Atomic and Molecular Physics

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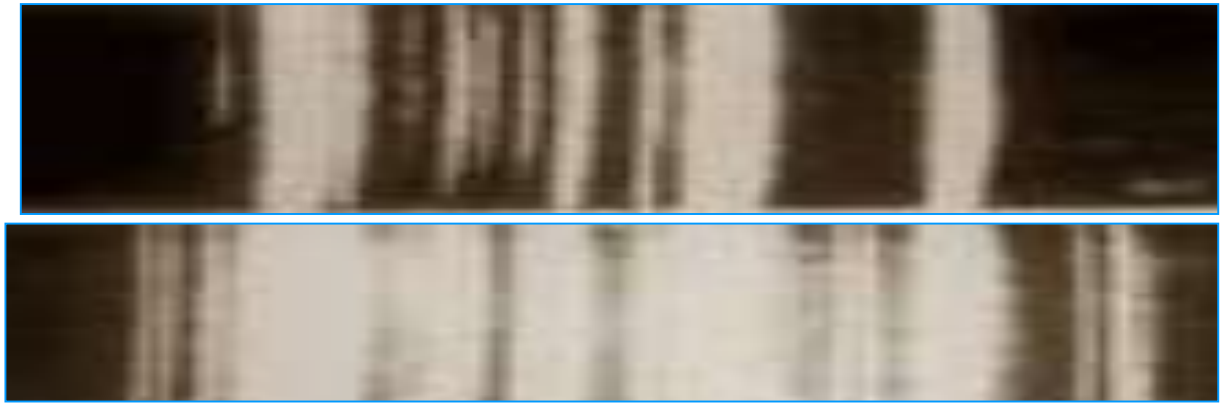
Raman Effect

Sir. C.V. Raman received the Nobel Prize in Physics in 1930 “for his work on the scattering of light and for the discovery of the effect named after him.” The first spectrum taken in 1928 by C.V. Raman and his colleague K.S. Krishnan is shown on the left (from R. Singh, Phys. Perspect. 2002). The left photograph shows the incident light from a mercury arc lamp after passing through a blue filter; the right photograph shows the same spectrum after passing through liquid benzene.

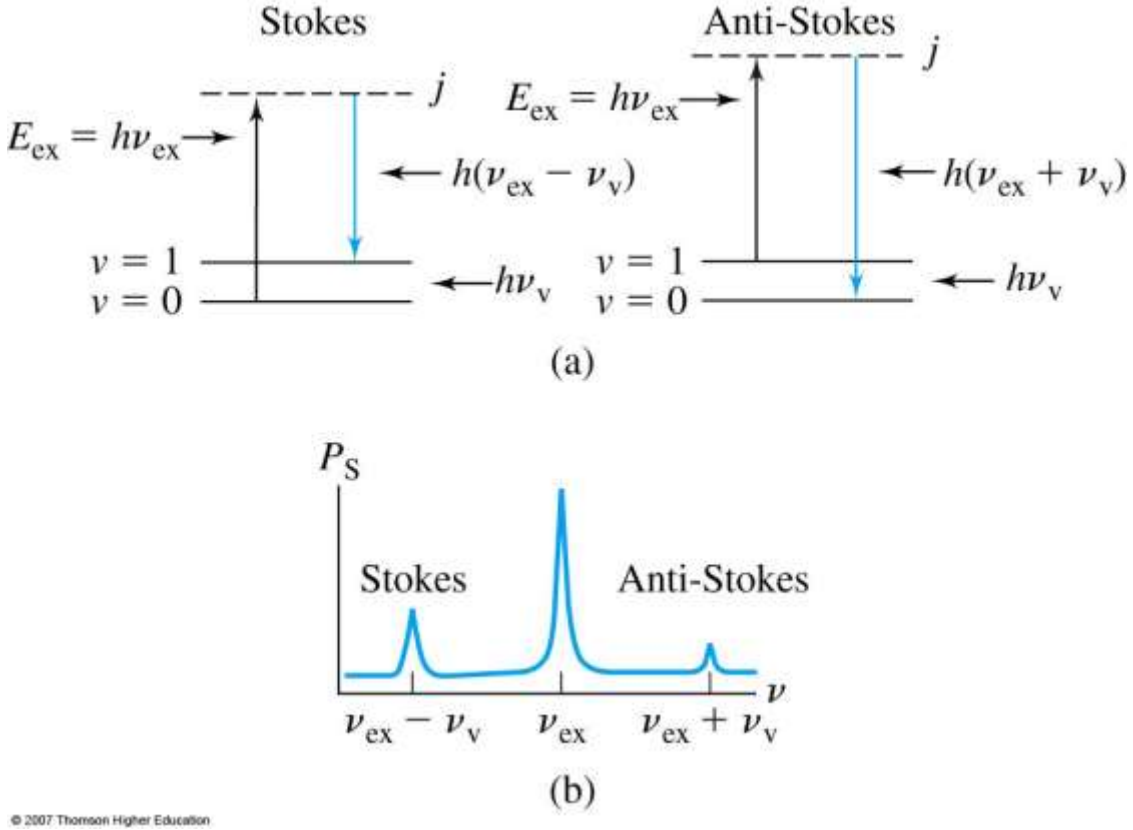


Extra in-elastically scattered lines - Raman Effect

Excitation of Raman Spectra

A Raman spectrum can be obtained by irradiating a sample of carbon tetrachloride (Fig 18-2) with an intense beam of an argon ion laser having a wavelength of 488.0 nm (20492 cm^{-1}). The emitted radiation is of three types:

1. **Stokes** scattering
2. **Anti-stokes** scattering
3. **Rayleigh** scattering



INSTRUMENTATION

Instrumentation for modern Raman spectroscopy consists of three components:

A laser source, a sample illumination system and a suitable spectrometer.

Source

The sources used in modern Raman spectrometry are nearly always lasers because their high intensity is necessary to produce Raman scattering of sufficient intensity to be measured with a reasonable signal-to-noise ratio. Because the intensity of Raman scattering varies as the fourth power of the frequency, argon and krypton ion sources that emit in the blue and green region of the spectrum have and advantage over the other sources.

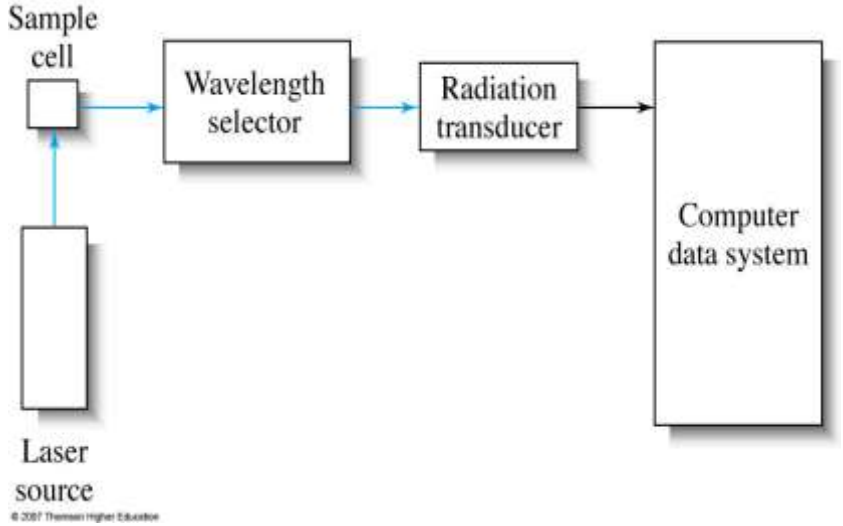
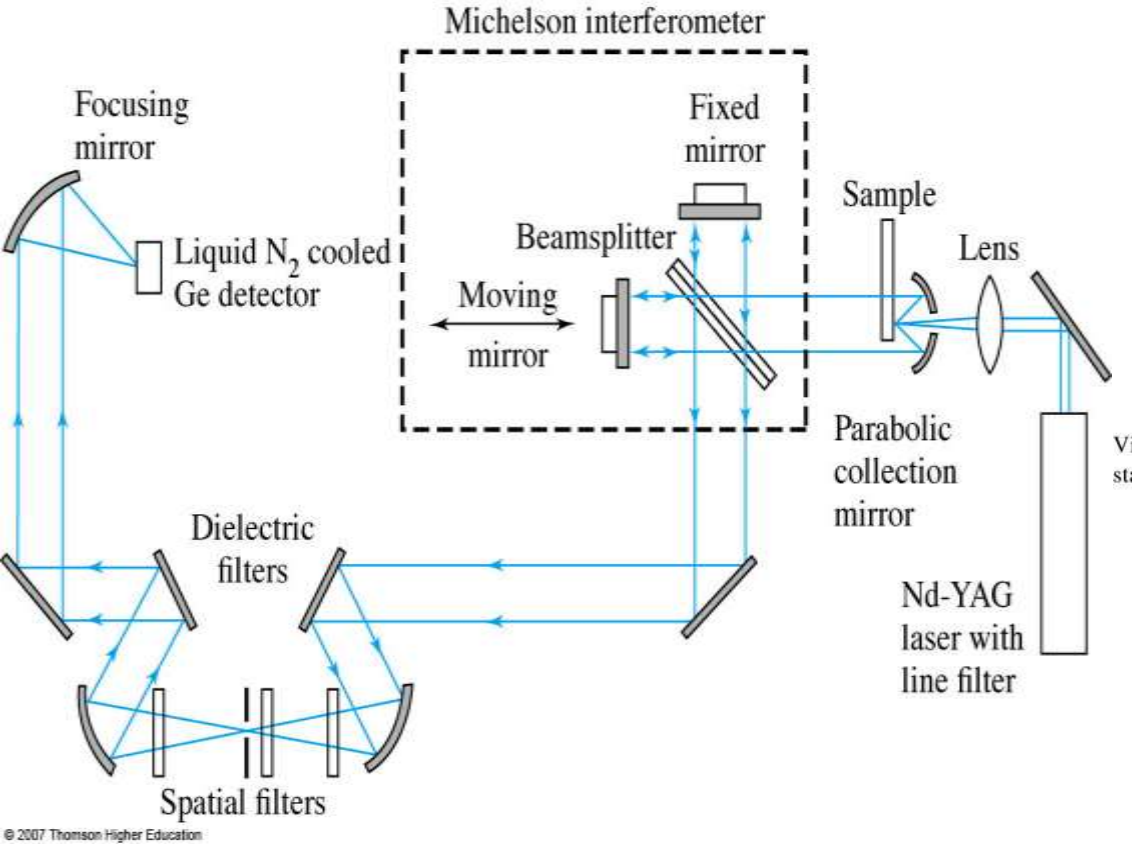
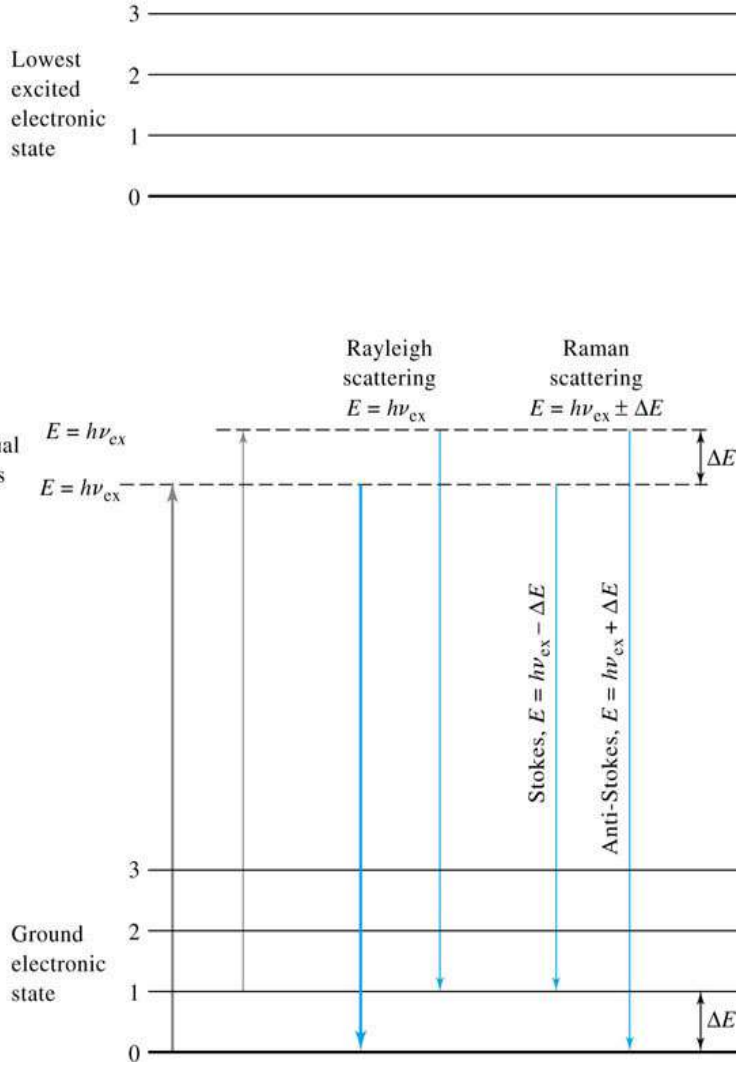


TABLE 18-1 Some Common Laser Sources for Raman Spectroscopy

Laser Type	Wavelength, nm
Argon ion	488.0 or 514.5
Krypton ion	530.9 or 647.1
Helium-neon	632.8
Diode	785 or 830
Nd-YAG	1064





Resonance Raman Spectroscopy

The most important application of resonance Raman spectroscopy has been to the study of biological molecules under physiologically significant conditions; that is , in the presence of water and at low to moderate concentration levels. As an example, the technique has been used to determine the oxidation state and spin of iron atoms in hemoglobin and cytochrome-c. In these molecules, the resonance Raman bands are due solely to vibrational modes of the tetrapyrrole chromophore. None of the other bands associated with the protein is enhanced, and at the concentrations normally used these bands do not interfere as a consequence.

Surface-Enhanced Raman Spectroscopy (SERS)

Surface enhanced Raman spectroscopy involves obtaining Raman spectra in the usual way on samples that are adsorbed on the surface of colloidal metal particles (usually silver, gold, or copper) or on roughened surfaces of pieces of these metals. For reasons that are not fully understood, the Raman lines of the adsorbed molecule are often enhanced by a factor of 10^3 to 10^6. When surface enhancement is combined with the resonance enhancement technique discussed in the previous section, the net increase in signal intensity is roughly the product of the intensity produced by each of the techniques. Consequently, detection limits in the 10^{-9} to 10^{-12} M range have been observed.