

The Photon as Billiard Ball: the Raman Effect

Kevin Jones, Williams College

The Raman effect¹ can be viewed as an inelastic version of the Compton effect. A photon bounces off of a molecule, leaving the molecule in a vibrationally excited state. Conservation of energy requires that the scattered photon be at a longer wavelength than the incident photon. In addition to reinforcing the lessons of the Compton effect, this experiment serves as an introduction to the use of a pulsed nitrogen laser, spectrometer and boxcar integrator. We use this as one half of a three hour lab in a junior level quantum mechanics/advanced lab course.

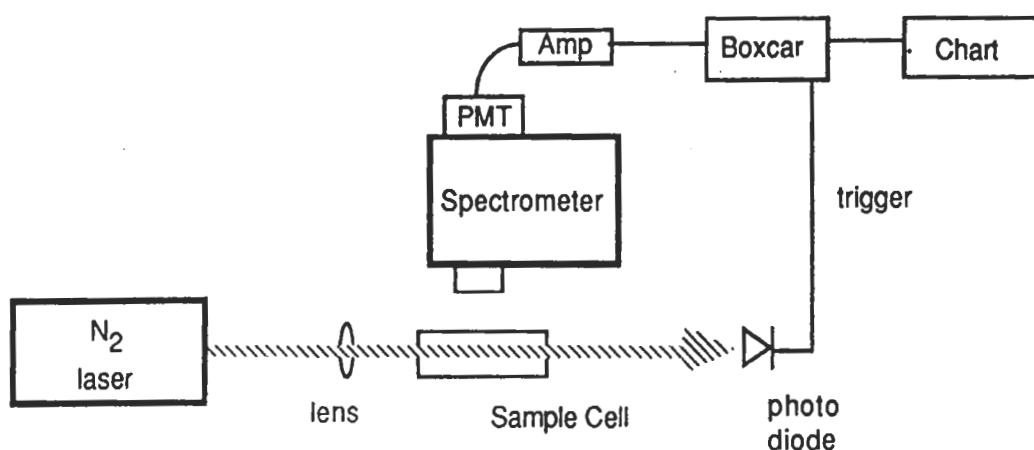


Figure 1. Experimental arrangement for observing Raman Scattering

The experiment uses a small nitrogen laser (PRA LN-120 now sold by Laser Photonics) with a energy per pulse of 70 μJ and a repetition rate of 20 Hz. A 10 cm, quartz, cylindrical, fluorescence cell (Hellma Cells) is filled with liquid benzene. A quartz lens serves to collimate or loosely focus the beam in order to reduce scattering from the cell walls. The cell is placed in front of the entrance slit of a 0.34 meter monochromator (Spex Industries 340E). The monochromator observes light scattered at approximately 90 degrees. No sophisticated light collection optics are required. A photomultiplier (such as 1P28) serves as the detector. A homemade amplifier increases the signal size and stretches the pulse length to about 10 μsec . The boxcar integrator is an inexpensive card from Evans Associates (4130 gated integrator board) which has been built into a box with switched capacitors to vary the integration time and a LS123 one shot chip to provide a variable length gate signal (total cost about \$300). The boxcar is triggered by a visible photodiode (Hamamatsu S2386-8K) used in photoconductive mode. To protect the diode, and convert the UV to visible light, a sheet of writing paper is placed over the front of the diode.

Students locate the huge elastically scattered peak at 337 nm and then scan to the red until they see something. Benzene has a strong, sharp Raman peak at a shift of 990 cm^{-1} (which corresponds to about 350 nm in figure 2). Other smaller lines are visible in the same region and as shown in the figure, there are additional strong lines further to the red. The 990 cm^{-1} line corresponds to excitation of the "breathing

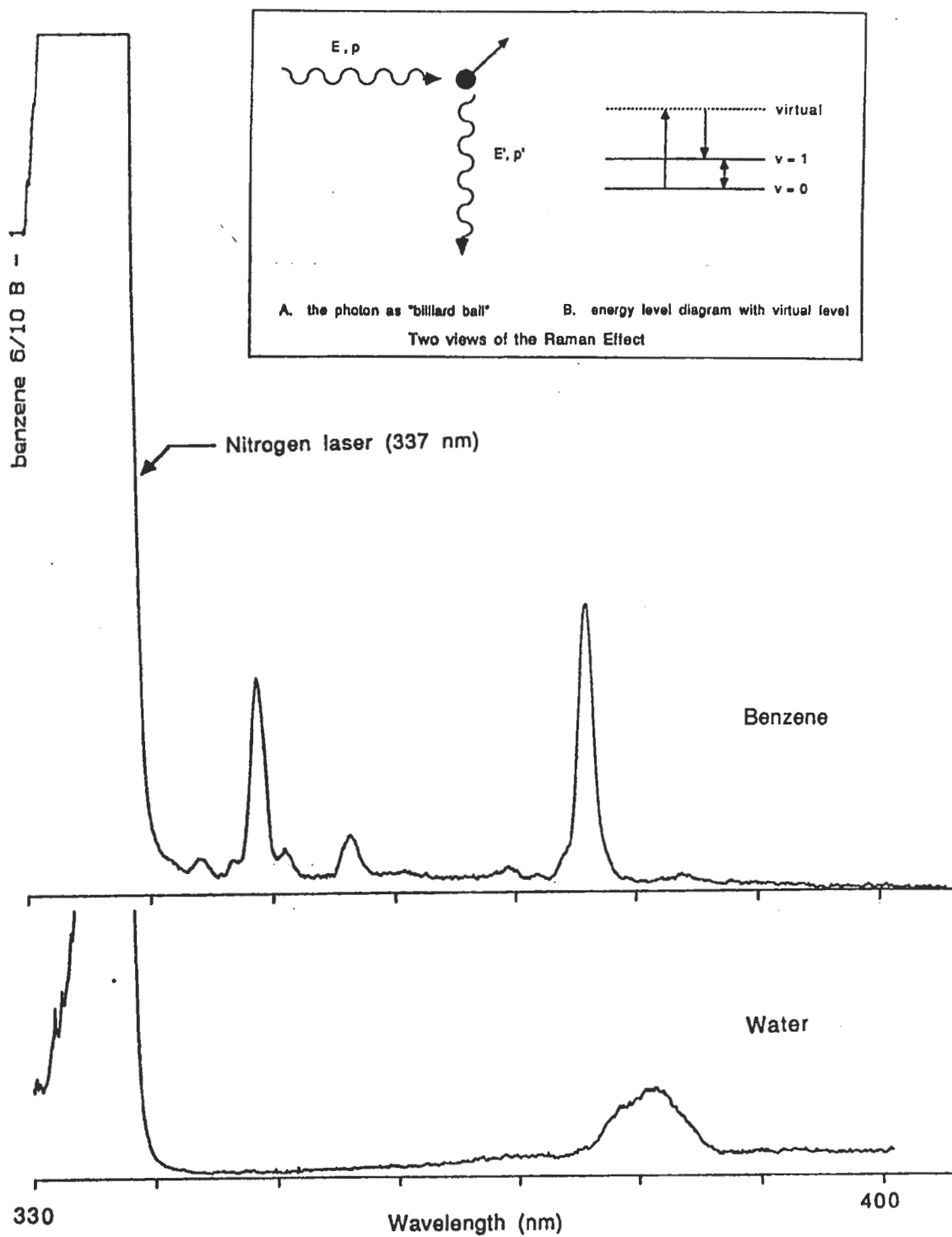


Figure 2. Raman Spectra of Benzene and Water

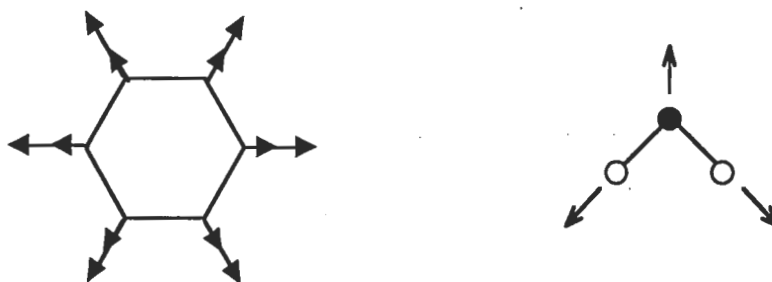


Figure 3. Vibrational modes of benzene (992 cm^{-1}) and water (3655 cm^{-1}) which give rise to the observed Raman lines²

mode” in which all of the carbons and the hydrogens move away from the center of the ring. To verify that the location of the Raman peak depends on the choice of molecule, water is substituted for benzene. The spectrum shows a different shift and a much broader peak, presumably as a result of the interactions of the polar water molecules.

Before coming to lab, students are asked to apply conservation of energy and momentum to a visible photon- molecule collision and predict that there should be no observable effect. Upon finding that, in fact, some of the photons undergo a large wavelength shift, they are asked to modify the picture to account for this observation. Most are able to deduce that the photon-molecule collisions are inelastic, with the molecule absorbing some of the energy in a vibrational mode. In order to rule out resonant absorption and subsequent fluorescence, one should vary the wavelength of the laser and show that the energy shift is constant. Since that is not easy to do with this particular apparatus, the instructor has to supply this additional information. It is possible with this apparatus to observe anti-Stokes scattering in which a photon gains energy by deexciting a thermally excited benzene molecule but the signal is much weaker than for the Stokes lines and thus we do not normally include that as part of the lab. In addition to reinforcing the basic lessons learned in the Compton experiment, the Raman effect is interesting in itself, both for its use as an analytical technique and as an example of a nonlinear optical process, although we do not emphasize this viewpoint in this particular class.

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¹ See for example J.I Steinfeld, “Molecules and Radiation,” MIT press, second edition (1985) pg 134 or Eisberg and Resnick, “Quantum Physics,” J. Wiley, second edition (1985) pg 432.

² G. Herzberg, “Molecular Spectra and Molecular Structure II: Infrared and Raman Spectra of Polyatomic Molecules,” Van Nostrand Reinhold Co (1945).