2)$$

where T_e is the electron kinetic energy, $v_{Ne}(r,R)$ is the electron-nuclear Coulomb potential, and $V_{ee}(r)$ is the electron-electron potential. The nuclear positions are assumed fixed and are treated as

parameters. The Coulomb repulsion of the nuclei is accounted for in an effective nuclear potential

$$\varepsilon_n(R) = E_n(R) + V_{NN}(R), \quad (3)$$

and the Schrödinger equation for the nuclei is

$$[T_N(R) + \varepsilon_n(R)] \Phi_{nv}(R) = E_{nv} \Phi_{nv}(R). \quad (4)$$

For small vibrations of the nuclei about their equilibrium positions, the potential is approximately parabolic and the problem reduces to a coupled set of simple harmonic oscillators. In general, therefore, the normal coordinates of the nuclear problem are obtained through classical physics.

Simplest Case: The Hydrogen Molecule

The case of H_2^+ (two protons and one electron) is covered in Baym (Chapter 21), where the form of $\varepsilon(R)$ is derived. The variational method is used in which the trial wavefunction (a linear combination of hydrogen 1s states) is localized on each nucleus. Two solutions emerge, one with even and the other with odd parity. The corresponding results are

$$\varepsilon(R) = -13.6 \text{ eV} \frac{2 \left(\frac{1}{a_0} + x \right) e^{-2x} - 1 \pm \left[\frac{1}{a_0^2} - 1 \left(\frac{1}{a_0} + x + \frac{x^2}{3} \right) - 2 \left(\frac{1}{a_0} + x \right) \right] e^{-x}}{1 \pm \left(\frac{1}{a_0} + x + \frac{x^2}{3} \right) e^{-x}}, \quad (5)$$

where a_0 is the Bohr radius (0.529 Å), $x=R/a_0$, and the “±” refers to even and odd parity states, respectively. The latter has no bound state, but the former has a minimum at 1.3 Å nuclear separation ($x=2.5$), reasonably close to the experimental value of 1.06 Å (Fig. 1).

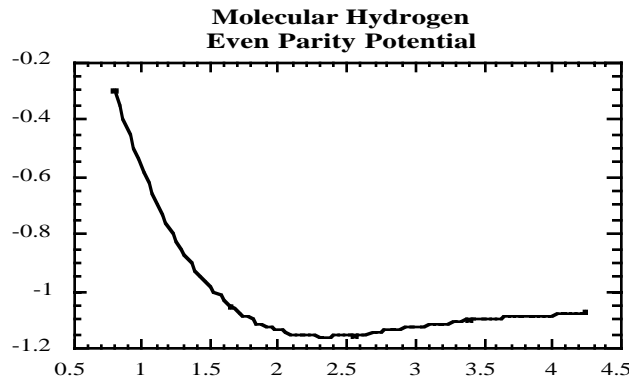


Figure 1: The even-parity potential function for molecular hydrogen, with $x = R/a_0$.

Vibrational and Rotational Modes

Classically, atomic nuclei remain at the equilibrium separation only at very low temperature. For small displacements the potential is approximately parabolic and so the molecule vibrates with simple harmonic motion. Quantum mechanics gives discrete vibrational states with energy

$$E_n = (n+1/2) S\omega, \quad (6)$$

where ω is the natural frequency of the oscillator. Assuming that the molecule is not spherically symmetric it can also possess quantized rotational modes with energies

$$E_l = (S^2/2I) l(l+1); \quad l = 0, 1, 2, \dots \quad (7)$$

Although the total energy becomes complicated when electronic, vibrational, and rotational states are all taken into account, one can simplify by considering a manifold of closely spaced vibrational and rotational states superimposed upon the widely-spaced electronic levels. Transitions between electronic states are thus “smeared out” by the possible variations in n and l . Raman scattering allows us to disentangle these contributions.

Raman Scattering

Raman scattering (Sir Chandrasekhar Venkata Raman, Indian: 1888-1970; 1930 Nobel) is due to the relationship between scattering and the vibrational and rotational modes. A classical analysis of the vibrational contribution provides an illustration, which we begin with the molecular electronic polarizability α . This relates the induced dipole moment p to the local electric field E :

$$p = \alpha E. \quad (8)$$

It is easy to imagine that α is a function of atomic separation R and therefore depends on the vibrational state. This varies the polarizability in time, as

$$\alpha = \alpha_0 + \alpha_1 \cos \omega_0 t. \quad (9)$$

Suppose that we now shine a beam of monochromatic light of frequency ω on an ensemble of molecules and measure the scattered light propagating perpendicular to the incident beam. What does its spectrum look like? Consider the polarization density

$$P = N\alpha E = N\alpha E_0 \cos \omega t = N\alpha_0 E_0 \cos \omega t + N\alpha_1 E_0 \cos \omega_0 t \cos \omega t, \quad (10)$$

of which the last term can be rewritten

$$(N\alpha_1 E_0/2) [\cos(\omega+\omega_0)t + \cos(\omega-\omega_0)t]. \quad (11)$$

Thus some terms in the polarization density, which determines the scattered spectrum, oscillate at frequency shifted by $\pm\omega_0$ (the vibrational mode frequency) from the incident radiation. We use the convention that labels the downshifted frequency $(\omega-\omega_0)$ the *Stokes* signal and the upshifted one

$(\omega+\omega_0)$ the *anti-Stokes* signal.

A rigorous quantum mechanical treatment also shows Stokes and anti-Stokes frequencies for vibrational levels as well as for rotational state transitions, determines the conditions for Raman activity through selection rules, and generates the relative intensities of the Stokes and anti-Stokes contributions. While we will not perform this derivation here, we can graphically represent the process using the *virtual transition*, an important concept that will at least help illustrate these effects.

A virtual transition can occur for a photon whose energy is below the ground-to-first-excited-state gap (Fig. 2). A strong light source can produce a distorted (perturbed) excited state due to the change in the potential caused by the external electromagnetic field, represented as a virtual superposition of the free molecular states. Raman Scattering consists of a dipole transition from the ground state to this new state, followed by a transition back down to another ground state with different rotational and vibrational energy. The process is “virtual” because the two transitions are not directly observed. Because there are fewer molecules in the higher-energy rotational and vibrational states, the Stokes process (final state energy greater than initial state energy) should be more common than the anti-Stokes process (in which the reverse is true). Therefore it should be more common to see scattered photons shifted to lower rather than higher frequency.

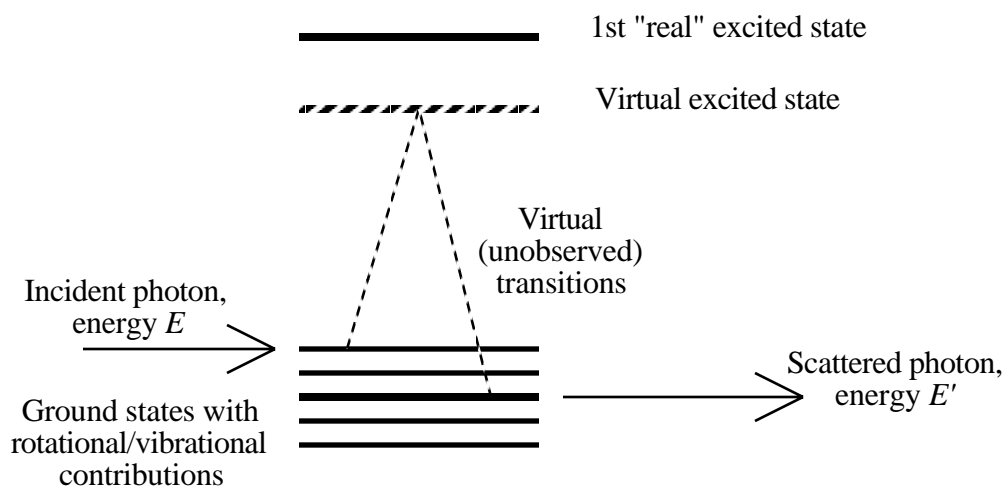


Figure 2: Raman scattering through a virtual state. The photon energy is shifted by the difference in rotational and vibrational energies of the initial and final states.

THE RAMAN SCATTERING APPARATUS

Raman scattering is an important spectroscopic tool because it allows precise measurements of small energy transitions without requiring far infrared sources and detectors. In addition the setup is simple because the energy of the scattering source is not critical (except for *resonant* Raman Scattering, a subject we won't discuss).

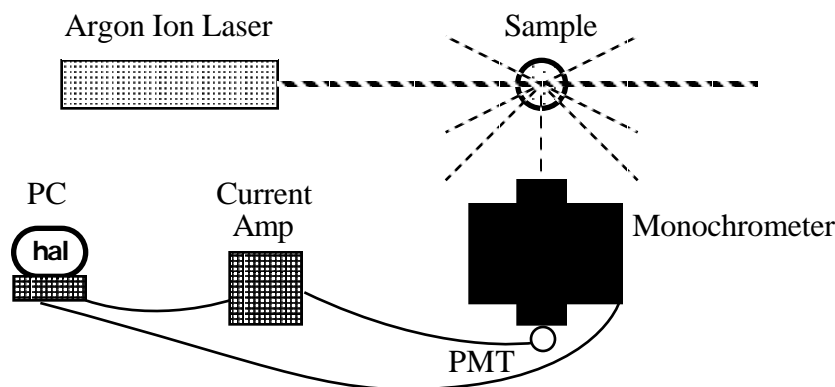


Figure 3: The Raman scattering equipment.

Fig. 3 shows the experimental setup. A monochromatic light beam (the argon laser) is focused on a liquid sample. A small amount of light is scattered in all directions, most of which is Rayleigh scattering (elastic scattering without change in the photon energy). Some, however, is the result of inelastic Raman scattering. The monochromator observes the resultant signals using a photomultiplier tube (PMT) to convert light intensity into an electronic signal. The entire apparatus is computer controlled. The monochromator is a basic Czerny-Turner spectrometer (Fig. 4).

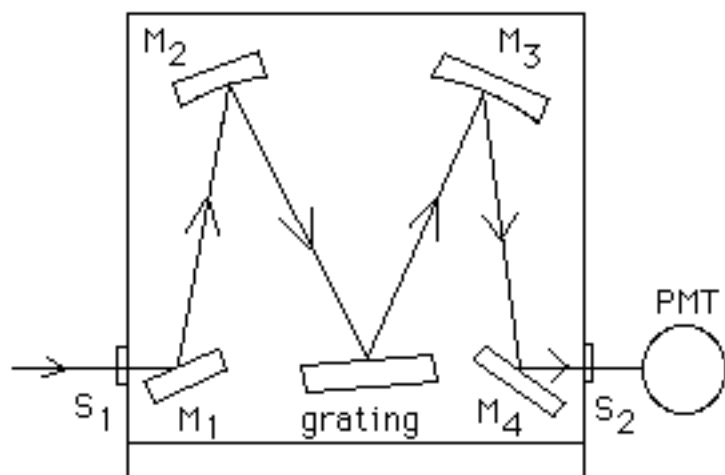


Figure 4. The Czerny Turner spectrometer. The entrance slit is S_1 , M_1 - M_4 are front-surface mirrors, and a photomultiplier detector is situated at the exit slit (S_2).

Light entering the Czerny-Turner device is directed to a diffraction grating, which can be rotated to direct light of different wavelengths to the exit slit. This wavelength selection technically makes the instrument a *monochromator*, but the term spectrometer is also commonly used. All of the mirrors are front-surface to avoid aberrations inside the optical elements (remember that the index of refraction is a function of wavelength, so normal silver-backed glass mirrors would not affect all colors of light equally). Mirrors M_2 and M_3 are spherical rather than flat mirrors so that an image of S_1 is formed on the grating. The narrower the slit, therefore, the better the resolution (and, of

course, the less light will be observed). As the grating is rotated the spectrum can be recorded. The photomultiplier signal is amplified and converted to digital via a current amplifier and PC running Labview.

This experiment employs high voltage for the photomultiplier and the gas discharge tube. Use caution whenever manipulating either of these devices. Avoid touching hot discharge tubes as they could cause burns and/or shatter.

The spectral resolution depends upon the quality of the optics, the length of the monochromator, the external optics, and the entrance and exit slit widths; of these, only the latter two can be changed. Begin the lab by varying these in order to obtain the best possible separation of the Hg Doublet at 5789.7 and 5790.7 Å. Determine the resolution of the spectrometer from the full width at half maximum (fwhm) of the peak

The spectrometer does have a wavelength indicator on it, but for accurate measurements it is necessary to calibrate it. This can be done by observing additional Hg lines (see the MIT tables) in order to find the relationship between true wavelength l and the indicated reading l' . Use a linear approximation:

$$l = a + bl' \quad (12)$$

THE RAMAN SCATTERING EXPERIMENT

Never allow collimated laser light to enter the eye. Be particularly mindful of reflected beams, which can appear unexpectedly. The argon laser used in this lab is capable of permanent eye damage and is strong enough to burn exposed skin. Proper safety goggles must be worn at all times.

Acquire data consisting of the light intensity (proportional to the Raman scattering cross section) as a function of frequency. The sample is the triatomic molecule carbon disulfide (CS_2) and there are two vibrational modes. One mode is Raman active and the other is not, though it can be observed due to collisions. Classically, collisions truncate the oscillation cycle and allow a non-zero contribution to the light radiation (it would be zero otherwise). Use these data to determine which vibrational ground states are populated and which transitions are allowed.

Goals

A complete laboratory report will

- Describe Raman Spectroscopy,
- Explain Raman active and Raman non-active modes,
- Calculate the vibrational energy levels,
- Compare the observed transition energies with a simple “ball and spring” model.