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RAMAN SPECTROSCOPY IS A SPECTROSCOPIC TECHNIQUE USED TO DETECT VIBRATIONAL, ROTATIONAL, AND OTHER STATES IN A MOLECULAR SYSTEM

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ABSTRACT:

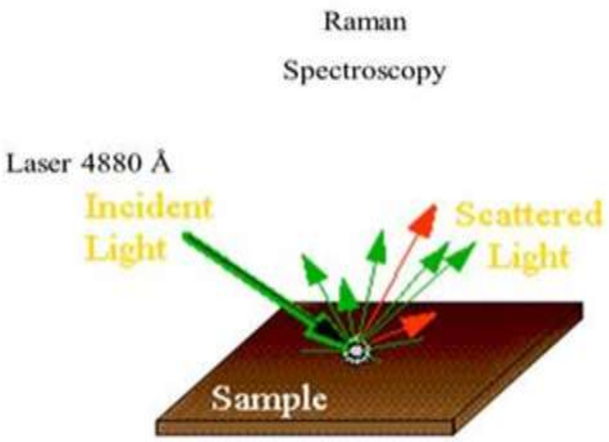
For material identification and analysis of molecular structure Raman spectroscopy a useful technique. There is one important distinction to make between the Raman spectra of gases and liquids, and those taken from solids (like crystals). For gases and liquids of the different vibrational energy levels of the individual molecules which make up the material. So, the whole crystal lattice undergoes vibration in macroscopic level. These macroscopic vibrational modes are called phonons. Raman Spectroscopy is a popular technique and is now considered complementary to infrared spectroscopy. Raman spectroscopy is based on the Raman effect, which was first found by the Indian physicist Chandrasekhara Venkata Raman in 1928.

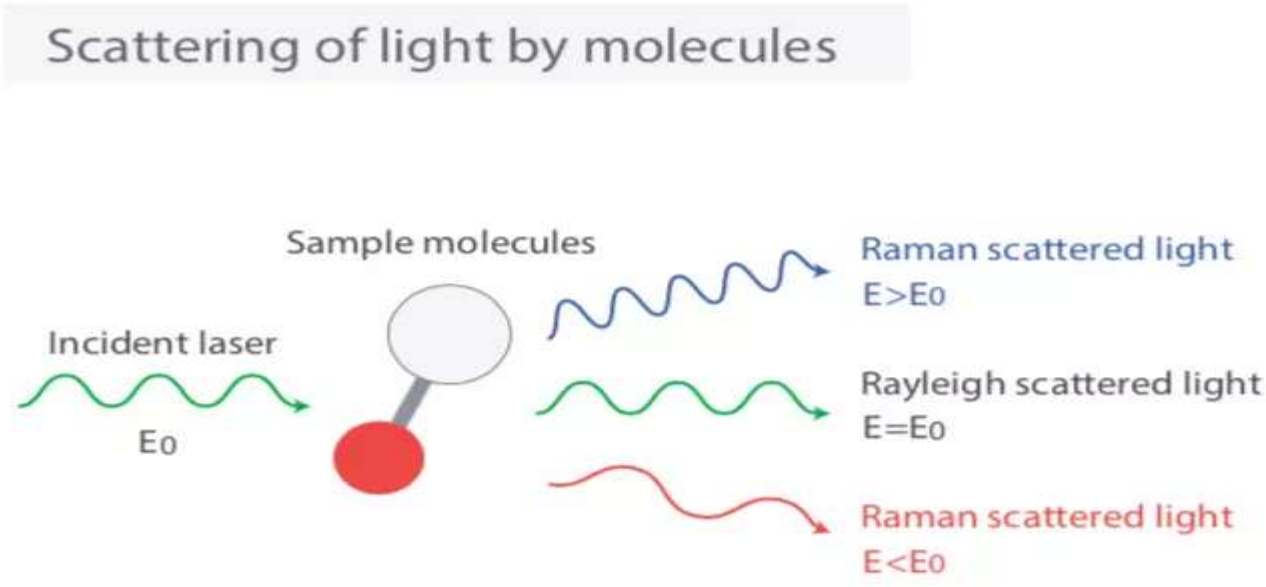
The molecule may be advanced to a virtual state of higher energy when photons interact with a molecule. From this higher energy state molecule comes down to vibrational energy level by producing photon of some different materials from than that of its beginning state.

An important advantage of Raman Spectra that can be obtained from aqueous solutions because water does not cause interference. Raman discovered that the visible wavelength of a small fraction of the radiation scattered by certain molecules differs from that of the incident beam.

INTRODUCTION

Raman Spectroscopy is a popular technique for the analysis of molecular structure which is based on the Raman effect according to which when incident light excites molecules in a tissue, the molecules will reflect light in a different wavelength and is now considered complementary to infrared spectroscopy. Raman spectroscopy is based on the Raman effect, which was first found by the Indian physicist Chandrasekhara Venkata Raman in 1928. According to quantum mechanics, when photons interact with a molecule, the molecule may be advanced to a virtual state of higher energy. From this higher energy state, there can be a few possible outcomes. One such outcome can be that the molecule comes down to some vibrational energy level different than that of its beginning state, by producing a photon of some Different materials have different vibrational modes, and therefore their own characteristic Raman spectra. If the energy of the incident photon is not large enough to excite the molecule from the ground state to the lowest electronic state, the molecule will be excited to some virtual state between the two states. But, the electron of that excited molecule cannot stay long in the virtual state and needs to immediately go back to the ground state. now, if the electron goes back to its original state (ground state in this instance), the wavelength of the emitted photon is then the same as that of the incident light photon. This type of scattering phenomenon is known as Rayleigh scattering. On the other hand, it is also possible for the electron to go to a virtual state that is different from where it is excited, giving rise to an energy difference between the emitted photon and the incident photon, and therefore a shift in wavelength (therefore an energy shift also) for the emitted photon as compared to the incident photon. This is known as Raman scattering. If the emitted photon has energy smaller than that of the incident photon, this scattering process is known as Stokes scattering and when the incident photon has a higher energy compared to the emitted photon, it is known as anti-Stokes scattering





A. Rayleigh Scattering

1. The electron of the excited molecule is excited to any virtual state.
2. The electron of the excited molecule relaxes back to its original state.
3. The photon is scattered elastically, leaving with its original energy (without any sort of change in energy).

B. Stokes Scattering

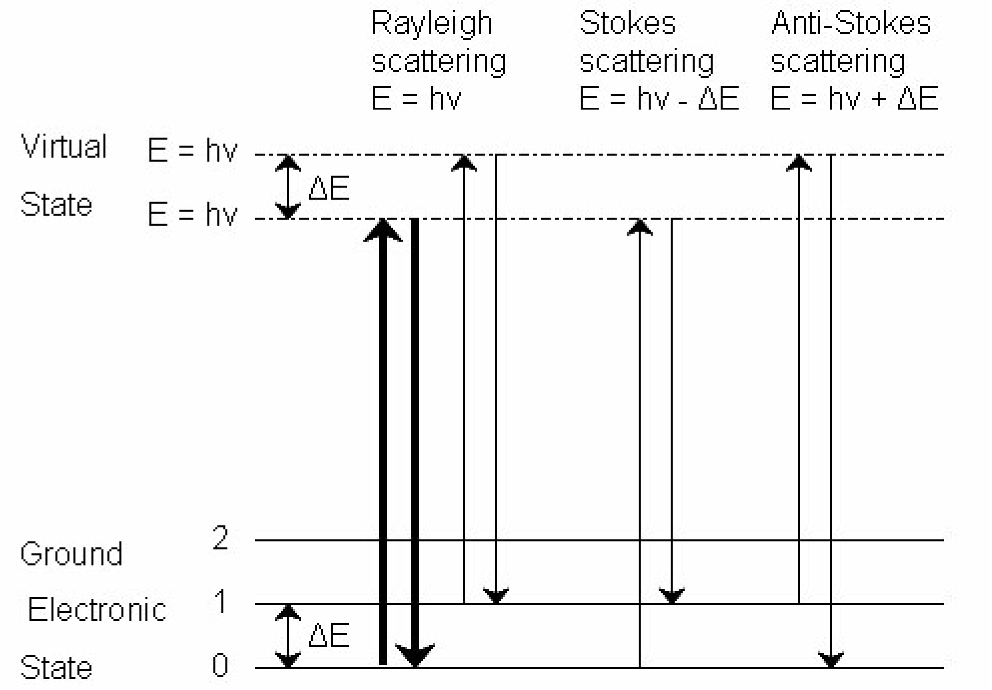
1. The electron of the excited molecule is excited to any virtual state.
2. The electron of the excited molecule relaxes back to a higher vibrational state than it had originally.

3. The photon leaves with energy h_ □ _E and has been scattered inelastically.

C. Anti-Stokes Scattering

1. The electron of the excited molecule begins from a vibrationally excited state.
2. The electron of the excited molecule is excited to any virtual state.
3. The electron of the excited molecule relaxes back to a lower vibrational state than it had originally.
4. The photon leaves with energy hv_ + _ῡE , and has been scattered super elastically.

illustrates the differences between Rayleigh scattering, Stokes scattering and anti-Stokes scattering from the quantum mechanical point of view.
and anti-Stokes scattering.
Rayleigh scattering is the most common transition, as, in this case, no change has to occur in the vibrational state of the molecule.

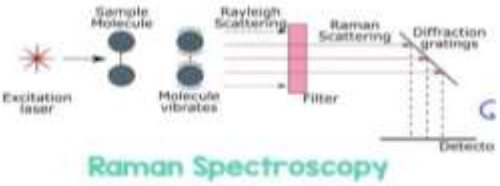


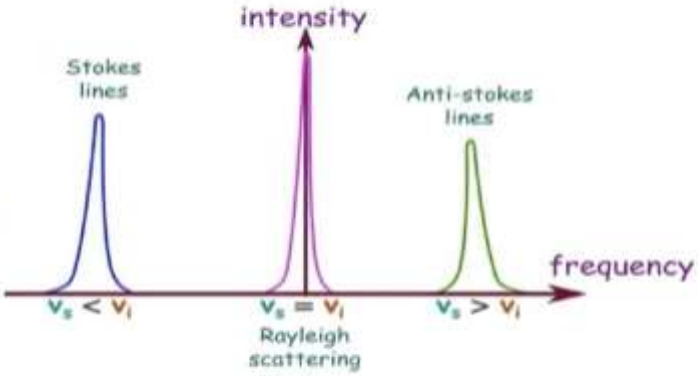
Energy level diagram showing the states involved Raman Spectra

Raman spectroscopy observes the change in energy between the incident and scattered photons associated with the Stokes and anti-Stokes transitions. This is typically measured as the change in the wavenumber (cm□1),from the incident light source. Because Raman measures the change in wavenumber, measurements can be taken using a source at any wavelength. Raman Spectroscopy looks at changes in a molecular bonds polarizability, which is the measure of the deformability of some bond in an electric field

The theory of Raman scattering shows that the phenomenon results from the same type of quantized vibrational changes that are associated with infrared absorption. Thus, the difference in wavelength between the incident and scattered visible radiation corresponds to wavelengths in the mid-infrared region.The Raman scattering spectrum and infrared absorption spectrum for a given species often resemble one another quite closely.

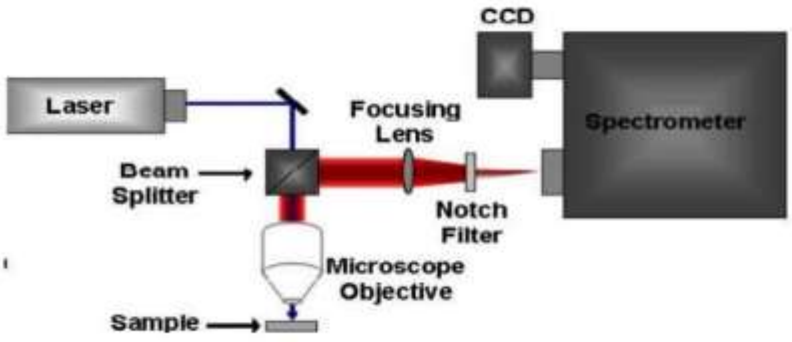
An important advantage of Raman spectra over infrared lies in the fact that water does not cause interference; indeed, Raman spectra can be obtained from aqueous solutions. In addition, glass or quartz cells can be employed, thus avoiding the inconvenience of working with sodium chloride or other atmospherically unstable window materials.



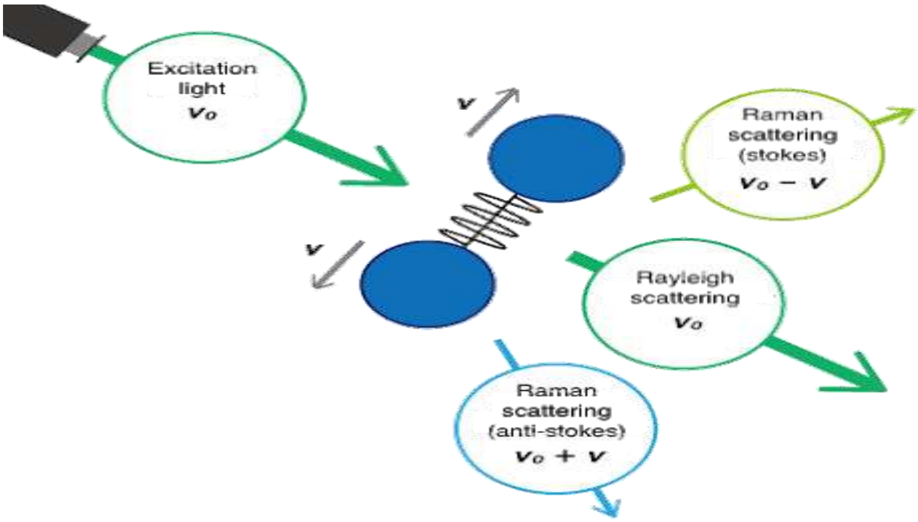


THEORY OF RAMAN SPECTROSCOPY:

Raman spectra are acquired by irradiating a sample with a powerful laser source of visible or near-infrared monochromatic radiation. During irradiation, the spectrum of the scattered radiation is measured at some angle (often 90 deg) with a suitable spectrometer.



Raman Spectrometer Design



Intensity of Normal Raman Peaks

The intensity or power of a normal Raman peak depends in a complex way upon the polarizability of the molecule, the intensity of the source, and the concentration of the active group. The power of Raman emission increases with the fourth power of the frequency of the source; however, advantage can seldom be taken of this relationship because of the likelihood that ultraviolet irradiation will cause photodecomposition. Raman intensities are usually directly proportional to the concentration of the active species.

Raman Depolarization Ratios

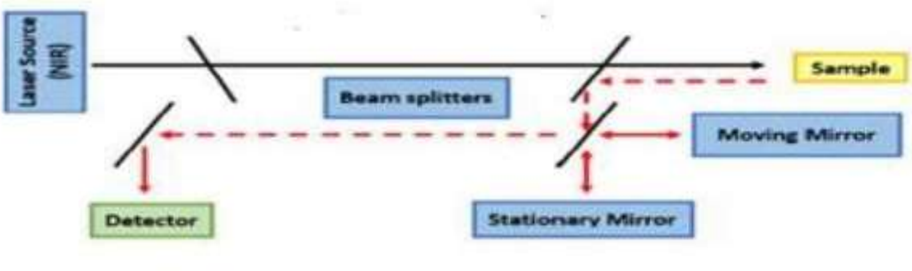
Polarization is a property of a beam of radiation and describes the plane in which the radiation vibrates. Raman spectra are excited by plane-polarized radiation. The scattered radiation is found to be polarized to various degrees depending upon the type of vibration responsible for the scattering.

INSTRUMENTATION

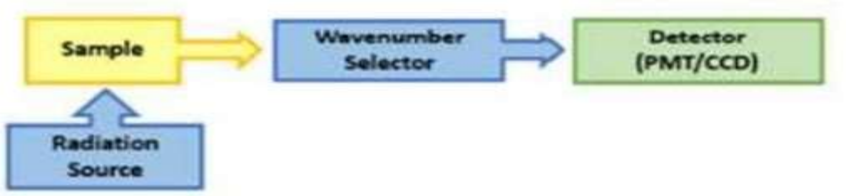
Instrumentation for modern Raman spectroscopy consists of three components: A laser source, a sample illumination system and a suitable spectrometer. The sources used in modern Raman spectrometry are nearly always lasers because their high intensity is necessary to produce Raman scattering of sufficient 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

Raman Spectrometers

Raman spectrometers were similar in design and used the same type of components as the classical ultraviolet/visible dispersing instruments. Most employed double grating systems to minimize the spurious radiation reaching the transducer. Photomultipliers served as transducers. Now Raman spectrometers being marketed are either Fourier transform instruments equipped with cooled germanium transducers or multichannel instruments based upon charge-coupled devices.



FT Raman Spectrometer



Dispersive Raman Spectrometer

APPLICATIONS OF RAMAN SPECTROSCOPY

Raman Spectra of Inorganic Species. The Raman technique is often superior to infrared for spectroscopy investigating inorganic systems because aqueous solutions can be employed. It is used in industry for a variety of application, including: Crystallization, polymorphism identification, polymerization reactions, Hydrogenation Reactions, Chemical Synthesis, Biocatalysis and Enzymatic Catalysis and synthesis reactions.

Biological Applications of Raman Spectroscopy

Biological Applications of Raman Spectroscopy Raman spectroscopy has been applied widely for the study of biological systems. The advantages of his technique include the small sample requirement, the minimal sensitivity toward interference by water, the spectral detail, and the conformational and environmental sensitivity.

Resonance Raman Spectroscopy

Resonance Raman scattering refers to a phenomenon in which Raman line intensities are greatly enhanced by excitation with wavelengths.

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.

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.

References:

1. *Gardiner, D.J. (1989). Practical Raman spectroscopy. Springer-Verlag. ISBN 978-0-387-50254-0.*
2. *Hammes, Gordon G. (2005). Spectroscopy for the biological sciences. Wiley. ISBN 9780471733546. OCLC 850776164.*
3. *K. S. Krishnan; Raman, C. V. (1928). "The Negative Absorption of Radiation". Nature.* ***122*** *(3062): 12–13. Bibcode:1928Natur.122...12R. doi:10.1038/122012b0. ISSN 1476-4687. S2CID 4071281.*
4. ^ Jump up to:[a] [b] [c] [d] [e] [f] [g] *McCreery, Richard L. (2000). Raman spectroscopy for chemical analysis. New York: John Wiley & Sons. ISBN 0471231878. OCLC 58463983.*
5. ^ *Gordon, Geoffrey P. S. Smith Gregory S. Huff Keith C. "Investigating Crystallinity Using Low Frequency Raman Spectroscopy: Applications in Pharmaceutical Analysis". spectroscopyonline.com. Retrieved 2019-07-21.*
6. ^ *"BragGrate- Bandpass ASE Suppression Filters". optigrate.com. Retrieved 2019-07-21.*
7. ^ *"SureBlock- Ultra Narrow-band Notch Filters". coherent.com. Retrieved 2021-03-25.*
8. ^ *Khanna, R.K. (1981). "Raman-spectroscopy of oligomeric SiO species isolated in solid methane". Journal of Chemical Physics.* ***74*** *(4): 2108. Bibcode:1981JChPh..74.2108K. doi:10.1063/1.441393. hdl:2060/19800020960.*
9. ^ *Butler, Holly J.; Ashton, Lorna; Bird, Benjamin; Cinque, Gianfelice; Curtis, Kelly; Dorney, Jennifer; Esmonde-White, Karen; Fullwood, Nigel J.; Gardner, Benjamin; Martin-Hirsch, Pierre L.; Walsh,*

Michael J.; McAinsh, Martin R.; Stone, Nicholas; Martin, Francis L. (2016). "Using Raman spectroscopy to characterize biological materials". Nature Protocols. **11** (4): 664–687. doi:10.1038/nprot.2016.036. PMID 26963630. S2CID 12315122. Retrieved 2017-05-22.

10. ^ Taylor, P.D.; Vinn, O.; Kudryavtsev, A.; Schopf, J.W. (2010). "Raman spectroscopic study of the mineral composition of cirratulid tubes (Annelida, Polychaeta)". Journal of Structural Biology. **171** (3): 402–405. doi:10.1016/j.jsb.2010.05.010. PMID 20566380. Retrieved 2014-06-10.
11. ^ Ben Vogel (29 August 2008). "Raman spectroscopy portends well for standoff explosives detection". Jane's. Archived from the original on 2008-12-03. Retrieved 2008-08-29.
12. ^ "Finding explosives with laser beams", a TU Vienna press-release
13. ^ Jump up to:[a] [b] Misra, Anupam K.; Sharma, Shiv K.; Acosta, Tayro E.; Porter, John N.; et al. (2012). "Single-Pulse Standoff Raman Detection of Chemicals from 120 m Distance During Daytime". Applied Spectroscopy. **66** (11): 1279–85. Bibcode:2012ApSpe..66.1279M. doi:10.1366/12-06617. PMID 23146183. S2CID 44935369.
14. ^ "Working Groups | raman4clinics.eu". raman4clinics.eu. Retrieved 2017-05-22.
15. ^ Howell G. M. Edwards, John M. Chalmers, Raman Spectroscopy in Archaeology and Art History, Royal Society of Chemistry, 2005
16. ^ McCann, Lowell I.; Trentelman, K.; Possley, T.; Golding, B. (1999). "Corrosion of ancient Chinese bronze money trees studied by Raman microscopy". Journal of Raman Spectroscopy. **30** (2): 121–132. Bibcode:1999JRSp...30..121M. doi:10.1002/(SICI)1097-4555(199902)30:2<121::AID-JRS355>3.0.CO;2-L. ISSN 1097-4555.
17. ^ Trentelman, Karen; Turner, Nancy (2009). "Investigation of the painting materials and techniques of the late-15th century manuscript illuminator Jean Bourdichon". Journal of Raman Spectroscopy. **40** (5): 577–584. Bibcode:2009JRSp...40..577T. doi:10.1002/jrs.2186. ISSN 1097-4555.
18. ^ Raman Spectroscopy at ColourLex
19. ^ Dariz, Petra; Schmid, Thomas (2021). "Trace compounds in Early Medieval Egyptian blue carry information on provenance, manufacture, application, and ageing". Scientific Reports. **11** (11296): 11296. doi:10.1038/s41598-021-90759-6. PMC 8163881. PMID 34050218.
20. ^ Quinn, Eamon (May 28, 2007) Irish classic is still a hit (in calfskin, not paperback). New York Times
21. ^ Candeias, Antonio; Madariaga, Juan Manuel (2019). "Applications of Raman spectroscopy in art and archaeology". Journal of Raman Spectroscopy. **50** (2): 137–142. doi:10.1002/jrs.5571. ISSN 1097-4555.
22. ^ "Home | IRUG". www.irug.org. Retrieved 2020-05-15.
23. ^ Marcet, S.; Verhaegen, M.; Blais-Ouellette, S.; Martel, R. (2012). Kieffer, Jean-Claude (ed.). "Raman Spectroscopy hyperspectral imager based on Bragg Tunable Filters". SPIE Photonics North. Photonics North 2012. **8412**: 84121J. Bibcode:2012SPIE.8412E..1JM. doi:10.1117/12.2000479. S2CID 119859405.
24. ^ David Tuschel (2016). "Selecting an Excitation Wavelength for Raman Spectroscopy". Spectroscopy Online. **31** (3): 14–23.
25. ^ Shan Yang; Ozan Akkus; David Creasey (2017). "1064-nm Raman: The Right Choice for Biological Samples?". Spectroscopy Online. **32** (6): 46–54.
26. ional normal modes of a single molecule with atomically confined light". Nature. **568** (7750): 78–82. Bibcode:2019Natur.568...78L. doi:10.1038/s41586-019-1059-9. ISSN 1476-4687. PMID 30944493. S2CID 92998248.
27. ^ "Raman scattering". cryst.ehu.es. Retrieved 2019-07-04.
28. ^ Khanna, R.K. (1957). "Evidence of ion-pairing in the polarized Raman spectra of a Ba^{2+}—CrO_4^{2-} doped KI single crystal". Journal of Raman Spectroscopy. **4** (1): 25–30. Bibcode:1975JRSp....4...25G. doi:10.1002/jrs.1250040104..

29. ^ Chao RS; Khanna RK; Lippincott ER (1974). "Theoretical and experimental resonance Raman intensities for the manganate ion". Journal of Raman Spectroscopy. **3** (2–3): 121–131. Bibcode:1975JRSp....3..121C. doi:10.1002/jrs.1250030203.
30. ^ Lombardi JR; Birke RL (2008). "A Unified Approach to Surface-Enhanced Raman Spectroscopy". Journal of Physical Chemistry C. **112** (14): 5605–5617. doi:10.1021/jp800167v.
31. ^ Hou, J. G.; Yang, J. L.; Luo, Y.; Aizpurua, J.; Y. Liao; Zhang, L.; Chen, L. G.; Zhang, C.; Jiang, S. (June 2013). "Chemical mapping of a single molecule by plasmon-enhanced Raman

scattering". Nature. ***498*** *(7452): 82–86. Bibcode:2013Natur.498...82Z. doi:10.1038/nature12151. ISSN 1476-4687. PMID 23739426. S2CID 205233946.*

32. ^ *Hermann, P; Hermeling, A; Lausch, V; Holland, G; Möller, L; Bannert, N; Naumann, D (2011). "Evaluation of tip-enhanced Raman spectroscopy for characterizing different virus strains". Analyst.* ***136*** *(2): 1148–1152. Bibcode:2011Ana...136.1148H. doi:10.1039/C0AN00531B. PMID 21270980.*

33. ^ *Kneipp K; et al. (1999). "Surface-Enhanced Non-Linear Raman Scattering at the Single Molecule Level". Chem. Phys.* ***247*** *(1): 155–162. Bibcode:1999CP....247..155K. doi:10.1016/S0301-0104(99)00165-2.*