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# Significant decrease of the optical losses in the coupling between colloidal CdSe/CdS nanocrystals and a flat gold film at cryogenic temperature

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We investigate the influence of the temperature (between 4K and room temperature) on the fluorescence of colloidal thick-shell CdSe/CdS nanocrystals coupled with a flat gold film. First, we deduce the complex dielectric function  $\tilde{g}$  from the spectrophotometric measurements on the flat gold film. Then, when compared to a nanocrystal deposited on a glass coverslip, calculations show that the enhancement of the photoluminescence decay rate is divided by a factor 2.3 between 4 K and 293 K due to the reduction of optical losses. Our analysis well accounts for the experiments performed on single CdSe/CdS nanocrystals.

PACS numbers:

## I. INTRODUCTION

Metallic structures have attracted great attention since they are very promising for applications such as spectroscopy [1], light harvesting in photovoltaic devices [2], optical sensors measuring the concentration of chemicals [3], and optical devices for biology [4] or nanomedicine [5]. In the field of nanophotonics, the use of plasmonic nanostructures represents a relevant approach to enhance the fluorescence of nanoemitters and to collect it efficiently [6–9]. Indeed, in contrast with dielectric structures, plasmonic ones offer the possibility to achieve subdiffraction confinement of light and to manipulate the electromagnetic field at the nanoscale [10]. However, metals that are commonly used such as silver or gold exhibit high optical losses, especially at visible wavelengths [11–13]. For practical applications, techniques to remedy this drawback are then on high demand.

The imaginary part of dielectric permittivity of metal quantifies the optical losses. It is also proportional to the electron ohmic resistivity. Joule and optical losses are then closely linked. Recently, the reduction of ohmic losses was investigated in flat silver films [14, 15]. The crucial role of the film crystallinity and the surface roughness has been highlighted. Beyond these structural effects, electron-phonon scattering ultimately limits the plasmon damping. It can be reduced with low temperature operation. In the case of a flat silver film, the plasmon propagation length at the film interface can be enhanced by a factor 1.5 when decreasing the temperature from 293 K to 4 K. For an ensemble or individual

gold bypyramid nanoparticles free of surface roughness, Liu *et al.* also reported a decrease of 30 % of the homogeneous plasmon resonance linewidth [16].

In this paper, the effects of low temperature operation on the optical properties of a gold film are first investigated. For temperature ranging between 11 K and 293 K, the complex dielectric function  $\epsilon$  of a low roughness film is determined from spectroscopic absorption measurements and from the fit of the experimental data by a Drude model with critical points (DCP). The imaginary part of  $\epsilon$  that is at the root of optical losses decreases by a factor of the order of 2.5 around  $\lambda = 600$  nm. The opportunities offered by the dramatic decrease of the optical losses are next illustrated through the coupling of colloidal nanocrystals (NCs) with the flat gold film. When compared to NCs deposited on glass, we predict and measure that the enhancement of the decay rate is 2.3 lower at 11 K than at 293 K due to the reduction of the ohmic energy dissipation (the enhancement is equal to 15 at 293 K and 6.5 at 11K). At the same time, the radiative quantum efficiency (QE) is 3.2 times greater.

## II. EXPERIMENTS

### A. Samples

The flat gold film was fabricated by thermal evaporation at room temperature of gold on a cleaned glass substrate under ultra-high vacuum ( $10^{-9}$  torr). The mass measured with a quartz balance shows that the continuous film has a thickness of 25 nm. Atomic force microscope measurements over a  $1 \mu\text{m} \times 1 \mu\text{m}$  indicates that the roughness is equal to 1.1 nm.

The chemical synthesis of CdSe/CdS core-shell NCs is

detailed in [26]. The core radius measures 3 nm while the mean value of the shell thickness is 6 nm. The surface is encapsulated by ligands with a mean length of 2 nm. In the following, we will consider that the shell and the ligands act as a spacer and that the NC corresponds to a degenerate dipole [17] located 10 nm above the surface they are deposited on. At room temperature, the emission wavelength is centered at 620 nm. At 4 K, it is about 590 nm.

## B. Experimental setups

The NCs are suspended in a mixture of 90 % hexane and 10 % octane. They can be spin coated on a glass coverslip or a flat gold film so that single NCs can be studied with a confocal microscope setup operating between 4 K and 293 K (Cryostat attoDRY1100, low temperature confocal microscope attoCFM-I, attocube) without any drift for several hours. The NCs are optically excited by a pulsed laser diode (LDH 485, Picoquant, wavelength operation of 485 nm, pulse duration  $\sim 100$  ps). The NC emission is collected with a 0.82 numerical aperture objective and detected by a Hanbury-Brown and Twiss setup (MPD avalanche photodiodes, time resolution of 50 ps) connected to a data acquisition card (PicoHarp 300 module, Picoquant, 64 ps time resolution). The instrumental function response (IRF) of the overall setup was determined experimentally and is of the order of 200 ps.

The transmission measurements were driven with a spectrophotometer (Perkin Elmer LAMBDA 850) extended with a cryostat (CCS-400H-204, Janis), so that the sample temperature can be adjusted between 11 K and 800 K. The absorption spectrum was measured between 11 K and 293 K for wavelengths ranging from 400 nm to 800 nm.

## III. RESULTS - DISCUSSIONS

### A. Gold film dielectric constant and decay rate

The dielectric function  $\epsilon$  of gold is tabulated in several data table such as the ones of Johnson and Christy [18] or in the ref. [19]. However, when considering a thin gold film, one has to take into account its thickness and roughness. More fundamentally,  $\epsilon$  also depends on the temperature and very few data on gold nanostructures optical properties were reported for cryogenic temperatures [16, 20].

In order to characterize the studied gold film, the dielectric constant was determined by fitting the measured transmission coefficient of a glass/gold/air slab as a function of the wavelength. The glass dielectric constant is taken from tabulated data, assuming a Cauchy wavelength dependency. Gold dielectric constant is assumed to follow a Drude-Lorentz model with critical points

(DCP) in order to describe the metal optical response near the interband transitions [21] (see Eq. 1).

$$\epsilon(\omega) = \epsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega u_p} + \sum_{i=1} \frac{A_i \omega_i e^{i\phi_i}}{\omega_i - \omega - iu_i} + \frac{A_i \omega_i e^{-i\phi_i}}{\omega_i - \omega + iu_i} \quad (1)$$

The two first terms refer to the Drude like contribution with  $\epsilon_{\infty}$  the high frequency limit of the dielectric constant and  $u_p$  the damping rate. The sum describes the interbands transition with two critical points transitions at energies  $k\omega_{1,2}$ , with a broadening  $u_{1,2}$  and a weight  $A_{1,2}$ .  $\phi_{1,2}$  is the phase of the pole describing the interband transition. For null phase, the critical point transition behaves like a Lorentz oscillator. The inclusion of a phase factor takes into account direct and indirect interband transitions within the Brillouin zone [22].

We present in Figure 1 typical behaviours for two working temperature (11 K and 293 K). We consider the parameters fitted by Vial and Laroche for tabulated data at ambient temperature as initial guess for our model [23]. The fitted parameters are presented as a function of the temperature in appendix A. The main changes concern the losses rates. We notably observe a strong increase of the Drude loss rate  $u_p$  and interband losses rates  $u_{1,2}$  near 125 K.

The mean total  $\Gamma_{\text{tot}}$  and non-radiative  $\Gamma_{\text{NR}}$  decay rates of NCs above the gold film can be finally calculated using the Chance Prock and Silbey model [24, 25], as presented in Figure 2 (the average is calculated for a distribution of NCs modeled as a 2D dipole and presenting a random orientation). We observe a decrease of the normalized decay rates (the normalization is made with respect to glass surface) at cryogenic temperatures, due to lower losses. Moreover, the decay rates are higher for smaller wavelengths, close to the gold interband transitions. In addition, the non radiative rate strongly increases above 125 K, due to higher metal losses as revealed by the DCP model.

The relative contribution of  $\Gamma_{\text{NR}}$  with respect to  $\Gamma_{\text{tot}}$  also increases at 11 K. When the temperature increases, the gap between the non radiative (dashed line) and total (continuous line) decay rates decreases, that is the radiative rate decreases. Simultaneously the decay rates raise up. As a consequence, the radiative QE also increases at cryogenic temperatures (Figure 3). The total radiated power over  $4\pi$  steradian represents 3.3 % of the total power at 293 K while it reaches 11 % at 4 K.

### B. NCs fluorescence

To illustrate the dramatic effect of the temperature on the coupling between a gold film and single NCs, we compare the results obtained at room temperature and the lowest temperature that be reached with the cryostat

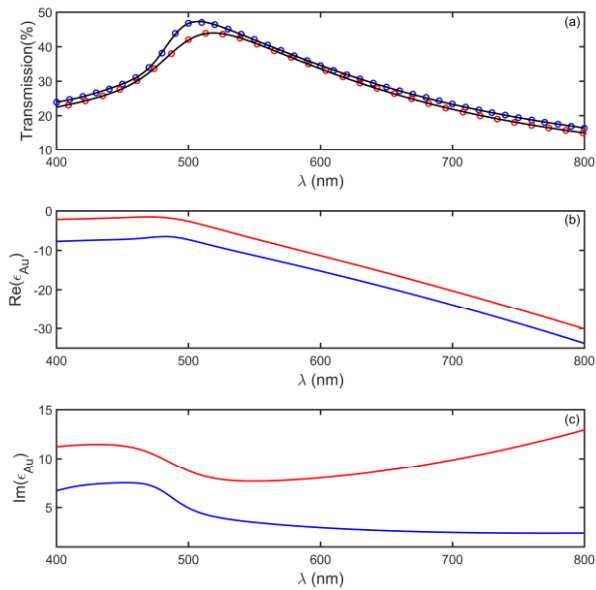


FIG. 1: (a) Transmission measured as a function of the wavelength for two temperatures: 11 K (blue circles) and 293 K (red circles). The experimental data are fitted using a Drude-critical points model for the gold dielectric constant (black lines). (b) Real part of the gold film dielectric constant estimated from the fit at 11 K (blue line) and 293 K (red line). (c) The same for the imaginary part.

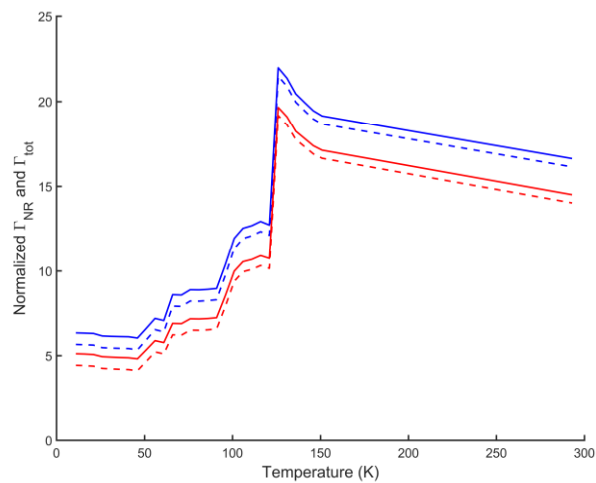


FIG. 2: Non-radiative (dashed lines) and total (continuous lines) decay rates as a function of temperature estimated considering the experimental gold dielectric constant of Fig. 1b and 1c (the values are normalized to the ones obtained for a glass coverslip). The emission wavelength is  $\lambda_{em} = 590$  nm (blue) or 620 nm (red). The NC is 10 nm above the gold film.

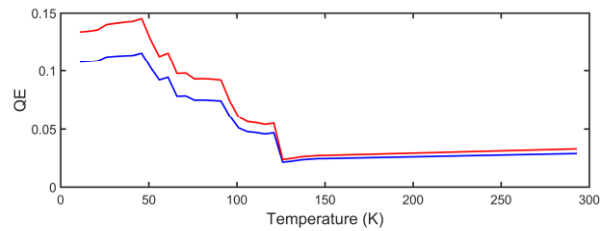


FIG. 3: QE as a function of the temperature. The emission wavelength is  $\lambda_{em} = 590$  nm (blue) or 620 nm (red).

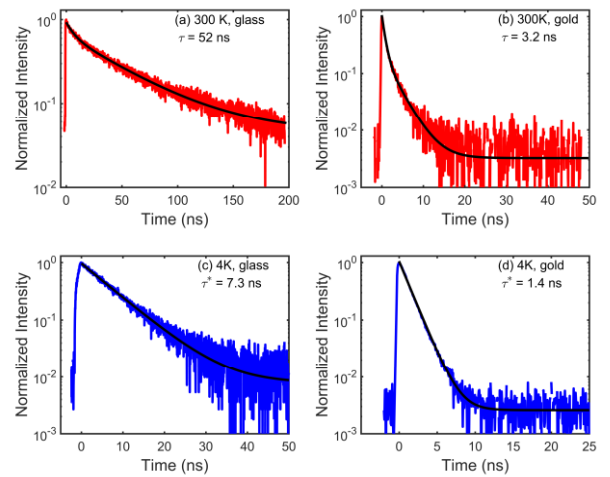


FIG. 4: (a) PL decay of a single NC deposited on glass at 293 K. The black line is a bi-exponential fit (lifetime of 7 ns and 52 ns). (b) PL decay of a single NC deposited on the flat gold film at 293 K. The black line is a bi-exponential fit (lifetime of 0.7 ns and 3.2 ns). (c) PL decay of a single NC deposited on glass at 4 K. The black line is a monoexponential fit (lifetime of 7.3 ns). (d) PL rate of a single NC deposited on the flat gold film at 4 K. The black line is a monoexponential fit (lifetime of 1.4 ns).

(4K). To start with, the emission of single NCs deposited on a glass coverslip is characterized at room temperature. In the following, we operate with low power excitation such as the probability to generate one electron-hole pair per pulse is much higher than the probability to create several ones. Thick-shell CdSe/CdS NCs are then known to alternate between a bright state when the NC is neutral and a “grey” state when it is ionized. For the bright state, the radiative quantum efficiency is close to 1 and close to 40 % for the grey one due to the competition between the radiative and the Auger recombinations for the trion. Adjusting the PL decay with a biexponential curve, we find that the mean lifetime of the exciton  $\tau$  is 49 ns, in agreement with previous measurements [27] (see Figure 4.a).

To compare the results obtained when NCs are coupled to the flat gold film, we took care to keep the pumping rate constant. We then reduced the pumping power tak-

ing into account the reflectivity of the film at 485 nm (41 % at 293 K and 49 % at 4K according to the spectrophotometric measurements). Still at 293 K, the PL decay of NCs coupled to the flat gold film occurs much faster as expected (Figure 4.b). As previously reported [27, 28], the PL decay also exhibits two components. The long component with a mean value of 3.4 ns still corresponds to the exciton recombination. The fast component  $\sim 0.7$  ns corresponds to the trion desexcitation and to a large contribution of noise due to the low QE. The decay rate enhancement induced by the gold film is then equal to 14, a value very close to the one predicted in the previous section ( $\Gamma_{\text{tot}}/\Gamma_{\text{glass}} = 15$  at  $\lambda = 620$  nm and room temperature, see Fig. 2).

The modification of the PL decay rate enhancement at 4 K is now investigated. Under vacuum, the PL decay and intensity measurements demonstrate that the NC remains in the charged state [29]. Due to the absence of air and water, once the NC is ionized, its neutralization cannot happen. At cryogenic temperatures, another crucial modification concerns the strong reduction of Auger recombinations efficiency leading, for the trion, to a QE close to 1 under 30 K [29]. The QE for the charged biexciton can also reach values as high as 60 % [30], with high variation from a NC to another [31], and the recombination of this state can contribute to the total fluorescence. At 4 K, the PL decay of NCs on glass is then well fitted by a monoexponential decay or a bi-exponential decay depending on the potential contribution of the biexcitonic emission. The mean trion lifetime  $\tau^*$  is 8.1 ns (7.3 ns for the data plotted in Figure 4.c). For few NCs, we also detected very long lifetimes components ( $\sim 20$  ns, with a weight of 10 %) that can be attributed to surface traps [32].

When NCs are coupled to the flat gold film at 4 K, the PL decay is well fitted by a monoexponential with very short lifetimes (Figure 4.d). The mean value is 1.6 ns so these measurements are not affected with the finite resolution of the experiment. Once again, for some NCs, we observed very long components ( $\sim 5$  ns) with small amplitudes (few percents) corresponding to the formation of long-live emission states.

From the 2 values of the trion lifetime measured at 4 K (8.1 ns on glass et 1.6 ns on gold), we calculate that the PL decay enhancement at this cryogenic temperature is equal to 5.1, a value close to the one predicted ( $\Gamma_{\text{tot}}/\Gamma_{\text{glass}} = 6.3$  at  $\lambda = 590$  nm and 11 K, see Fig. 2). As already highlighted in section III A, the decrease of the Purcell effect from 14 at 293 K to 5.1 at 4 K is due to the strong reduction of Joule losses and is associated to an enhancement of the overall radiative QE.

#### IV. CONCLUSION

In conclusion, the modification of the coupling between thick-shell CdSe/CdS NCs and a flat gold film at 4 K was investigated in detail. Measuring the variation of

the flat film absorption spectrum with the temperature and fitting the spectra with a DCP model, we predict a dramatic reduction of the optical losses and an enhancement of the QE of the NCs. These results are in agreement with the experimental data obtained at single NC level.

Our results open new opportunities in terms of plasmonics applications. The reduction of the temperature in addition to the control of the film quality (surface defects, cristallinity of the metal) represents a relevant approach to reduce optical losses. The potentiality to enhance by a factor 3 the radiative QE provides a strong motivation for future studies at cryogenic temperature, especially in the domain of quantum optics for which the reduction of the temperature also results in an improvement of the emitter optical properties (linewidth, QE). This strategy can also be extended to other nanoscale emitters.

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#### APPENDIX A: TEMPERATURE DEPENDENCE

We represent on Fig 5-7 the DCP parameters used to fit the gold dielectric constant as a function of temperature. Concerning the Drude contribution (Fig. 5), the plasma frequency  $\omega_p = \sqrt{Ne^2/m^*\epsilon_0}$  does not significantly varies on the temperature range. This originates from a small decrease of the carrier density  $N$  with temperature that is compensated by a decrease of the effective mass  $m^*$  [34].

The decay rate  $u_p$  is divided by ten freezing from ambient to cryogenic temperatures, with a strong modification close to 125 K. The Drude decay rate originates from electron-electron ( $u_{ee}$ ) and electron-phonon ( $u_{ep}$ ) scattering processes [20]

$$u_p = u_{ee} + u_{ep} \quad (\text{A1})$$

$$u_{ee} = \frac{\pi^3 \Gamma \Delta}{12 k E_F} (k_B T)^2 + \frac{k \omega}{2\pi} \quad (\text{A2})$$

$$u_{ep} = \omega_0 \left[ \frac{2}{5} + \frac{4T^5}{T_D} \int_0^{T_D/T_0} \frac{z^4}{e^z - 1} dz \right] \quad (\text{A3})$$

where  $T_D$  is the gold Debye temperature.

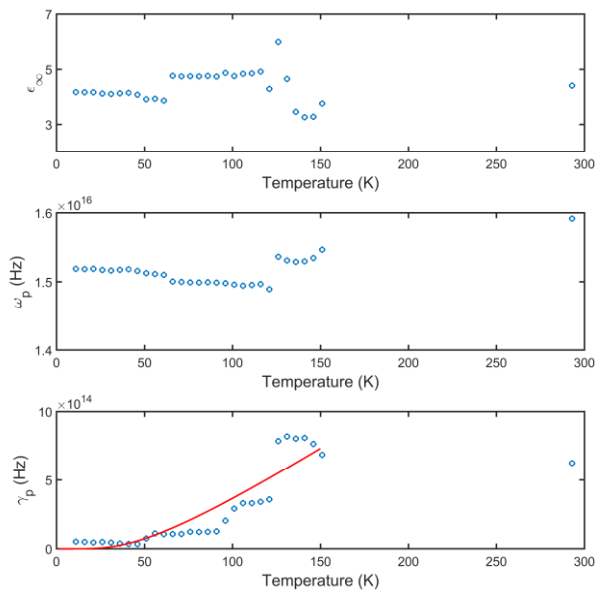


FIG. 5: Drude parameters  $g_\infty$ ,  $\omega_p$  and  $\gamma_p$  as a function of the temperature.

Note that electron-electron scattering depends quadratically on both the temperature and the angular frequency (see  $u_{ee}$  expression). The temperature contribution is negligible compared to the frequency term. We moreover assume a frequency independent behaviour as generally guess for Drude models. The line fit in Fig. 5c assumes the bulk Debye temperature  $T_D = 185$  K and qualitatively reproduces the Drude decay behaviour up to 150 K. We have considered only the ambient temperature above this value so that it is difficult to discuss of the general trend but it seems that the losses does not significantly change above 150 K. We attribute this to the grain boundaries that would govern the losses in the metal above the Debye temperature. Discussion of the role of surface roughness and grain boundaries on the optical losses as a function of the temperature is out of the scope of this work but could benefit from the extended work accomplished to describe the temperature dependence of metal resistivity (see e.g. [33]).

The two critical points describe the metal behavior close to interband transitions. The first point dominates

at angular frequency  $\omega_1 \approx 4.5 \times 10^{15}$  rad/s (corresponding to a wavelength  $\lambda \approx 420$  nm) whereas the second point dominates at angular frequency  $\omega_2 \approx 3.9 \times 10^{15}$  rad/s (corresponding to a wavelength  $\lambda \approx 480$  nm). The corresponding oscillator strength  $A(T)$ , frequency and damping rate are shown in Fig. 6, 7 as a function of temperature. We again observe an important variation (about 65%) from cryogenic to ambient temperatures with a jump close to 125 K. These behaviors qualitatively obey the following standard phenomenological

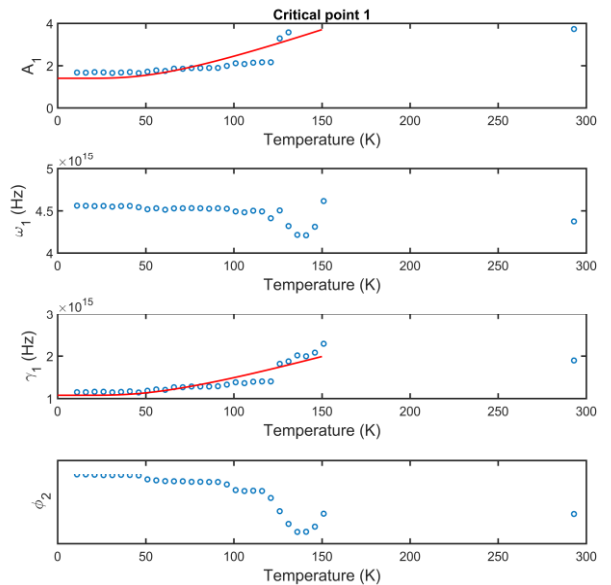


FIG. 6: Critical point 1 parameters  $A_1$ ,  $\omega_1$ ,  $\gamma_1$  and  $\phi_1$  as a function of the temperature. The red line is a fit of the Drude losses with  $\gamma_p = \gamma_{ee} + \gamma_{ep}$ , where the electron-electron scattering  $\gamma_{ee}$  is assumed constant and the electron-phonon scattering  $\gamma_{ep}$  obeys eq. A3.

model [34].

$$A_i = A_{i0} + \alpha_i \coth \frac{T_D}{T} \quad (A4)$$

$$u_i = u_{i0} + g_i \coth \frac{2T}{T_D} \quad (A5)$$

- 
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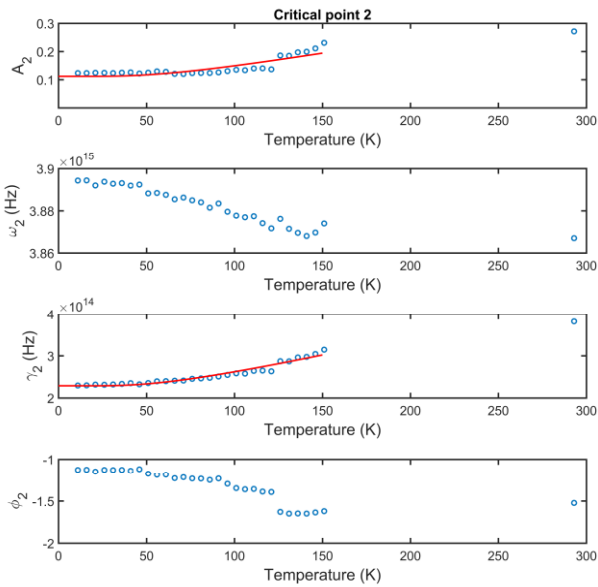


FIG. 7: Critical point 2 parameters  $A_2$ ,  $\omega_2$ ,  $\gamma_2$  and  $\phi_2$  as a function of the temperature. The red lines are fit of oscillator strength  $A_2$  and interband losses  $\gamma_2$  with eq. A4 and A5, respectively.

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