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Citation: [Review of Scientific Instruments](#) **67**, 2490 (1996); doi: 10.1063/1.1147203

View online: <http://dx.doi.org/10.1063/1.1147203>

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Design considerations and performance of a spectro-streak apparatus applying a planar LIGA microspectrometer for time-resolved ultrafast fluorescence spectroscopy

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(Received 28 December 1995; accepted for publication 22 March 1996)

Results of a pilot study with a spectro-streak apparatus applying a grating microspectrometer with a self-focusing reflection grating are reported. The microspectrometer chip (dimensions: 17×6.4 mm²; 125 μm effective thickness of the three-layer x-ray resist system), fabricated with the versatile LIGA technique, has been adapted to a picosecond streak camera. Performance tests have been carried out with a fluorescent probe exhibiting a dynamic Stokes shift of the exciplex fluorescence band due to solvation of the charge transfer dipole within about 400 ps. The use of a LIGA microspectrometer in ultrafast spectroscopy proved to be of advantage in time-resolved studies of complex luminescence spectra where a moderate spectral resolution is required and a large spectral range must be covered. © 1996 American Institute of Physics. [S0034-6748(96)00907-0]

I. INTRODUCTION

The high-speed streak camera has become an indispensable tool in many areas of time-resolved studies in scientific research and engineering. Researchers in biology, chemistry, and physics use the streak camera to measure the fluorescence and absorption kinetics of ultrafast light phenomena. In particular, fluorescence measurements in the picosecond time domain are conveniently performed with this kind of detector.¹⁻⁴ Streak cameras are based on the conversion of temporal information into spatial information. Photons striking the photocathode of the streak tube produce emission of electrons in proportion to the incident light intensity. The electrons are accelerated via an accelerating mesh^{4,5} or via a proximity focused nonamplifying channel plate.⁶ They are then electrostatically swept at a known rate over a known distance, converting temporal information into spatial information. The photoelectrons (in some designs, after passing a channel plate intensifier) impinge upon a phosphor screen forming the streak image which is viewed by a video readout system.

Conventional streak camera apparatus measures fluorescence time functions at fixed wavelengths. In many photo-physical and photochemical kinetic studies, however, such as solvent relaxation, exciplex formation, electron, proton or energy transfer, conformational changes, excimer formation, and ionization reactions, etc., fluorescence emission must be measured simultaneously as a function of time and wavelength. Global analysis is required in order to determine kinetic rate constants and thermodynamic properties related to those processes. Spectrally and time-resolved data covering the desired wavelength range can be obtained by taking measurements successively at many different wavelengths and

then normalizing the kinetic data to a relative scale. This procedure requires knowledge of the relative intensities of the measured data, which is often not available. In a recent paper we have described the performance of a spectro-streak apparatus which is characterized by the combination of a polychromator objective with a conventionally designed grating coupled to a commercial streak camera.^{7,8} Meanwhile, this instrument has provided numerous valuable spectroscopic data, which would not have been obtainable as readily with other measuring techniques. The most striking examples lie in studies of molecular dynamics,⁸ in particular, solvation dynamics^{8,9} and preferential solvation.¹⁰

In the last few years, highly sophisticated designs of optical microsystems have been created which can possibly be employed with advantage in time-resolved ultrafast spectroscopy. In this article, we describe the results of a feasibility study carried out with a spectro-streak apparatus which uses a LIGA microspectrometer^{11,12} in ultrafast spectroscopy for the first time (Fig. 1). The combination of the compact micro-optical device with a conventional streak camera allows simultaneous measurement of light intensity (I) as a function of wavelength (λ) and time (t). The streak camera output provides an $I(t, \lambda)$ histogram making the dynamics of chromatic fluorescence changes directly visible after only one excitation event.

II. THE SPECTRO-STREAK SETUP

A commercial picosecond streak camera (Hamamatsu, type 1370-01, 2-ps resolution) was used for this pilot study. Fluorescence light from the laser-excited sample (S) is directly received by the input fiber in contact with the excited microvolume or is relayed by an achromat system (L1) to the input fiber of the grating microspectrometer (GMS); cf. Fig. 1. The dispersed light output of the GMS is focused sharply with an achromat (L2) onto the photocathode (PHC, sensi-

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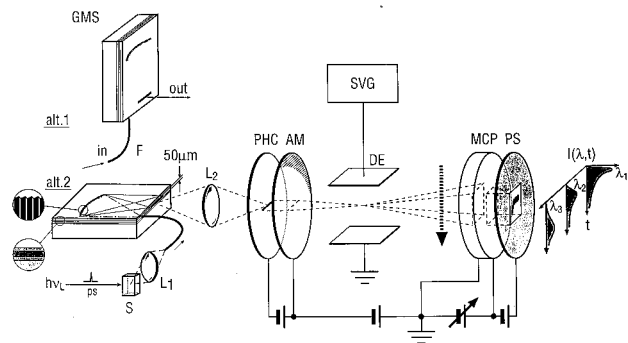


FIG. 1. Schematic representation of a spectro-streak arrangement composed of a streak tube and a planar LIGA GMS chip, in front, with gradient index fiber input (F). Shown are two alternative constructions (alt. 1 and alt. 2). A ps laser pulse excites the sample S (microvolume) which then emits exciplex fluorescence light that varies from a ps to ns time scale due to solvation and recombination processes. The components of the Hamamatsu streak tube are (see the text): PHC; AM; DE; SVG; MCP; and PS.

tivity S20), which is deposited on the inside of the glass envelope of the streak tube. In this pilot study we used a GMS chip of the alternative design, alt. 1 (cf. Fig. 1). The streak tube incorporates an accelerating mesh (AM), the deflection electrodes (DE), and a microchannel plate amplifier (MCP) which intensifies the photoelectron beam current before it reaches the phosphor screen (PS). An external microchannel plate, a CCD camera (Photometrics, STAR 1 with 384×576 pixels and $25 \mu\text{m}$ pixel size) and a personal computer complete the spectro-streak apparatus (the latter three components are not shown in Fig. 1). Sample excitation in our experiments is accomplished with single pulses from a frequency tripled Nd:glass laser (351 nm, 7 ps half-width). The magnification of the dispersed spectral pattern from the GMS was about 1:2, yielding a nominal spectral resolution per $25 \mu\text{m}$ at the photocathode of about 3 nm.

III. THE MICROSPECTROMETER

The microspectrometer based on a polymeric multimode waveguide with a self-focusing and blazed reflection grating, adjusted fiber fixing groove, and with a tilted (alt. 1) or non-tilted (alt. 2) focus line have been developed at FZK/IMT (Forschungszentrum Karlsruhe, Institut für Mikrotechnik).¹³ The reflection grating which is patterned into the integrated waveguide works in the spectral range from 400 nm–1100 nm with a maximum transmission of 24% at the blaze wavelength of 740 nm. More data of the GMS are given in Table I. Other designs, optimized for shorter and longer wavelengths, have been fabricated too.

The complete optical arrangement of the grating microspectrometer is structured in one process sequence taking advantage of the LIGA technique.^{14–20} By this technique, all components are adjusted with respect to each other and no further alignment is required. The LIGA process is based on a combination of x-ray lithography, electroforming, and replication techniques, and allows the fabrication of 3D microstructures with high aspect ratios. The structural heights of LIGA microstructures are normally several hundred micrometers, while the minimum lateral dimensions are on the order of $1 \mu\text{m}$ or less.¹⁴ Due to the high parallelity of the

TABLE I. Data of the grating microspectrometer GMS.

Grating constant	2.5	μm
Order	1	...
Spectral range	400–1100	nm
Spectral resolution	0.24	nm/ μm
Blaze wavelength	740	nm
Transmission (blaze)	24	%
Attenuation to scattered light	25	dB
Optical fiber	50/125 gradient index	μm
Dimensions of GMS chip (length/width)	17.25/6.4	mm/mm
Thickness of planar waveguide	50	μm
Time resolution of grating; Eq. (3)	~6	ps
Group delay, calculated (400–530 nm); Eqs. (1) and (2)	3–5	ps

synchrotron radiation and the high selectivity of the developer specially tailored to polymethylmethacrylate (PMMA), which is used as the x-ray sensitive material, submicron accuracy over the total height of the microstructures can be achieved and vertical walls can be obtained. As the LIGA process does not rely on the use of the crystal orientation of any material, there are no restrictions in lateral patterning.¹⁴

The waveguide consists of a PMMA core layer with refractive index $n=1.49$ at 589 nm and cladding layers from copolymers of PMMA and tetrafluoropropyl methacrylate (TFPMA) with $n=1.425$. The material attenuation in the visible and NIR spectral range up to 1100 nm for a PMMA core is of the order of 0.3 dB/cm which is small enough with regard to the optical path length of 2–3 cm.²⁰

The thickness of the different layers of the GMS is matched to the fiber parameters ($50/125 \mu\text{m}$ multimode fiber, $NA=0.2$) by which the light is launched into the waveguide. The position of the fiber-end face is given by a fiber-fixing groove and is adjusted to the grating on a Rowland circle. The blazed reflection grating is structured with optimized individual positions of each single-grating tooth. Thus, imaging losses on the linearized focal line can be neglected.^{19,20} A high reflectivity is achieved by coating the grating with a 100-nm-thick silver layer.¹⁸

As mentioned above, the PMMA resist used in the LIGA process shows good optical transmission properties in the visible and near-ir regions. In order to be able to fabricate micro-optical components with proper characteristics by deep-etch x-ray lithography, it is also essential that the roughness of the vertical walls is preferably lower than 1/10 of the wavelength of the light. Phase shifting interferometry experiments have demonstrated that this requirement has been achieved: The surface roughness turned out to be only on the order of 30–40 nm.¹⁴ The attenuation to scattered light—which is an important figure of merit in optical microdevices, particularly in spectro-streak applications—has been determined as 25 dB for the complete GMS used in this study (cf. Table I).²⁰

For applications in ultrafast spectroscopy, a delay in time, due to group velocity dispersion in PMMA generally has to be taken into account in the lower picosecond regime. Wave groups centered at different wavelengths λ_1 and λ_2 , having traversed optical material of length L and refractive index $n(\lambda)$, suffer a delay in time Δt , with respect to each other.^{21–23}

$$\Delta t = L \left(\frac{1}{v_g(\lambda_1)} - \frac{1}{v_g(\lambda_2)} \right), \quad (1)$$

with group velocity

$$v_g = c \left(n - \lambda \frac{dn}{d\lambda} \right)^{-1}. \quad (2)$$

For PMMA and for, e.g., $\lambda_1=400$ nm, $\lambda_2=530$ nm, and $L=2-3$ cm, Δt is of the order of 3–5 ps.

The time resolution of the grating itself is about 6 ps, calculated for a wavelength of 450 nm. We define the time resolution of a grating as the time delay δt between the marginal diffracted first-order rays,²²

$$\delta t = \frac{\lambda d}{ac} = \frac{d}{af}, \quad (3)$$

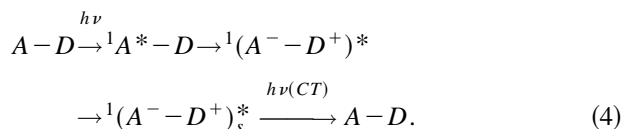
where λ is the wavelength, d is the length of the grating, a is the grating constant, c is the velocity, and f the frequency of light.

The tolerated length of the GMS's input fiber in spectro-streak applications in ultrafast spectroscopy is determined by its group velocity dispersion (GVD) in the spectral range of the transmitted light to be analyzed as function of time and wavelength. Spectral broadening of the input light due to self-phase modulation (SPM) becomes effective only at high light intensities in fibers several meters in length.

Grating microspectrometers (particularly designed for ir spectroscopy) with an air waveguide, and free of group delay, have also been produced at FZK/IMT.

IV. EXPERIMENTS AND DISCUSSION

Results of this pilot study are presented, demonstrating the performance of the spectro-streak apparatus with the grating spectrometer chip. The fluorescent sample under investigation is an electron-donor/acceptor (D/A) system [pyrene-dimethylaniline, (PyDMA), in octanol, depicted in Fig. 2(a)] that shows ultrafast charge separation after excitation to the locally excited state (LE) with a picosecond UV laser pulse followed by an emission of exciplex fluorescence^{9,24} as given by the general scheme,^{25,26}



The exciplex fluorescence band undergoes a dynamic Stokes shift within about 400 ps due to solvation of the charge transfer dipole in the protic solvent octanol [Fig. 2(b)]. The lifetime of the relaxed charge-transfer species (CT_s), however, is ten-times longer. The quantitative elucidation of the solvation dynamics is the aim of such a spectro-streak experiment, which is considered as a feasibility study and as a test of the LIGA microspectrometer as a tool in ultrafast spectroscopy.

Figure 3 shows the spectro-streak image which represents the intensity-wavelength-time histogram $I(\lambda, t)$, containing information about the charge transfer kinetics, the solvation dynamics, and the charge recombination kinetics. Figure 4 displays the binning readout of the streak image

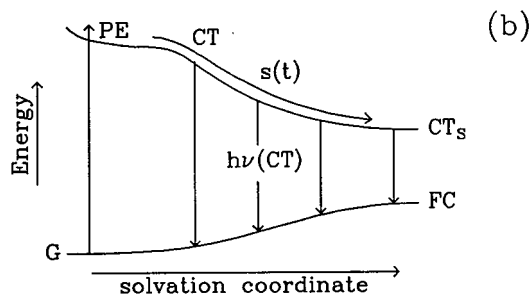
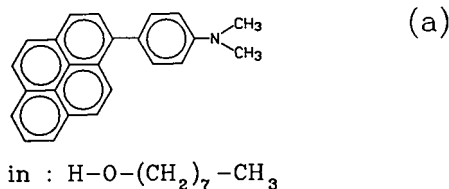


FIG. 2. Molecular charge transfer system used for the test. (a) Structure of the molecules: pyrene-dimethylaniline (PyDMA) in octanol (Ref. 9). (b) Schematic representation of the dynamic Stokes shift of the charge transfer (CT) emission during solvation (s), with transitions to the Franck-Condon (FC) ground state.

(not intensity corrected) for quantitative evaluation. The left set of graphs shows λ - t plots. The right set of graphs exhibits t - λ plots. The important feature is the temporal development of the CT band, i.e., the dynamic Stokes shift due to solvation of the CT dipole. Relaxation of the CT emission maximum toward the equilibrium position takes place in about 400 ps ($1/e$ time). Calibration and correction procedures for spectro-streak setups have been described in detail elsewhere;⁷ furthermore, the application of a band-averaged correction factor is required in dynamic Stokes shift spectroscopy for quantitative global analysis, as pointed out earlier.^{9,24}

V. DISCUSSION

The results obtained in this pilot study with a LIGA microspectrometer compare very well with those obtained earlier,⁹ applying a polychromator with spherical holographic grating (65 mm diam, 133 lines/nm). Note, however, that the solvent used in this experiment was n -octanol (with dielectric constant $DK=10$ and a longitudinal relaxation time $\tau_{L1} \approx 360$ ps), while it was n -hexanol in the former ($DK=12.5$ and $\tau_{L1} \approx 180$ ps).⁹

A number of LIGA GMS prototypes with varying design features and different spectral characteristics, e.g., with spectral dispersion of 0.23, 0.08, 0.14, and 0.22 nm/ μ m, have been reported recently.¹⁷ It is possible to select an optimal GMS chip in combination with active electron-optical components like streak cameras²⁷ or electro-optical devices like Kerr-gate shutters, as well as for other spectral detection systems (time-correlated single photon counting²⁸ or steady state).

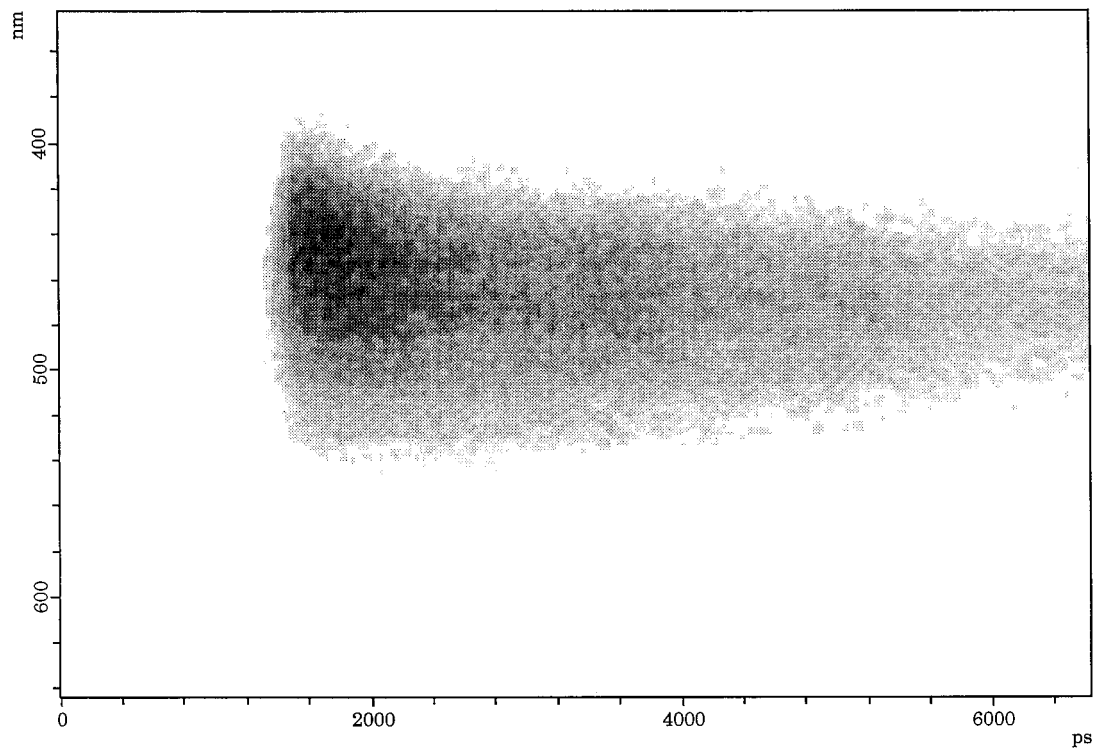


FIG. 3. Spectro-streak image of excited PyDMA in octanol solution representing the intensity-wavelength-time histogram $I(\lambda, t)$.

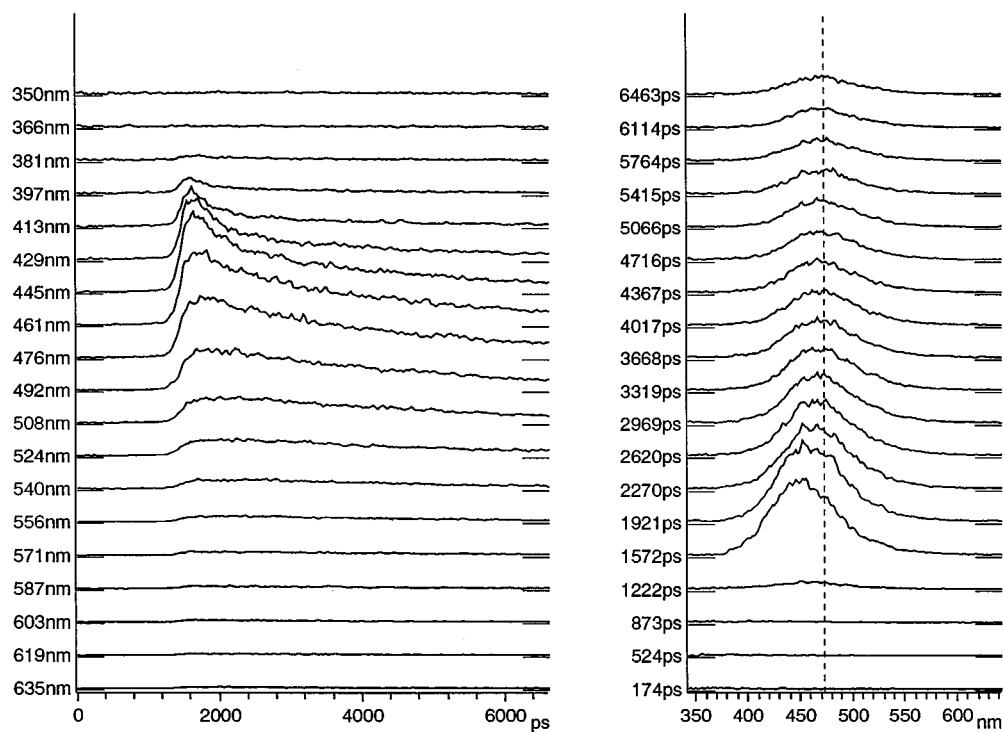


FIG. 4. Temporal development of the fluorescence emission from the CT of the aromatic compound PyDMA in *n*-octanol at room temperature. The graph on the right exhibits the dynamic Stokes shift due to solvation of the CT dipole; relaxation of the CT emission maximum toward the equilibrium position takes place in about 400 ps.

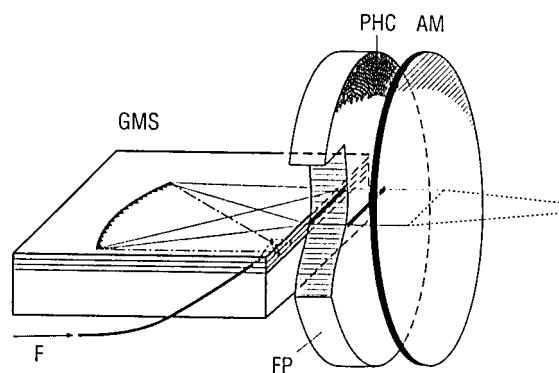


FIG. 5. GMS in contact with the streak tube input window which is a fiber optic plate (FP); the PHC, small in size to keep the dark current background low, is deposited on the vacuum side of the FP (cf. Fig. 1) and receives the "slit" image directly 1:1. Sectional view of the FP in the drawing is to show details.

At least the following new design proposals emerge from this study:

- (i) Figure 5 shows a design proposal of a GMS with a free contact surface for direct coupling to a fiber optic input window (FP) instead of using a coupling achromat, thus obtaining a higher overall transfer efficiency. A GMS with a nontilted output beam (similar to alt. 2 in Fig. 1) provides the narrowest "slit image" of the dispersed spectrum, given by the thickness of the core layer (e.g., 50 or 100 μm). The slit image arriving at the photocathode determines, among other parameters, the time resolution of the spectro-streak apparatus.⁷
- (ii) Figure 6 depicts schematically a concept of a multi-story microspectrometer with three floors and displaced outputs being streaked simultaneously. Such a device would allow (a) time-resolved spectral diagnostics from different locations of sample targets simultaneously. Possible examples are numerous, e.g., in physics: plasma spectroscopy in discharge studies; in biology and medicine: propagation of Ca^{2+} waves among communicating cells in the dye-loaded intact organ,²⁹ etc. (b) By using gratings having different characteristics, we study the same event in different spectral ranges or with different resolutions.

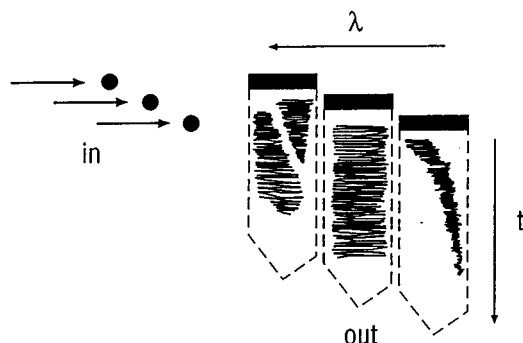


FIG. 6. Concept of a three-story GMS with displaced spectro-streak fields.

- (iii) A two-story microspectrometer with fiber input and nondisplaced output windows coupled to a double-diode array for a picosecond broadband transient absorption spectrometer, similar to conventional designs.³⁰

At present there appear to be no fundamental difficulties in constructing such multistory and cross-talk-free microsystems with, e.g., 2–3 floors with the LIGA technique. Such multistory microsystems are likely to broaden substantially the range of application of steady state and time-resolved spectroscopy.

ACKNOWLEDGMENTS

The test compound has been synthesized by Dr. W. Kühnle (see also Ref. 9). The authors thank B. Frederichs and H. Meyer (both MPI Göttingen) for technical assistance.

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troscopic measurements can be achieved with recently developed synchroscan streak cameras which apply photon counting techniques (Hamamatsu C4334).

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