THE SHORT-RANGE COMPONENT OF SERS:
RESULTS OF BIOPOLYMERS
E. Koglin, J. Séquaris

To cite this version:
E. Koglin, J. Séquaris. THE SHORT-RANGE COMPONENT OF SERS : RESULTS
<10.1051/jphyscol:19831098>. <jpa-00223556>

HAL Id: jpa-00223556
https://hal.archives-ouvertes.fr/jpa-00223556
Submitted on 1 Jan 1983

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
THE SHORT-RANGE COMPONENT OF SERS : RESULTS OF BIOPOLYMERS

E. Koglin and J.M. Séquarís

Chemistry Department, Institute of Applied Physical Chemistry, Nuclear Research Center (KFA), Juelich, F.R.G.

Résumé. - La composante à courte portée de la diffusion Raman exaltée de surface (SERS) est étudiée à l'aide des biopolymères, DNA et poly-A. Les deux molécules forment une double hélice (diamètre d'environ 20 Å). Les chaînes sont disposées avec l'armature sucre-phosphate à l'extérieur et les bases nucléiques face au centre. Sur une surface d'Argent chargée positivement (colloïdes, électrode), ces biomolécules sont principalement adsorbées par l'intermédiaire de l'armature sucre-phosphate chargée négativement. Les bases nucléiques, situées au centre de l'hélice, ne présentent aucun signal Raman. Cependant, après la destabilisation de la structure en double hélice, les bases nucléiques interagissent directement avec la surface et donnent des signaux Raman importants. Ces observations indiquent que l'importante amplification constatée pour DNA et poly-A sur des colloïdes et des électrodes d'Argent est due à un mécanisme à courte portée, sur des distances à la surface inférieures à 5 Å.

Abstract. - The short-range component of surface enhanced Raman scattering (SERS) is investigated using the biopolymers, DNA and poly-A. Both molecules form a double stranded helix (diameter about 20 Å). The chains are arranged with the sugar-phosphate backbone on the outside and the nucleic bases facing the center. At a positively charged silver surface (colloids, electrode) these biomolecules are adsorbed mainly through the negatively charged sugar-phosphate backbone. Nucleic bases, located in the center of the helix do not exhibit any Raman signals. However after the destabilization of the double helical structure the nucleic bases interact directly with the surface and show strong SERS signals. These experimental observations indicate that the strong enhancement for DNA and poly-A on silver colloids and electrodes is caused by a short range mechanism for distances smaller than 5 Å from the surface.

There are both short-range and long-range enhancements contributing to the total surface enhanced Raman scattering (SERS) intensity (1,2). It was our goal to exploit the natural geometry of the biomolecules deoxyribonucleic acid (DNA) and polyriboadenyllic acid (poly-A) to clarify the range of the short-range component of the enhancement. These biomolecules consist of a double stranded helix with a weak scatterer (sugar-phosphate-group) on the outside of the molecules and strong Raman scatterers (nucleic bases) located in the center of the helix. The distance of the center of DNA, measured from the phosphate group, is about 10 Å. Our previous investigations of the nucleic bases adsorbed on silver electrodes and silver colloids have shown that
these building stones of DNA and poly-A exhibit strong SERS (3,4). Prominent SERS bands for the nucleic acid bases are the ring-breathing modes at 648 cm$^{-1}$ (electr.), 653 cm$^{-1}$ (coll.) in guanine, 728 cm$^{-1}$ (electr.), 728 cm$^{-1}$ (coll.) in adenine, 782 cm$^{-1}$ (electr.), 789 cm$^{-1}$ (coll.) in thymine and 798 cm$^{-1}$ (electr.), 797 cm$^{-1}$ (coll.) in cytosine. These specific Raman frequencies are usually found in the normal solution Raman scattering (NSRS) of DNA. However, in the case of the SERS spectrum of DNA adsorbed at a high positively charged silver electrode, Fig. 1 bands appear predominantly at 245 cm$^{-1}$ and 818 cm$^{-1}$ which can be respectively assigned to a silver-phosphate group vibration and to the backbone vibration of the polymeric-deoxyribose-phosphate chain.

The presence of these Raman bands indicate a preferential interaction of the nucleic residues lying outside the helical structure. The nucleic bases, located in the center of the helix exhibit no signals or very weak SERS signals. Thus, these experimental results show that the Raman enhancement is limited to the sugar phosphate residues at 5 Å maximum distance from the electrode surface.

It is interesting now to compare these SERS results from the intact double helical structure of native DNA and the SERS spectra of $\gamma$-irradiated DNA. It is well known that ionizing radiation causes different damages in DNA. These damages in modified nucleic acid residues, consist of strand breaks which induce the labilization of the helical structure.
Fig. 2 shows the SERS spectra of the intact and \( \gamma \)-irradiated DNA in the spectral range of the ring modes of the bases. The most striking features are the new pronounced lines at 734 cm\(^{-1} \) and 1334 cm\(^{-1} \). These characteristic bands can be assigned to the adsorbed adenine base vibrations. It follows that the nucleic base adenine becomes more accessible to the electrode surface. Thus, this result confirms that the short-range interactions play an important role in the enhancement factor of the Raman scattering.

In view of these results obtained with a rough silver electrode surface, we also investigated the Raman scattering from biomolecules adsorbed on dispersed silver particles of the silver colloids. Using the results of the strong interaction of the adenine base with the colloidal silver surface (4) we turned our attention to a polynucleotide based solely on the adenine-monophosphate: that is the polyriboadenylic acid, poly A. This biomolecule forms a double stranded helix at acid pH. The strands are also arranged with the sugar-phosphate backbone on the outside and the adenine base facing the center. The SERS spectrum of this polynucleotide and its building stones (adenine, adenosine-5'-phosphate and ribose-5'-phosphate) adsorbed at silver colloids are shown in Fig. 3. The most characteristic vibrations of the poly-A spectrum (cf. Fig. 3) are located at 606, 796 and 1282 cm\(^{-1} \). For the interpretation of these bands it is necessary to assign precise frequencies of the SERS bands of the building stones. Adenine and adenine 5'-monophosphate exhibit the characteristic ring breathing modes at 726 cm\(^{-1} \) and 721 cm\(^{-1} \). Prominent SERS bands for the ribose 5'-phosphate are at 600 cm\(^{-1} \) and 1282 cm\(^{-1} \). Comparing these results, we can thus conclude that in the case of poly-A we only observe the
SERS signals of the ribose-phosphate groups lying outside of the helical strands. The appearance of a band at 796 cm\(^{-1}\) in the SERS spectrum of poly-A corresponding to the stretching of the ribose-phosphate backbone confirms that the ribose-phosphate group is preferentially adsorbed. The adenine molecule located at a distance of about 5 Å from the phosphate group does not give any SERS signals.

Fig. 3
SERS spectra of poly-A and its building stones, adenine, adenosine 5'-monophosphate and ribose 5-phosphate. Freshly prepared silver colloids, pH 4.5; 4.10\(^{-4}\) M adenine, 5'-AMP or ribose 5-phosphate added; poly-A concentration 1.6 mg/ml; Laser excitation line: \(\lambda = 514\) nm, laser power 200 mW. (The drawing of poly-A shows the adenine base /black/ and the sugar-phosphate backbone outside the molecule)

In summary we have presented surface enhanced Raman spectra from biomolecules adsorbed at silver surfaces (electrodes and colloids) and discussed the influence of the short-range component in SERS. The observations show that an enhancement for the helical biomolecules is only detected at distances ranging up to 5 Å.

Acknowledgement
We thank H.H. Lewinsky for the measurements of \(\gamma\)-irradiated DNA and Dr. P. Valenta for helpful discussion. We are indebted to Prof. Dr. H.W. Nürnberg for his interest in this work.

References
5. S.C.Erfurth and W.L.Peticolas, Biopolymers 14, 247 (1975)