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ENHANCED INFRARED ABSORPTION BY RHODAMINE 6G DYE ON DIFFRACTION GRATING OF THE Au/Pd THIN FILM

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ABSTRACT

Today, IR nanosensors have many applications in science and technology. Extraordinary optical transmission (EOT) through an array of ordered subwave holes in a thin metallic film is used to create some kind of high-sensitivity sensor. In this work, we performed micro-hole arrays fabrication in thin film Au/Pd (80 / 20 %) by ablation technology using femtosecond laser pulses Micro-holes with diameters $d \approx 2 \div 3$ μm and periods $p \approx 5$ μm were produced. We studied the enhanced infrared absorption by Rhodamine 6G (R6G) dye on diffraction grating of the Au/Pd thin film. A deposited rhodamine layer exhibits infrared absorption, which is enhanced in the range of 1400–1600 cm^{-1} when approaching the edge of the first band gap with the maximum gainof about 10.

Keywords: infrared absorption, transmittance, micro-hole, metal thin film, Rhodamine 6G.

1. INTRODUCTION

Since the discovery of the effect of extraordinary transmission of light through an array of ordered subwave holes in a thin metallic film [1, 2] as compared to transmission through individual (or noninteracting) holes [3], studies of the possibility of using this effect for sensorics problems continue [4]. Indeed, the main reason for extraordinary transmission is the excitation of surface electromagnetic waves (SEW) [5], which are responsible for the enhancement of a local electromagnetic field near the surface. Highly sensitive sensors for molecular compounds or even biological objects on arrays of nanoholes were created on the basis of surface-enhanced Raman scattering (SERS) [6], surface-enhanced infrared absorption (SEIRA) [7-10], and dependence of the position of the maximum transmission of light on the effective dielectric constant of the environment of a metallic film. The surface-enhanced infrared absorption (SEIRA) method is quite sensitive and makes it possible to detect a monolayer of the deposited substance and to use not only noble metals (which is necessary for SERS) but also

transition metals or even some alloys, because they have similar optical properties in the infrared range.

The fabrication of such arrays of periodically ordered subwavelength holes faces the technological problem of the impossibility of their mass production by the ion-beam lithography method used to create them for laboratory studies. At the same time, the highly efficient laser ablation method allows the creation of nanoholes and microholes in thin metal films [11]. It is noteworthy that ultrashort laser pulses (USP) make it possible to obtain high-quality holes in a wide range of their dimensions (up to 0,1–0,2 μm, which is several times smaller than the wavelength) without the use of near-field optical elements.

The absorptance (A) was determined by $A = 1 - R - T$ [8], R - the reflectance and T – the transmittance. The reflectance R is very much small when the width of the holes becomes smaller than the wavelength of the probing light $d << \lambda$. The extraordinary IR transmission through an array of these meshes means that we can use them to obtain enhanced IR absorption spectra of molecular species at the metal's surface simply by placing the mesh in transmission mode.

In this work, a two-dimensional square transmission diffraction grating of microholes with a period of about 6 μm is formed on the surface of a thin gold film under the single-pulse action of ultrashort laser pulses of the visible range. A deposited rhodamine layer exhibits infrared absorption, which is enhanced in the range of 1400–1600 cm^{-1} when approaching the edge of the first band gap with the maximum gain of about 10.

2. MATERIALS AND METHODS

As a sample, we used a film of an 80/20 gold–palladium alloy with the thickness $h \approx 60$ nm deposited in an argon atmosphere on a CaF_2 substrate by magnetron sputtering SC7620, Quorum Technologies. The radiation of the fundamental harmonic of the Nd:YAG – laser $\lambda = 1030$ nm was doubled in frequency with the yield of ultrashort laserpulses of the second harmonic at a wavelength of 515 nm with an FWHM of about 200 fs [12]. The spatial distribution of radiation at the output from a single-mode fiber corresponded to the TEM_{00} mode. Laser radiation was focused onto a spot with the radius $R_{1/e} \approx 1.5$ μm on the surface of the sample in air through the objective of a microscope Levenhuk 870T with the numerical aperture NA = 0.25. Holes with the diameter $d \approx 3$ μm and period $p \approx 6$ μm (Fig. 1) in the film located on a three dimensional Ox, Oy, Oz motorized holder with computer control were formed under the action of single laser pulses focused by the micro objective at the constant energy E = 32 nJ [12]. We used a thin coat of dye R6G 99.99 % to deposit on above sample by using experimental needles with small capacity, to drip the first R6G on diffraction grating in thin Au/Pd and CaF_2 substrate and to wait drying of its layer. The second R6G is driped up, so on to the end of the 3rd drops. The grating was visualized by means of a JEOL 7001F scanning electron microscope with a magnification up to 500000×, as well as an Al'tami-6 optical metallographic microscope with an instrumental magnification up to 2000×. The infrared spectra of the transmittance of a diffraction grating without and with a deposited rhodamine layer (Figs. 2 and 3) were recorded in the range of 2–10 μm with a Vertex V-70 Fourier spectrometer (Brucker) under the conditions of evacuation of the measurement cell [12].

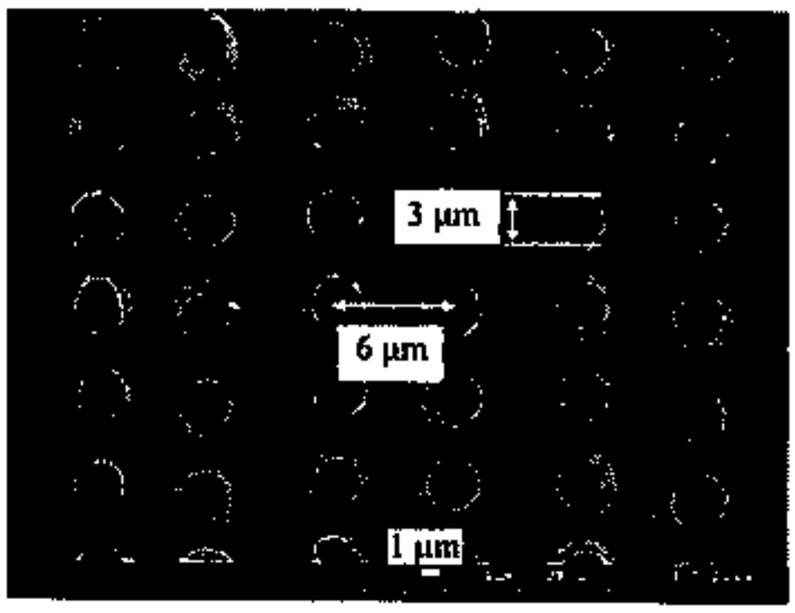
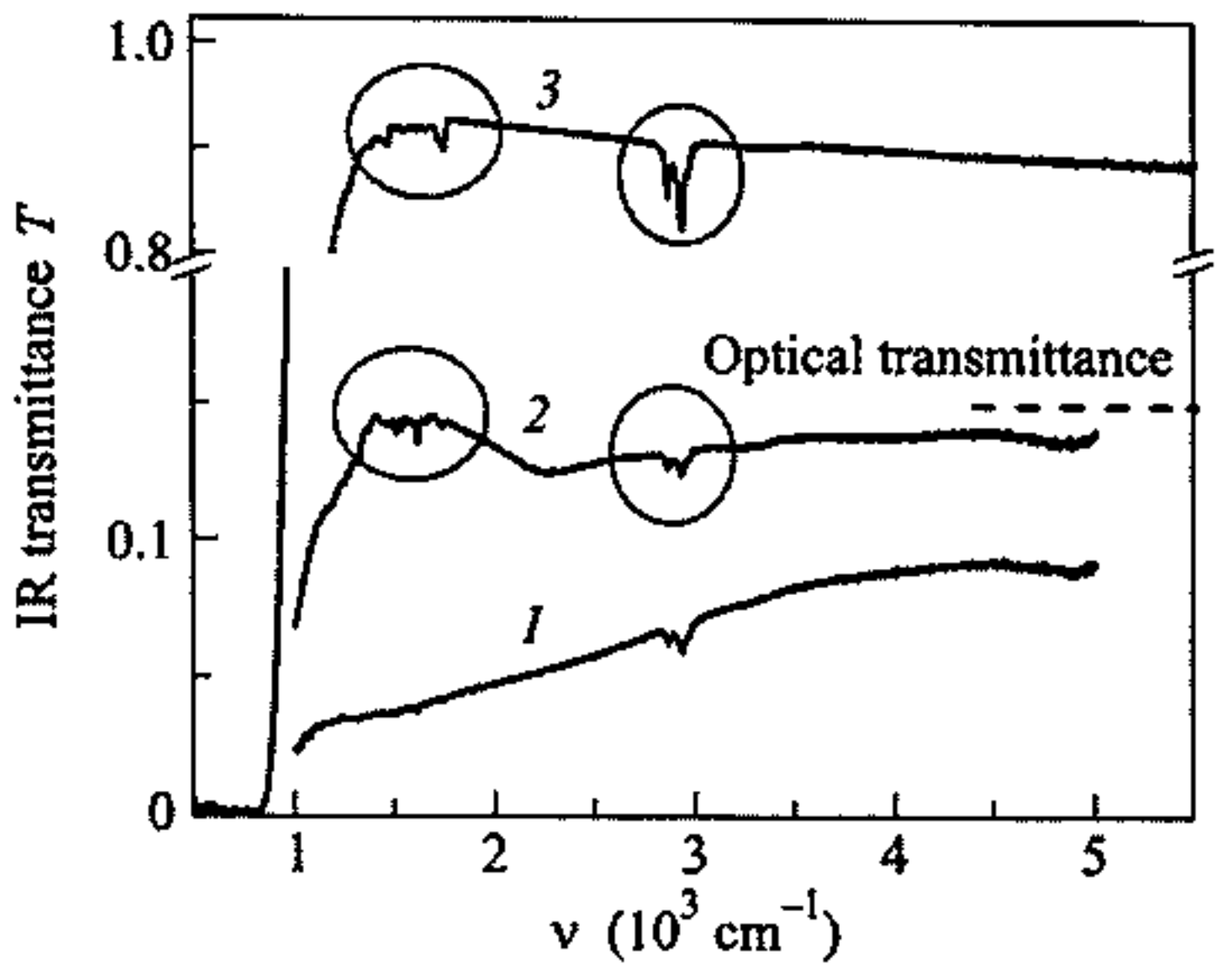
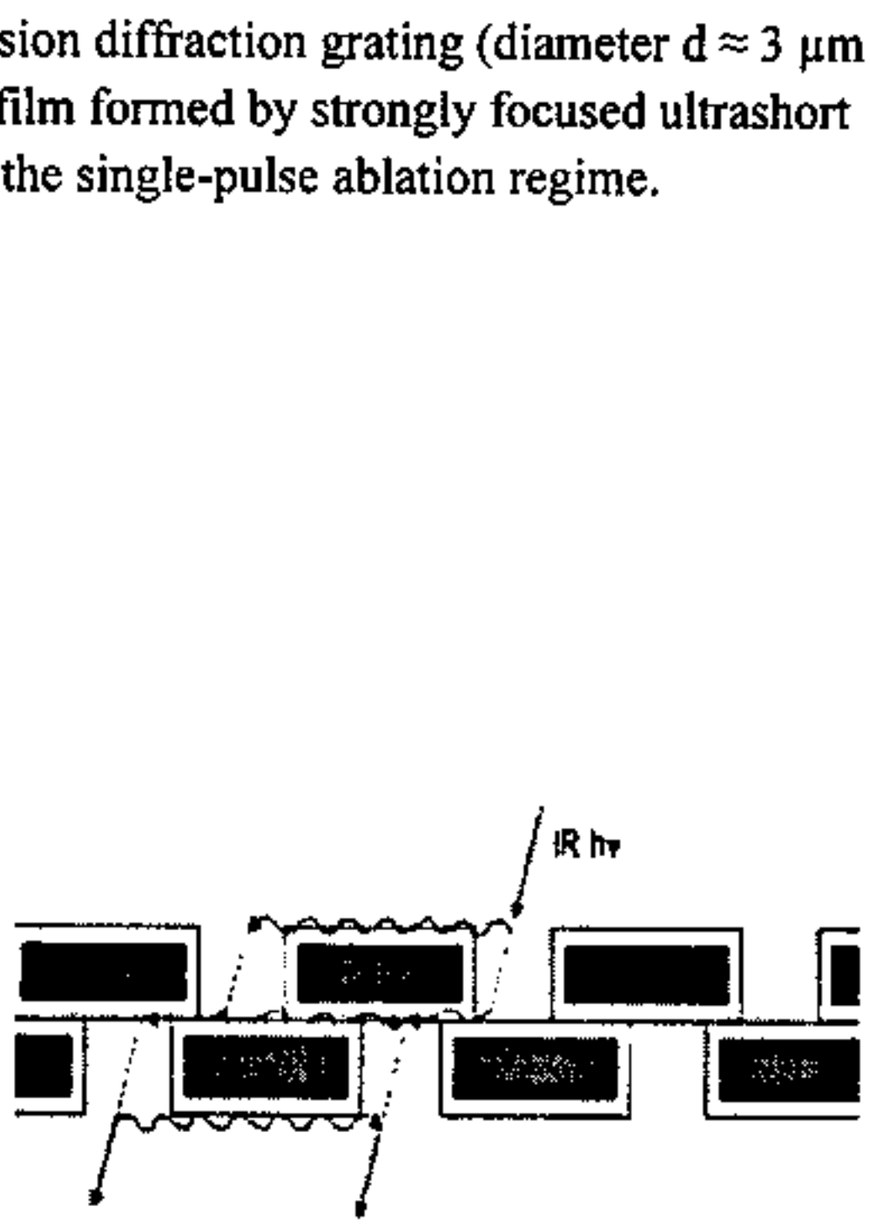


Figure 1. Scanning electron microscopy image of the transmission diffraction grating (diameter d ≈ 3 μm and period p ≈ 6 μm) of microholes in the Au/Pd (80 / 20 %) film formed by strongly focused ultrashort laser pulses with the energy density F = 0.5 J/cm^2 in the single-pulse ablation regime.



(a)



(b)

Figure2. (a) (Color online) Infrared spectra of the transmittance T of the (1) initial film, (2) diffraction grating on this film, and (3) dye layer R6G on CaF_2 substrate. The dashed line is the asymptotic transmittance of the grating in the visible region. Circles indicate spectral features associated with the deposited dye layer. (b) Schematic of how light travels through the mesh [10].

3. RESULTS AND DISCUSSION

After normalization to the transmittance of the infrared transparent CaF_2 substrate with R6G (line 3inFig. 2), the infrared spectrum of the transmittance T of the diffraction grating (line 2) exhibits a number of features as compared to the initial film (line 1). First, a characteristic nonlinear increase is observed in the region of low spectral wavenumbers ν and the subsequent maximum is observed near $q_{max} \approx 1500$ cm^{-1} (line 2 in Fig. 2), whose position can be related to the dimension of the holes of the grating as 1/(2d)[12], not excluding a certain contribution of plasmon–polariton effects. The amplitude of the maximum relatively low as compared to the

calculated curves is related in our case to the uncollimated infrared beam from the source of the Fourier spectrometer.

In the case of a plane wave through the holes has a radius much smaller than the wavelength of the light incident on the metal thin film $qa = \frac{2\pi a}{\lambda} \ll 1$, to the transmittance is calculated by the formula (Bethe 1944, Bouwkamp 1950) [1]:

$$T = \frac{64}{27\pi^2}(qa)^4 \sim \left(\frac{a}{\lambda}\right)^4$$

in which: a - the radius of the hole, λ - wavelength of incident light. Saturation value of transmittance T = 0.14 in a shorter wavelength range (2000-5000 cm^{-1}) is a good result compared with the above theoretical calculations and quantity - with the value of T, what is directed measurement of the optical range (≈ 0.15).

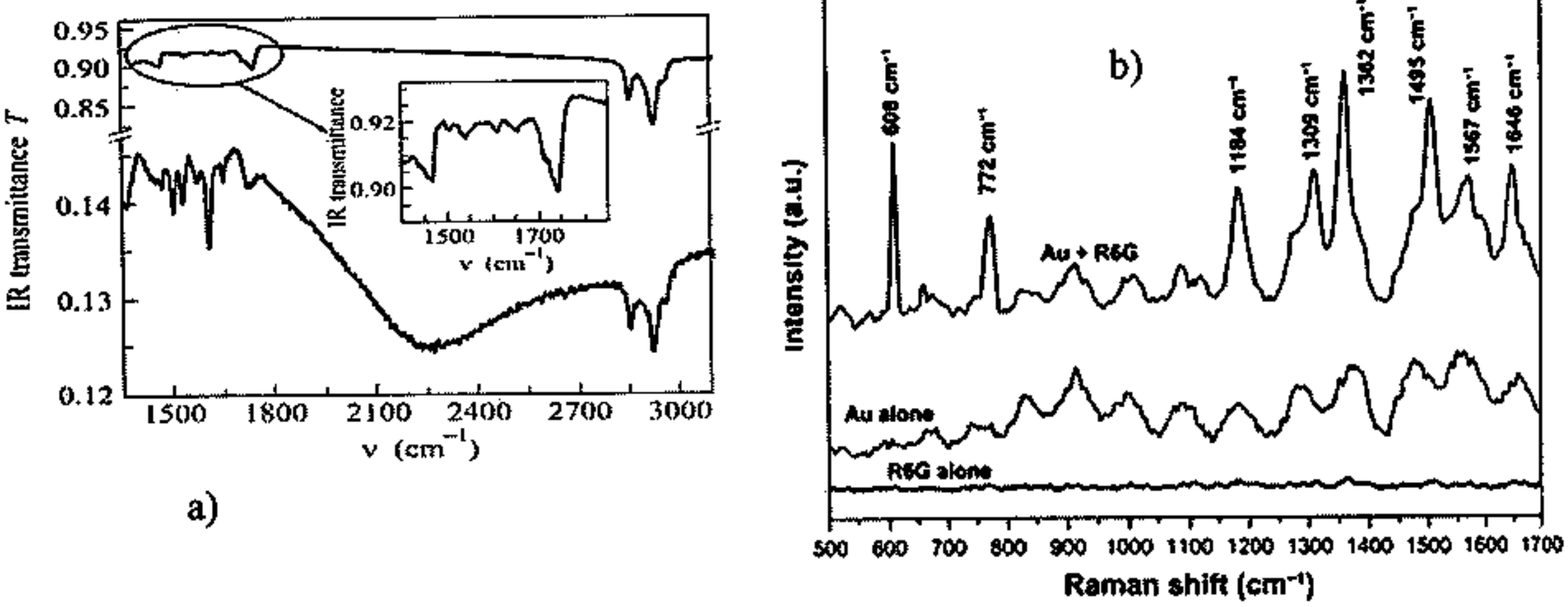


Figure 3. (a) (Color online) Infrared spectra of the transmittance T of the dye layer on (lower curve) diffraction grating and (upper curve) CaF_2 substrate. The inset shows the magnified image of the low frequency spectrum of the dye on the substrate. (b) Characteristic spectra of Au + R6G [13].

In addition to the indicated spectral features characteristic of the diffraction grating, when a R6G dye layer is deposited, the spectral lines of infrared active vibrations of rhodamine molecules appear in the regions ν = 1400–1800 and 2800 - 3000 cm^{-1} in infrared spectra (Fig. 3a, b).The infrared spectra of the dye in the "red" region drastically differ for its layers on the surface of the substrate and on the grating. In the former case, the intensity of lines decreases rapidly with an increase in the wavenumber (Figs. 3 and 4). The opposite tendency to an increase in the intensity of lines with a monotonically increasing gain reaching ~10 is observed for the grating. However, the absorption line near 1750 cm^{-1} in the latter case is suppressed and partially cut. The ratio of the intensities of the 2850 and 2920 cm^{-1} lines in the blue region (2800-3000 cm^{-1}) for the substrate and grating does not change (Figs. 3 and 4), whereas their absolute intensities (amplitudes of the maxima in Fig. 3) for the substrate and grating are proportional to the transmittance.

The plane between CaF_2 substrate and the thin gold film (dielectric/metal) born plasmon, the incident light can be used to excite coherent oscillations in the metal's conducting electrons at a dielectric/metal interface; that is, surface plasmons (SP) can be excited. Metals have many free electrons, free electrons will oscillate under the influence of external electromagnetic fields as light. The SPs propagate along the surface of the mesh, perhaps on both sides, to another hole

where they decouple, producing photons that emerge in the same direction as the incident beam (Fig. 2b) [10]. Surface plasmon resonance (SPR) is the resonant oscillation of conduction electrons at the interface between a negative and positive permittivity material stimulated by incident light. The essence of the absorption spectrum is due to the phenomenon of SPR [7, 8]. Hole size has a dramatic effect on the appearance of transmission spectra, and the smaller hole size reveals more resonances. The SPs are not bouncing back and forth within the hole as with an etalon; rather, absorption is due primarily to propagation along the front and back metal surfaces. The main advantage of the use of an array of ordered subwave holes is the possibility of spectrally selective enhancement of a signal from molecules controlled by the period of a grating consisting of holes. When a R6G dye layer is deposited on the nano-diffraction grating, the molecules of R6G will stimulate stronger oscillations of the free electron on the surface, to increase localized surface plasmon, thereby increasing the surface plasmon resonance. That is the cause of the increase in infrared absorption of the diffraction grating with R6G.

The observed spectral features can be attributed to the features of the band structure of this grating; thisstructure is schematically shown in Fig. 5. For the extreme wavenumber of the grating $q_\infty \approx 1700\ cm^{-1}$ at the edge of the first, lowest allowed, band, the density of spectral modes increases rapidly when approaching this edge, which results in an increase in the rate of photoprocesses (infrared absorption in this case). As a result, the inversion of the infrared spectrum of the dye on the grating as compared to its spectrum on the substrate with an increase in the intensity of absorption lines with an increase in the wavenumber ν is observed in the region ν = (1400-1600) cm^{-1} (Fig. 4). On the contrary, the spectral region ν = (2800-3000) cm^{-1}, in which the grating effect is absent, can correspond to the waveguide transmission mode of shorter wavelength light through holes of the grating.

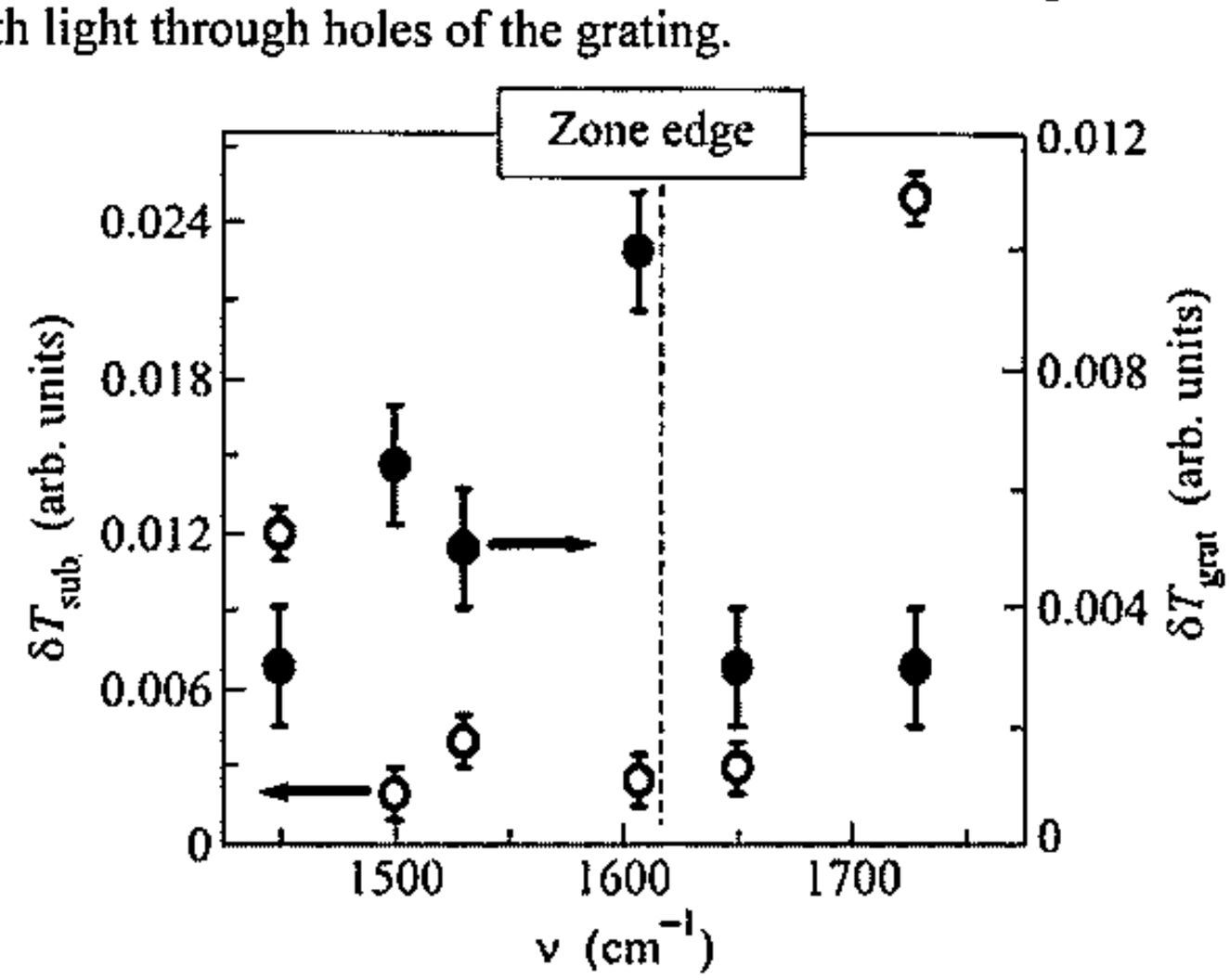


Figure 4. Intensity of the lines of infrared absorption (modulation of the transmittance) of the dye layer on the (δT_{sub}, open circles) CaF_2 substrate and (δT_{grat}, closed circles) diffraction grating manifested in Fig. 3 at the corresponding values. The vertical dashed line (zone edge) indicates the inversion cut region on the energy axis ν.

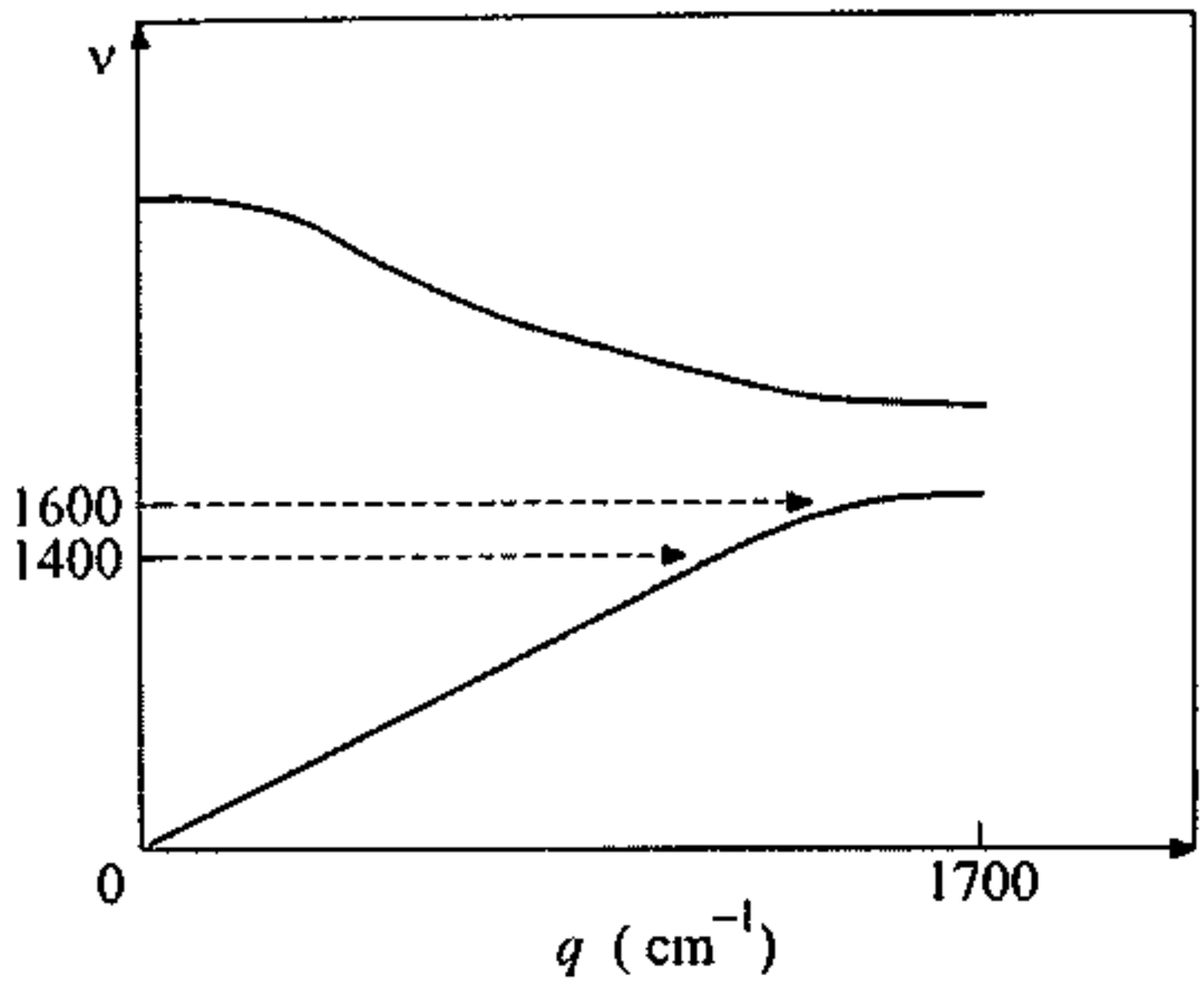


Figure 5. Schematic ν - q band structure for the diffraction grating under study in the infrared region. The arrows indicate the region of low-frequency infrared spectroscopy of rhodamine 6G.

4. CONCLUDING REMARKS

The observed strong enhancement of absorption of dye molecules for certain regions of the infrared spectrum of the transmittance of the transmission diffraction grating, which correspond to the edge of its allowed band with a high density of states, can be of significant interest for nanophotonics. This effect implies the possibility of creating infrared sensors for certain functional groups or even pair combinations of functional groups of organic or inorganic molecules by the corresponding choice of different periods of the two-dimensional transmission diffraction grating and unpolarized infrared radiation.

In summary, a two-dimensional square transmission diffraction grating consisting of micro-holes in a Au/Pd (80/20 %) film with the diameter $d \approx 3$ μm and period of about 6 μm was produced by ultrashort laser pulses. It exhibits surface enhanced infrared absorption of rhodamine 6G in the range of 1400–1600 cm^{-1} near the edge of the lower allowed band with a gain of about 10. This effect has very high application in the manufacture of infrared sensors (IR-sensor).

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TÓM TẮT

TĂNG CƯỜNG SỰ HẤP THỤ ÁNH SÁNG HỒNG NGOẠI BỞI THUỐC NHUỘM RHODAMINE 6G TRÊN LƯỚI NHIỄU XẠ Au/Pd

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Ngày nay cảm biến nano (nanosensor) hồng ngoại có rất nhiều ứng dụng trong khoa học công nghệ, y tế và đời sống. Hiệu ứng truyền ánh sang bất thường (extraordinary optical transmission – EOT) qua mảng nhiễu xạ lỗ nano tuần hoàn trên màng mỏng kim loại được sử dụng để tạo ra một số loại cảm biến có độ nhạy cao. Trong công trình này chúng tôi nghiên cứu sự tăng cường hấp thụ hồng ngoại bởi thuốc nhuộm Rhodamine 6G (R6G) của lưới nhiễu xạ trên màng mỏng vàng pha tạp paladin Au/Pd (80 / 20 %) độ dày h ≈ 60 nm với đường kính trung bình mỗi lỗ d ≈ 3 μm và chu kì của lưới (khoảng cách giữa hai tâm của lỗ liền kề nhau) p ≈ 6 μm, thông qua hiệu ứng EOT, cho thấy trong khoảng bước sóng 1400 - 1600 cm^{-1} hệ số hấp thụ hồng ngoại của lưới nhiễu xạ được khuếch đại lên khoảng 10 lần so với chất nền CaF_2.

Từ khóa: hấp thụ hồng ngoại, hệ số truyền qua, lỗ micro, màng mỏng kim loại, Rhodamine 6G.