RAMAN DIFFERENCE SPECTROSCOPY

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Received 8 March 1972

A method is devised for obtaining Raman difference spectra by subtracting signals collected from two samples alternately. The advantages of this technique are for cancellation of unwanted components and for detection of frequency shifts. Various applications are outlined.

In many forms of spectroscopy unwanted components of spectra are cancelled out by comparison techniques. In infrared spectroscopy for example, double beam spectrophotometers are used to eliminate effects due to absorption by H_2O and CO_2 in air, and to examine impurity spectra by comparison of a sample with impurity (placed in the sample beam) to one without (placed in the reference beam). A simple method is reported here, which has been devised for obtaining Raman spectra of this type. With this method signals from two samples are subtracted from each other, hence the term "Raman difference spectroscopy" (RDS). The basic advantages of RDS over conventional Raman spectroscopy are twofold. Firstly, various signals common to both samples can be cancelled to facilitate observation of certain effects. Secondly, frequency shifts between signals from the two samples can be measured with an accuracy which is determined by the resolution of the spectrophotometer rather than by its reproducibility.

The basic system is illustrated in fig. 1. The laser source B is split into two beams by a semi-circular chopping mirror C. Each beam is focused separately into one of two different samples S_1 and S_2, using lenses L_1 and L_1'. The Raman scattered light from each sample is collected independently using lenses L_2 and L_2', and coupled into a monochromator with lens L_3.

The photomultiplier (PM) output is amplified (AMP) in conjunction with a phase sensitive detector

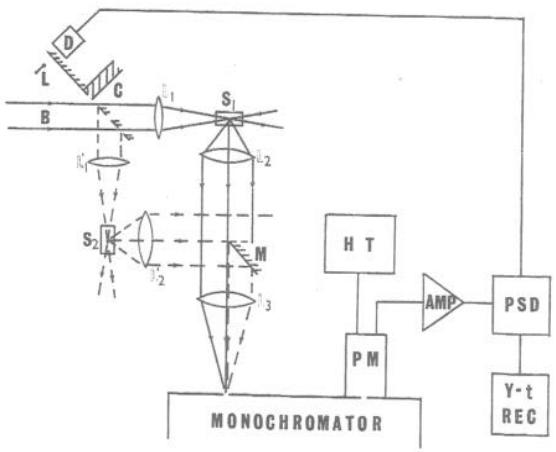

Fig. 1. Block diagram of system.

(PSD) synchronised to the chopper. The resulting signal is displayed on a (y, t) chart recorder which plots the Raman intensity as a function of wavenumber, i.e., $I\ [\nu]$.

This system results in the addition of the two signals 180° out of phase. Thus, when the two paths are well matched, insertion of similar samples into the two beams results in complete cancellation. If however the samples are not similar, the spectrum obtained will consist only of the difference between the two signals. Thus the intensity of the recorded spectrum is a function

$$I[\nu] = F_1(S_1, \nu) - F_2(S_2, \nu),$$

where $F_1(S_1, \nu)$ and $F_2(S_2, \nu)$ are the intensities of the Raman scattered light from the two samples respectively. In this way the change in the spectrum as function of a parameter x can be measured directly by switching between two samples, each held at different constant values of x. Such a system may be simply constructed as a detachable extra for most existing commercial Raman spectrophotometers. In this case a modified Cary model 81 Raman spectrophotometer [1] was used. The reference signal for the phase sensitive detector was obtained from a light switch D activated by a lamp L behind the rotating chopper. In principle the signal intensity for each of the samples in RDS is reduced by a factor of four, and thus the signal to noise ratio by a factor of two, compared with conventional spectra taken under identical conditions. This reduction is due to beam splitter C and recombination mirror M, assuming 100% reflectivity at the reflecting surfaces. Rotation of the mirror M synchronously with C to collect alternately from each sample would appreciably increase the collection efficiency of the system. A detailed description of the system and instrumentation will be published.

To illustrate the effect of this system the Raman spectrum of CBr_4 was examined. A liquid phase spectrum of CBr_4 may be obtained by using CCl_4 as a solvent. The Raman spectrum of solvent and solute are of approximately equal intensity. Both molecules have a T_d tetrahedral structure and some molecular interactions may be expected. Fig. 2 shows the Raman

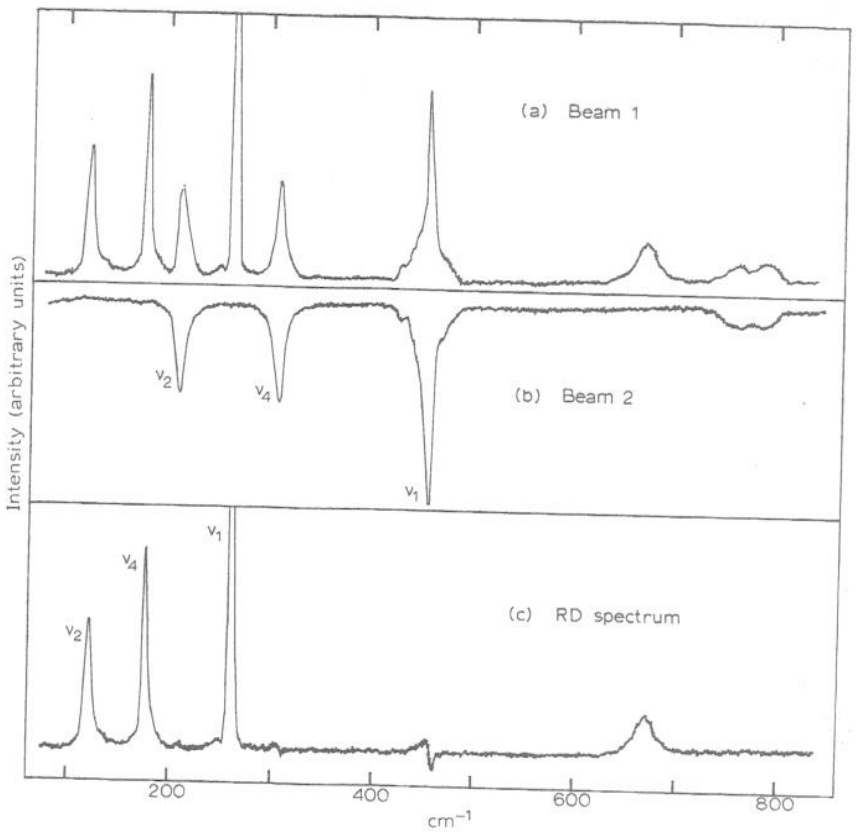

Fig. 2. Spectra of CBr_4 and CCl_4. (a) CBr_4 in CCl_4 (approximately 2:1 concentration). (b) CCl_4 [180° out of phase with (a)]. (c) CBr_4 in CCl_4 minus CCl_4. Spectral resolution 4 cm^{-1}, exciting wavelength 488 nm, time constant 0.3 sec, scan speed 1 cm^{-1} per sec.

spectrum of CCl_4; CBr_4 in CCl_4; and the RD spectrum of CBr_4 in CCl_4 minus CCl_4. The first two spectra were obtained on the difference system by blocking off one of the beam paths. From the third spectrum it is apparent that some interaction between the CCl_4 and CBr_4 molecules exists. The CCl_4 "breathing" mode is shifted to slightly lower frequency when in the presence of CBr_4 molecules. This is shown by the derivative shaped feature centred around 460 cm^{-1}. The major contributing factor to the noise level in these spectra is an unstable chopping system, and an improved chopper is presently being installed.

We conclude by outlining some applications of RDS. As illustrated by the example above, it is often impossible to obtain a spectrum of a compound in solution without having a large contribution due to the solvent. The solvent spectrum may obscure part of the solute spectrum, and frequency shifts can be produced in either the solvent or solute spectrum by the solvent –solute interactions. By the RDS method the former can be eliminated, and the presence of the latter indicated. Another type of application of RDS arises from the ability to cancel out varying backgrounds due, for example, to anisotropy scattering in liquids, fluorescence, and grating ghosts.

In single crystal spectroscopy, identification of particular mode types may be facilitated, for example in $NaClO_3$ [2] where A type modes of vibration are deduced from spectra of (A+E) modes in $Z(XX)Y$ geometry and E modes in $Z(Y'X')Y'$ geometry (Porto notation [2]). In RDS, deduction of A type modes may be facilitated by recording the spectrum

$$I\,[\nu(Z(XX)Y - Z(Y'X')Y')] = F_1(S_1,\nu) - F_2(S_2,\nu)\,.$$

Although the E modes in the (A+E) spectrum and in the E spectrum are of different relative intensities, individual cancellation of E type modes in the RDS spectrum (A+E)–E should give a clear indication of the A type modes.

For investigation of the dependence of vibrations on external forces, the intrinsic spectrum can be eliminated in order to record only the net effect of the force [3]. (This has been achieved previously in Raman spectroscopy by modulation of the external parameter [4].) Similarly, impurity spectra can be obtained by RDS free from the spectrum of the host lattice. In the study of linewidth as function of a parameter x, such as temperature, pressure, or solvent, fine variations can be detected by subtracting spectra of two similar samples at different values of x.

Thus it has been demonstrated that RDS can reasonably be developed into a useful and versatile extension of the standard methods of investigating the light scattering properties of matter.

Helpful remarks of Drs. A.T. Collins and W.F. Sherman, are gratefully acknowledged. We wish to thank the Science Research Council for grants which made the work possible.

References

[1] B.J. Berenblut and P. Dawson, J. Phys. E (1972), to be published.
[2] C.M. Hartwig, D.L. Rousseau and S.P.S. Porto, Phys. Rev. 188 (1969) 3.
[3] M. Cardona, Modulation spectroscopy, Solid State Physics Suppl. 11 (Academic Press, New York, 1969).
[4] P.A. Fleury and J.M. Worlock, Phys. Rev. 174 (1968) 613.