

Some recent trends in Raman spectroscopy

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1. Introduction

Even after sixty years since the discovery^{1,2} of the Raman Effect in 1928, Raman spectroscopy continues to be an exciting field of research, covering an increasingly wider spectrum of extremely important problems in physics, chemistry, biology and other branches of science and technology. Ordinarily, this should not be surprising because the frequency-shifted Raman lines, corresponding to inelastic scattering of incident photons by a material medium, directly give the most basic information about the possible excitations in the system. This is obviously very useful in determining the structure and the nature of the material medium at the microscopic level. However, the spontaneous Raman scattering is a very weak second-order electronic process; the scattering cross-section for the Raman process involving vibrational excitations in a typical liquid being only of the order of 10^{-30} cm² per molecule. The signal is extremely small, if the scattering volume is small or the observation time is very short. Moreover, in most cases, while detecting the Raman signal one is faced with a large unwanted fluorescence background arising from the two-step real absorption and emission of photons by impurities, etc., in the sample. In spite of these difficulties, the reason for Raman spectroscopy to remain so popular and extensive is, of course, due to major revolutionary developments which are taking place in optics since the discovery of lasers in the early sixties. These not only relate to the availability of powerful laser sources which can be tuned in a wide range of frequencies and also generated as ultrashort picosecond and femtosecond pulses³, but also to the development of extremely sensitive optical photon-detection systems and multi-channel analysers⁴. They have indeed opened up a vast range of new possibilities in the field.

The main aim of this presentation is not to attempt an exhaustive review of all the recent important developments in the field, but to select an illustrative list of some of these topics for discussing their importance as well as typical results obtained so far. Hopefully, this would bring out, at least partially, the flavour of present trends in research in modern Raman spectroscopy.

In recent years, there has been a greater emphasis on the use of Raman spectroscopy to study the dynamics of a given system and its excitations, instead of just its structural

properties. This is best accomplished by using the so-called time-resolved Raman spectroscopy⁵, with pulsed-laser sources in the appropriate temporal range. This technique will be discussed in some detail in Section 2. In the conventional CW experiment, this information is buried in the shape and the width of the Raman line which, very often, can not be analysed easily for obtaining the relevant dynamical parameters.

The increasing role being played by Resonance Raman Spectroscopy⁶ (RRS) in the investigation of various biological, chemical and other delicate systems like molecules adsorbed on surfaces will be discussed in Section 3. Next, we will consider various types of new studies involving high-vibrational overtone spectroscopy, nonlinear Raman spectroscopies and Fourier-Transform (FT) Raman spectroscopy. Before concluding, we will also mention briefly some recent work on superlattice structures as well as theoretical calculations of Raman intensities for vibrational excitations in molecules.

2. Time-resolved Raman studies

The time-domain optical study of fast dynamical processes at the microscopic level requires ultrashort light pulses, during which the temporal property of the system must not change appreciably. Vibrational energy relaxation in liquids and solids as well as excited-state chemical reactions and energy transfers at the chemical-bond level from one part of a biological molecule to another, represent dynamical processes on the picosecond and subpicosecond time scales. Highly excited nonequilibrium carriers (electrons and holes) in semiconductors can exchange energy among themselves and with lattice phonons on similar ultrashort time scales. In fact, in many cases, the nature of electronic-excited states can change appreciably even in a few femtoseconds. In principle, the time-resolved Raman spectroscopy, in which vibrational (ionic) or electronic excitations of the system are probed by short pulses at different time-delays with respect to the initial time at which the system is prepared in the required state, is an ideal technique for such temporal studies because the intrinsic time of such Raman scattering processes themselves is less than 10^{-15} seconds. In actual practice, the application of the Raman technique for ultrafast time-resolved studies has been slow, mainly because of the difficulties in detecting extremely small Raman signals and in synchronising various steps, including the preparation of the system in the required initial state. However, with the introduction of position-sensitive micro-channel plate photo-multipliers, CCD cameras, powerful monochromators, new pulsing techniques, and various optical data acquisition and processing systems, this situation is changing fast. In the years to come, time-resolved Raman measurements are expected to be a substantial part of the activity in Raman spectroscopy. This is mainly because, in the conventional Raman experiments, one faces serious difficulties in separating various dynamical processes responsible for the line broadening, including inhomogeneous broadening due to a distribution of mode frequencies. Measurements in time-domain directly determine relevant relaxation rates or temporal evolution (whether exponential or not), *e.g.* of mode population, vibrational dephasing, concentration of different transient species, etc.

In the earliest time-resolved Raman experiments⁷, the studies were made mainly of the dynamics of vibrational modes in the electronic ground state of a condensed

medium. Usually, a strong optical pump-pulse was used to prepare the initial state of the system by exciting coherent vibrational modes in liquids like CH_3CCl_3 or phonons in solids like diamond, through the stimulated Raman scattering process or resonant infrared absorption. A series of weak probe pulses at different time delays was then used to measure the vibrational dephasing time (T_2') or the population life-time (T_1), using coherent Raman scattering or the usual incoherent anti-Stokes Raman scattering. In chemistry, it is extremely important to determine the flow of energy between different degrees of freedom in a chemical solution, *i.e.* the complete pathway⁸ for T_1 -relaxation. Molecules in solutions can remain in nonequilibrium (hot) for hundreds of picoseconds. For proper understanding of chemical reactions in solutions, one has to study the vibrational mode frequencies and their dynamics by determining the changes in the potential function for the nuclear motion due to the presence of solvent and other molecules. In general, the investigation of chemical reaction dynamics and the decay of transient species is very important for time-resolved Raman studies in chemistry⁹. Recent incoherent pump-probe Raman experiments, with picosecond-time resolution, have shown that it is indeed possible to obtain such information in a wide range of systems, including pyrrole, haemoglobin, etc. In such a pump-probe technique, the pump beam merely acts to prepare the system far from equilibrium involving *incoherent* superposition of various excitations, and the weak probe beam monitors their population as a function of time *via* Raman scattering from these excitations.

A typical pump-probe set-up is shown in fig. 1, in which both the strong pump and the weak-probe pulses are generated by the same laser beam, but the probe beam is delayed with respect to the pump beam by introducing an additional variable optical length in its path. Ideally, one would like to avoid the detection of the Raman signal arising from the pump beam by choosing the probe frequency quite different than the pump-laser frequency. However, because of technical difficulties, it may not be possible to do so in many situations. In such a case, the real Raman signal from the probe beam is discriminated against the pump scattering by using different polarizations for the pump and probe beams dictated by appropriate polarization selection rules for the excitations¹⁰. The dependence of Raman scattering signal from the probe beam on the delay time t_d at which the probe beam is switched on for a short time t_p , arising from a given excitation mode λ of frequency ω_λ decay constant Γ_λ and occupation number $n_\lambda(t)$, is approximately determined by the temporal functions

$$G_{\text{Stokes}}^\lambda(t = t_d + t_p) = \left| \int_0^{t_p} d\tau e^{-i(\omega_s - \omega_i + \omega_\lambda - i\Gamma_\lambda)\tau} [n_\lambda(t_d + t_p - \tau) + 1]^{1/2} \right|^2 \quad (1)$$

$$G_{\text{A.Stokes}}^\lambda(t = t_d + t_p) = \left| \int_0^{t_p} d\tau e^{-i(\omega_s - \omega_i - \omega_\lambda - i\Gamma_\lambda)\tau} [n_\lambda(t_d + t_p - \tau)]^{1/2} \right|^2 \quad (2)$$

where ω_s and ω_i are scattered and incident frequencies, respectively^{11,12}. If one assumes that during the short-probe pulsewidth, the system properties including $n_\lambda(t)$ do not change appreciably, the above expressions lead to the signals proportional to $n_\lambda(t_d) + 1$ and $n_\lambda(t_d)$, with Raman lines of width π/t_p at the frequencies $\omega_s = \omega_i \mp \omega_\lambda$, respectively, for $1/\Gamma_\lambda$ large compared to the pulsewidth t_p . This implies that for spectral resolution of

microchannel plate photomultiplier/CCD

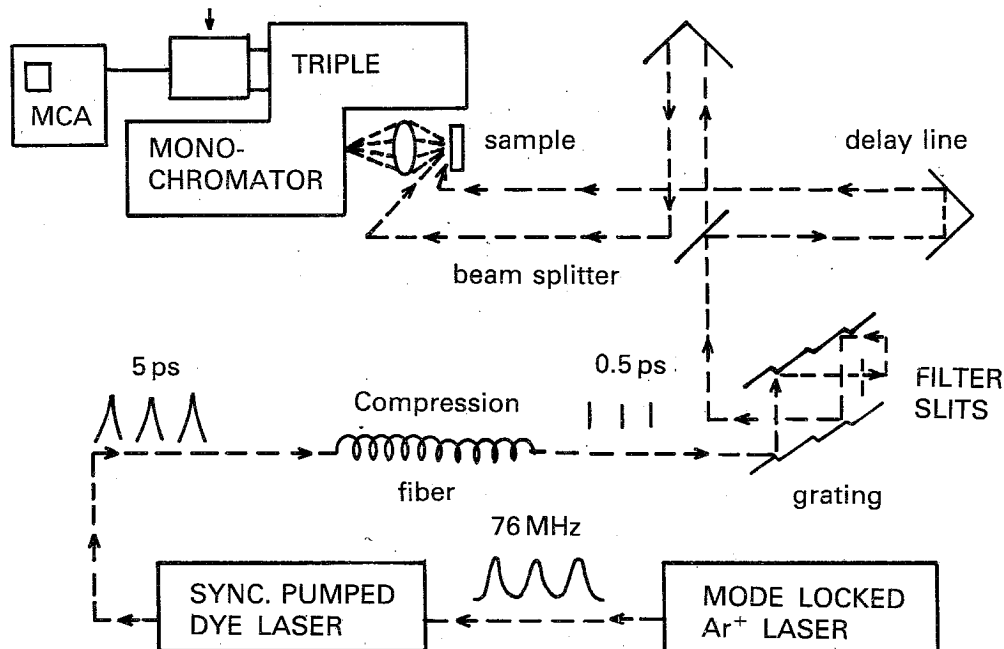


FIG. 1. Typical pump-probe Raman scheme.

at least 100 cm^{-1} , one can not use pulses shorter than 200 femtoseconds¹². For shorter pulses, one can only monitor much higher frequency vibrational modes or electronic excitations, because of the uncertainty principle.

Recently, dynamics of nonequilibrium carriers and LO-phonons have been studied^{13,14} in several polar semiconductors like GaAs, InAs, $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $\text{In}_x\text{Ga}_{1-x}\text{As}$, using subpicosecond pump-probe Raman technique. A very short laser pulse, with photon energy above the band gap of the intrinsic semiconductor, pumps electrons from its valence bands to the conduction band with carrier densities in the range of 10^{16} to 10^{18} cm^{-3} , depending on the total pump-laser energy. Because of the strong Fröhlich interaction of carriers with LO-phonons, electrons and holes relax towards band extrema by emitting long-wavelength LO-phonons on a time scale of 150 to 200 femtoseconds. Since the lifetime of the generated LO-phonons is much longer (several picoseconds), their occupation number first increases from its equilibrium value as a function of time t_d , before decreasing towards the equilibrium value. The Raman signal of the probe beam, either on the anti-Stokes side or on the Stokes side, directly monitors this temporal evolution as a function of the time delay t_d . The initial rising slope gives the electron-LO-phonon scattering time (about 160 femtoseconds in GaAs) and the later fall determines the LO-phonon decay time, for different lattice temperatures of the sample. Because of the current interest in fabricating fast electronic devices, these studies are also being extended to quantum-well and superlattice structures of GaAs and AlAs.

3. Resonance Raman Spectroscopy (RRS)

The advent of powerful lasers in the early sixties, allowed increased source intensity with an extremely narrow spread of incident frequencies, and the resulting increase in signals for the spontaneous Raman scattering. However, this ease in detection was not very useful for investigating many delicate biological and chemical systems or for studying processes at solid surfaces involving very small scattering volumes. In such systems, one faces severe limitations in increasing the incident laser intensity because that can heat and alter the nature of the system itself, which is under study. On the other hand, with easy availability of tunable lasers in the late sixties and early seventies, it was realised that one could enhance the basic Raman scattering process itself by several orders of magnitude by tuning the incident laser frequency close to one of the electronic intermediate states of the medium under study. Since Raman transition polarizability is a second-order perturbation process involving the interaction of the electrons in the system with the incident photons (ω_i) and the scattered photon (ω_s), the cross section has also a resonance structure when ω_i or ω_s is close to an electronic intermediate state of the system. The essential point is that in the so-called Resonance Raman Spectroscopy (RRS), the signal can be increased by a factor of approximately $(\hbar\omega_i)^2/(\hbar\Gamma_{ni})^2$, where $\hbar\Gamma_{ni}$ is the transition width of the intermediate electronic state n .

The extension of RRS up to the ultraviolet (UV) region of the incident frequency has allowed the study of many important biological molecules and processes. Prosthetic groups such as heme, flavin, retinal and metal-ion centres, and aromatic chromophores in complex environments have been recently investigated using visible and UV excitations¹⁵. Apart from other studies of nucleic acid structures, lipids and related systems, new studies of benzene, benzene derivatives, ammonia, oxygen, etc., have also been made using far UV-RRS to determine changes in the excited-state geometry and highly excited vibrational levels of the ground electronic state¹⁶. By pulsing the incident laser, it has also been possible to couple RRS with the time-resolved studies of protein dynamics. In RRS, partial depolarization of the resonance Raman signal from molecular vibrations is present if the molecules could rotate during the time interval between the absorption and emission steps. In fact, the measurement of the depolarization ratios in RRS can give very important data on fast collisional processes in liquids, because the efficiency of RRS depends essentially on the dephasing time of the intermediate electronic state. The excited-state rotation and collisions with solvent molecules give a value of the dephasing time of the order of 10^{-13} seconds, which leads to a partial depolarization of RRS.

The study of adsorption and reaction dynamics of a very small number of layers of molecules on the surfaces of metals and semiconductors has become possible in recent years, because of the development of the so-called Surface-Enhanced Raman Spectroscopy (SERS) and the new highly sensitive optical-detection techniques. For many molecules adsorbed on metals like Ag, Au, Pt, Al, etc., there is a large enhancement of Raman cross-sections for various vibrational modes of the molecules¹⁷, due to resonance of the incident and/or scattered frequencies with the electromagnetic surface-plasmon-polariton modes of the medium or with the charge-transfer band of the surface complex formed by the molecule and the solid substrate. SERS has been used to study many

important processes at electrodes and in biological molecules. Of course, new optical-detection techniques have now allowed observation of very weak Raman signals from adsorbed molecules, even without any apparent resonance enhancement.

4. Vibrational overtone, FT Raman, and nonlinear Raman spectroscopies

In polyatomic molecules, anharmonicity of nuclear motion on a potential energy hypersurface becomes increasingly important with increasing amplitude of vibration. In fact, small amplitude normal-mode picture collapses as the amplitude of vibration approaches bond dissociation. Because of the lowering of the restoring force at the outer turning points, the separation between vibrational levels in a diatomic molecule decreases with increase in vibrational energy. In general, bond-stretching vibrations decouple from other molecular motions and get localized, if we increase vibrational energy in that bond. The measurement of overtone vibrational frequencies in the region of very high vibrational energies gives essential information in constructing the complete potential energy hypersurface which is important in understanding the mechanism of any chemical reaction involving such molecules. With increased sensitivity of optical detectors, it is expected that the observation of Raman scattering from high vibrational overtones will complement similar studies using infrared spectroscopy.

The use of Raman scattering technique for analytical purposes has always been slow because of the need to eliminate background fluorescence signal which can sometimes be much stronger than the Raman signal. This problem is more severe, if one is not analysing samples of single-component compounds. With the development of Fourier-transform (FT) infrared spectroscopy in recent years, it is now possible to obtain FT Raman spectra with almost no fluorescence background. When samples are irradiated in the near infrared, there is only weak absorption due to excitations of overtones and combinations of fundamental vibrations, and fluorescence is almost absent with the usual energy of infrared laser being used in Raman experiments. Instead of the dispersive elements used in detecting optical signals in the conventional Raman spectroscopy, a Michelson interferometer, or other interferometric method is used to detect signals in FT-Raman spectroscopy. This results in very high resolution and allows measurement of even very small-frequency shifts, with the possibility of a better accuracy in absolute frequency measurements. The optimization of various systems in FT-Raman instrumentation is still continuing, but its application to various interesting systems in future seems very promising.

Development of intense tunable lasers with high spatial and temporal coherence has also allowed the use of nonlinear Raman spectroscopies to solve problems which can not be tackled otherwise. These arise because of the third-order term involving $\chi^{(3)}\overline{E}\overline{E}\overline{E}$ in the induced-polarization \overline{P} of the medium. When incident radiation fields at frequencies ω_1 and ω_2 (let $\omega_1 > \omega_2$) are present in coincidence in space and time in the medium, such that $\omega_1 - \omega_2$ is equal to the frequency ω_0 of a Raman-active excitation, because of the $\chi_R^{(3)}(\omega_1, -\omega_2, \omega_1)$ term one can study the gain in the amplitude of the wave at the lower frequency ω_2 (Raman-gain spectroscopy), or a loss at the higher-frequency wave at ω_1 (Inverse Raman spectroscopy), or the growth of the amplitude of a new wave at $2\omega_1 - \omega_2$

(CARS). Whereas the changes in intensities of the waves at ω_1 and ω_2 are related to the imaginary part $\chi_R^{(3)''}$, the CARS intensity is related to $|\chi_{\text{CARS}}^{(3)}|^2 = |\chi_R^{(3)'} + \chi_{\text{NR}}|^2 + |\chi_R^{(3)''}|^2$. Here, the signals in these nonlinear spectroscopies are background free because of the special need for temporal and spatial coincidence of beams in these processes. However, due to the nonresonant contribution χ_{NR} in CARS, there are distortions in the line shapes in CARS as opposed to, *e.g.*, Raman-gain (amplification) spectroscopy. Since gases can withstand very high power needed in these spectroscopies, they have been applied very successfully in recent years for very high-resolution Raman studies in such systems. Using picosecond-pulsed lasers, Raman amplification technique can also be used in the condensed phase, *e.g.*, in a single crystal of ion-exchange resin which is otherwise extremely fluorescent. In high-order processes beyond $\chi^{(3)}$, one can generate new waves when $\omega_1 - \omega_2$ is equal to a subharmonic of the active Raman mode ω_0 . For example, with $\chi_R^{(5)}$ ($\omega_1, -\omega_2, \omega_1, -\omega_2, \omega_1$), one creates waves²¹ at $\omega_1 - \omega_2 = \omega_0/2$. However, these signals may not necessarily contain any more information than that obtained in the lower-order nonlinear spectroscopies.

5. Concluding remarks

Before concluding, let us emphasize here that in this article we have touched upon only a very small sub-set of present interesting topics in Raman spectroscopy. Among many other important investigations like high-pressure Raman experiments, etc., we have not said anything about the beautiful Raman studies of acoustic phonons in periodic semiconductor lattices as well as non-periodic (Fibonacci quasi-periodic, random, etc.) lattices. These structures consist of sequences of two building blocks of GaAs and AlAs layers of thickness of the order of 20 to 40 Å or so. Because of zone-folding in the \vec{q} -space, in the direction of the superlattice structure, acoustic phonons have many different sets of longitudinal and transverse branches, starting from $\vec{q} = 0$, with a much shorter first Brillouin-zone in the \vec{q} -space. Long-wavelength ($\vec{q} \rightarrow 0$), finite-frequency modes can then be observed *via* Raman scattering. This provides extremely useful information about the structural and elastic properties of these layered materials²². In a sense, acoustic-Raman scattering studies in a periodic superlattice can approximately map the acoustic phonon dispersion relations of the original bulk materials up to the large original Brillouin-zone in the \vec{q} -space, in the direction of the superlattice structure.

Substantial progress has also been made in calculating Raman-scattering intensities for vibrational excitations in various molecules, from first principles. Since the computation of absolute Raman cross-sections has always been a troublesome theoretical problem, one is often content with only relative comparisons of experimental results with theoretical predictions. However, recent *ab initio* calculations²³ of the polarizability derivatives in molecules like H₂O, etc., *via* direct computation of electronic energy derivatives, have been quite promising.

The present activity in the field of Raman spectroscopy is quite vast and very extensive. Since it covers many diverse disciplines in science, it has been difficult to do justice to various exciting developments taking place in the field, in an article like this. The vitality of the field is proved by the exciting proceedings of biennial international confe-

rences on Raman spectroscopy, and by the increasing number of interesting papers being published in the field in a large number of research journals. With the rapid growth of sophistication and sensitivity in optical detection and data-processing techniques, and the progress made in controlling and generating tunable optical sources which can be pulsed to the level of a few femtoseconds, different forms of Raman spectroscopy are expected to remain in the limelight for decades to come.

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