

Characterization of photons produced in solid films of organic molecules by the impact of ^{252}Cf -fission fragments

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Abstract

Experiments on photon production in solid films of organic molecules by the impact of ^{252}Cf -fission fragments are presented. The samples were mainly prepared with Coronene or POPOP sprayed onto an aluminized polyester foil using the nebulizer spray technique. It is demonstrated by scanning electron micrographs that this technique is a suitable method to prepare homogeneous solid films of organic compounds by producing layers of microcrystals. Time profiles and photon spectra have been determined by bombarding these samples with ^{252}Cf -fission fragments as well as, for comparison, by exciting with light. The results give evidence that the photons induced by fission fragment bombardment originate from molecular fluorescence in the solid sample. Approximately 500 photons per fission fragment have been produced within a 100 ns time window in about 2 μm thick POPOP samples. The photon yield has been observed to increase linearly with the thickness of the sample up to about 16 μm . Only very few photons per fission fragment has been obtained with Rhodamine 6G samples and the same low photon yield has been observed under the bombardment with 2 keV electrons. These results probably indicate that the excitation of molecular species by energetic δ -electrons is the necessary step in the process of photon production by fast heavy ions. Photons which have been additionally produced when extracting positive ions come also from molecular fluorescence in the samples. But this fluorescence is excited by electrons which originate from impacts of fission fragments on components of the acceleration system and which are accelerated back to the sample.

1. Introduction

Fission fragments of ^{252}Cf are used since 1974 in plasma desorption mass spectrometry (PDMS) as primary MeV energy heavy ions to deposit energy into the electronic system of solid samples [1]. By this excitation process, large secondary ions can be produced from the surface of the solid [2]. Molecular mass analyses of protein samples with molecular weights extending to several 10000 Da is one important application of this electronic sputtering effect [3].

Much theoretical and experimental work has been done on the elucidation of the entire process which for example has led to substantial improvements of the PDMS technique [4–8]. In the last year, first reports have been published on the emission of photons induced by the impact of single high-energy ions [9–11]. The results presented give evidence that the photons produced (i) are prompt, (ii) are not correlated with a desorption of particular secondary ions, and (iii) come from radiative transitions within the bulk of the sample due to relaxations of the electronic system. The

observed spectra show broad wavelength distributions and no narrow emission lines. These basic properties were obtained independent of the energy of the primary ion (MeV as well as keV) and independent of the type of sample (alkali halide, amino acids or aromatic compounds). Therefore, general information on ion–solid interactions can be obtained by measuring and characterizing the photons arising in high-energy ion induced desorption events.

In this paper we describe experiments on fast heavy-ion induced photon emission. New results are presented allowing to characterize the observed photons. Time profiles and photon spectra have been determined from solid films of Coronene or POPOP which have been excited by bombardment with ^{252}Cf -fission fragments as well as, for comparison, by irradiation with light. Compared to former measurements, the experimental setup have been changed so that photons could be also observed in the UV spectral range. The origin of the photons arising additionally when secondary ions are extracted could be better addressed. In addition, first results on the effect of sample thickness are presented.

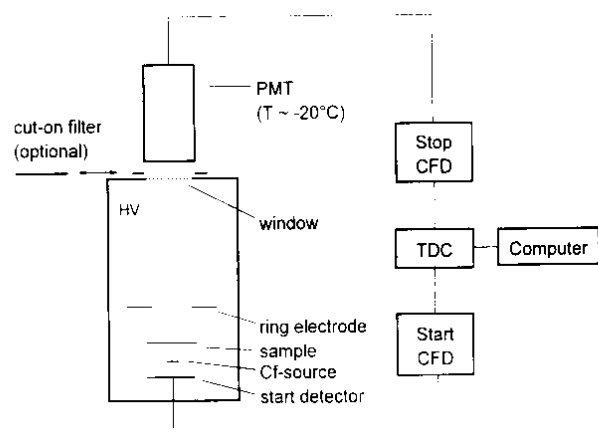


Fig. 1. Experimental set-up for the detection of single photons produced by the impact of ^{252}Cf -fission fragments; HV: vacuum chamber, PMT: photomultiplier tube, CFD: constant fraction discriminator, TDC: time-to-digital converter.

2. Experimental

2.1. Setup for photon emission measurements

The experimental setup for measuring photons emitted under the bombardment of ^{252}Cf -fission fragments is depicted in Fig. 1. The photons were produced in a plasma desorption ion source mounted in a time-of-flight spectrometer. The pressure was maintained at 10^{-6} to 10^{-7} mbar. The fission fragments emitted from the ^{252}Cf -source (effective rate about 100 ff/s) stroke the sample which had a typical thickness of a few μm so that the majority of the fission fragments could traverse the sample. The complementary fission fragments were used to create start pulses in a double-stage multi-channel plate detector. The secondary ions produced by the impact of the fission fragments could be accelerated by a ring electrode (diameter 13 mm) which was mounted 5 mm from the sample. The photons were detected directly through a sapphire view-port by a head-on type photomultiplier tube (Hamamatsu R 269) which has been mounted on a flange outside the ultra-high vacuum chamber. The distance between photocathode and sample was about 270 mm. The detection efficiency was estimated to about 1.2×10^{-4} resulting from the solid angle recorded by this arrangement, from the quantum efficiency of the photodetector (185–680 nm: 15% on average), and from reflection losses. The photodetector was maintained at -20°C to reduce the thermal background (about 30 counts/s at this temperature). A set of cut-on filters inserted in front of the photodetector was used for spectral analysis of the photons. Resolution was about 30 nm. Corrections with regard to the wavelength dependence of the collection efficiency were made when evaluating the data. Compared to the recently used setup [11], the main advantage of this setup is a clearly enlarged detection efficiency. Especially the detection of photons in the UV spectral range (until about 200 nm) was made possible.

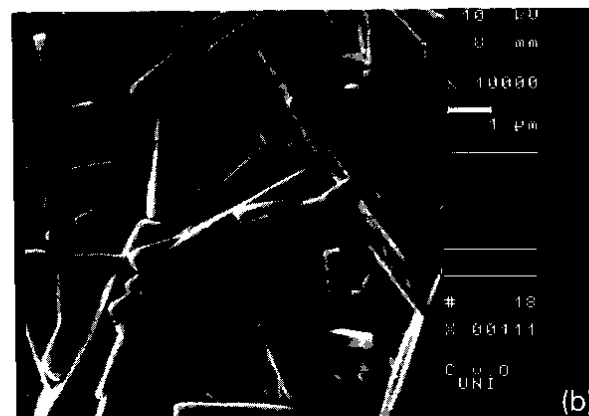
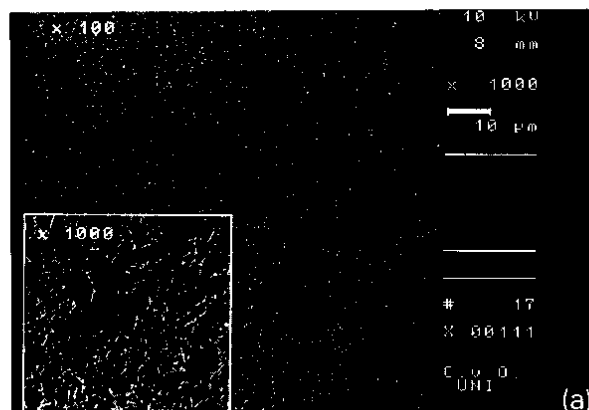


Fig. 2. Scanning electron micrographs of a Coronene sample; above: 100-fold magnification (1000-fold in the insert); below: 10000-fold magnification.

The photomultiplier pulses produced by the detection of single photons were amplified by a fast preamplifier (Ortec VT 120) and converted to standard pulses by a constant fraction discriminator (Ortec Quad CFD 934). The pulses were given to a multistop time-to-digital converter (CTN/M2, IPN, Orsay, France) as stop signals. The corresponding starts were produced by the antiparallel fission fragments. The time profile of the photon emission was obtained by recording the time interval distribution in a personal computer via a direct memory interface (DMI, also from IPN). The time resolution was 500 ps. The time uncertainty resulting from the fact that the two fragments of a spontaneous fission differ in energy and mass was much smaller and has been determined in this setup to about 250 ps.

2.2. Sample preparation

Solid films of Coronene or POPOP were prepared by spraying 10^{-3} M solution onto a $2 \mu\text{m}$ thick aluminized polyester foil using the nebulizer spray technique. Toluene was used as solvent for both substances. The film diameter was about 8 mm and approximately $150 \mu\text{l}$ were applied to

get a film thickness of $1\ \mu\text{m}$. Scanning electron micrographs of a $300\ \mu\text{l}$ sample of Coronene are presented in Fig. 2. They clearly show that the supporting foil was completely covered by a homogeneous microcrystalline layer. The crystals look like needles with diameters in the range of a few $100\ \text{nm}$. Crystal dimensions up to $1\ \mu\text{m}$ are also found with a POPOP sample. Thus, the applied nebulizer spray technique is a suitable method to prepare homogeneous solid films of the organic compounds considered here by producing layers of microcrystals.

2.3. Measurements with optical excitation

Steady state as well as time-resolved photon emission spectra of the samples have been measured by means of two self-built optical spectrometers: a cw-fluorimeter for the steady state and a picosecond-fluorimeter for the time-resolved measurements. They are built on the basis of single photon counting and for measuring ultra-short molecular lifetimes [12]. The measurements were performed with $330\ \text{nm}$ or $340\ \text{nm}$ excitation wavelength, with a spectral resolution of about $1\ \text{nm}$, and with $70\ \text{ps}$ time resolution. The steady state solution spectra were recorded at a concentration of $10^{-6}\ \text{M}$.

The picosecond fluorimeter uses the frequency-doubled output of a Nd:YAG-laser (Spectra Physics: Series 3000) to pump synchronously a dye laser (Spectra Physics 375 B; dye: DCM from Radiant Dyes). The repetition rate of the output pulses was reduced to $4\ \text{MHz}$ by a cavity dumper. The output of the dye laser ($\lambda = 660\ \text{nm}$) was frequency-doubled by means of a LiIO_3 crystal so that finally laser pulses at $330\ \text{nm}$ and with $7\ \text{ps}$ time duration could be used for sample excitation. The photons emitted from the sample were collected and focused onto the entrance slit of a double-monochromator (Jobin Yvon, $250\ \text{mm}$ focal length, $500\ \text{nm}$ blaze) by a $50\ \text{mm}$ lens. A double-stage MCP photodetector (Hamamatsu: R 1564U-07) mounted at the exit slit of the monochromator was used for photon detection. The detector started a time-to-amplitude converter (TAC) and the delayed signal of a fast photodiode illuminated by a low-intensity laser beam reflection was applied for stopping the TAC, i.e. the inverse time-correlated single photon counting technique has been used. The output of the TAC was given via an analog-to-digital converter to a multichannel analyzer for determining the time interval distribution by accumulation. The time profiles were finally stored and evaluated in a personal computer.

3. Results and discussion

3.1. Photon yields

By far the most results have been obtained with solid films of Coronene and POPOP. The typical number of photons per fission fragment observed with $300\ \mu\text{l}$ samples of these

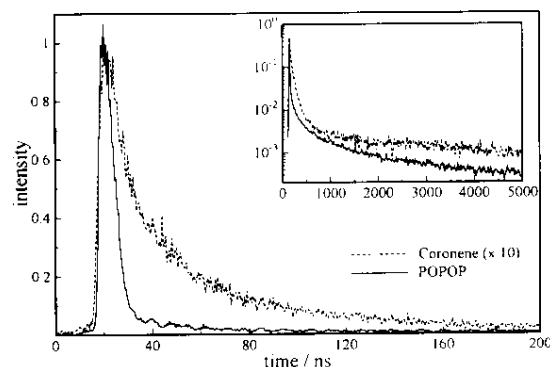


Fig. 3. Time profiles obtained with Coronene and POPOP under fission fragment bombardment.

substances within a $100\ \text{ns}$ time window (see Fig. 3) was 6×10^{-2} , i.e. about 500 photons per impinging fission fragment have been produced when the collection efficiency of about 1.2×10^{-4} is taken into account. The photon yield of Coronene samples is somewhat lower than that of POPOP samples in contrast to what we have found formerly [11]. But the results presented here are certainly more precise due to the much better sample preparation. The typical number of photons per fission fragment observed with blank samples was about 1.2×10^{-3} , i.e. about 10 photons per desorption event were produced. A nearly 10-fold higher photon yield has been obtained from blank samples with upside down mounted aluminized polyester foil. This indicates that the photons are mainly induced in the polyester foil and that the aluminium layer reflects or absorbs most of the photons.

Several samples prepared with other compounds have been investigated for comparison. The photon yield obtained with Stilbene 3 films is somewhat lower than that of POPOP samples, i.e. about 360 photons per fission fragment were induced in $300\ \mu\text{l}$ samples. The photon yield of PBBO films is about the same than that of POPOP samples. The yield of $300\ \mu\text{l}$ CsJ films have been determined to about 250 photons per fission fragment. The photon yield of amino acid samples was found to be very low in agreement with [10]. For example, only 15 photons per fission fragment were produced in $300\ \mu\text{l}$ Tyrosine samples. This yield is very close to that of blank samples. Rhodamine 6G samples have also a very low yield of only a few photons per incoming fission fragment. This result has not been expected because Rhodamine 6G is a laser dye provided with a high fluorescence quantum yield in solution. But the same low photon yield has been obtained in experiments with Rhodamine 6G bombarded by $2\ \text{keV}$ electrons, whereas with POPOP a lot of photons were observed under electron bombardment [13]. These facts probably indicate that the excitation of molecular species by energetic δ -electrons is the necessary step in the process of photon production by fast heavy ions and may open a new field to analyze the δ -electrons in plasma desorption.

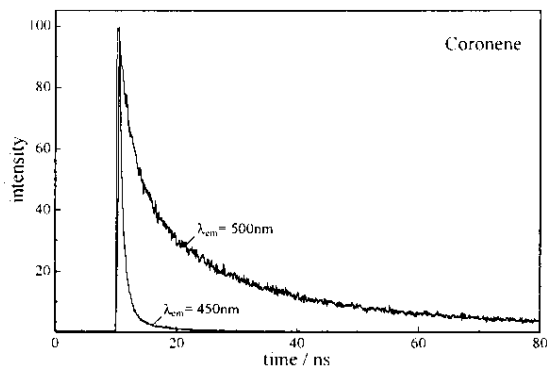


Fig. 4. Time-resolved photon emission from a Coronene film excited by ultra-short laser pulses and observed at 450 nm and at 500 nm.

3.2. Time profiles

The time profiles of the photon emission obtained by bombarding Coronene and POPOP samples with fission fragments are depicted in Fig. 3 on a scale up to 200 ns. The measurements were performed without inserting optical filters for spectral analysis. With both substances, non-exponential decay curves were obtained but the relaxation times evaluated by determining the centroids are clearly different. 30 ns is the relaxation time of Coronene and 9 ns that of POPOP. Both values agree very well with results obtained formerly [11]. When the data were evaluated on a larger time scale, a slow decay component of about 2 μ s was also found with both substances (see insert in Fig. 3). But the amplitude is rather small.

The photons emitted from Coronene and POPOP films when using ultra-short laser pulses for excitation have been measured for comparison. The time profiles are non-exponential decay curves as under the bombardment with fission fragments. The centroids have been determined to 31 ns for Coronene and to 7 ns for POPOP, respectively [11]. These relaxation times agree well with those obtained by fission fragment excitation. The photons were recorded in both cases with broad-band observation, i.e. the emitted photons were not subject to spectral analysis before being recorded. But the decay curves obtained with solid films as samples are strongly dependent on the wavelength of observation because of energy transfer processes [14]. With Coronene, two clearly different decay curves have been measured with laser pulse excitation and the centroids are 6.3 ns observed at 450 nm and 20.4 ns observed at 500 nm, respectively (see Fig. 4). With POPOP, three different decay curves have been measured and the relaxation times are 2.4 ns at 450 nm, 6.1 ns at 500 nm, and 9.8 ns at 550 nm, respectively (not presented). There are no corresponding measurements with fission fragment excitation yet. But we expect that future investigations on the wavelength dependence of the time profile will give valuable informations on the dynamics of photon production by high-energy ions.

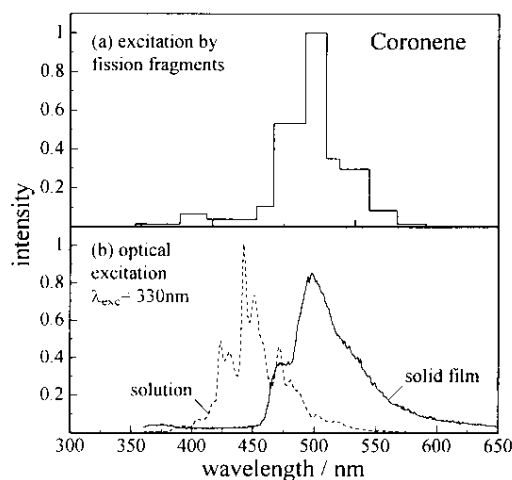


Fig. 5. Photon spectra of a Coronene film; (a) excited by fission fragments, (b) excited by light irradiation at 330 nm.

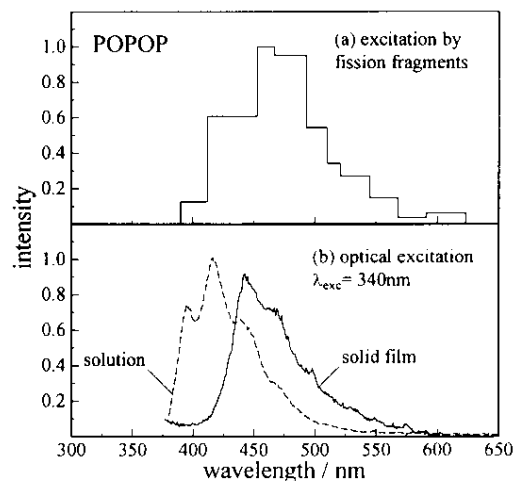


Fig. 6. Photon spectra of a POPOP film; (a) excited by fission fragments, (b) excited by light irradiation at 340 nm.

3.3. Photon spectra

The spectra of the photons emitted from Coronene and POPOP films under fission fragment excitation were measured by inserting various cut-on filters for spectral analysis. The intensity interval per unit wavelength obtained with two adjacent cut-on filters yields a spectrum which can be directly compared with optical spectra. The spectra of a 12 μ m thick Coronene film prepared by spraying 800 μ l 10^{-2} M solution are depicted in Fig. 5. The optical spectrum of the solid film reaches from 450 nm to nearly 650 nm with a broad maximum at about 500 nm. It differs clearly from the solution spectrum because it is shifted to longer wavelengths and less richly structured. The spectrum obtained by bombardment with fission fragments is very similar to the optical

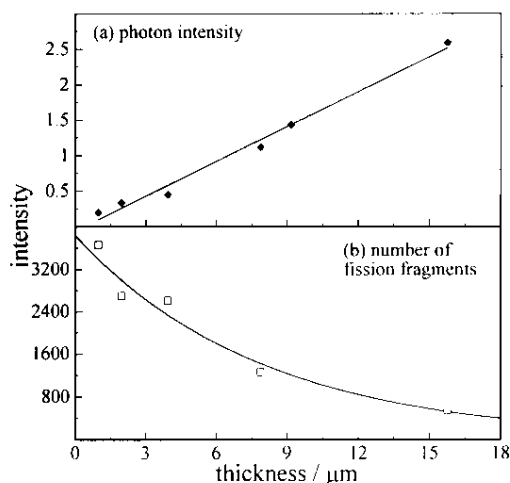


Fig. 7. Photon intensity (a) and number of fission fragments (b) for various thicknesses obtained with POPOP samples.

spectrum of the solid film. The spectra of a POPOP sample prepared as the corresponding Coronene sample are depicted in Fig. 6. A broad spectrum which is shifted to longer wavelengths when compared to the solution spectrum was obtained with the solid film as with Coronene, but the maximum is near 450 nm. The fission fragment induced spectrum resembles also the optical spectrum of the solid. These facts together with the observed time profiles give evidence that the photons observed in this study under fission fragment bombardment originate from molecular fluorescence in the solid sample.

3.4. Effect of sample thickness

The thickness of POPOP samples has been varied by spraying various amounts of solution. Six samples were prepared with a thickness reaching from 1 to 16 μm . The rate of fission fragments traversing these samples has been determined and the results show an exponential decrease with growing sample thickness which comes from scattering by nuclei in the sample (see Fig. 7). The range amounts to about 8 μm . But the photon yield obtained with these samples show a linear growth with increasing film thickness as is depicted in Fig. 7. Similar results were observed with Coronene. When the number of photons produced is proportional to the energy deposited in the solid film and when it is assumed that the energy deposition along the ion track is constant and that no noticeable part of photons disappears by scattering or absorption, a linear growth of photon intensity with sample thickness would be the consequence. But on the one hand, there really should be a distinct loss of photons in the solid film and in the spectral range of molecular fluorescence considered here it should be mainly due to scattering by the microcrystals. On the other hand, the energy deposited along the track is not necessarily constant

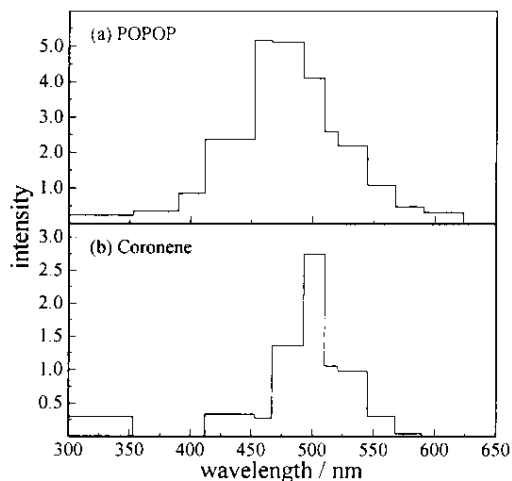


Fig. 8. Photon spectra obtained with Coronene and POPOP under fission fragment bombardment when extracting positive ions.

as indicated by the observed decrease of fission fragments traversing the sample. Therefore, more information on the energy deposition in these types of samples and on their optical characteristics is needed to discuss the effect of sample thickness in more detail.

3.5. Measurements with ion extraction

Much more photons per incident fission fragment and clearly different, voltage-dependent time profiles were observed when positive ions were extracted. The results are similar to those presented recently [11]. The spectra of the photons observed at 10 kV with Coronene and POPOP films have been measured by determining the intensity intervals per unit wavelength obtained with two adjacent cut-on filters. They are depicted in Fig. 8. The samples have been prepared by spraying 800 μl 10^{-2} M solution analog to the samples measured without ion extraction (see Subsection 3.3). Because of their higher yield it is advantageous to use thicker samples when running the various measurements necessary for spectral analysis. For example, the time needed for the POPOP measurements of Fig. 8 was about 30 hours. When compared to no ion extraction, a nearly 5-fold higher photon yield has been observed at 10 kV with both substances. But the amount of additionally produced photons has been generally found to decrease with growing sample thickness.

The spectra shown in Fig. 8 represent mainly the spectra of additionally produced photons and the observed distributions are nearly identical with those obtained without ion extraction. Therefore, it is concluded that the photons produced additionally when extracting positive ions come also from radiative transitions within the samples, i.e. molecular fluorescence, as has been found without ion extraction. With regard to the observed time profiles, the samples were obviously excited by electrons which originate from impacts of

fission fragments on components of the acceleration system mounted beyond the ring electrode and which are accelerated back to the sample. This interpretation was completely supplied by results obtained in the event-by-event analysis mode [13]. These measurements were performed with a mass detector mounted at the place of the photomultiplier and with an optical fibre introduced into the ion source for guiding photons to the photodetector outside the spectrometer (see [11] for details). The results clearly show that fission fragments striking the mass detector are strictly anti-correlated with additionally produced photons. The fact that no photons were additionally produced when negative ions were extracted fits also very well into this interpretation.

4. Conclusion

Experiments on photon production in solid films of organic molecules by the impact of ^{252}Cf -fission fragments has been presented. The samples were mainly prepared with Coronene or POPOP sprayed onto an aluminized polyester foil using the nebulizer spray technique. It is demonstrated by scanning electron micrographs that this technique is a suitable method to prepare homogeneous solid films of organic compounds by producing layers of microcrystals. Time profiles and photon spectra have been determined by bombarding these samples with ^{252}Cf -fission fragments as well as, for comparison, by exciting with light.

The results give evidence that the photons induced by fission fragment bombardment originate from molecular fluorescence in the solid sample. Approximately 500 photons per fission fragment have been produced within a 100 ns time window in about 2 μm thick POPOP samples. The photon yield has been observed to increase linearly with the thickness of the sample up to about 16 μm . Only very few photons per fission fragment have been obtained with Rhodamine 6G samples and the same low photon yield has been observed under the bombardment with 2 keV electrons. These results probably indicate that the excitation of molecular species by energetic δ -electrons is the necessary step in

the process of photon production by fast heavy ions. Photons which have been additionally produced when extracting positive ions come also from molecular fluorescence in the samples. But this fluorescence is excited by electrons which originate from impacts of fission fragments on components of the acceleration system and which are accelerated back to the sample.

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References

- [1] D.F. Torgerson, R.P. Skowronski and R.D. Macfarlane, *Biochem. Biophys. Res. Commun.* 60 (1974) 616.
- [2] B.U.R. Sundqvist and R.D. Macfarlane, *Mass Spectrom. Rev.* 4 (1985) 421.
- [3] R.J. Cotter, *Anal. Chem.* 60 (1988) 781A.
- [4] R.E. Johnson, *Int. J. of Mass Spectrom. and Ion Proc.* 78 (1987) 357.
- [5] E.R. Hilf, *Int. J. of Mass Spectrom. and Ion Proc.* 126 (1993) 25.
- [6] K. Barghorn and E.R. Hilf, *Nucl. Instr. and Meth. B* 88 (1994) 196.
- [7] G.P. Jonsson, A.B. Hedin, P.L. Håkansson, B.U.R. Sundqvist, B.G.S. Säve, P.F. Nielsen, P. Roepstorff, K.-E. Johansson, I. Kamensky und M.S.L. Lindberg, *Anal. Chem.* 58 (1986) 1084.
- [8] R.D. Macfarlane, Z.-H. Hu, S. Song, E. Pittenauer, E.R. Schmid, G. Allmaier, J.O. Metzger und W. Tuszynski, *Biol. Mass Spectrom.* 23 (1994) 117.
- [9] R.G. Kaercher, E.F. da Silveira, J.F. Blankenship and E.A. Schweikert, *Phys. Rev. B* 51 (1995) 7373.
- [10] T.R. Ariyaratne, D.D.N.B. Daya, P. Håkansson and B.U.R. Sundqvist, *Int. J. of Mass Spectrom. and Ion Proc.* 152 (1996) 31.
- [11] W. Tuszynski, K. Koch and E.R. Hilf, *Nucl. Instr. and Meth. B* 107 (1996) 160.
- [12] J. Allgermissen, T. Weber and K. Maier-Schwartz, *Engng. Optics* (1992) 111.
- [13] M. Wehofsky, Diploma Thesis, Carl von Ossietzky-Universität, Oldenburg, 1996.
- [14] see for example: *Polymer Photophysics*, D. Phillips, ed. (Chapman and Hall, London, 1985).