

Study of Photoionization of Solids—Resonance Ionization

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Multiphoton ionization (MPI) mechanism in the solid state being still controversial we coupled a tunable laser to the LAMMA 500 microprobe to reinvestigate, using different UV irradiations, the ionization of some organic and organometallic solid compounds. Two polycyclic aromatic hydrocarbons (PAH) anthracene and pyrene and metallic derivatives of copper and cadmium were tested. Preliminary results are consistent with thermal desorption of neutral molecules as the first step followed by photoionization in the vapor phase.

Thus the ionization mechanisms described for gases or vapors, and in particular some REMPI or RIS processes appear to apply to our experimental conditions.

INTRODUCTION

Molecular photoionization requires high photon fluxes which can be supplied only by lasers. These light sources have led to an extension of newer soft ionization techniques, as applied to mass spectroscopy both in gaseous and solid states.

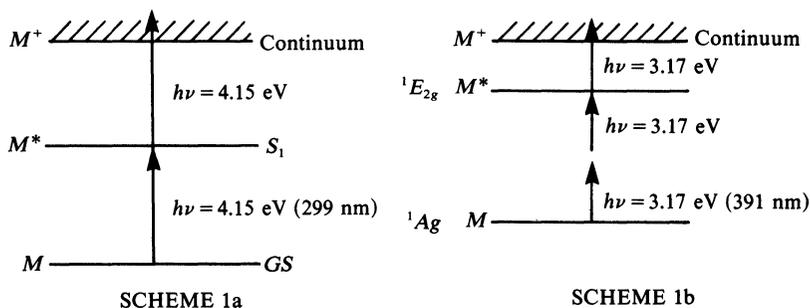
The possibility of varying the irradiation wavelength allows a selective ionization of some specific molecules in a gaseous mixture.^{1,2}

We connected a Quantel TDL III tunable dye laser to a laser microprobe mass analyser (LAMMA 500) in order to investigate the effect of wavelength variation on ionization in solid samples.^{3,4}

In the gas phase, photoionization is based on an absorption of several photons by the molecules (M.P.I.: Multiphoton Ionization).⁵ When the energy of the photons irradiating the molecules corresponds exactly to the energy of some specific electronic transitions, the

molecules absorb much of the radiation and change over to metastable excited states (resonance). The lifetime of some of these excited states allows a subsequent absorption of one or more other photons, which then causes the ionization of the molecules (REMPI: resonance enhanced multiphoton ionization).

Depending on the energy of the photons and on the energetics of the excited states of the molecules, two types of photoionization mechanisms have been proposed as illustrated by naphthalene (Scheme 1a) and benzene (Scheme 1b).



In the solid phase, laser photoionization at various irradiation wavelengths is still a controversial issue.

Cotter⁷ suggests that ion formation is independent of the laser wavelength. Thus, when the laser beam energy is not very high (10^6 – 10^7 W/cm²) the mass spectra are comparable to those obtained with other traditional desorption methods (F.A.B.: Fast Atom Bombardment, F.D.: Field Desorption, ²⁵²Cf P.D.M.S.: Californium 252 Plasma Desorption Mass Spectroscopy). This holds in particular for thermally unstable or non volatile molecules, which can not be investigated by traditional methods of gaseous phase mass spectrometry.^{10,11}

However, Hillenkamp,¹² has suggested that other ionization processes might exist depending on the range of wavelength used:

- IR or visible ionization could occur through a thermal process (by a superficial evaporation of ions, or neutral molecules which might ionize by reactions of ion molecule type).
- UV ionization should occur preferably through a photonic ionization process in the condensed phase. Hillenkamp uses the expression of “true desorption” for this situation.

Antonov arrived at similar conclusions¹⁴ has when he showed that the ionization yield of an anthracene monocrystal with the same low laser beam energy level ($2 \cdot 10^5$ W/cm²) was ten times higher at 249 nm than at 308 nm.

Thermal ionization could not be considered since the calculated sample temperature ranged from 2.5 to 10 K. The increase of the anthracene ionization yield can be paralleled to the increase of the molar absorption coefficient going from the first to higher energy absorption bands.

For Egorov *et al.*¹⁵ this photoionization mechanism is not convincing. According their experiments, the ionization occurs in two steps. At the first a thermal desorption of neutral molecules, and then a photoionization in the immediately superjacent gas phase. Thus all the energy absorbed in the crystal is thermalized completely and according to the relatively high volatility of the compounds studied, even a small increase of temperature is sufficient to induce a notable increase of neutral molecule desorption which can then be photo-ionized.

This paper gives the results that we obtained when we punctually irradiated some solid samples at different wavelengths.

EXPERIMENTAL^{3,4}

The LAMMA 500 system (Laser Microprobe Mass Analyser) in its usual structure permits a determination of the mass of the ions generated by a punctual interaction between a quadrupled pulsed Nd-Yag laser ($\lambda = 266$ nm – $\tau = 12$ ns) and the solids analyzed.

The irradiation wavelength of the solids is controlled by a dye laser pumped by the second harmonic of the LAMMA power laser ($\lambda = 532$ nm) (cf. Figure 1).

This equipment made it possible to investigate the ionization evolution in different accessible wavelength ranges using the dyes Rhodamines 590 and 640 (Exciton). The laser beam energy levels were measured with a photodyn XLA 66 photometer equipped with a model 400 sensorhead just before the objectives.

The range of energies measured on the sample is between 2 and 0.001 μ J.

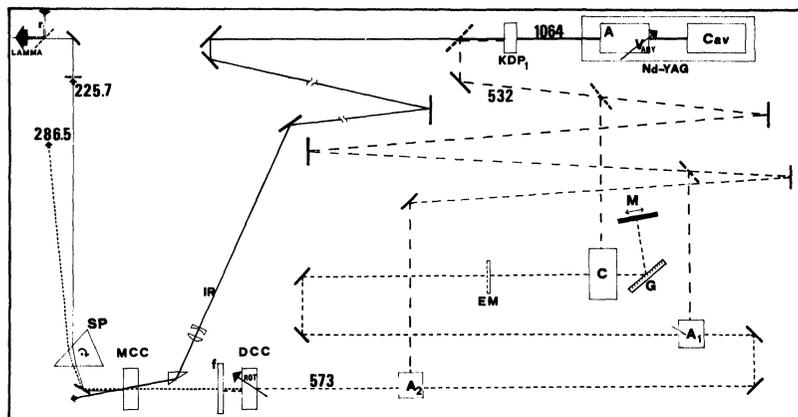


FIGURE 1 Coupling of the LAMMA's Neodymium-Yag laser (JK laser 2000) with a modified tunable laser Quantel TDL III. (—) Full line: total mirror reflecting prism, (---) dotted line: dichroic mirror, DCC: adjustable KDP crystal, MCC: mixing KDP crystal, SP: separating prism, EM, C, G, and M are elements of the cavity of the tunable laser i.e., respectively End Mirror, Capillary, Grating and tunable Mirror. V_{ANY} represents the variable voltage of the amplifier of the Neodymium Yag laser. A_1 , A_2 are the amplifiers of the tunable laser.

RESULTS

1. Evolution of the molecular peaks intensity of some organic molecules

Polycyclic aromatic hydrocarbons (PAH) were specifically investigated in the first place in order to compare our results with those of Antonov and Egorov.

The samples analyzed were cryptocrystalline films of anthracene or pyrene obtained by evaporating a toluenic solution of PAH on electron microscope grids (G 400 - ϕ 3.2 mm) adapted to the sample support of the LAMMA microprobe.

- (i) The two wavelengths selected were respectively 225.7 and 286.5 nm and correspond to very different molar absorption coefficients for both anthracene and pyrene in solution or gas phase. For the cryptocrystalline films (crystal form is not ob-

servable by a standard optical microscope) we suppose that the relative difference between the ϵ values are approximatively in the same order.

The mass peak of these two compounds showed up clearly at each irradiating wavelength, though a major difference was noticed concerning the energy threshold for the appearance of the M^{+o} peak when the wavelength was modified. Thus, the energy threshold from which M^{+o} molecular peak (and its satellite with a correct isotopic ratio of ^{13}C) appeared with the same anthracene film, passed from 0.05 μJ at 286.5 nm to 0.003 μJ at 225.7 nm.

A similar but smaller difference was also noticed with pyrene, the energy threshold passing from 0.1 μJ at 286.5 nm to 0.05 μJ at 225.7 nm.

The considerable rise of the mass peak noticed for anthracene when the wavelength was changed from 286.5 to 225.7 nm can be paralleled with the evolution of ϵ which is passed from $2.4 \cdot 10^2$ with $\lambda = 286.5$ nm to $7.9 \cdot 10^4$ with $\lambda = 225.7$ nm in solution or gas phase. In the case of pyrene, the small difference between the threshold energy levels at 286.5 and 225.7 nm might be explained by the small difference between its two molar absorption coefficients: $\epsilon_{286.5} = 2.6 \cdot 10^3$ and $\epsilon_{225.7} = 2.1 \cdot 10^4$.¹⁶ For these two compounds and at a same wavelength (227.5 or 286.5 nm) the threshold energy differences required to obtain the mass peak M^+ can be paralleled with their vapor pressure difference (volatility) at a same temperature: 403.15 K. For example anthracene (solid state) = 17.5 Pa and pyrene (solid state) = 0.228 Pa.^{17,18}

- (ii) To produce the mass peak of PAH microcrystals whose lattice energies are greater than that of cryptocrystalline films, it was necessary in the same conditions, to focalize a higher laser beam energy (anthracene at 225.7 nm; $E = 0.05 \mu\text{J}$) although there was also a superjacent gaseous phase above the solid for this type of sample. Conversely for cryptocrystalline films, when the lattice energy was higher (due to the polarity of the molecules) in particular for compounds such as 9 nitroanthracene,⁴ we have showed that the wavelength variations seem to be less sensitive to the energy threshold necessary to produce M^{o+} which is about 0.6 μJ at 225.7 nm or at 286.5 nm although

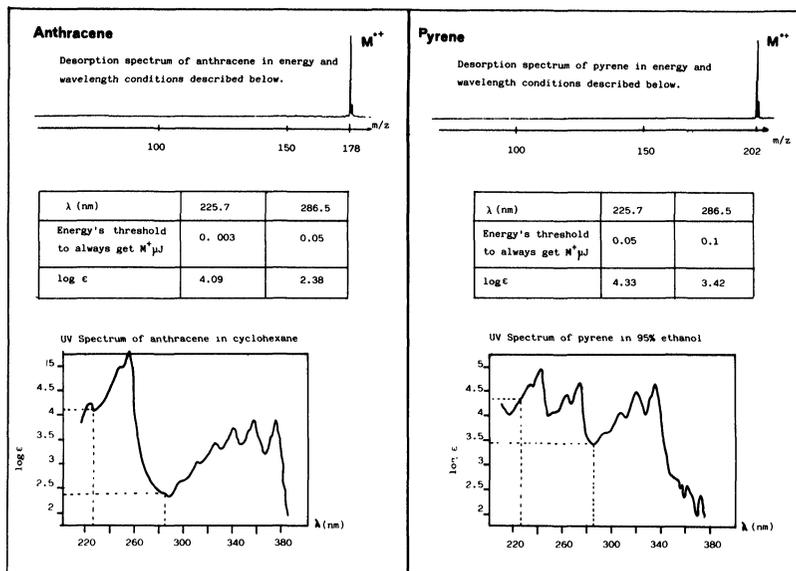


FIGURE 2 LAMMA's desorption spectra of anthracene and pyrene obtained at 225.7 and at 286.5 nm with the energy levels indicated in the table below the spectra. UV spectra of these compounds in the range of 200-400 nm,¹⁶ in solution.

the molar absorption coefficients $\epsilon_{286.5} = 1.6 \cdot 10^3$ and $\epsilon_{225.7} = 1.2 \cdot 10^4$ are significantly different.

Moreover there were more fragments on the spectra when the wavelength of irradiation was decreased.

Thus this evolution of the ionization energy threshold seems to be governed by two parameters: the volatility and the lattice energy of the sample studied.⁴

So our results are in good agreement with Egorov's conclusions, where a prior thermalization, which conditions the superjacent gaseous volume ionizable, is necessary before ionization.

Obviously it is possible, by decreasing the irradiation wavelength, to reduce considerably the energy level necessary to produce the specific P.A.H. molecular peak. Then we can hope to be in a position to detect the presence of absorbed P.A.H. without damaging the support.

2. Evolution of the ionization of metals

The resonant absorption is also widely used for a selective ionization of free atoms (atomized atoms), (R.I.S.: resonance ionization spectroscopy).^{8,9}

In the same manner that we showed that the ionization yield depends on the molar absorption coefficients of some organic molecules in the UV range, we examined the photoionization of some metals in the solid phase in relation to these atomic absorption properties. We paid special attention to the ionization of cadmium and copper in relation to the irradiation wavelength.

These two metals were included in polymers (Spurr and araldite) in the form of organometallic complexes with two acetylacetonate molecules ($\text{Cd}(\text{Acac})_2$ and $\text{Cu}(\text{Acac})_2$). Two specific phenomena appeared when modifying the wavelength, at constant energy level:

- (i) During the analysis of the polymer, the Cd^+ signal was multiplied three fold when the wavelength of the laser beam was identical to that of the more intense absorbing (or emitting) line of Cd (228.8 nm; transition $^1S_0 \rightarrow ^1P_1$) (Scheme 2a) as compared to the neighbouring wavelengths (226.5 or 231.3 nm).^{19,20}

This ratio was multiplied ten or even twenty-fold with longer wavelength (260–270 or 290–295 nm) where Cd has few weak absorbing (or emitting) lines (cf. Figure 3).
- (ii) With low energy ($E \approx 0.04 \mu\text{J}$) the irradiation of $\text{Cd}(\text{Acac})_2$ microcrystals also showed a sharp increase of the Cd ionization signal when 228.8 nm (resonance) light was used whereas at longer wavelength (291.8 nm) the presence of the $[(\text{Acac})_3\text{Cd}_2]^+$ cluster is observed.¹⁹
- (iii) The results obtained for copper are similar. Thus when wavelength of the laser beam was tuned to the more intense absorbing line of Cu doublet $^2S_{1/2} \rightarrow ^2P_{1/2}$ and $^2S_{1/2} \rightarrow ^2P_{3/2}$ at 327.39 and 324.75 nm respectively, we can see a notable increase of this metal ionization signal. We can also remark that the intensities of the peaks correctly reproduce the multiplicity of the *P* states. (cf. Figure 3.)

For copper the absorption of the photons at about 325 nm is not sufficient to cause ionization, but atoms are raised so close to their continuum that by collisions or/and electric field

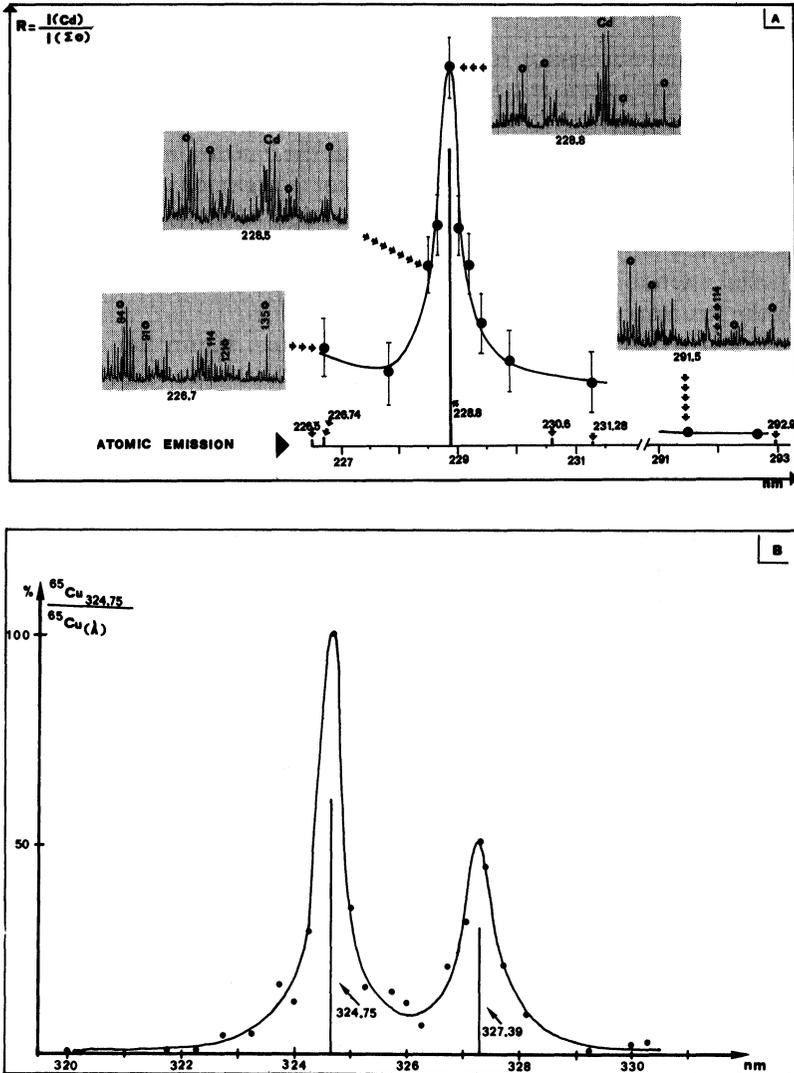
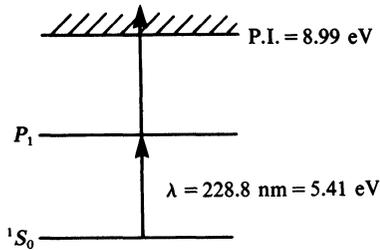
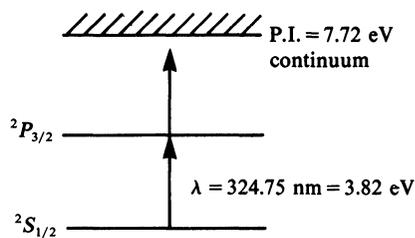


FIGURE 3 (a) Resonance ionization of Cadmium at 228.8 nm during the polymer doped film analysis. The ratio R of the Cd^+ peak intensity by the sum of the marked peaks varies from 0.45 to 1.35 in the range of 227 and 228.8 nm. At 228.8 nm the relative intensity of the emission ray of Cadmium is 1.500.¹⁸ (b) Evolution of Cu^+ signals via the wavelength variation. The two bars at 324.75 and 327.39 nm represent the relative intensity of the emission rays of copper (5000 and 2500 respectively).¹⁸

of the spectrometer extraction lenses, the ionization is obtained. This explanation was suggested at first by Hurst⁹ and reconsidered by Harrison *et al.*²¹

SCHEME 2a Case of Cd.¹⁰

SCHEME 2b Case of Cu.

Our results suggest that the mechanism of ionization of these inorganic derivatives could be similar to that occurring with the organic compounds. The irradiation wavelength corresponds indeed to an intense absorbing line of the metal under study, but the laser beam energies applied are rather high (0.04 μJ for $\text{Cd}(\text{Acac})_2$ and 0.3 μJ for polymer).

We recall that the mass peak of anthracene could be detected with an energy level of the order of 0.003–0.05 μJ (cryptocrystalline films or microcrystals) at 225.7 nm though there was no particular sharp resonance effect at this wavelength, but simply a strong radiation absorption.

This difference of behavior can be explained by the fact that atomization of metal requires more energy than the desorption of neutral organic molecules, and also the very different vapor pressure values of these two types of compounds.

Thus the first impinging photons of the *laser pulse* irradiating the solid might induce the formation of a microplasma—thermal stage—leading to an almost instantaneous emission of ions, neutral or charged molecules, atomized atoms, out of the solid. During this stage ion-molecule reactions can take place in solid phase (very low energy)⁴ or in the superjacent gas phase (higher energy). The atomized atoms can then reabsorb the radiation very strongly if the energy of the photons ($h\nu$) used corresponds exactly to an intense electronic transition (transitional R.I.S. mechanism).²¹

In the case of Cd or Cu, as examined here, the wavelengths used suggest that there would be photoionization according to the first of the five mechanisms put forward by G. S. Hurst: $\text{Cd}(\omega_1, \omega_1, e^-) \text{Cd}^+$ where ω_1 is the pulsation of the laser irradiating the sample.

CONCLUSION

The molar absorption coefficient of elements or organic molecules seems to be an important factor for the ionization of solids at ambient temperature.

The fact that ionization mechanisms deduced from gas experiments (in particular R.I.S.) are suitable for some metals included in polymer strengthens the ionization mechanism proposed by Egorov who assumes that a prior thermal stage takes place before the actual photoionization.

So it is possible to reduce selectively the detection threshold of all the elements which have some very intense absorbing line, in particular, in the UV range from 220 to 410 nm.

(The latter metals tested (Mo, Er) have also given good results.²²)

For organic molecules, the decrease of the ionization energy threshold, at very low wavelengths, has been observed for all the PAH studied at that time. This study, is continued with other series of molecules.

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