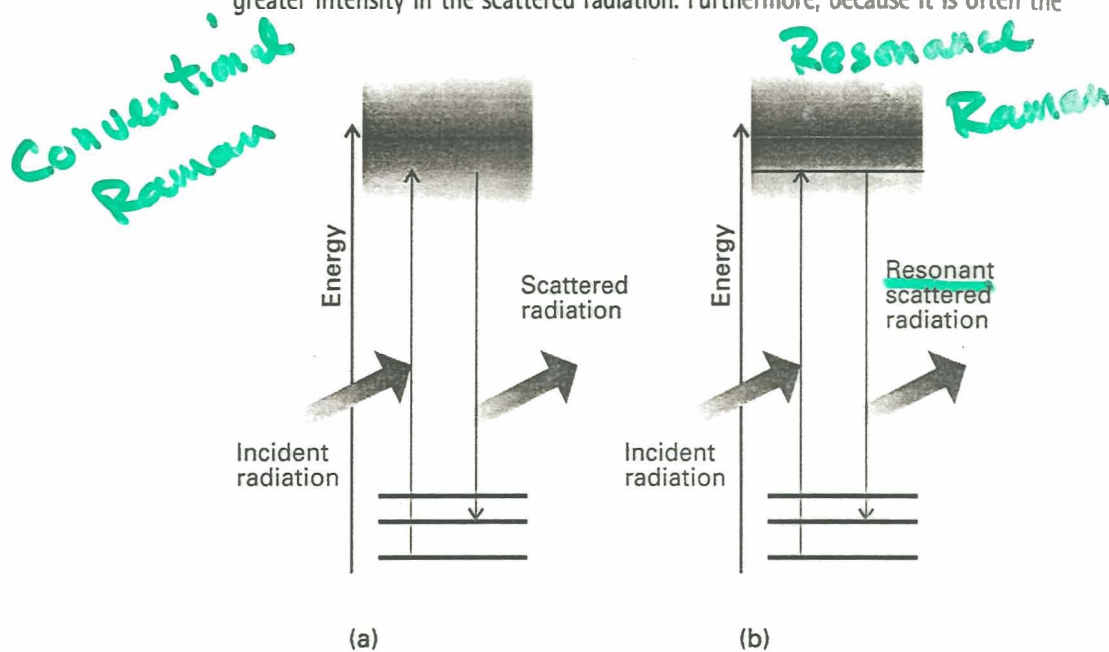


largely preserved. Vibrations that are not totally symmetrical give rise to depolarized lines because the incident radiation can give rise to radiation in the perpendicular direction to

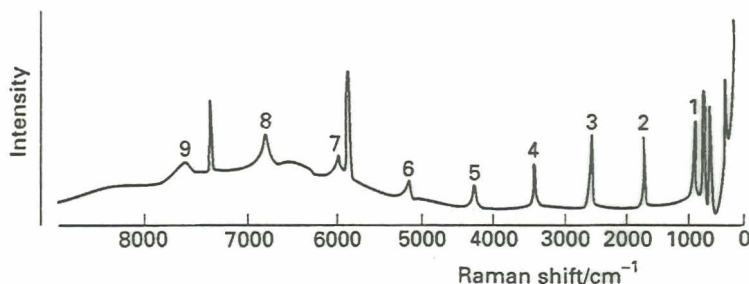
(c) Resonance Raman spectra

A modification of the basic Raman effect involves using incident radiation that near coincides with the frequency of an electronic transition of the sample (Fig. 16.52). The technique is then called resonance Raman spectroscopy. It is characterized by a much greater intensity in the scattered radiation. Furthermore, because it is often the



16.52 (a) In conventional Raman spectroscopy, the incident radiation does not match an absorption frequency of the molecule, and there is only a 'virtual' transition to an excited state. (b) However, in the resonance Raman effect, the incident radiation has a frequency that coincides with a molecular transition.

only a few vibrational modes contribute to the more intense scattering, the spectrum greatly simplified. The resonance Raman spectrum shown in Fig. 16.53, for example, is solid potassium chromate. The nine peaks that are identified are the Stokes lines that correspond to the excitation of the symmetric breathing mode of the tetrahedral CrO_4^{2-} and the transfer of up to nine vibrational quanta during the photon-ion collision. The high intensity of the resonance Raman transitions is employed to examine the metal ions in biological macromolecules (such as the iron in haemoglobin and cytochromes or the cobalt in vitamin B₁₂), which are present in such low abundances that conventional Raman spectroscopy cannot detect them. An additional advantage is that resonance picks out



16.53 The resonance Raman spectrum of solid K_2CrO_4 . The peaks are due to the totally symmetric stretching mode of the CrO_4^{2-} anion. (W. Kiefer and H.J. Bernstein, *Molec. Phys.* 23, 835 (1972).)