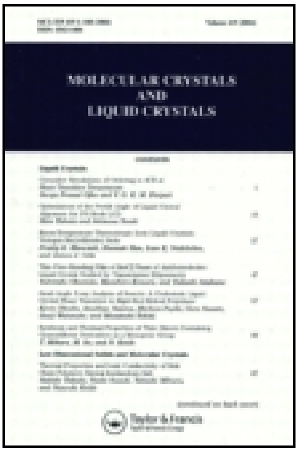

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Identification by Surface Enhanced Raman Speci'roscopy of Photodegradation Products in Organic Photochromes

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IDENTIFICATION BY SURFACE ENHANCED RAMAN SPECTROSCOPY OF PHOTODEGRADATION PRODUCTS IN ORGANIC PHOTOCHROMES

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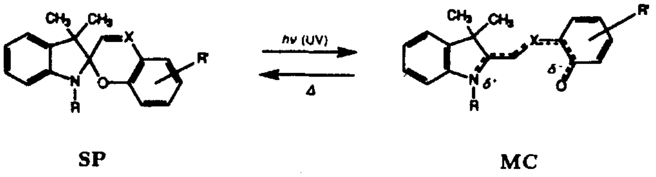
Abstract In this paper we described a recently developed method, using surface enhanced Raman scattering (SERS) in silver colloids, to detect and identify organic photochromes and their main photodegradation products. The reported SERS data were obtained on the classical 6-nitro-8-methoxy-indolinospirobenzopyran. It was observed that SERS spectra of this photochrome arise mainly from open species (photomerocyanines), and display vibrational features typical of the indolinic moiety. From specific SERS detection of totally degradated solutions, obtained under UV irradiation, it was possible to identify 5-nitrovanillin as the main photodegradation product and to estimate the proportions of this species and that of the remaining photochrome in various solvents (acetonitrile and dioxane).

INTRODUCTION

Owing to their ability to undergo photoinduced reversible coloration in solutions or in polymer matrix films, spiropyrans and spirooxazines are very interesting organic photochromes for various applications[1] (optical filters, data imaging and storage, molecular probes...). Photochromism in these systems is initiated by UV irradiation of the colorless spiro compounds, SP, which leads to cleavage of the C–O bond to give a deeply colored metastable merocyanine species, MC (scheme 1).

Scheme 1 : *Photochromic equilibrium between closed and open forms.*



Spiropyrans (BIPS) X=CH

Spirooxazines X=N

However, one of the major limiting factors for the industrial availability of these compounds is their progressive degradation with the loss of their photochromism after long exposures to repeated light–dark cycles.

While the kinetic mechanisms and the nature of short lived species participating in the photochromic reaction in solution have been studied in details using absorption and Raman spectroscopies, to date only very limited data are available concerning the photodegradation process.[2,3]

In a preceding study we have shown that surface enhanced Raman scattering (SERS) could be used to detect organic photochromes at very low concentration[4] (*ca.* 10^{-8}M). Indeed, huge enhancement of Raman spectra may be observed when organic molecules are adsorbed onto certain metallic surfaces like Ag, Au and Cu. We have recently developed a strategy, using Ag colloid SERS in complex biological media, for *ex-situ* and *in-situ* detection and characterization of drug metabolites at the level of traces.[5] This method is general and could be be applicable to detect and identify the main photoproducts involved in spiropyran photoaging. In this paper, we report SERS spectra obtained by irradiating the classical 6-nitro-8-methoxy-indolinospirobenzopyran (NMBIPS) in various solvents. In order to assist the analysis and assignments of Raman data, model molecules, which mimicked respectively indolinic and benzopyran moieties of the photochrome and fragments expected in the degradation process, have been synthesized and their Raman spectra (spontaneous and SERS) recorded. From the comparison of the SERS spectra of irradiated NMBIPS solutions with those of the reference compounds, identification of the main photoproducts involved in the degradation process along with their distribution in various solvents is discussed.

EXPERIMENTAL.

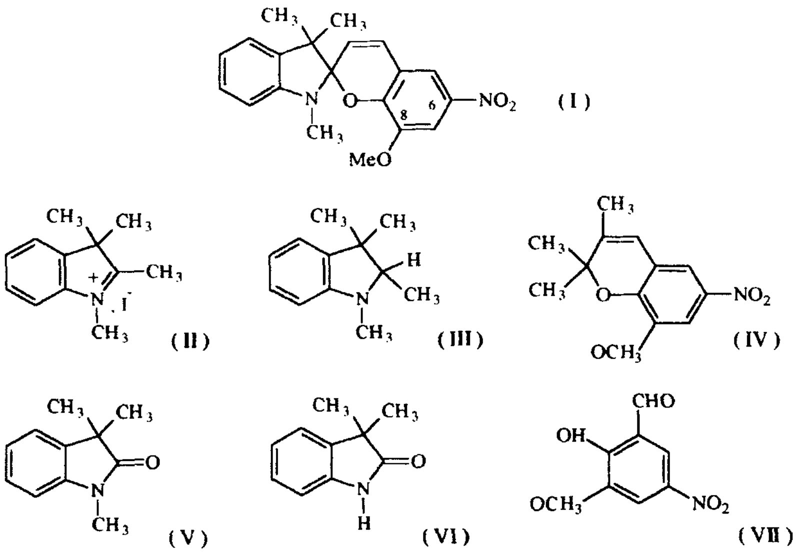


FIGURE 1 Chemical formula of the photochrome (I), the model moeities (II–IV) and the reference molecules (V–VII).

Synthesis and purification of 6 nitro-8-methoxy BIPS (I) and model molecules, 1,2,3,3 tetramethylindoleninium (II), 1,2,3,3 tetramethylindoline (III), and 2,3,3 trimethyl-6-nitro-8-methoxy-benzopyran (IV), were reported previously.[4] The synthesis of the reference samples of the photodegradation products, respectively 1,3,3 trimethyloxindol (V), 3,3 dimethyloxindol (VI), and 5 nitrovanillin (VII) were performed by one of us (KK) according to Baillet *et al.*[2]. For the recording of the SERS spectra of compounds I–VII, a few microliters of stock solution (*ca.* 10^{-2} to 10^{-4} M) were diluted in one $m\ell$ silver colloid obtained from the reduction of silver nitrate with an excess of sodium borohydrure ($NaBH_4$). This colloidal preparation has been shown recently to be very "SERS active" in the case of anionic and zwitterionic organic molecules,[8] and is well adapted for SERS studies of spiropyran photochromes (closed or open forms), and model molecules. In our experiments, the final concentrations were in the range 10^{-5} to 10^{-7} M for I, and 10^{-4} to 10^{-6} M for model molecules II to VII. SERS spectra from Ag sols were excited with 514.5 nm line of an Ar^+ laser and recorded on a Dilor XY multichannel Raman spectrometer.[4] Raman spectra of neat compounds (in either powders for I, II, IV, and VII or liquids for III, V, and VI) were recorded with a NIR-FT Raman spectrometer (Perkin Elmer, system 2000) equipped with Nd-Yag laser (1.06 μm excitation). In all experiments, the laser power was kept low enough (approximately 100 mW or less) to avoid thermal decomposition of the samples.

Degradation experiments were performed by UV irradiating 10^{-3} M solutions of I (acetonitrile or dioxane) using a focused 150 W high pressure mercury lamp. Small aliquots (a few $\mu\ell$), taken at regular time intervals, of the irradiated solutions were poored into the 1 $m\ell$ Ag sols and their SERS spectra recorded.

RESULTS AND DISCUSSION.

Assignments of SERS spectra of 6-nitro-8-methoxy BIPS (I).

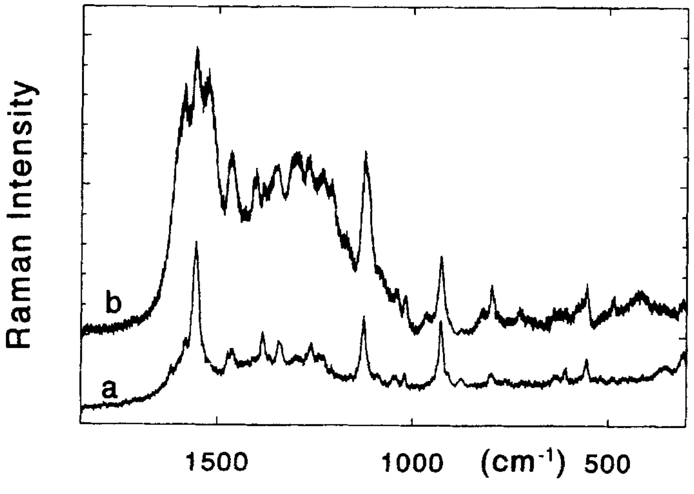


FIGURE 2 SERS spectra of photochromes I (b) and BIPS (a) in Ag colloids (5×10^{-6} M). Laser excitation, 514.5 nm, 50 mW.

The SERS spectrum of compound I in acetonitrile, in the absence of any UV irradiation, is shown in Fig. 2 (spectrum b). Upon a few seconds UV illumination, short enough to not degradate the solution, a blue deep coloration, typical of open forms, appears. The SERS spectra obtained in these conditions are very intense and identical (intensities and positions) to that reported in Fig. 2b. This is a strong evidence indicating that the SERS spectrum of I arises, at least for a part, from open merocyanine species (MC; see scheme I). Other arguments, in favor of this conclusion, are given below.

The SERS spectrum of BIPS, the parent compound of I but without any substitution on 6 and 8 positions, is also reported in Fig. 2 (spectrum a). Important differences are observed between the spectra, particularly in the spectral region above 1200 cm^{-1}. Aside some minor shifts in band positions, the intensity distribution in the spectrum b (I) is very different to that observed for the BIPS spectrum (Fig. 2a). Since this spectral region involves mainly ring stretch vibrations, which are very sentive to the electronic distribution, this would indicate a strong modification in the π electron delocalization between I and BIPS. Taking into account that in the closed form of spirocompounds there is no conjugation between indoline and benzopyran moieties, one must consider that open forms participate to the observed SERS spectrum of compound I.
In Fig. 3 we have compared the SERS spectrum of I with those of indoline (III) and nitro-benzopyran (IV) model molecules, recorded under the same experimental conditions. As observed, evident analogies in the line positions appear between spectra b (III) and d (I). On the other hand, the very strong lines observed at *ca.* 1320–1330 cm^{-1} in the NIR-FT Raman spectrum of I (neat compound; not shown) are absent in the SERS spectrum (Fig. 3d). These observations indicate that the SERS spectrum of I is mainly dominated by the vibrational characteristics of the indolinic moiety, in agreement with our previous SERS assignments of indolinospiropyran derivatives.[4] However, even if it appears several analogies between spectra b and d, (Fig. 3) their intensity distribution is very different. As suggested above, this is probably due to the difference in the π electron distribution of the species giving rise to the SERS spectra. Therefore, in order to complete our spectral analysis, the SERS spectrum of the methylindoleninium (II) was recorded (Fig. 3c). This compound was chosen on purpose since it has structural features and electronic distribution very close to those of indolinic moiety of the zwitterionic open forms in 6-nitrospiropyran series.[1] Comparison between spectra of compounds III, II, and I (Fig. 3, resp. b,c, and d) reveals similarities in line positions for all spectra but, more interestingly, strong analogies in the intensity distribution for only c and d spectra. This suggests that the SERS spectrum of I arises mainly from a species which the structural features and the electronic distribution are very close to those of methylindoleninium (II).

All these observations confirm the conclusion that open forms are present in the solution of I in the absence of any UV light irradiation. Probably solvatochromism which is very efficient in the case of 6-nitro derivatives is responsible for this situation.[1] These results may be compared with those of recent SERS experiments performed by Schneider *et al.*,[6] which have postulated that SERS spectra of nitro-BIPS derivatives in methanolic solutions, originated from neutral open merocyanine forms. Since photomerocyanines are colored red absorbing species, they present a strong resonance Raman effect; their detection with 514.5 nm laser excitation in Ag colloidal solutions is thus favored by resonant SERS (SERRS) with respect to the non resonant closed forms. It should be noted that the SERRS detection efficiency for cyanine dyes is very hight and spectra in Ag sols from 10^{-17} M solutions have been reported recently.[7]

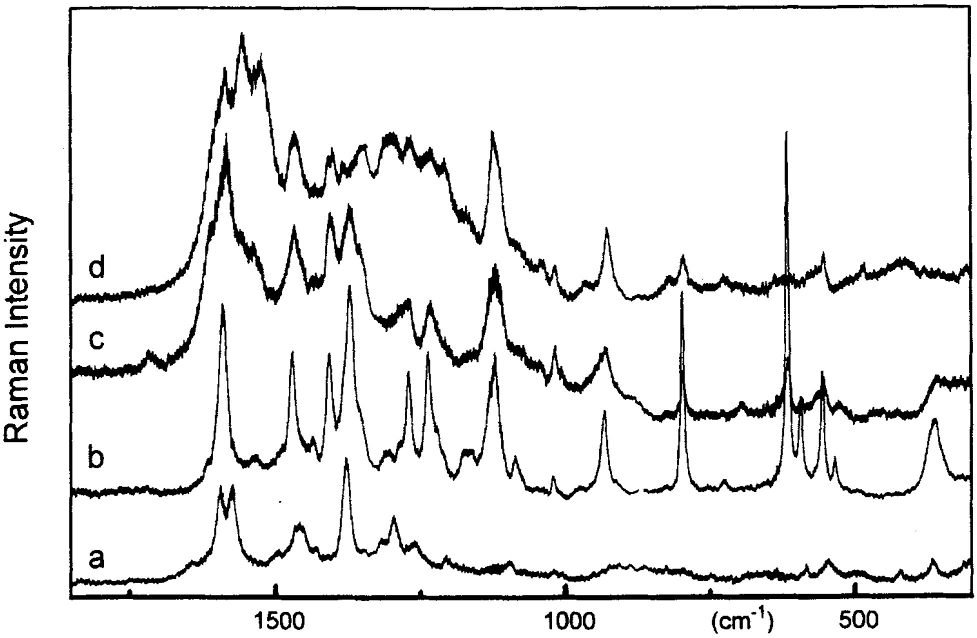


FIGURE 3 SERS spectra in silver sols of model molecules II to IV (a to c) and photochrome I (d). Laser excitation, 514.5 nm, 20–100 mW.

SERS analysis of UV irradiated solutions.

Different solutions of compounds I (acetonitrile and dioxane) were UV irradiated until their complete degradation. In our experimental conditions, after 4 hours of extensive irradiation, in acetonitrile, the photochrome has lost totally its photochromism properties. The yellow color solution thus obtained did not evolve any longer. In dioxane, the degradation kinetics is faster and complete degradation of the solution lasted about half an hour. SERS spectra were obtained by taking at regular time intervals, few *μℓ* aliquots of the irradiated solution, which were immediately deposited on 1 *mℓ* silver colloids. It was observed that once adsorbed onto Ag surfaces, further degradation did not develop, and SERS spectra were reproducible from experiment to experiment. The SERS spectrum of the non irradiated compound I along with the spectra recorded after 10 minutes and 4 hours of intense UV photolysis in acetonitrile, are shown in Fig. 4. Comparison between spectra 1, 2 and 3 shows that UV irradiation leads to important spectral changes (intensities and wavenumbers). The SERS spectrum of the totally degradated solution (spectrum 3) is then expected to give structural information on the main final products involved in the degradation process. Since a direct vibrational analysis of these SERS spectra is difficult, their assignments were obtained by comparison with spectra of synthetic reference compounds.

It has been shown that indolinospiropyran degradation in solution and in polymer matrices was mainly a photooxydation process, which proceeds essentially through the open merocyanine forms.[3] In the case of 6-nitro derivatives this process would lead to a mixture of tri- and di- methyloxindols (compounds V and VI) and 5-nitrovanillin (VII), the composition of which depends on the nature of the solvents.[2] Therefore, the SERS spectra of these compounds have been recorded under the same experimental conditions as used for irradiated solutions. The SERS spectrum of the model compound VII, shown in Fig. 4 (spectrum 4) is very similar, apart from very thin differences, to the SERS spectrum of the totally degradated solution (spectrum 3).

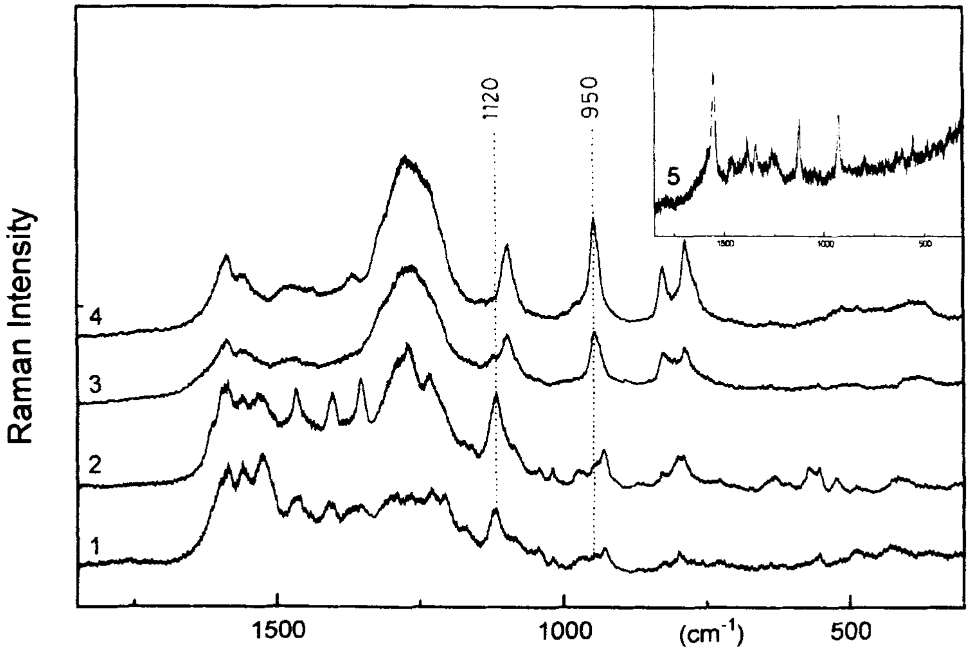


FIGURE 4 SERS spectra in silver colloids (40 mM $NaNO_3$) of I (10^{-5} M). (1) Non irradiated acetonitrile solution; (2) 10 minutes UV irradiated; (3) 4 hours UV irradiated. (4) SERS spectrum in Ag colloid (40 mM $NaNO_3$) of the model compounds VII (5-nitrovanillin). (5) SERS spectrum in Ag colloid (30 mM NaCℓ) of the 4 hours UV irradiated solution. Laser excitation. 514.5 nm, 100 mW.

We have demonstrated recently that specific SERS detection can be achieved when different salts are added in Ag colloids.[8] Thus, neutral or zwitterionic species are only detected in the presence of nitrate anions while the detection of organic cations are favored in the presence of chlorides. In this latter case, neutral or anionic molecules are exchanged, from the very Ag surface to the bulk, by these very reactive anions leading to the quenching of SERS spectra.[8] Such a specific detection, monitored by the nature of the salts added to the Ag sols, is clearly illustrated in the present photodegradation experiments. Whereas the SERS spectrum of the totally degradated acetonitrile solution of I, obtained in the presence of 30 mM NO_3^- (spectrum 3, Fig. 4), reveals essentially the presence of 5-nitrovanillin, the SERS spectrum obtained in the presence of $C\ell^-$ (see insert in Fig. 4), is exactly that of BIPS (Fig. 2a). This indicates that in the presence of chloride only the remaining photochrome I is detected.

Such a specific detection of either the remaining photochrome ($C\ell^-$) or photoproducts (NO_3^-) makes any quantitative SERS analysis very tricky. Moreover in the absence of an internal standard, only rough estimates of the amount of 5-nitrovanillin and remaining photochrome, present in the various degradated solutions, may be given. To this purpose, we have considered intensity ratios between the 950 and 1120 cm^{-1} lines specific respectively of the model compound VII (spectrum 4) and of the photochrome (spectrum 1). The estimates obtained by this procedure are reported in Table I and compared with the results of analytical chromatography experiments performed in the same solvents. These SERS results are in fair agreement with the data from chromatographic analyses.

TABLE I Photoproduct distributions (%) from UV irradiation of photochrome I in various solvents at 25°C. Comparison between chromatographic analyses (CA) and SERS.

Photoproducts	Acetonitrile		Dioxane	
	CA	SERS	CA	SERS
V	22	traces ?	9	10 - 20
VI	5	not detected	8	not detected
VII	70	$\gtrsim 80$	81	60 - 70
remaining photochrome	3	$\simeq 5$	2	traces ($\lesssim 1$)

CONCLUSION

This study is a clear demonstration of the usefulness of Ag colloidal SERS for specific detection and characterization of photochromes and their main photodegradation products, even at the level of traces.

It has been observed that the SERS spectra of 6-nitro-8-methoxy BIPS (NMBIPS) arise mainly from open photomerocyanine species. This conclusion has been confirmed by studying SERS spectra of the parent compound (BIPS) and those of model constitutive moieties (indoline, methylindoleninium and nitro- benzopyran). Analysis of these spectra reveals that the SERS spectrum of NMBIPS is dominated by the vibrational characteristics of the indolinic part. Moreover, comparison between SERS spectra of NMBIPS and methyl indoleninium confirms the zwitterionic structure of the photomerocyanines in this series.

From specific SERS detection it has been possible to identify 5-nitrovanillin as the main photodegradation product and to estimate the proportions of this species and that of the remaining photochrome in various solvents. These SERS data are in fair agreement with those reported from chromatographic analyses. The same strategy, using specific SERS detection, is currently underway to study the fatigue process and to identify the photoproducts in photochromic polymeric films.

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