Nanoscopic charge fluctuations in a gallium phosphide waveguide measured by single molecules

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We present efficient coupling of single organic molecules to a gallium phosphide subwavelength waveguide (nanoguide). By examining and correlating the temporal dynamics of various single-molecule resonances at different locations along the nanoguide, we reveal light-induced fluctuations of their Stark shifts. Our observations are consistent with the predictions of a simple model based on the optical activation of a small number of charges in the GaP nanostripe.

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One of the promising platforms for future quantum technologies is based on integrated nanophotonics, where a large number of quantum emitters and quantum states of light are efficiently interconnected via a labyrinth of subwavelength waveguides (nanoguides) and other nano-optical elements. The optimal choice of materials for achieving this goal has not been settled yet, but semiconductors (e.g., GaAs) and diamond architectures have made significant progress. In most cases, quantum emitters have been situated inside the host material of the nanoguides, e.g., AlGaAs quantum dots in GaAs or color centers in diamond. To decouple the choices of ideal quantum emitters, appropriate guiding architectures, and other nano-optical elements from each other, there is a large effort towards hybrid solutions.

Guiding light on a chip is best realized in a material with high refractive index, $n$. Common choices for waveguides in the visible and near-infrared regimes have been silicon nitride or titanium dioxide with $n \sim 2 - 2.5$. Semiconductors such as Si and GaAs offer considerably larger $n$ but at the expense of strong absorption for wavelengths smaller than 800 nm. Gallium phosphide (GaP) presents a very attractive alternative with $n \geq 3$ and a cutoff wavelength below 600 nm, and indeed, recent efforts have established fabrication of high-quality nanophotonic chips from this material. In this work, we show efficient coupling of single organic molecules to a GaP nanoguide. Furthermore, we investigate light-induced charge fluctuations in the nanoguide by analyzing the spatio-temporal features of single-molecule Stark shifts.

**Efficient coupling of molecules to a GaP nanoguide.**

The core of our experimental platform is a 50 µm long GaP nanoguide fabricated on a 2 µm thick SiO$_2$ layer on a silicon substrate. The nanoguide has a cross-section of 100 nm $\times$ 160 nm, is terminated on both sides by grating couplers and is decorated by sawtooth-shaped gold microelectrodes placed 2 µm from the nanoguide. The nanoguide supports two propagating modes of orthogonal polarization states, which have the majority of their energy concentrated in the evanescent field. In this work, we show efficient coupling of single organic molecules to a GaP nanoguide. Furthermore, we investigate light-induced charge fluctuations in the nanoguide by analyzing the spatio-temporal features of single-molecule Stark shifts.

**Figure 1.** (a) Schematic of a nanoguide interfaced with two electrodes. (b) Simulated intensity profile of the TE mode in the nanoguide. (c) Extinction (blue) and fluorescence (red) spectra of hundreds of molecules. (d) Extinction and fluorescence spectra of one single molecule.

by grating couplers and is decorated by sawtooth-shaped gold microelectrodes placed 2 µm from the nanoguide (see Fig.1a, b)). The nanoguide supports two propagating modes of orthogonal polarization states, which have the majority of their energy concentrated in the evanescent field (see Fig.1b). Fabrication details are presented in earlier works. The nanostructures are covered by a para-dichlorobenzene (pDCB) crystal confined in a nanochannel as described in previous publications. By doping the pDCB crystal with dibenzoterrylene (DBT) at a concentration of $2 \times 10^{-4}$ mol/mol, we realize a random distribution of the latter. At a temperature below 4 K, DBT molecules possess strong zero-phonon lines with a lifetime-limited linewidth of 30 MHz at a vacuum transition wavelength of 745 nm (frequency of 402 THz). Owing to variations in...
their nanoscopic crystal environment [24], the resonance frequencies of individual molecules span a range of about 4 nm (2 THz). The transverse electric (TE) mode of the nanoguide (see Fig. 1(b)) is excited by continuous-wave Ti:Sapphire laser beams (linewidth < 1 MHz), and the outcoupled radiation is detected on an avalanche photodiode. The blue curve in Fig. 1(c) displays the extinction spectra of several hundred molecules measured in transmission, while the red spectrum reports on the corresponding fluorescence via the vibrational levels of the ground state and phonon wings. In Fig. 1(d), we plot a closeup for a single-molecule extinction dip of 13%, comparable with the coupling efficiency achieved for illumination in a diffraction-limited focus spot [25].

**Monitoring the local electric field.** The molecule DBT has inversion symmetry and is thus expected to undergo a quadratic Stark shift. Figure 2(a) illustrates the parabolic spectra of three nanoguide-coupled molecules as a function of the voltage applied to the nearby electrodes. In some cases, local strain in the matrix leads to the addition of a linear Stark effect manifested by an offset in the turning points of the parabolas [25, 26]. A more noteworthy observation in these spectra is, however, that the resonances appear broader and less stable at larger slopes of the Stark tuning profile (see e.g., the spectra across the dashed line in Fig. 2(a)). We point out that this effect is consistently observed for all nanoguide-coupled molecules on all studied GaP samples. On the contrary, we have verified that molecules at about 10 μm away from the nanoguide are highly stable and have a lifetime-limited linewidth regardless of the applied Stark shift. For the latter measurements, we shined a focused laser beam normal to the plane of the chip.

We, thus, attribute the origin of the spectral instabilities for nanoguide-coupled molecules to electric field fluctuations originating from the GaP nanostructure. As we show in the following, the effect at hand is very different from previous reports of electric field-induced spectral instability and broadening of organic molecules, which were caused by two-level tunneling systems [30, 35] or electromechanical oscillations [36] in the host organic matrix.

To investigate the temporal dynamics of the spectral instabilities more quantitatively, we increased the frequency scan rate from 400 MHz/s in Fig. 2(a) to 10 GHz/s. This was sufficient to arrive at lifetime-limited Lorentzian resonances in individual frequency sweeps and, thus, resolve the wandering of their center frequencies over time. To characterize Stark spectra such as those shown in Fig. 2(a), we recorded a large number of individual scans. In this manner, we obtained a robust mean value (f) for the molecular resonance frequency and root mean square (RMS) frequency fluctuations (σf) at a given electrode voltage (V). By repeating this procedure for many applied voltages, we established the frequency tunability defined as δf/σf. Figures 2(b) and 2(c) display examples of spectral trajectories of a molecule, which we name M1, at two applied voltages. Figure 2(d-f) shows σf and the tunability for three exemplary molecules. For M1, δf/σf (orange) increases linearly with V, as shown in Fig. 2(d), implying a quadratic Stark behavior. Interestingly, σf (blue) also grows proportionally with δf/σf. Figure 2(e) presents the case of a second nanoguide-coupled molecule that behaves similarly although its turning point (δf/σf = 0) is shifted to a voltage of about 25 V. As a control experiment, in Fig. 2(f) we report on a molecule far away from the nanoguide. It is evident that, in this case, there is no correlation between δf/σf and σf, which stays at 4 MHz, given by the fit error.

Assuming that the field fluctuations originate from the nanoguide, we express the total Stark shift experienced by the molecule as δf ∝ |Ec−Ec+|Eeg|2, where Ec−, Ec+, and Eeg denote the fields created by the residual strain in the crystal, the electrodes, and the nanoguide, respectively. A cross term in this expression leads to the amplification of a small fluctuating Eeg by a large constant Ec− + Ec+. The former quantity causes σf while the latter dictates δf/σf such that σf becomes proportional to δf/σf, as observed in our measurements. The measured data in Fig. 2(e, d) and our knowledge of the electrode and nanoguide geometries let us deduce the RMS nanoguide field fluctuations to be around 40 kV/m at the position of the molecule. This corresponds to the field generated...
by a single electron at a distance of 100 nm, which is comparable to the typical separation of the evanescently-coupled nanoguide-molecule system.

**Temporal field correlations.** The ability to scan faster than typical electric field fluctuations allows us to determine the correlation function $C_{jk}(\Delta t)$ between the frequency fluctuations of molecules $j$ and $k$. Figure 3(a) plots the autocorrelation function $C_{11}$ computed for molecule M1 from 12,000 individual sweeps, 100 of which are displayed in Fig. 3(b). By fitting an exponential function to $C_{11}$, we extract the autocorrelation time $\tau = 1.0$ s.

Next, we studied the dependence of $\tau$ and $\sigma_f$ on the optical power ($P$) in the nanoguide. Figure 3(c, d) displays the outcome of measurements for one molecule, indicating an inverse proportionality relation between $\tau$ and $P$ over four orders of magnitude. This robust dependence clearly demonstrates that the fluctuations are photo-induced. We checked that the observed phenomenon is not caused by direct interaction of light with the molecule. To do this, we performed measurements, where up to 90% of the optical power inside the nanoguide was provided by a second laser beam detuned by 2 THz from the molecule and verified that the fluctuation rate ($1/\tau$) scaled with the total laser power in the nanoguide. Furthermore, we found that $\sigma_f$ remains independent of $P$ within our measurement precision (see Fig. 3(d)). This indicates that while the external illumination power dictates the spectral noise dynamics, it does not influence its amplitude.

**Spatial field correlations.** We now investigate the spatial properties of the observed electric field noise by simultaneous measurement of several molecules. Here, we coupled two independent laser beams into the nanoguide and performed time-multiplexed alternate frequency sweeps in two different frequency regions. In Fig. 4 we present an example, where the frequency fluctuations of three molecules (M1, M2 and M3; see Fig. 4(a)) were examined. The frequency variations and the cross-correlation functions $C_{12}, C_{23}$ displayed in Figs. 4(b) and 4(c), respectively, reveal that the spectral fluctuations in M1 and M2 are correlated, but M3 behaves independently. Considering the error in extracting resonance frequencies, we infer almost perfect correlation between M1 and M2. By determining the positions of each molecule through localization microscopy, we revealed that, in

![Figure 3](image3.png)

![Figure 4](image4.png)
Indeed, M1 and M2 were separated by only 26 ± 5 nm, while M3 was about 2 μm away from them. For another correlated pair separated by about 80 nm we saw that the peak spectral cross-correlation drops to ~ 30%, verifying that the field fluctuations are very local.

To provide further evidence for the local character of the field fluctuations, we also conducted single-molecule measurements under illumination by an auxiliary laser beam that was frequency detuned by 6 GHz. Here, we scanned the focal spot of this second beam along the nanoguide across the molecule position (see Fig. 4(d,e)) and recorded changes in \(1/\tau\). The blue symbols in Fig. 4(d) confirm that \(1/\tau\) follows the intensity profile of the auxiliary light beam shown by the red curve (full width at half-maximum 1 μm).

Theoretical modelling. Regardless of the details of the process at work, electric field fluctuations generated by the nanoguide can be attributed to charge fluctuations. Redistribution of charges in semiconductors can be caused by many effects such as trapped or wandering charges [37,38], impurities [39], or ligand rearrangements [40,41] and have also been shown to be driven by light with energy below the bandgap [42]. We consider a simple model in which electric field fluctuations result from the rearrangement of randomly distributed point charges with density \(n_\text{q}\) in the GaP nanoguide. We assume that each charge stays in the vicinity of its original position, but it experiences an average displacement \(d\) upon scattering one photon. In other words, while the field fluctuation rate scales with the optical power \(P\), \(n_\text{q}\) and \(d\) remain independent of it. It can then be shown that \(\sigma_f \propto d\sqrt{n_\text{q}}\). Furthermore, the randomness of the jumps and the quadratic fall-off of the Coulomb field lead to a short correlation length, approximately equal to the molecule-waveguide distance.

In the limit of large \(n_\text{q}\), one expects a Gaussian statistics for the frequency steps. The upper panel of Fig. 5(a) shows that the histogram of the measured data clearly deviates from a Gaussian distribution shown in grey. To compare the statistical properties of the frequency fluctuations with the predictions of our model, we simulated time traces of the molecular resonance frequencies for different \(n_\text{q}\) values and used the same analysis procedure applied to the experimental data to generate a histogram of the frequency steps. The upper panel of Fig. 5(b-d) displays the outcome for three synthetic data sets. It turns out that at the lowest considered density, corresponding to the effect of only ~ 5 charges, the molecular resonance experiences jump-like frequency shifts, causing a non-Gaussian frequency step-size distribution.

To quantify the deviations from a Gaussian distribution, we consider the ratio of the occurrence to the corresponding Gaussian fit distribution as plotted in the lower panel of Fig. 5(a-d). Next, as presented in Fig. 5(e), we introduce a measure of non-Gaussianity (\(\eta\)), defined as the area under this curve above one. The experimentally measured \(\eta\) marked by the blue line corresponds to a density of charges around \(n_\text{q} = 2.5 \times 10^{22} \text{m}^{-3}\), or equivalently to about one charge per (35 nm)³. Although this analysis only established an estimate, the result is in agreement with the typical density of defects, impurities or charge traps seen in such systems [43] and implies that an average of 50 charges govern the frequency fluctuations of our molecules. Given this density and the experimentally measured magnitude of the frequency fluctuations, we can estimate \(d \approx 20\) nm. We also note that owing to the small width of the nanoguide, surface and volume charges lead to similar results.

Conclusions. We have used single molecules as nanometer-sized probes for investigating the spatio-temporal behavior of a low number of charges activated in GaP nanoguides. The small size, excellent spectral properties, large achievable concentrations and the inhomogeneous distribution of their resonance frequencies make organic molecules a promising tool for ultrasensitive characterization of nanoscopic charge dynamics in a range of systems such as single electron transistors, quantum dots or superconductors [47,52]. Our findings also advance the use of GaP as a platform for integrated quantum photonics [1,2,4,21]. The observed light-induced field fluctuations are small and slow enough to be tolerated or eliminated by more sophisticated fabrication schemes [42,53]. However, even in their current form, the estimated density of charges and their light absorp-
tion probability signified by the slope of Fig. 3(c) point to a loss coefficient of about 0.5 dB/cm, which would allow for resonator quality factors in the order of $10^6$.

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[1] J. Wang, F. Sciarrino, A. Laing, and M. G. Thompson, Nat. Photonics 14, 273 (2020).
[2] J.-H. Kim, S. Aghaeine-mibodi, J. Carolan, D. Englund, and E. Waks, Optica 7, 291 (2020).
[3] A. W. Elshaar, W. Pernice, K. Srinivasan, O. Benson, and V. Zwiller, Nat. Photonics 14, 285 (2020).
[4] V. Sandoghdar, Nano Lett. 20, 4721 (2020).
[5] P. Türschmann, H. L. Jeeonne, S. F. Simonsen, H. R. Haak, S. Götzinger, V. Sandoghdar, P. Lodahl, and N. Rottenberg, Nanophotonics 8, 1641 (2019).
[6] H. Thyrrestrup, G. Kiršanskė, H. L. Jeannic, J. Pernolato, L. Zhai, L. Raahauge, L. Mildo, N. Rottenberg, A. Jawadi, R. Schott, A. D. Wieck, A. Ludwig, M. C. Löbl, I. Söllner, R. J. Warburton, and P. Lodahl, Nano Lett. 18, 1801 (2018).
[7] D. Hallett, A. P. Foster, D. L. Hurst, B. Royall, P. Kok, E. Clarke, I. E. Itskevich, A. M. Fox, M. S. Skolnick, and T. Pregnolato, Nano Lett. 5, 644 (2015).
[8] J. Q. Grim, A. S. Brucker, M. Zalabudinov, S. G. Carter, A. C. Kozen, M. Kim, C. S. Kim, J. T. Mlack, M. Yakes, B. Lee, and D. Gammon, Nature Materials 18, 963 (2019).
[9] M. Atatüre, D. Englund, N. Vamivakas, S.-Y. Lee, and J. Wachtrop, Nat. Rev. Mater. 3, 38 (2018).
[10] A. V. Akimov, A. Mukherjee, C. L. Yu, D. E. Chang, A. S. Zibrov, P. R. Hemmer, H. Park, and M. D. Lukin, Nature 450, 402 (2007).
[11] P. Türschmann, N. Rotenberg, J. Renger, I. Harder, O. Lohse, T. Utikal, S. Götzinger, and V. Sandoghdar, Nano Lett. 17, 4941 (2017).
[12] P. Lombardi, A. P. Ovvyannikov, S. Pazzagli, G. Mazzanuto, G. Kews, O. Neitzke, N. Gruhler, O. Benson, W. H. P. Pernice, F. S. Cataliotti, and C. Toninelli, ACS Photonics 5, 126 (2018).
[13] S. Grandi, M. D. Nielsen, J. Cambiasso, S. Boissier, K. D. Major, C. Reardon, T. F. Krauss, R. F. Oulton, E. A. Hinds, and A. S. Clark, APL Photonics 4, 086101 (2019).
[14] C. U. Hail, C. Höller, K. Matsuzaki, P. Rohner, J. Renger, V. Sandoghdar, D. Poulikakos, and E. Waks, Optica 7, 18501 (2020).
[15] J. E. Fröch, S. Kim, N. Mendelson, M. Kianinia, M. Toth, and I. Aharonovich, ACS Photonics 14, 7085 (2020).
[16] N. H. Wan, T.-J. Lu, K. C. Chen, M. P. Walsh, M. E. Trusheim, L. De Santis, E. A. Bersin, I. B. Harris, S. L. Mouradian, I. R. Christen, E. S. Bielejec, and D. Englund, Nature 583, 226 (2020).
[17] D. Rattenbacher, A. Shkarin, J. Renger, T. Utikal, S. Götzinger, and V. Sandoghdar, New J. Phys. 21, 062002 (2019).
[18] P. E. Barclay, K.-M. C. Fu, C. Santori, and R. G. Beausoleil, Applied Physics Letters 95, 191115 (2009).
[19] J. Wolters, A. W. Schell, G. Kews, N. Nüsse, M. Schoenhen, H. Döscher, T. Hannappel, B. Löchel, M. Barth, and O. Benson, Applied Physics Letters 97, 141108 (2010).
[20] M. Gould, E. R. Schmidgall, S. Dadgostar, F. Hatami, and K.-M. C. Fu, Phys. Rev. Applied 6, 011001 (2016).
[21] D. J. Wilson, K. Schneider, S. Hönl, M. Anderson, Y. Baumgartner, L. Czornomaz, T. J. Kippenberg, and P. Seidel, Nat. Photonics 14, 57 (2020).
[22] S. Hönl, H. Hahn, Y. Baumgartner, L. Czornomaz, and P. Seidel, J. Phys. D: Appl. Phys. 51, 185203 (2018).
[23] K. Schneider, P. Weller, Y. Baumgartner, H. Hahn, L. Czornomaz, and P. Seidel, J. Lightwave Technol. 36, 2994 (2018).
[24] B. Gmeiner, A. Maser, T. Utikal, S. Götzinger, and V. Sandoghdar, Phys. Chem. Chem. Phys. 18, 19585 (2016).
[25] A. A. L. Nicolet, P. Bordat, C. Hofmann, M. A. Kolichenko, B. Kozankiewicz, R. Brown, and M. Orrit, ChemPhysChem 8, 1929 (2007).
[26] N. R. Verhart, G. Lepert, A. L. Billing, J. Hwang, and E. A. Hinds, Opt. Express 22, 19633 (2014).
[27] G. Wrigge, I. Gerhardt, J. Hwang, G. Zmunoﬁen, and V. Sandoghdar, Nature Phys. 4, 60 (2008).
[28] M. Orrit, J. Bernard, A. Zumbusch, and R. Personov, Chem. Phys. Lett. 196, 595 (1992).
[29] A. Moradi, Z. Ristanović, M. Orrit, I. Deperasinsky, and B. Kozankiewicz, ChemPhysChem 20, 55 (2019).
[30] W. A. Phillips, J. Low Temp. Phys. 7, 351 (1972).
[31] A. Heuer and R. J. Silbey, Phys. Rev. Lett. 70, 3911 (1993).
[32] H. Maier, R. Wunderlich, D. Haarer, B. M. Kharlanov, and S. G. Kulikov, Phys. Rev. Lett. 74, 5252 (1995).
[33] J.-M. Segura, G. Zmunoﬁen, A. Renn, B. Hecht, and U. Wild, Chem. Phys. Lett. 340, 77 (2001).
[34] M. Bauer and L. Kador, J. Chem. Phys. 118, 9069 (2003).
[35] I. Gerhardt, G. Wrigge, and V. Sandoghdar, Mol. Phys. 107, 1975 (2009).
[36] Y. Tian, P. Navarro, and M. Orrit, Phys. Rev. Lett. 113, 135505 (2014).
[37] J. Müller, J. M. Lupton, A. L. Rogach, J. Feldmann, D. V. Talapin, and H. Weller, Phys. Rev. B 72, 205339 (2005).
[38] G. Sallen, A. Tribu, T. Aichele, R. André, L. Besombes, C. Bougerol, M. Richard, S. Tatarenko, K. Kheng, and J. P. Poizat, Phys. Rev. B 84, 1 (2011).
[39] R. Bardoux, T. Guillart, P. Lefebvre, T. Taliere, T. Bretagnon, S. Rousset, B. Gil, and F. Semond, Phys. Rev. B 74, 195319 (2006).
[40] J. Wolters, S. Sadzak, A. W. Schell, T. Schröder, and O. Benson, Phys. Rev. Lett. 110, 027401 (2013).
[41] A. Thoma, P. Schnauber, M. Ghchrey, M. Seifried, J. Wolters, J.-H. Schulze, A. Strittmatter, S. Rodt, A. Carmele, A. Knorr, T. Heinzel, and S. Reitzenstein, Phys. Rev. Lett. 116, 036301 (2016).
[42] J. Liu, K. Komhasinghe, M. Davanc, J. Lawall, V. Anant, V. Verna, R. Mirin, S. W. Nam, J. D. Song, B. Ma, Z. S. Chen, H. Q. Ni, Z. C. Niu, and K. Srinivasan, Phys. Rev. Applied 9, 064019 (2018).
[43] M. Hauck, F. Sellmeier, S. E. Beavan, A. Badorato, P. M.
Petroff, and A. H"ogele, Phys. Rev. B 90, 235306 (2014).
[44] M. J. Fernée, T. Plakhotnik, Y. Louyer, B. N. Littleton, C. Potzner, P. Tamarat, P. Mulvaney, and B. Lounis, J. Phys. Chem. Lett. 3, 1716 (2012).
[45] A. P. Beyler, L. F. Marshall, J. Cui, X. Brokmann, and M. G. Bawendi, Phys. Rev. Lett. 111, 177401 (2013).
[46] J. J. W. Tomm, Spectroscopic Analysis of Optoelectronic Semiconductors (Springer, 2016).
[47] M. Rezai, J. Wrachtrup, and I. Gerhardt, Phys. Rev. X 8, 031026 (2018).
[48] J. M. Caruge and M. Orrit, Phys. Rev. B 64, 1 (2001).
[49] M. Fauré, B. Lounis, and A. I. Buzdin, EPL 77, 17005 (2007).
[50] A. N. Vamivakas, Y. Zhao, S. Fält, A. Badolato, J. M. Taylor, and M. Atatüre, Phys. Rev. Lett. 107, 1 (2011).
[51] C. Arnold, V. Loo, A. Lemaitre, I. Sagnes, O. Krebs, P. Voisin, P. Senellart, and L. Lanco, Phys. Rev. X 4, 1 (2014).
[52] S. Faez, S. J. van der Molen, and M. Orrit, Phys. Rev. B 90, 205405 (2014).
[53] B. Guha, F. Marsault, F. Cadiz, L. Morgenroth, V. Ulin, V. Berkovitz, A. Lemaitre, C. Gomez, A. Amo, S. Combrè, B. Gérard, G. Leo, and I. Favero, Optica 4, 218 (2017).