Excitonic Fano resonance in free-standing graphene

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Graphene, a one-atom-thick layer of carbon atoms arranged in a honeycomb lattice, exhibits extraordinary material properties which are closely connected to its atomic structure. Using optical spectroscopy, one can get insight into the electronic structure of graphene and especially gain a deeper understanding of the nature of the excited states. Such an investigation is of essential importance on the route toward applications of graphene in optoelectronics, for example in modulators or detectors. Most of graphene's physical properties can be explained by a tight-binding model of uncorrelated electrons. The characteristic band structure which results from this model is shown in Fig. 1. Due to the linear dispersion relation at the K point, where the so-called Dirac cones are formed, the optical absorption in the infrared is constant. It can be expressed in terms of fundamental constants only as $A \approx n\pi\alpha$, where n is the number of graphene layers and $\alpha \approx \frac{1}{137}$ denotes the fine structure constant in vacuum.

Here, we demonstrate that the common non-interacting particle picture fails to describe the absorption spectrum of free-standing graphene in the visible and ultraviolet regime [1]. However, the asymmetric shape of the prominent peak in the UV can be understood when many-body effects like electron-hole interactions are taken into account [3]. We show that our experimental data can be described quantitatively over a broad spectral range with a simple Fano model. In this picture, a discrete exciton state forms near the saddle point M in the band structure and couples to the continuum of states descending from the saddle point.

To fabricate the free-standing graphene monolayer and bilayer samples, the flakes are first exfoliated from natural graphite using the sticky tape method and are transferred on a silicon dioxide substrate. The number of layers can be identified by the optical contrast in a microscope and by Raman spectroscopy. The sample is then spin-coated with a 500 nm thick layer of a transparent plastic (PMMA). To achieve the free-standing character of the graphene flakes, 8 μm diameter holes are written on top of the flakes using electron beam lithography and the silicon dioxide substrate is etched in a sodium hydroxide solution. Figure 2a shows a microscope image of a measured graphene flake.

The optical transmission of the free-standing graphene flakes is measured with a confocal microscope (see Fig. 2b). With a light source combining a deuterium and a halogen lamp, spectra can be taken over a broad range of photon energies from 1.5 to 5.5 eV. The light is focused onto the sample by an all-reflective Cassegrain objective. The transmitted light is collected by a UV objective and analyzed with a spectrometer consisting of a monochromator and a CCD camera. The ratio of the transmitted light intensity through the graphene layer to the transmitted light intensity through an empty reference aperture gives the transmittance T. Since the reflectance of the free-standing sample is negligible, the absorbance can be determined as A = 1 - T.

The measured transmission spectra for monolayer and bilayer graphene are shown in Fig. 3a. At photon energies below 2 eV, the absorption spectra are almost flat and approach the predicted values of $\pi\alpha$ and $2\pi\alpha$ for the monolayer and the bilayer sample, respectively. Towards higher energies, the absorption slowly increases until it reaches a peak at approx. 4.5 eV. Beyond the resonance, it steeply decreases again, which results in an asymmetric line shape. The fact that a peak arises in the UV which shows an asymmetric line shape agrees

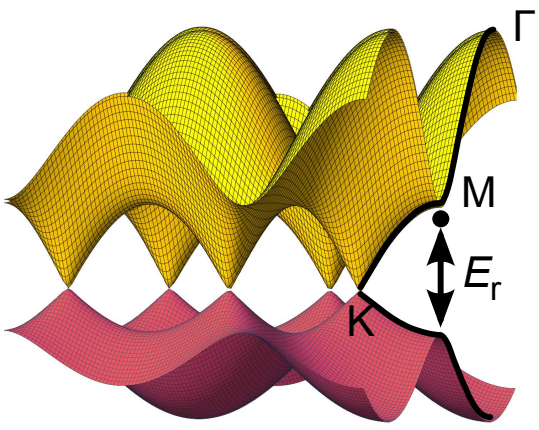

Figure 1: Electronic band structure of graphene. Dirac cones with a linear dispersion relation form at the K points. At the Γ point, in the center of the Brillouin zone, the conduction band reaches its maximum. A saddle point is found at the M point. The excitonic state is marked schematically by a dot.

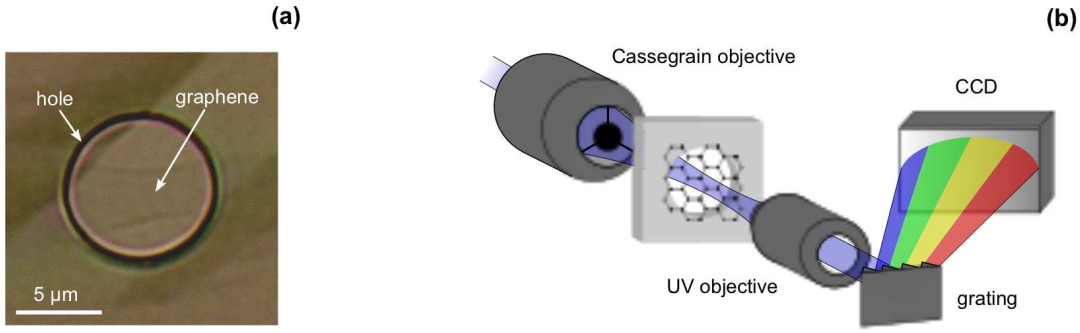

Figure 2: (a) Optical microscope image of a measured graphene layer taken in transmission mode. The free-standing flake on top of the PMMA aperture can be identified due to graphene's opacity of $\pi\alpha \approx 2.3\%$. (b) Schematic view of the experimental setup.

with the findings from ellipsometric measurements as well as recent measurements of the optical conductivity of supported graphene [2].

To model the measured data, we first draw on the commonly used picture of uncorrelated electrons which predicts a symmetric line shape of the peak in the UV. However, this cannot be brought into agreement with our measurement as is shown in the close-up in Fig. 3b. Hence, the single particle picture fails to describe the absorption spectrum of free-standing graphene in the visible and UV regime and we conclude that many-body effects need to be taken into account.

As it is known from semiconductors, an excitonic state can form near a saddle point in the band structure. The excitonic resonance is at an energy slightly below that of the saddle point. In graphene, this discrete state near the M point in the band structure overlaps with the continuum of states descending from the saddle point down to the Dirac point, the so-called Dirac continuum (see Fig. 1). When a discrete state couples to a continuum, the classical theory by Fano can be used to model the system. The resulting absorption spectrum has the form

$$A_{\text{Fano}}(E) = C\left(1 + \frac{q^2-1}{1+s^2} + \frac{2qs}{1+s^2}\right) = C\,\frac{(s+q)^2}{1+s^2}. \tag{1}$$

An illustrative interpretation of the Fano resonance is that of an interference between the transition to the discrete state and to the continuum. The three terms in the parantheses of Eq.(1) correspond to the constant absorption of the Dirac continuum, the discrete state, and the interference. Here, the discrete exciton state is modeled as Lorentzian resonance of width γ and energy E_r and determines the parameter $s = 2\,(E\text{-}E_r)\,/\,\gamma$. The asymmetric line shape of the absorption peak is caused by the interference term. The Fano parameter q is given by the ratio of the transition probabilities to the discrete state and to the continuum. C is an overall scaling factor. As can be seen from Fig. 3a, the model excellently fits our measured data for both monolayer and bilayer graphene.

From the fit parameters, the absorption in the low energy limit can be calculated and turns out to be in good agreement with the predicted integers of $\pi\alpha$. Moreover, we can estimate the exciton binding energy from the difference between the resonance energy E_r and the energy of the saddle point (see Fig. 3a). With 400 meV, the exciton binding energy in monolayer graphene seems to be substantially higher than in bilayer graphene, for which a value of 250 meV is obtained. This behavior can be explained by a screening effect: the screening ability of the electrons in a material depends on the density of states near the Fermi energy, i.e. near the Dirac point K in the band structure of graphene. While the density of states at the K point vanishes for a monolayer, it is constant and nonzero for a bilayer. The screening ability of the electrons is therefore larger in bilayer graphene and the binding energy of the exciton is expected to be reduced compared to monolayer graphene. This finding is in line with the behavior that has been observed for materials of different dimensionality: in three-dimensional bulk metals, strong screening prevents the formation of excitonic states, whereas excitons can clearly be found in one-dimensional metallic carbon nanotubes.

In conclusion, we investigated the role of electron-hole correlations in the absorption of free-standing graphene using optical transmission spectroscopy from the near-infrared up to the UV regime. The asymmetric peak in the UV can be described by a Fano model which includes an excitonic resonance near the saddle point in the band structure that couples to the Dirac continuum. In contrast, the common single particle picture of non-interacting

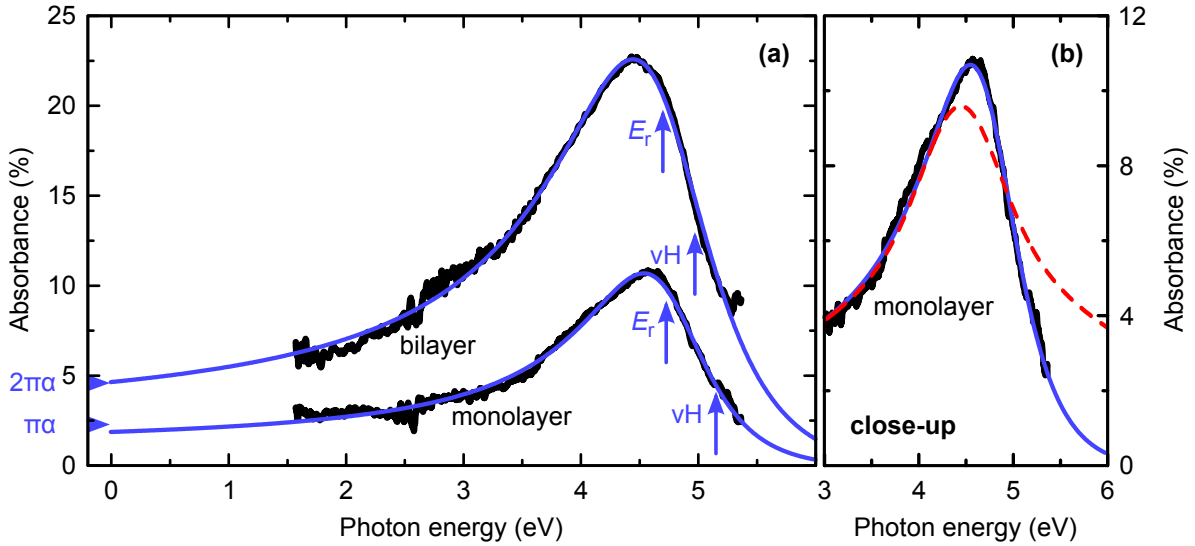

Figure 3: (a) Absorbance (= 1 - transmittance) spectra of free-standing monolayer and bilayer graphene (black thick lines) are well described by a Fano model (blue thin lines). The difference between the resonance energy E_r of the discrete state and the saddle point energy (van Hove singularity, vH) determines the exciton binding energy. (b) Close-up of the monolayer spectrum (black thick line) with the Fano fit (blue thin line) compared to a model neglecting electron-hole correlations (red dashed line).

electrons gives a symmetric line shape and thus cannot describe our measurement. Remarkably, the Fano model fits the measured data all the way down to low energies where the expected values of $n\pi\alpha$ are reproduced. This fact suggests that the optical response of graphene is fully determined by the topology of the band structure, whereas its detailed shape seems to be less relevant.

References:

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