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Sample and plume luminescence in fast heavy ion induced desorption

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Abstract

The luminescence arising in ^{252}Cf -fission fragment induced desorption events has been measured using the time-correlated single photon counting technique. Photons emitted from the sample have been guided from a plasma desorption ion source to a photodetector by an optical fibre. Spectra and decay functions have been obtained using thin layers of Coronene or POPOP as samples. The results are strongly dependent on the acceleration field applied for ion extraction. Approximately 10 photons per fission fragment have been produced when applying no accelerating voltage. The results clearly show that these photons come from radiative electronic relaxations of molecules in the solid sample. Considerably more photons per fission fragment have been produced when applying a positive acceleration voltage. The intensity increases almost linearly for acceleration fields below 10 kV/cm and saturates at a nearly 10-fold higher value when compared to no acceleration. The intensity is also affected by the homogeneity of the accelerating field. These additional photons are attributed to radiative electronic relaxations of desorbed neutral molecules in the plume excited by inelastic collisions with accelerated positive ions. No additional photons have been observed when extracting negative ions. The negative ions produced do obviously not hit and/or excite desorbed neutral molecules, presumably due to their specific desorption characteristics. The experimental data have been analyzed by comparing with the cw and time-resolved sample luminescence obtained by optical excitation. The findings demonstrate that valuable information on ion-solid interactions, on specific desorption quantities and on processes in the plume can be obtained by measuring and analyzing the luminescence induced by the impact of high energy primary ions.

1. Introduction

Using ^{252}Cf -fission fragments as primary MeV energy heavy ions we investigated the photon emission arising in fast heavy ion induced desorption events. When penetrating thin samples, ^{252}Cf -fission fragments deposit energy into the electronic system of the sample through electronic stopping. A collective relaxation of electrons excited by this process disperses the energy to molecular or lattice vibrations leading finally to a transition of solid surface material into the gas phase and to a production of secondary ions. An important advantage of this effect, i.e. that large molecules can be desorbed as intact molecular ions, is widely used in plasma desorption mass spectrometry (PDMS) [1,2].

In PDMS, the ions produced are identified by their time-of-flight. Positive as well as negative ions are observed depending on the polarity of the acceleration field applied. The negative ion spectrum observed from layers of organic molecules, e.g. pure carbon or hydrocarbon compounds, shows always a very intense C_nH_x -series ($n = 1, 2, 3, \dots$; $x = 0, 1, 2, \dots$) and sometimes no molecular ion peak. From

hydrodynamic adiabatic expansion calculations it has been concluded that these ions are formed very close to the track of the impinging heavy ion by condensation subsequent to a complete destruction of the molecular structures [3]. The observed positive ions are assumed to be ejected from the ultratrack and some of them break up through an entropic fragmentation mechanism [3]. The temporal development of desorption as previously simulated by molecular dynamic calculations with keV energy primary ions shows three distinct processes: an early explosive process, a surface ablation by a surface shock wave, and a final thermal evaporation [4]. The angular distribution of total sputtering yield was found in this calculations to be nearly independent on the impact angle and to have a clear maximum at an ejection angle of about 50° . Time-of-flight experiments indicated that the emission angle of organic ions is correlated to the direction of the primary ion track in the solid [5] and in some cases a clearly reduced ion emission at 0 degree was observed by means of a position-sensitive detector [6]. But there are no experimental data on the ejection angle of neutrals which are expected to be by far the most abundant particles sputtered by MeV ions [7].

Luminescence from CsI films induced by the impact

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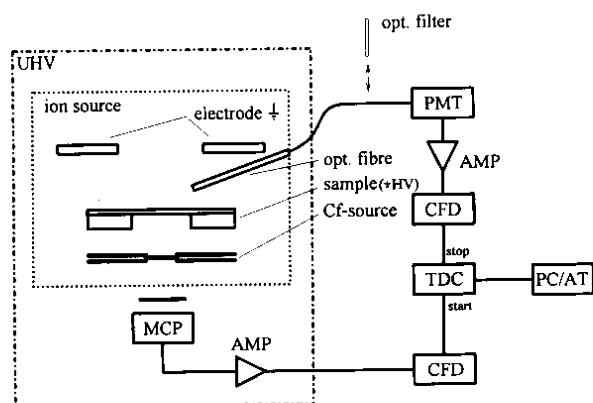


Fig. 1. Experimental set-up for single photon detection in a plasma desorption ion source; UHV: ultra-high vacuum chamber, MCP: double stage microchannel plate start detector, AMP: fast preamplifier, PMT: photomultiplier, CFD: constant fraction discriminator, TDC: time-to-digital converter, PC/AT: personal computer.

of single keV ions has been observed recently [8]. The photon yield was found to be proportional to the energy deposited into the electronic system of the target directly through electronic stopping and indirectly via the collision cascade. The observed luminescence originates from within the bulk of the target and was attributed to the radiative decay of self-trapped excitons. In our experiments, films of organic molecules suitable for luminescence measurements have been bombarded by single MeV ions. In addition to the luminescence of the sample, the photon emission arising in the plume when applying an accelerating voltage has been investigated for the first time. The analysis of the luminescence data yields valuable information on ion–solid interactions and may be useful for determining important desorption quantities in the future.

2. Experimental

The experiments were performed by introducing an 1.5 m optical fibre into the plasma desorption ion source of a time-of-flight spectrometer (see Fig. 1). The optical fibre was mounted between sample and acceleration system (distance 5 mm) aligned at an angle of about 70° to the target surface normal. Photons induced by the impact of ^{252}Cf -fission fragments (effective rate about 150 ff/s) and emitted from the whole 50 mm^2 active area of the sample into the direction of the optical fibre were guided to a photomultiplier (Hamamatsu R 269) placed outside the ultra-high vacuum chamber. The detection efficiency is estimated to about 10^{-3} mainly due to the small solid angle recorded by the optical fibre. The spectral range accessible by this arrangement is 300 nm to 750 nm limited by transmission of the optical fibre and by detector response. Because of the low photon intensity, a set of 8 optical filters inserted in front of the photodetector was used for spectral analysis (resolution about

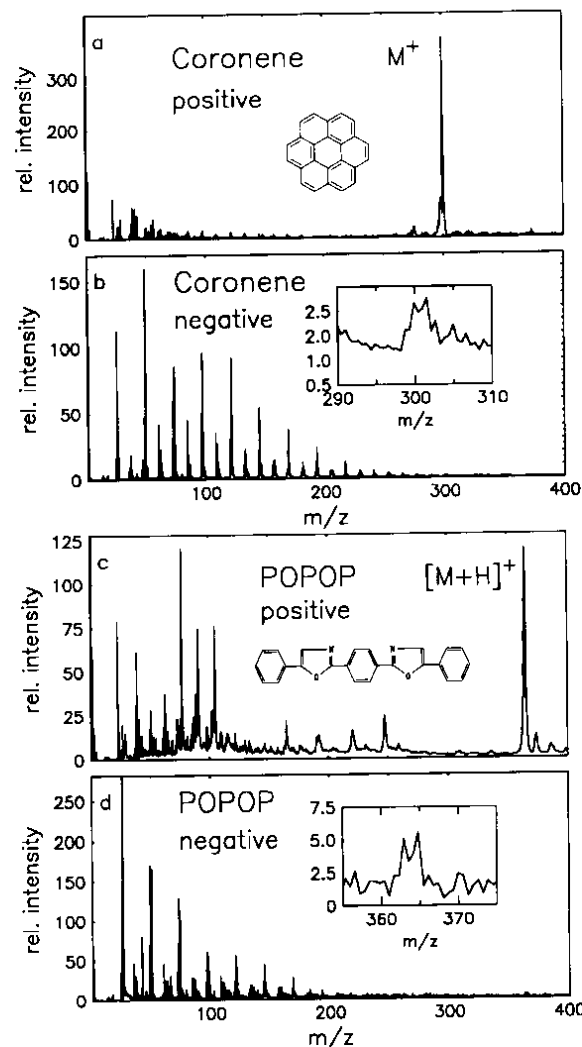


Fig. 2. Positive and negative ion PD mass spectra of the samples; negative ion spectra in the mass range of the molecular ion peaks are inserted into the figure on a larger scale.

30 nm). A background of about 200 counts/s was registered in the voltage range applied for acceleration ($< 15\text{ kV}$). The background signal increased rapidly at higher voltages due to spontaneous desorption.

The photomultiplier pulses arising from detection of single photons were amplified by a fast preamplifier (Ortec VT 120) and then converted to standard pulses by a constant fraction discriminator (Ortec Quad CFD 934). The photons were counted by collecting into a direct memory interface card (DMI, from IPN, Orsay, France) of an IBM PC/AT via a time-to-digital converter (CTN/M2 also from IPN). The time resolution was 500 ps. Start signals were obtained by the antiparallel fission fragments detected by a double stage MCP detector as usual in time-of-flight measurements.

Approximately $2\ \mu\text{m}$ thick layers of Coronene or POPOP deposited onto aluminized polyester foil were used as samples. Both substances are suitable for use in scintil-

lation spectrometry. Samples were prepared by spraying 300 μl 10^{-3} M solution using a nebulizer. For Coronene benzene was used as solvent and ethanol for POPOP. The positive and negative ion PD mass spectra of the samples are shown in Fig. 2. The positive ion spectra are clearly dominated by the molecular ion peak of Coronene M^+ at m/z 300 and of POPOP $[\text{M}+\text{H}]^+$ at m/z 365, respectively. The negative ion spectra are very similar showing the intense C_nH_x -series as expected but no molecular ion peak.

The cw luminescence spectra of the samples irradiated at 340 nm were measured by means of a photon emission spectrometer built on the basis of single photon counting. A strong molecular fluorescence reaching from 400 nm to 650 nm with the highest maximum near 500 nm was observed with both samples. The decay functions of the sample luminescence were determined by means of a picosecond-fluorimeter built for measuring ultra-short molecular lifetimes [9]. The measurements were performed with excitation at 330 nm, broad-band observation, and a time resolution of 70 ps. Non-exponential decay curves were obtained with both samples, but the mean relaxation times are clearly different. The data analysis (evaluation by determining the centroid) yields 31 ns for Coronene and 7 ns for POPOP. For comparison, a monoexponential decay was observed when measuring a 10^{-6} M solution of these substances. Lifetimes are 24 ns and 2 ns, respectively. Spectra and relaxation times clearly show that the origin of the sample photon emission is molecular fluorescence. Emission from excimers built e.g. by a self-trapping mechanism may occur in the long wavelength range of the luminescence band.

3. Results and discussion

The luminescence induced by the impact of ^{252}Cf -fission fragments was obtained as time-resolved photon intensity observed on the nanosecond scale. The results are strongly dependent on the acceleration field applied for extracting ions.

3.1. Luminescence observed without ion extraction

The photon intensity observed up to 100 ns without ion extraction is presented in Fig. 3. The number of photons per fission fragment registered with Coronene and POPOP amounts to a total of 12×10^{-3} and 4×10^{-3} , respectively. For comparison, the value obtained without sample layer is 5×10^{-4} . Therefore, nearly 12 or 4 photons per fission fragment were produced considering the detection efficiency of approximately 10^{-3} . The higher yield of Coronene is probably due to a larger quantum efficiency.

The time dependence of the photon intensity observed with Coronene and POPOP layers is non-exponential but clearly different (see Fig. 3). The centroids are at 30 ns and 9 ns, respectively. These values agree very well with those determined by optical measurements (see Section 2).

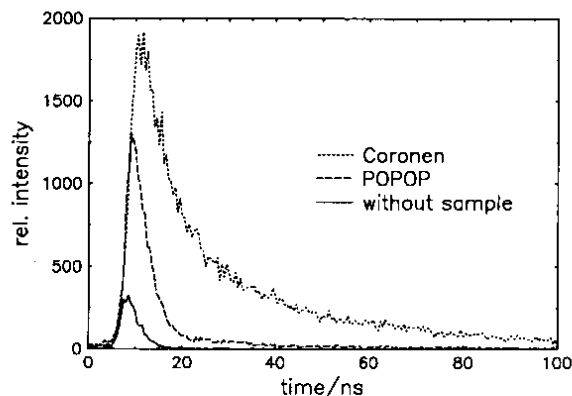


Fig. 3. Time-resolved photon intensity without ion extraction.

The photon spectrum obtained from Coronene by fission fragment excitation is depicted in Fig. 4. For comparison, the spectrum obtained by optical excitation and converted into the same spectral resolution is also shown in this diagram (Fig. 4c). The spectra look very similar. Therefore, from the correspondence of temporal characteristics and spectra it is concluded that the luminescence induced by the impact of ^{252}Cf -fission fragments come from radiative electronic relaxations, i.e. molecular fluorescence, in the solid samples.

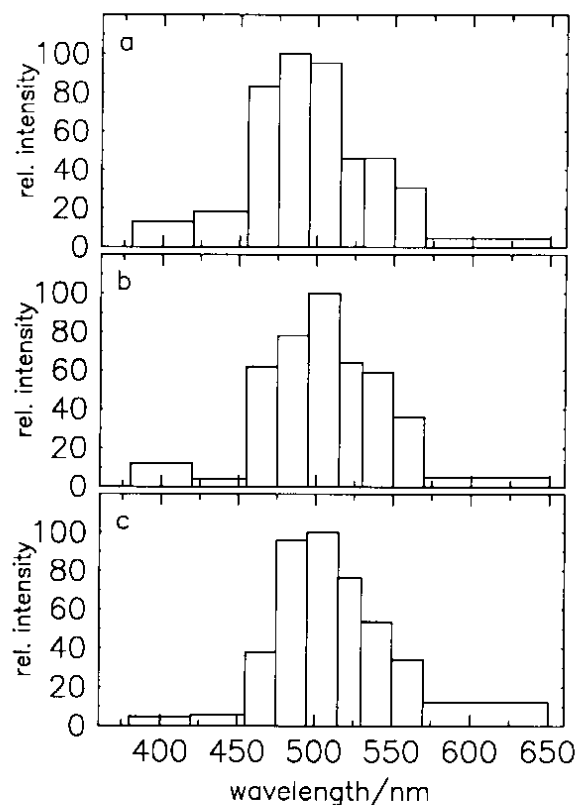


Fig. 4. Luminescence spectra of a Coronene film: (a) excited by ^{252}Cf -fission fragments without ion extraction; (b) excited by ^{252}Cf -fission fragments with +10 kV ion extraction; (c) excited by irradiation at 340 nm.

3.2. Luminescence observed with ion extraction

Depending on the polarity of the acceleration field applied, positive or negative ions are extracted (see Fig. 1). Usually, the acceleration was carried out by a grid, but in this investigation a single ring electrode (diameter 13 mm) was also used instead of a grid to study the effect of field homogeneity.

3.2.1. Positive ion extraction

Considerably more photons per fission fragment were generally observed when extracting positive ions. For example, the total photon yield obtained with POPOP when accelerating at +14 kV with a grid is approximately 5-fold enhanced when compared to no acceleration (see Fig. 5). But the most striking feature is the fact that the time dependence of the photon intensity observed with positive ion extraction is completely different and not monotonously decreasing. A lot of additional photons were registered even at times larger than 30 ns leading to a distinct shoulder in this time domain.

A further enhancement of the photon yield and more information is obtained when using a ring electrode instead of

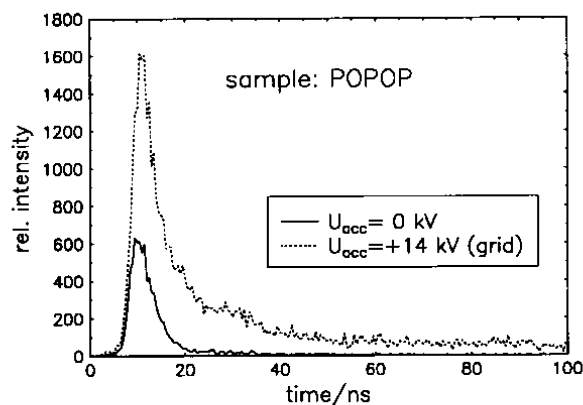


Fig. 5. Time-resolved photon intensity with and without ion extraction; acceleration with a grid.

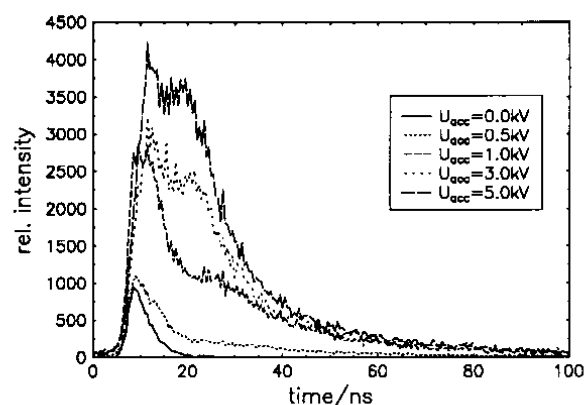


Fig. 6. Time-resolved photon intensity at various acceleration voltages; acceleration with a ring electrode; sample: POPOP.

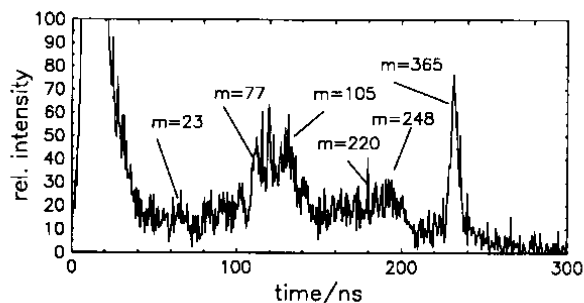


Fig. 7. Time-resolved photon intensity at times larger than 60 ns; acceleration with a metallic film; sample: POPOP.

a grid. The photon intensity observed with POPOP at various positive acceleration voltages when using a ring electrode is depicted in Fig. 6. The photon yield increases almost linearly and amounts at +5 kV to a total of 34×10^{-3} per fission fragment, i.e. 30 photons per desorption event are additionally produced when compared to no acceleration. The corresponding value of the Coronene sample is 73×10^{-3} . The photon yield saturates at voltages larger than +5 kV. The alteration of the time dependence observed with increasing acceleration voltages is striking (see Fig. 6) and an additional production of photons is obtained always in the same time domain (compare also Fig. 5). A distinct shoulder is observed already at +0.5 kV which changes into a clear second maximum at +1 kV. The maximum then shifts to shorter times at higher voltages.

The spectrum of the additionally produced photons has been measured with a Coronene sample (see Fig. 4b). The acceleration was +10 kV carried out with the ring electrode. The spectrum applies to the same wavelength region as the one obtained by optical excitation or at 0 kV and has also the same maximum. This correspondence is a strong indication that the additionally observed luminescence comes from Coronene molecules. Excitation of the sample by electrons produced by fission fragments hitting the grid or ring electrode and accelerated back to the sample can be excluded. These electrons would produce photons only in the time domain of the first few nanoseconds even at 0.5 kV. Therefore, the acceleration field dependent temporal characteristics of the photon intensity are much better explained by excitations of already desorbed neutral molecules colliding with positive ions. A careful analysis of the various time dependencies [10] yields that the neutral molecules should then be desorbed at energies of a few eV with a preferred ejection angle of about 50° . The positive ions should run after the neutral molecules delayed by a few picoseconds and come probably from a final thermal evaporation. Further work is needed to evaluate more precisely the observed temporal characteristics. But in any case, the experimental luminescence data are so far a strong indication that the desorption of the neutral molecules is not isotropic like an explosion.

Additional luminescence photons were observed also at times larger than 60 ns when accelerating positive ions by a grid. This effect can be strongly enhanced by using a metal-

lic foil instead of a grid. The photon intensity observed with POPOP at +5 kV in this time domain is shown in Fig. 7. Several maxima were obtained up to nearly 240 ns. These maxima are well explained by an additional luminescence produced by the impact of electrons on the sample. These electrons were sputtered from the grid or metallic foil by the 5 keV ions coming from the sample and were then accelerated back to the sample. The calculated running times of the ions indicated in the diagram fit very well with the observed maxima. Therefore, this additional delayed luminescence comes unambiguously from the sample.

3.2.2. Negative ion extraction

No additional photons per fission fragment were observed when extracting negative ions. This remarkable result was obtained independent of the sample or of the acceleration voltage. This experimental fact is not completely understood, but may be attributed to a special type of negative ion production. There is only an intense C_nH_x -series and no molecular ion in the negative ion spectra (see Fig. 2). These ions are formed very close to the track of the impinging fission fragment by condensation subsequent to a complete destruction of the molecular structures [3]. Therefore, the probability that some of these ions hit already desorbed neutral molecules may be very small due to spatial or temporal separation.

4. Conclusion

The luminescence arising in ^{252}Cf -fission fragment induced desorption events were measured using time-correlated single photon counting technique. Spectra and decay functions were obtained using thin layers of Coronene or POPOP as samples. The results are strongly dependent on the acceleration field applied for ion extraction. Approximately 10 photons per fission fragment were produced when applying no accelerating voltage. The results clearly show that these photons come from radiative electronic relaxations of molecules in the solid sample. Considerably more photons per fission fragment were produced when applying a positive acceleration voltage. The intensity increases almost linearly for acceleration fields below 10 kV/cm and satu-

rates at a nearly 10-fold higher value when compared to no acceleration. These additional photons are attributed to radiative electronic relaxations of desorbed neutral molecules in the plume excited by inelastic collisions with accelerated positive ions. No additional photons were observed when extracting negative ions. The negative ions produced do obviously not hit and/or excite desorbed neutral molecules presumably due to their specific desorption characteristics. The experimental data were analyzed by comparing with the cw and time-resolved sample luminescence obtained by optical excitation. The findings demonstrate that valuable information on ion–solid interactions, on specific desorption quantities and on processes in the plume can be obtained by measuring and analyzing the luminescence induced by the impact of high energy primary ions.

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