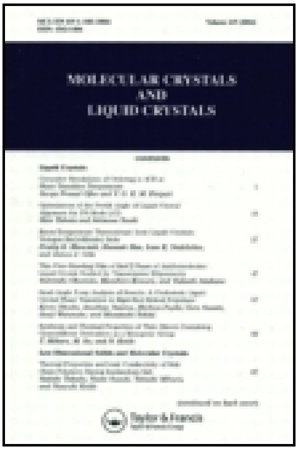

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Surface Enhanced Raman Spectroscopy of Photochromic Spiroxazines and Related Spiropyrans

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SURFACE ENHANCED RAMAN SPECTROSCOPY OF PHOTOCHROMIC SPIROXAZINES AND RELATED SPIROPYRANS.

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Abstract The surface enhanced Raman spectroscopy (SERS) of a spiroxazine and spiropyran photochromes in silver colloids is presented. A qualitative description of the structure and orientation of adsorbed species is given. This work is a preliminary step in order to study photochromic molecules in polymer matrices using SERS.

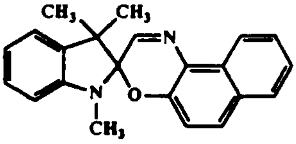
INTRODUCTION.

While the photochromism of spiropyrans has been intensively studied, comparatively few studies concerning the closely related spiroxaxines have been performed.(1) However, spiroxazines reveal more interesting properties, particularly they show a good balance between photocoloration and photodegradation and thus are good candidates for industrial applications. Therefore, our recent works have been focused on the synthesis of new structures in the oxazine series and on the study of their spectrokinetic and photodegradation parameters.(2,3) Apart from these spectral measurements in organic solutions, involving absorption and Raman spectroscopies, we have investigated the vibrational spectra of some photochromes in silver colloids. Indeed, surface enhanced Raman spectroscopy (SERS) may occur when molecules are adsorbed onto certain metallic surfaces with enhancement factors up to 10^8, thus allowing the study of molecular properties and orientation of photochromes at very low concentrations (*ca.* 10^{-8} M). Moreover, such studies can be envisaged not only in colloidal solutions but also within polymer matrices.(4) In this paper, we report SER spectra of spiro[indoline-naphthoxazine] with those of its closely related spiro[indoline-naphthopyran] for comparison. In order to assist the analysis of these spectral data, the model molecules of indoline and naphthopyran moieties have been synthetised and their Raman spectra (ordinary and SERS) recorded. Finally a strategy for using Ag colloid SERS in polymer matrices for structural studies of photochromes and identification of their degradation products is discussed.

EXPERIMENTAL SECTION

Synthesis and purification of spiroxazine (I) and spiropyran (II) were reported previously(2); the synthesis of the models, respectively 1,2,3,3 tetramethylindoline (III) and the chromene, 3,3 dimethylnaphtho[2,1-b]pyran (IV), was performed by one of us. (EB)

For the measurement of Raman spectra, a few microliters of stock solutions ($10^{-3}/10^{-4}$ M for I and II, $10^{-1}/10^{-2}$ M for III and IV) were diluted in 1 *ml* citrate reduced Ag colloids. In our experiments the final concentrations were in the ranges $10^{-5}/10^{-7}$ M for the photochromes and $10^{-3}/10^{-4}$ M for model molecules. SER spectra, from Ag sols, were excited with the 514.5 *nm* line of an Ar^+ laser and recorded on a Dilor XY multichannel Raman spectrometer.(5) The sample cell (1 *cm* quartz cuvette) was illuminated using a 180° configuration. Raman spectra of pure compounds (either powders for I, II and IV or liquid for III) were collected on a NIR-FT Raman spectrometer (Perkin-Elmer, system 2000) equipped with a Nd-YAG laser with 1.06 *μm* excitation.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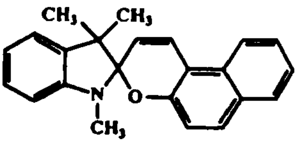
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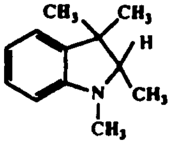
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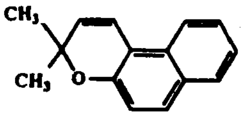
IV

RESULTS AND DISCUSSION.

Figure 1 compares the SER spectra on Ag colloids of photochromes (I,II) with those of indoline (III) and chromene (IV) model molecules. First it should be noted that SER spectra of photochromes show high S/N ratios (at 10^{-7} M) and are rather similar, both in positions and intensities, as expected from their very close chemical structures (see chem. formula). Second it appears that the medium or strong lines at *ca.* (in cm^{-1}), 360, 555, 609, 795, 877, 1022, 1048, 1087, 1127, 1242, 1264, 1343, 1369, 1410, 1460 and 1580, common to photochromes I and II (with only slight frequency shifts), are also present in model indoline moiety but with very different relative intensities. On the other hand, we observed two lines at *ca.* 1384 and 1556 cm^{-1} in II (1393 and 1565 cm^{-1} in I), which are absent in the SER spectrum of indoline (III) but are very intense in the SER spectrum of the chromene (resp. 1380 and 1568 cm^{-1}; spectrum IV in Fig. 1). These lines are characteristic of ring vibrations of disubstituted naphthalene, thus indicating they are issued from chromene moiety in the photochromes. Likewhise the lines at, 929, 1474 and 1630 cm^{-1} in II (resp. 938, 1494 and 1630 cm^{-1} in I), which solely appear in IV (but with very different relative intensities), probably correspond to in plane (ν and δ) ring vibrations of naphthopyran moiety as revealed by the detailed vibrational analysis of NIR-FT Raman spectra of pure molecules.(6)

On the basis of the above results it is clear that SER spectra of photochromes are mainly dominated by the spectral contribution from indoline moiety. This is consistent with the observation of strong SER spectra for N-heterocycle molecules(5). Moreover, recent studies on naphthalene derivatives have shown that their SER spectra involved essentially two strong lines at *ca.* 1380 and 1560 cm^{-1},(7) as it is observed in the present experiments for naphthopyran model molecule (IV) and photochromes (I and II). Thus, the SER spectrum of photochromes appears to be simply the addition of the SER spectrum of each constitutive moiety (ie. heterocycle and chromene) with weak coupling between these two parts.

It should be noted that this result is in agreement with previous vibrational analysis of spiropyran photochromes.(8)

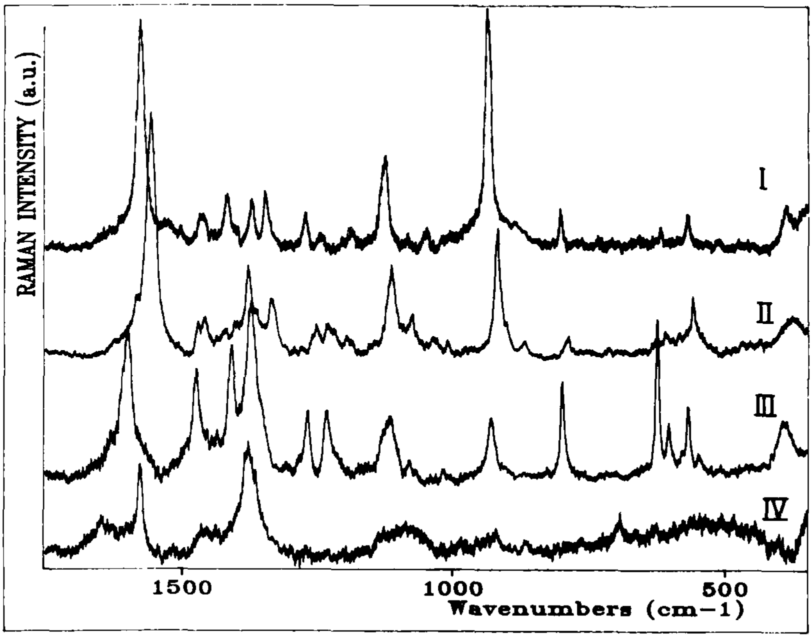

FIGURE 1. SER spectra in Ag colloids of photochromes (I and II, concentration 10^{-7} M) and model molecules, indoline (III, 10^{-4} M) and chromene (IV, 10^{-3} M). Laser excitation, 514.5 nm, 50 mW.

However, in the present experiments, the important intensity variations between the SER spectra of photochromes and their model constitutive parts implies that indoline and chromene (III and IV) have orientations, with respect to the silver surface, different from the ones they have in photochromes. In our case, the model molecules are adsorbed with their plane normal to the Ag surface, via the nitrogen atom for the indoline(5) and the naphthalene side for the chromene.(7) For the photochromes, deviation from these geometries must be considered to account for the large intensity variations observed. Indeed, since the Raman modes involving vibrations of atoms interacting with the surface are particularly enhanced, these intensity variations are probably due to the orientation of photochrome which takes place with its chromene and indoline planes no longer perpendicular to the surface. In figure 2 we have modelised the photochrome molecule and one of its possible orientations with respect to Ag surface.

CONCLUSION

This preliminary study has established that SERS is an efficient method to detect very small amounts of photochrome adsorbed onto Ag surfaces. A qualitative description of possible structure and orientation of adsorbates has been proposed on the basis of SER spectra of photochromes and their model constitutive moieties (indoline and chromene). Due to its hight detectivity and specificity SERS could be interesting to use for the detection and characterisation of photochromes and photodegradation products within polymer matrices.

The quenching of any fluorescence and particularly that of the polymer matrices should be a decisive advantage to use SERS in this case. However, for this purpose, polymers must be doped with fine Ag particles of which the size and the shape are controlled in order to obtained SERS effect. Moreover, "in situ" identification of species within polymers will necessitate building up a "SERS data base" of the expected photodegradation fragments and this implies the synthesis of numerous model compounds.

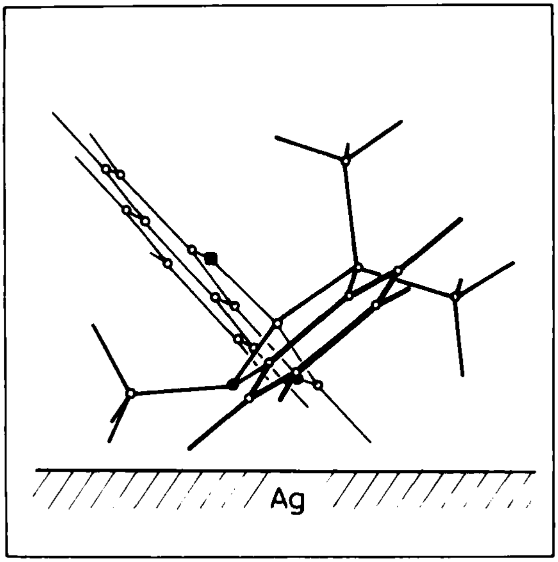

FIGURE 2 Orientation of photochrome adsorbed onto silver surface. This molecule has been modelised using the molecular graphic software SYBYLand its geometry optimised by a semi-empirical quantum mechanical method (AM1 from QCPE). The above orientation has been obtained using HOMO, LUMO and isopotential surfaces geometry.

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