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Redshift of the Fröhlich Resonance and Electron Pinning at the Surface of a Spherical Copper Nanoparticle Surrounded by Protons

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Received May 16, 2025
Revised July 1, 2025
Accepted July 2, 2025

This work proposes a model describing the attachment of C−H bond protons to the surface of copper nanoparticles in an amorphous carbon nanocomposite modified with copper nanoclusters (a-C:H:⟨Cu⟩). It is shown that non-covalent interactions between the dipole moments of C−H bonds and induced charges in copper nanoparticles lead to electron localization near the particle surface — a phenomenon termed *electron pinning*. This effect is accompanied by shifts in the infrared absorption bands of C−H bonds and a reduction in electron density within the nanoparticle volume. As a result, the plasma frequency of the nanoparticle decreases, causing a redshift of the Fröhlich resonance into the infrared spectral region.

Keywords: amorphous carbon, non-covalent interactions, Fröhlich resonance, plasmonics.

DOI: 10.61011/PSS.2025.06.61698.132-25

1. Introduction

Over the past decades, nanocomposite materials containing metallic nanoparticles have attracted considerable attention due to their widely tunable physicochemical and optical properties [1,2]. A key factor is the mutual influence of the properties of metal nanoparticles and the host matrix, which manifests on short- and medium-range length scales and results in shifts of the Fröhlich (or Mie) resonance across the infrared to ultraviolet spectral range. For instance, prior work [2] attributed such spectral shifts to dipole–dipole interactions between adjacent copper nanoparticles forming dimers. However, the role of the chemical composition of the matrix in these shifts remains underexplored. In particular, the amorphous carbon used to encapsulate copper nanoparticles may contain hydrogen in the form of C−H bonds. When in direct contact with a metal surface, protons from these bonds can localize electrons near the nanoparticle surface, depleting the particle volume of electrons and shifting the resonance frequency toward the infrared region.

This phenomenon may have significant implications for applications such as optical filters based on copper-modified hydrogenated amorphous carbon (a-C:H:⟨Cu⟩). The present study investigates the influence of C−H bonds localized near the surface of copper nanoparticles on the behavior of the Fröhlich resonance (localized surface plasmon resonance). To predict the Fröhlich resonance frequency in novel materials containing C−H bonds, it is essential to determine whether non-covalent interactions between the dipole moments of these bonds in a-C:H:⟨Cu⟩ nanocomposites affect the resonance frequency shift. Furthermore, quantifying proton concentration near metal nanoparticle surfaces is promising, as the proposed model may help address challenges in applied betavoltaics.

2. Experimental

Copper-modified a-C:H:⟨Cu⟩ layers were deposited onto potassium bromide and amorphous quartz substrates by simultaneous DC magnetron sputtering of graphite and copper targets in an argon–hydrogen plasma. Detailed process parameters are reported in Ref. [2]. Copper plates covered 15% of the erosion zone of the graphite target. The deposited films were characterized by infrared (IR) spectroscopy using a Specord 75 IR double-beam spectrometer. Transmission and reflection spectra were recorded with a Hitachi U3410 spectrophotometer.

As shown in Figure 1, absorption bands are observed in both copper-containing and copper-free samples in the spectral region corresponding to C−H stretching vibrations of sp^3-hybridized carbon atoms [3]. This confirms that hydrogen is primarily incorporated into the films in carbon-bound form. Spectral decomposition in Figure 1 reveals changes in both line shape and peak position. For copper-free samples, the spectra are accurately described by a sum of Lorentzian oscillators. For a-C:H:⟨Cu⟩ samples, Gaussian line shapes are required, as evident from the figure. A comparison of Figures 1, *a* and *b* shows that IR absorption in the presence of copper consists of three Gaussian components, compared to seven Lorentzian components in copper-free samples. Thus, encapsulation of copper nanoclusters substantially modifies the IR spectrum.

Spectral changes may arise from interactions between C−H stretching vibrations near copper nanoparticles and the electrons within the particles. Lorentzian line shapes

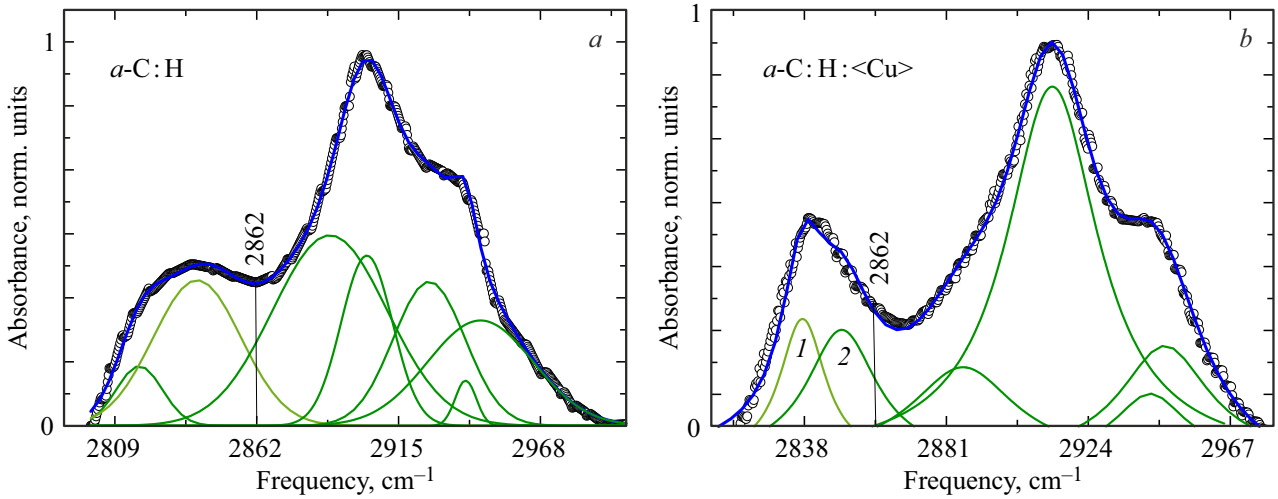

Figure 1. *a* — Decomposition of an IR absorption spectrum fragment of hydrogenated amorphous carbon (copper-free sample) into a sum of Lorentzian contours in the region of C−H stretching vibrations for sp^3-hybridized carbon. *b* — Decomposition of an IR absorption spectrum fragment of hydrogenated amorphous carbon modified with copper nanoparticles into a sum of Gaussian contours. Decomposition of IR absorption spectra for (*a*) a copper-free sample and (*b*) a copper-modified sample.

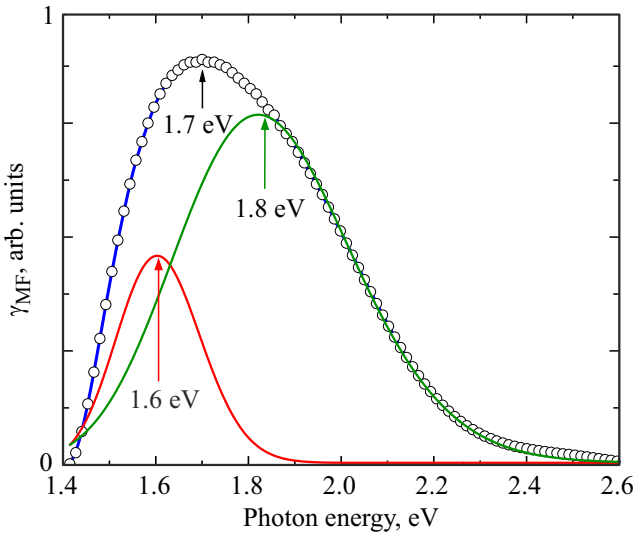

Figure 2. Contribution of copper nanoclusters to the absorption spectrum of a-C:H:⟨Cu⟩, shown as open circles. Log-normal Gaussian decomposition is presented with red and dark-green contours. The blue curve connecting the circles represents the sum of the dark-green and red contours. Arrows indicate peak positions.

are typical of homogeneously broadened bands determined by intrinsic harmonic oscillator parameters (e.g., C−H vibrations). In contrast, Gaussian line shapes indicate inhomogeneous broadening, which may result from interactions between C−H vibrations and metal-induced oscillators, combined with statistical averaging over oscillators at varying distances from the nanocluster surface.

Figure 2 shows the processed absorption spectrum of a-C:H:⟨Cu⟩ layers across the near-infrared, visible, and ultraviolet ranges. The absorption band peaks at 1.7 eV. The experimental data decompose into two log-normal distributions with maxima at 1.6 eV and 1.8 eV (red and dark-green curves, respectively). For the Fröhlich resonance, log-normal distributions may arise from fluctuations in nanoparticle size and local dielectric environment. The identified bands correspond to a redshifted Fröhlich resonance associated with plasma oscillations of electrons in spherical copper nanoparticles. Previous estimates [2] placed the unsifted Fröhlich resonance near 2 eV. The following sections present a model explaining this redshift.

3. Electron Pinning Model

As noted earlier, copper significantly alters the IR absorption spectra in the 2862−2990 cm^{-1} range (cf. Figures 1, *a* and *b*). Given the amorphous nature of the material and limited structural data, determining the precise geometric arrangement of terminal C−H bonds relative to nanoparticle surfaces is challenging. Nevertheless, key factors influencing spectral changes can be identified.

Figure 3 presents a **qualitative** model of the interaction between C−H bond vibrations and nanoparticles on the short-range order scale. C−H vibrations can be modeled as oscillating dipoles near the surface, inducing corresponding dipoles in the nanoparticle. Two limiting configurations are considered: perpendicular and parallel orientation of the dipole axes relative to the surface.

In the perpendicular orientation (Figure 3, *a*), the total dipole moment of the pair increases, enhancing the intensity of the corresponding absorption band. In the parallel orientation (Figure 3, *b*), opposing dipole directions yield a zero net moment, reducing intensity. Interactions between C−H dipoles and induced dipoles in copper (Figure 3, *a*) cause

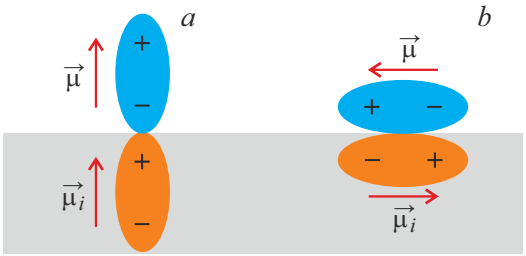

Figure 3. **Qualitative** schematic of dipole interactions near the surface of a copper nanoparticle. In the upper half-plane, the C−H bond dipole is shown in blue; in the lower half-plane, the image dipole is shown in orange. (*a*) Stretching vibrations with normally oriented dipole moments activate an IR absorption band. (*b*) Bands corresponding to parallel dipole moments are suppressed due to mutual cancellation.

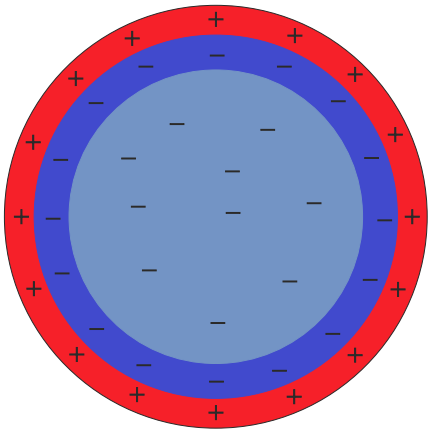

Figure 4. **Qualitative** model of electron redistribution inside a copper nanoparticle surrounded by protons (red shell) in the dipole binding configuration shown in Figure 3, *a*. Dark blue indicates regions of elevated electron concentration near the surface; light blue indicates electron-depleted regions in the volume.

charge redistribution within the nanoparticle. Positively charged protons from C−H bonds near the surface attract free copper electrons, forming electron-rich regions near the surface and electron-depleted regions in the volume. This reduces the plasma frequency and induces a redshift of the Fröhlich resonance.

Figure 4 illustrates a **qualitative** model of inhomogeneous charge distribution due to protons near the copper nanoparticle surface. Regions containing C−H protons are shown in red. Electron localization near the surface is depicted in dark blue, while depleted regions are in light blue. The stability of this charge configuration (Figure 4) is temperature-dependent, as elevated temperatures can disrupt dipole interactions. Reference [4] estimated proton–bulk copper interaction energies exceeding 2 eV per bond across various crystallographic directions.significantly greater than thermal energy at room temperature. Thus, the configuration in Figure 4 is stable, enabling quantitative assessment of electron pinning effects on the Fröhlich resonance frequency using surface proton concentration as a parameter.

4. Calculation of Free Electron Concentration in a Copper Nanoparticle Surrounded by Protons

The previous section introduced a **qualitative** model of electron pinning. Here, a quantitative analysis is provided. The spatial distribution of free electron concentration $n_e(r)$ in copper nanoparticles is calculated using the equation from Ref. [5]:

$$n_e(r) = n_0 \left(1 - \frac{u(r)}{\varepsilon_{0f}}\right)^{3/2}, \tag{1}$$

where $\varepsilon_{0f} = \frac{\hbar^2}{2m}(3\pi^2 n_0)^{2/3}$, n_0 is the average electron density in bulk copper, and m is the electron mass.

The electron potential energy is:

$$u(r) = -e\varphi(r), \tag{2}$$

where e is the elementary charge and φ is the electrostatic potential.

The potential satisfies Poisson's equation:

$$\nabla^2\varphi = -4\pi\rho. \tag{3}$$

The model considers a sphere with uniformly distributed fixed positive charge on the surface (surface density n_p) and non-uniform mobile negative charge inside.

The charge density inside the sphere is:

$$\rho = e(n_0 - n_e) = en_0\left[1 - \left(1 + \frac{e\varphi(r)}{\varepsilon_{0f}}\right)^{3/2}\right].$$

Poisson's equation inside the nanoparticle becomes:

$$\nabla^2\varphi = -4\pi en_0\left[1 - \left(1 + \frac{e\varphi(r)}{\varepsilon_{0f}}\right)^{3/2}\right]. \tag{4}$$

Outside the sphere ($\rho = 0$):

$$\nabla^2\varphi = 0. \tag{5}$$

Boundary conditions (particle radius R):

$$\begin{cases} \varphi(R-0) = \varphi(R+0), \\ \left.\dfrac{d\varphi}{dr}\right|_{R-0} - \left.\dfrac{d\varphi}{dr}\right|_{R+0} = -4\pi en_p, \\ \left.\dfrac{d\varphi}{dr}\right|_{0} = 0, \\ \left.\dfrac{d\varphi}{dr}\right|_{\infty} = 0. \end{cases} \tag{6}$$

Solutions are presented in Figure 5 as $\xi = n_e/n_0$.

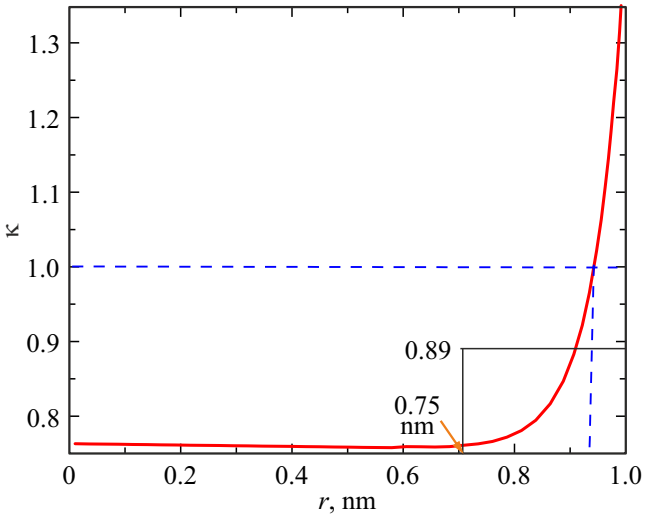

Figure 5. Electron distribution in a spherical copper nanoparticle of diameter $D = 2\,\text{nm}$ with surface proton concentration $n_p = 6.8\,\text{nm}^{-2}$. The blue dashed line shows the distribution in a cluster without protons. The red curve is the normalized electron concentration as a function of distance from the center (0) to the surface. The intersection of the vertical blue line with the red curve indicates the point where the electron concentration equals that of bulk copper.

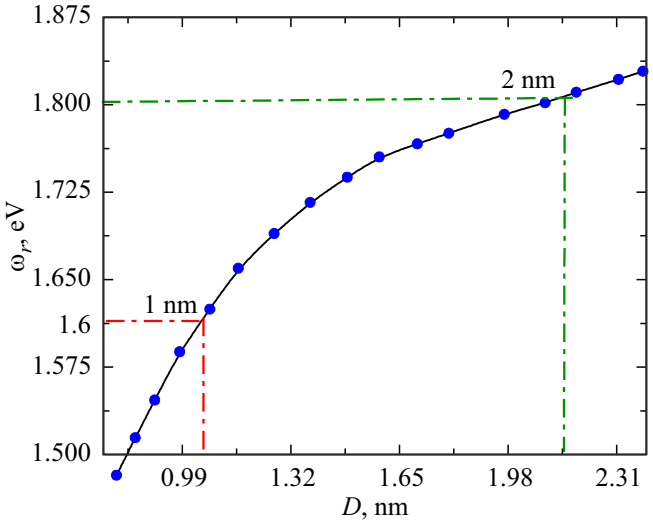

Figure 6. Dependence of the Fröhlich resonance frequency on copper nanoparticle size, calculated using Eq. (8). Dark-green and red lines correspond to the maxima in Figure 2.

5. Assessment of Pinning Effects on Optical Properties

Calculations (Figure 5) reveal enhanced electron localization near the surface, decaying to bulk values at approximately 0.75 nm from the center (0.25 nm from the surface). The non-uniform electron distribution complicates quantitative inclusion of localized electron contributions to the dielectric function. Therefore, the effect was estimated via changes in plasma frequency due to reduced free electron count.

The nanoparticle absorption cross-section C_{ext} is given by [6]:

$$C_{\text{ext}} = 4\pi k \varepsilon_m^{1/2}\,\text{Re}(i\alpha), \tag{8}$$

where α is the polarizability, k is the wave number, and $\varepsilon_m \approx 4$ is the dielectric permittivity of the matrix (a-C:H) [2].

$$\alpha = R^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}. \tag{9}$$

The dielectric function of bulk copper is [6]:

$$\varepsilon = \varepsilon_1 - \frac{\omega_{p0}^2}{\omega(\omega + i\gamma)}, \tag{10}$$

where γ is the damping constant, ω is the electromagnetic frequency, and ε_1 is the high-frequency dielectric constant.

For spherical particles of diameter D, γ is replaced by γ_{eff} [6]:

$$\gamma_{\text{eff}} = \gamma + \frac{2v_F}{D}, \quad v_F = 1.56 \cdot 10^6\,\text{m/s}. \tag{11}$$

The Fröhlich resonance condition is:

$$\text{Re}(\varepsilon) + 2\varepsilon_m = 0. \tag{12}$$

The resonance frequency ω_r is:

$$\omega_r = \sqrt{\frac{\omega_{p0}^2}{\varepsilon_1 + 2\varepsilon_m}\left(1 - \frac{6n_s}{n_0 D}\right) - \gamma_{\text{eff}}^2}. \tag{13}$$

Calculations used $n_0 = 84.9\,\text{nm}^{-3}$ ($\omega_{p0} = 8.0\,eV$ [6]).

The squared plasma frequency for modified electron density is:

$$\omega_p^2 = \omega_{p0}^2\left(1 - \frac{3n_s}{n_0 R}\right), \quad \omega_{p0} = \sqrt{\frac{4\pi n_0 e^2}{m_e}},$$

where $n_p \approx n_s$, $R = D/2$.

Figure 6 shows calculations using Eq. (13). A resonance at 1.6 eV corresponds to 1 nm particles, while 1.8 eV corresponds to 2 nm particles. The coexistence of two populations may arise from characteristics of the magnetron sputtering process: variations in nucleation and growth conditions lead to discrete size distributions. Previous electron microscopy [2] identified the 2 nm fraction; 1 nm particles may be indistinguishable due to projection overlap.

6. Conclusions

Protons from C–H bonds can localize copper nanocluster electrons near the surface, reducing the plasma frequency and shifting the Fröhlich resonance into the infrared region. The observed absorption spectra in a-C:H:⟨Cu⟩ nanocomposites are explained by two copper nanocluster populations with diameters of 1 nm and 2 nm, each surrounded by a proton shell with surface density $n_p = 6.8\,\text{nm}^{-2}$.

Conflict of Interest

The authors declare no conflict of interest.

References

[1] S. Tamulevičius, Š. Meǩinis, T. Tamulevičius, H.-G. Rubahn. Rep. Prog. Phys. **81**, 024501 (2018). https://doi.org/10.1088/1361-6633/aa966f
[2] I. Istomin, S. Yastrebov, M.R. Singh. Diam. Relat. Mater. **136**, 109962 (2023). https://doi.org/10.1016/j.diamond.2023.109962
[3] A. Grill, V. Patel. Appl. Phys. Lett. **60**, 2089 (1992). https://doi.org/10.1063/1.107098
[4] K. Cao, A. Füchsel, A.W. Kleyn, L.B.F. Juurlink. Phys. Chem. Chem. Phys. **20**, 22477 (2018). https://doi.org/10.1039/C8CP03386B
[5] C. Kittel. Introduction to Solid State Physics, 8th ed. (Wiley, New York, 2005).
[6] C.F. Bohren, D.R. Huffman. Absorption and Scattering of Light by Small Particles (Wiley, New York, 1983).