

## *Supporting information*

# **An IR modulator based on the self-assembly of gold nanoparticles on germanium**

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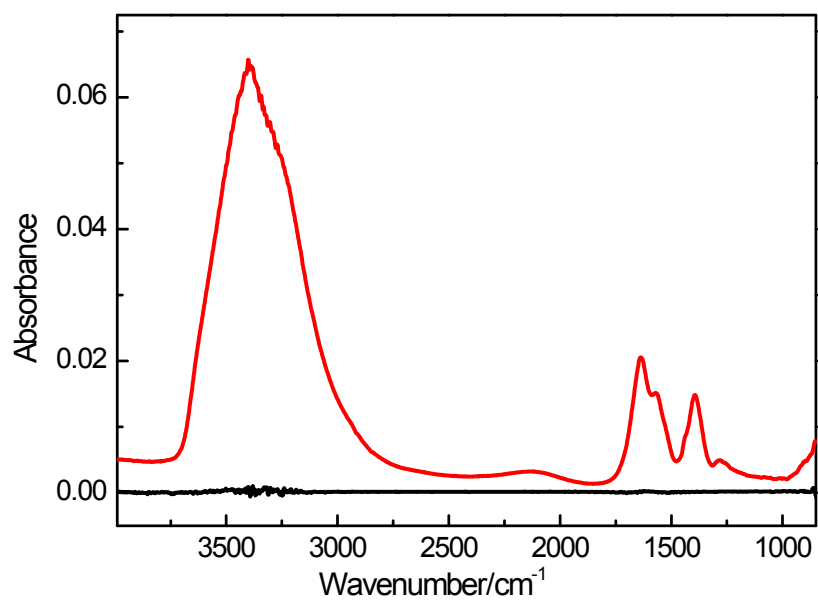
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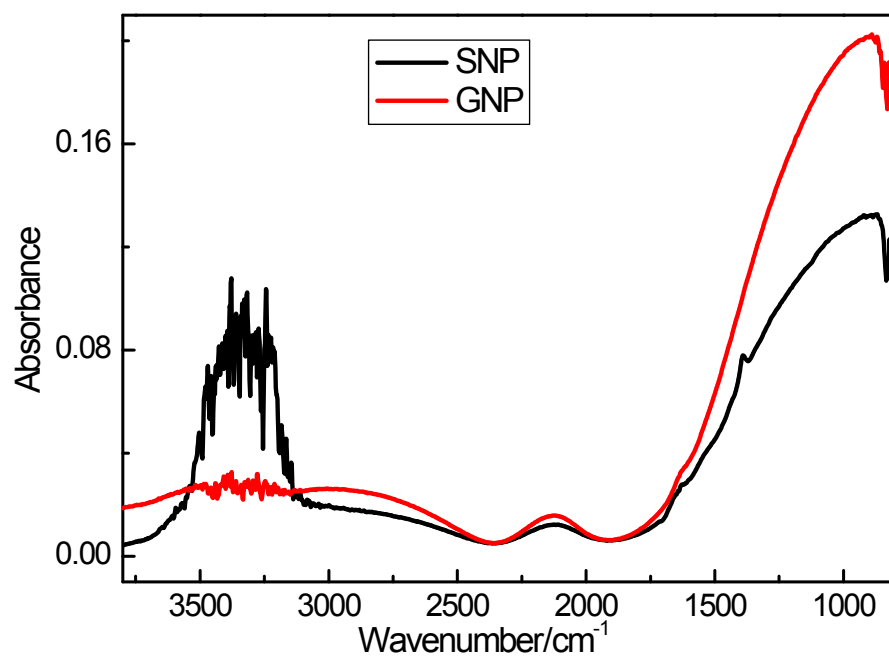
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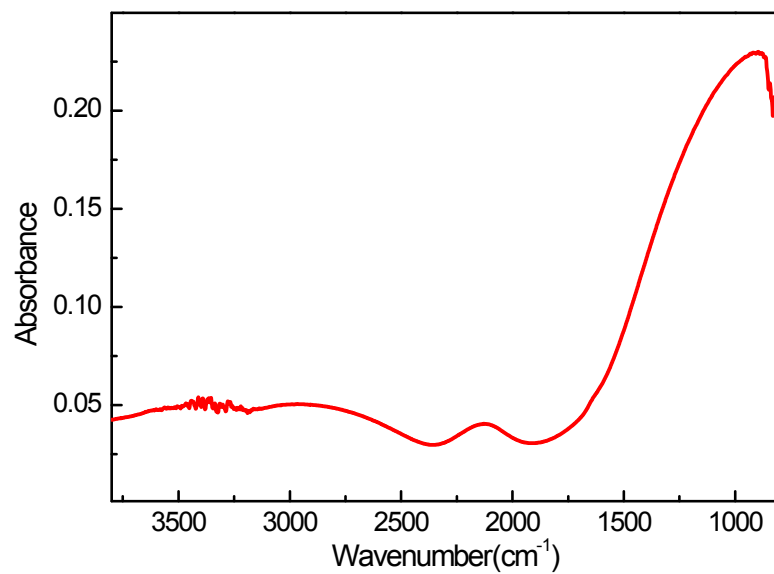
[thomas.buergi@unige.ch](mailto:thomas.buergi@unige.ch)



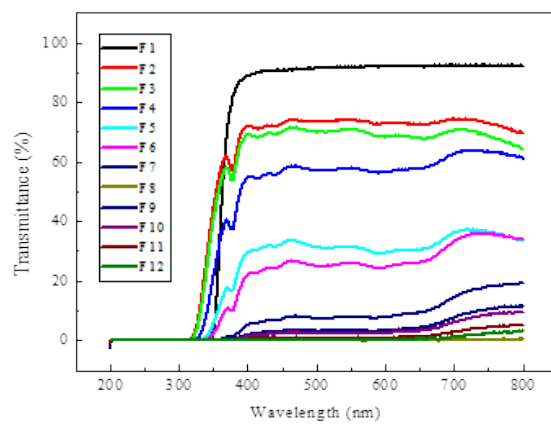
**Figure S1.** ATR-IR spectra of gold nanoparticle (GNP) adsorption on a PAH functionalized Ge IRE. Spectra were measured after 40 minutes of GNP adsorption. The background (black spectrum) was taken just before GNP adsorption. Bands at 1640 and 3400  $\text{cm}^{-1}$  are due to water (enhanced IR absorption); bands at 1390 and 1570  $\text{cm}^{-1}$  are due to citrate molecules. The latter are adsorbed on the nanoparticles but also on PAH (from free citrates in solution).



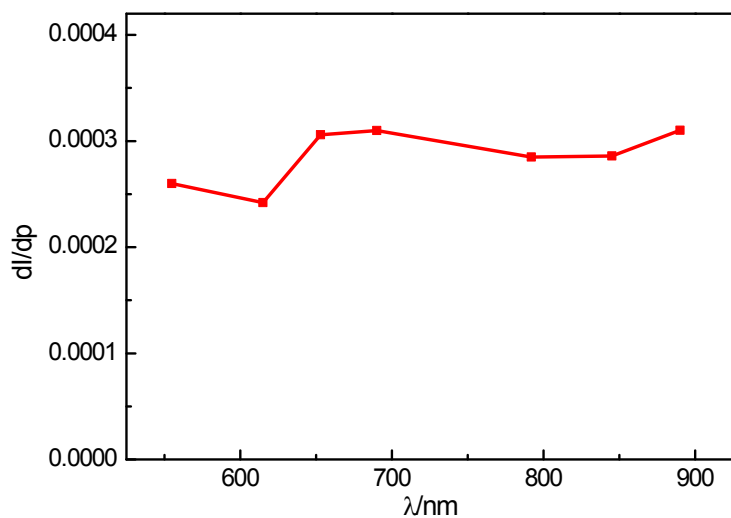
**Figure S2.** ATR-IR spectra of a Ge internal reflection element functionalized by PAH polyelectrolyte and nanoparticles (gold nanoparticles (GNP) and silver nanoparticles (SNP)) during illumination with a Xe lamp. After nanoparticles adsorption the background was recorded in the dark and the ATR-IR spectra were measured. The comparison shows that the effect is more pronounced for the gold nanoparticles.



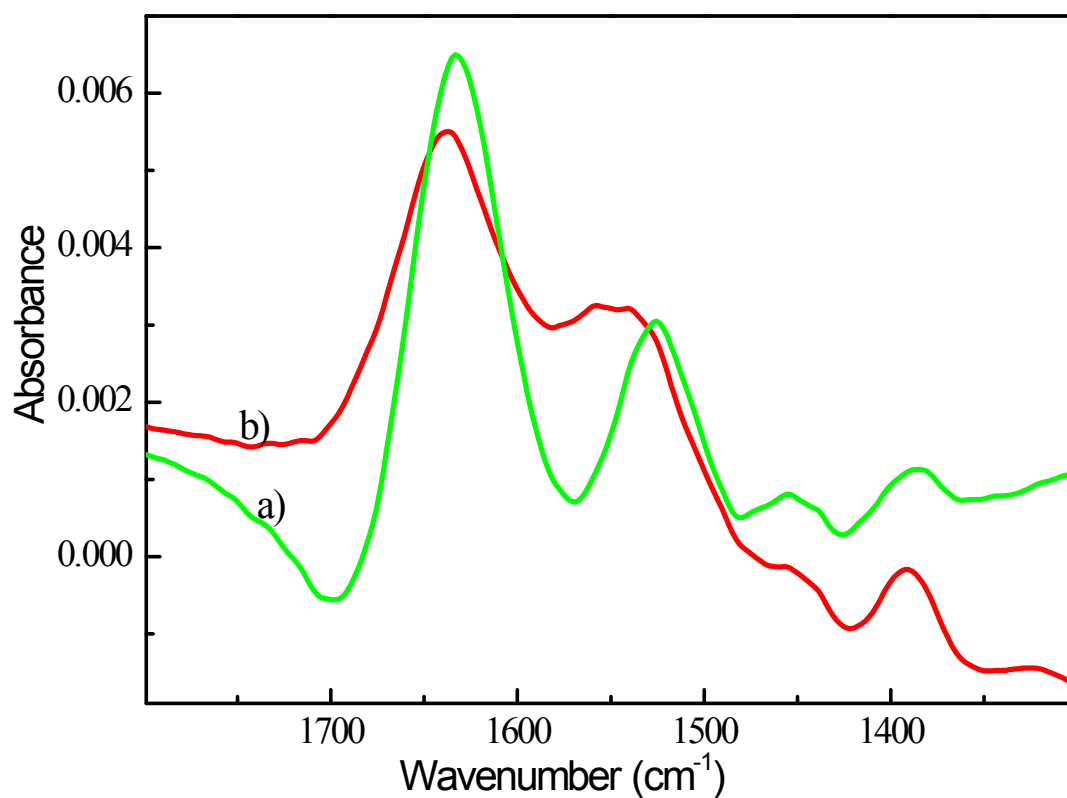
**Figure S3.** ATR-IR spectra of the Ge element covered by GNPs recorded during illumination with a Xe lamp. The spectrum was measured at the end of an experiment that was conducted entirely in the dark. First GNPs were adsorbed for 40 min followed by washing for three hours. The background was measured and the finally the spectrum was measured during illumination. This is the first time that the sample is exposed to light. The experiment shows that light is not necessary for the processes that leads to the development of the effect.



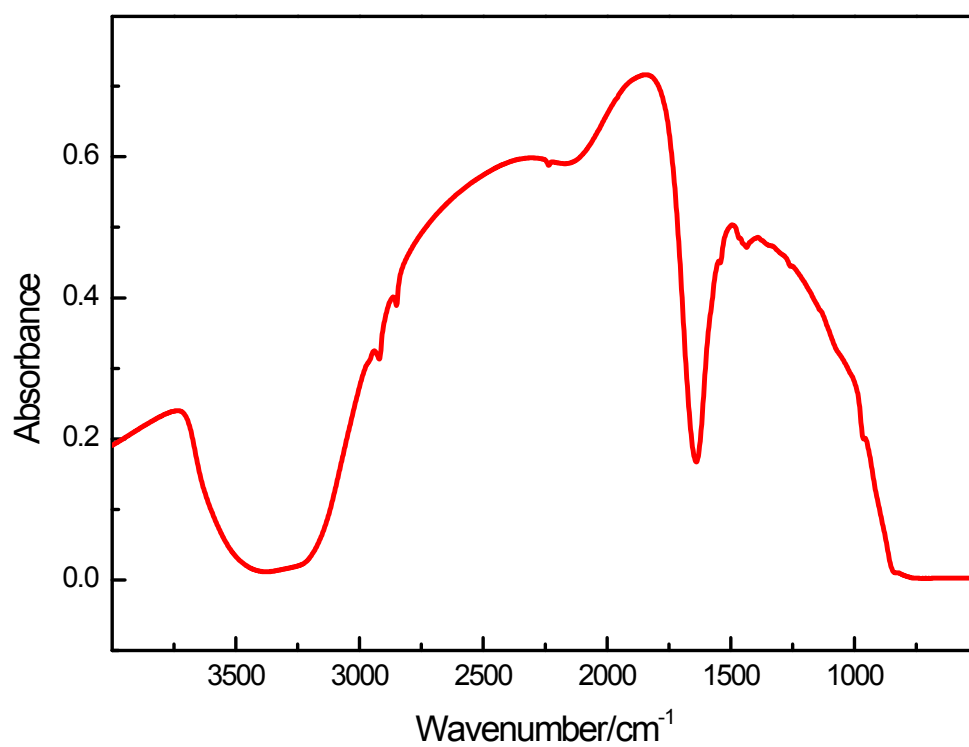
**Figure S4.** Transmittance of grey filters used to study the dependence of the absorbance in the IR (due to holes in the Ge) on the irradiance of the visible / NIR light.



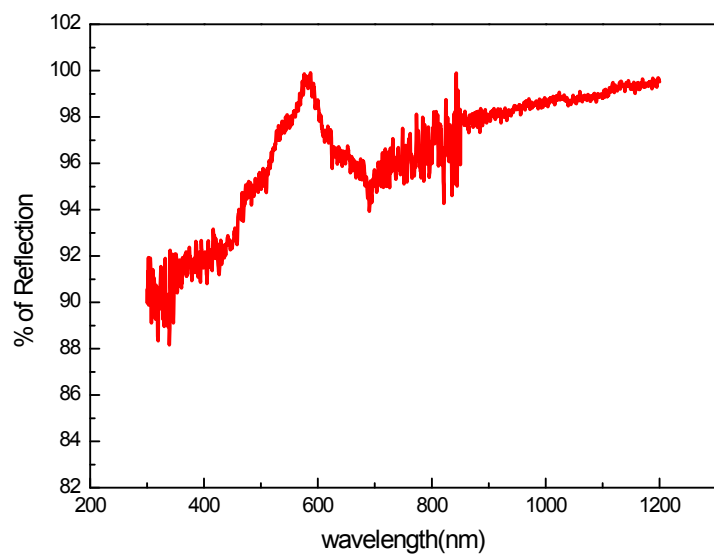
**Figure S5.** Absorbance at  $950\text{ cm}^{-1}$  divided by the irradiance as a function of wavelength. The Ge sample covered by GNPs was illuminated by a Xe lamp transmitted through a band pass filter. The observed IR absorbance at  $950\text{ cm}^{-1}$  was measured and divided by the irradiance measured at the sample ( $dI/dp$ ) for different band pass filters. The wavelength corresponds to the middle of the band pass filter transmittance. The curve shows no strong dependence on wavelength, which indicates that the plasmon of the gold nanoparticles is not directly involved in the generation of higher signals in the IR due to the holes in Ge.



**Figure S6.** ATR-IR spectra recorded during adsorption of PAH and subsequent washing. a) Polyelectrolyte (PAH) adsorption from 0.1 M NaCl solution, b) washing for 90 minutes with neat water. For both spectra the reference was recorded while flowing neat water before the adsorption step. The most prominent bands are due to the amine groups of PAH. The experiment confirms the adsorption of positively charged PAH on the Ge surface. The changes during washing with water are due to removal of NaCl.



**Figure S7.** Single channel spectrum of a Ge ATR element in contact with water. This spectrum shows the accessible wavenumber range of the ATR measurements.



**Figure S8.** Reflectance spectrum of gold nanoparticles attached on Ge ATR crystal surface. As the reference served the Ge ATR element before gold nanoparticle adsorption. The feature at 583 nm is ascribed to the plasmon of the gold nanoparticles, which is shifted with respect to isolated gold nanoparticles due to the large refractive index of Ge.