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► **To cite this version:**

Thomas Liu, Baptiste Carles, Christine Elias, Claire Tonnelé, Daniel Medina-Lopez, et al.. Vibronic fingerprints in the luminescence of graphene quantum dots at cryogenic temperature. *The Journal of Chemical Physics*, 2022, 156 (10), pp.104302. 10.1063/5.0083282 . hal-03585050

HAL Id: hal-03585050

<https://hal.science/hal-03585050>

Submitted on 30 Oct 2023

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Cite as: J. Chem. Phys. **156**, 104302 (2022); <https://doi.org/10.1063/5.0083282>

Submitted: 23 December 2021 • Accepted: 21 February 2022 • Accepted Manuscript Online: 21 February 2022 • Published Online: 09 March 2022

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Submitted: 23 December 2021 • Accepted: 21 February 2022 •

Published Online: 9 March 2022












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Note: This paper is part of the JCP Special Topic on The Ever-Expanding Optics of Single-Molecules and Nanoparticles.

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ABSTRACT

Atomically precise graphene quantum dots synthesized by bottom-up chemistry are promising versatile single emitters with potential applications for quantum photonic technologies. Toward a better understanding and control of graphene quantum dot (GQD) optical properties, we report on single-molecule spectroscopy at cryogenic temperature. We investigate the effect of temperature on the GQDs' spectral linewidth and vibronic replica, which we interpret building on density functional theory calculations. Finally, we highlight that the vibronic signatures are specific to the GQD geometry and can be used as a fingerprint for identification purposes.

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I. INTRODUCTION

Graphene quantum dots (GQDs) offer a wide range of tunable properties related to their size, symmetry, and edge shape.^{1,2} Their “bottom-up” synthesis ensures an atomic control of their structure. It leads to homogeneous intrinsic properties. A wide variety of GQD structures have been synthesized, providing a large playground for physicists and for device developments.^{2–8} As an example of interesting properties, we demonstrated recently that GQDs can be bright and stable single photon emitters at room temperature with tunable optical properties through edge functionalization.^{9,10} Nevertheless, to fully unleash the potential of GQDs, an important work remains ahead to deeply understand their photophysics. As an example, we recently highlighted the central role played by the vibrations as regards the coupling of light to the GQD's delocalized π -electrons. Indeed, we showed that a singlet state, dark by symmetry, can be brightened by GQD distortions.¹¹ Toward a better understanding

of GQD photophysics, we report on pioneering experimental investigation of photoluminescence (PL) spectroscopy of single GQDs with a large number of atoms (i.e., 96 atoms) at cryogenic temperatures.¹² We show a strong narrowing of the emission lines at low temperature, which we use to characterize and identify vibrational replicas that are characteristic to GQDs. These observations are discussed in light of density functional theory (DFT) calculations. Finally, the temporal stability of the GQD emission (spectral diffusion) is discussed.

II. RESULTS AND DISCUSSION

In order to perform the cryogenic-temperature spectroscopy of C₉₆ triangular GQDs [Fig. 1(a)], we use a single-molecule microscopy setup. A typical fluorescence raster scan of a GQD sample is shown in Fig. 1(b). The bright spots correspond to single fluorescent

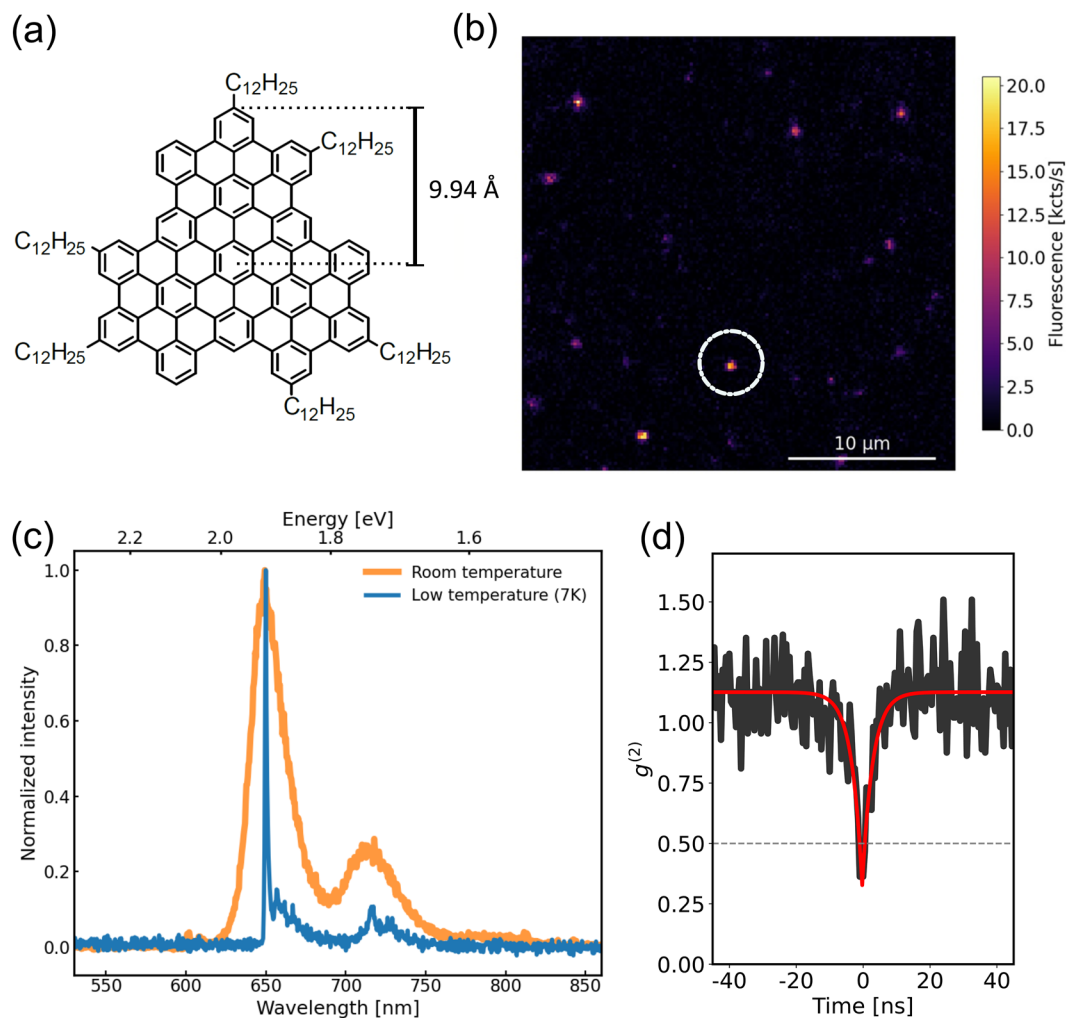


FIG. 1. (a) Chemical structure of the investigated GQD. (b) Photoluminescence raster scan of the GQD embedded in a polystyrene matrix. (c) Photoluminescence spectra of two different GQDs at room temperature (orange curve) and at 7 K (blue curve). (d) Photon autocorrelation measurement performance at 7 K. $g^{(2)}(0) < 0.5$ is a signature that a single emitter is addressed.

objects as shown by the anti-bunching signature observed in the fluorescence autocorrelation function measured on a diffraction-limited spot ($g^{(2)}(0) < 0.5$). Note that the observed $g^{(2)}(\tau) > 1$ for the longer delays τ is a signature of a metastable triplet state, as previously reported.¹⁰ Room-temperature measurements on single GQDs give spectra composed of a main peak at ~ 650 nm together with the vibronic replica at an energy that is characteristic of the C=C bond.¹⁰ When we decrease the temperature to $T_{\text{cryo}} \approx 7$ K, we observe a narrowing of the spectral features, as shown by the blue curve in Fig. 1(c). At low temperature, the spectra show sharp lines. The central energy is, on average, similar to the ones measured at room temperature. Moreover, we observe additional lines that were unresolved at room temperature due to the temperature broadening. The spectra are characteristic of single molecules at low temperature, consisting of a zero-phonon line (ZPL), associated

with the purely electronic transition, followed by redshifted vibronic features resulting from electronic transitions associated with phonon emission. The zero-phonon line of the spectrum given in Fig. 1(c) (blue line) has a linewidth of 0.8 nm (2.3 meV). The lowest value of the linewidth measured on our samples is 1.6 meV. Though much narrower than at room temperature (~ 80 meV), it remains orders of magnitude above the fundamental lifetime-limited linewidth. Indeed, for the previously reported lifetime of few ns,¹⁰ we expect a lifetime limited spectral linewidth of the order of less than 1 μeV .¹³ We attribute this broadening to the amorphous polystyrene host matrix as observed for other single molecules.¹⁴ The use of other environments such as Sh'polskii matrices¹⁴ or inclusion in molecular crystals¹⁵ may unlock this issue and help reach the intrinsic limit. Moreover, the dispersion of the wavelength of the ZPL for a large number of objects identified as single GQDs is

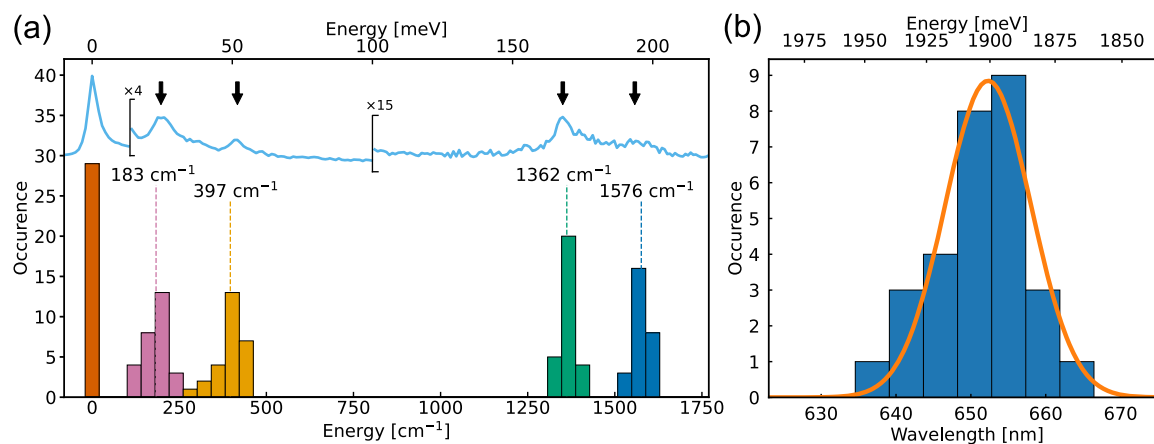


FIG. 2. (a) (Bottom) Histograms of the energy of the different vibronic replicas. (Top) Typical spectrum of a single GQD at 7 K. The spectrum is shifted to put the zero-phonon line at zero-energy. A different scale is applied to the different vibronic replicas for an easier visualization. (b) Histogram of the energy of the zero-phonon lines. The orange curve is a fit to a normal distribution.

plotted in Fig. 2(b). We observe a quasi-normal distribution centered at 651.3 nm with a standard deviation of 5.9 nm. A possible mechanism behind this ZPL dispersion is dielectric screening of the excitons. Such screening can vary significantly at the local scale due to the inhomogeneity of the polystyrene matrix at the nanoscale.¹⁶ Likewise, inhomogeneities in the local strain felt by the GQDs could also contribute to this dispersion.

The red-shifted replicas, relatively to the ZPL, correspond to transitions assisted by phonon creation. The red shift is a measurement of the frequencies of the associated vibrational modes. These replicas yield very accurate spectroscopic signatures, some of them being characteristic of the emitter. As shown in Fig. 2(a), we observe four characteristic lines in the GQD spectra recorded at 7 K. We attribute the two higher frequency modes to localized vibrational modes of the molecule. The lines at 1362 and 1576 cm^{-1} coincide well with the frequencies typically associated with C=C bond stretching modes in polycyclic aromatic hydrocarbons (PAHs).^{17,18} In contrast, the two lower frequency modes (183 and 397 cm^{-1}) are more probably related to global vibrations of the molecule and should therefore be characteristic of the size (and possibly the geometry) of the investigated GQD. Interestingly, one can notice that the splitting between the two high energy modes and the two low energy modes is of 214 cm^{-1} . It is probably a coincidence, but it deserves to be mentioned. Moreover, the lowest-frequency mode at 183 cm^{-1} may be related to a breathing-like mode of the whole molecule. By analogy to the radial breathing-like mode (RBLM) in graphene nanoribbons, the characteristic vibrational frequency corresponding to the global-stretching mode of the GQD should decrease with the increasing size of the object.^{19,20} This hypothesis is supported by a recent theoretical proposal for the estimation of such RBLM frequency for a graphene circular disk of radius R . Estimating the radius of our C_{96} GQD to be $R \approx 9.94 \text{ \AA}$, we find $\omega_{\text{RBLM}} \approx 208 \text{ cm}^{-1}$ in good qualitative agreement with our experimental measurement of 183 cm^{-1} . To go further in the assignation of these modes, we performed some calculations. Molecular geometry of the GQD ground state was optimized in the gas phase in the framework of Density

Functional Theory (DFT) at the B3LYP/6-31G(d) level. On the basis of this structure, normal modes of vibration were computed at the same level of theory. All calculations were performed using the Gaussian 16 package.²¹ It turns out that the low-frequency normal modes are indeed characterized by in-plane collective radial breathing and bending vibrations. Some of them have their energy fitting well with the values of the low frequency vibronic replica observed in our measured spectra at low temperature. The detailed description of these modes are depicted in Fig. S1.

Finally, the low frequency mode at 183 cm^{-1} (respectively, 397 cm^{-1}) shows a standard deviation of its central energy of 36 cm^{-1} (respectively, 39 cm^{-1}), while the higher energy modes both have a standard deviation of 19 cm^{-1} . The narrower dispersion of the higher-frequency modes is consistent with the fact that localized vibrational modes are less sensitive to environmental modifications. Conversely, we expect delocalized modes to be more sensitive to environmental perturbations, such as strain induced by the polymer matrix.^{17,22} In a first approximation, if strain was the main origin of the energy dispersion of the zero-phonon line and of the delocalized vibrational mode, one would observe a correlation between the energy of the zero-phonon line and the ones of the vibronic replica. Interestingly, we do not observe such correlation (see Fig. S2).

Beyond the understanding of vibronic modes and the role of environment on the photophysics of GQDs, this study also has a second important outcome. As we have shown, the lower-energy modes are a fingerprint of the investigated GQDs. As such, it could be used to unequivocally distinguish the GQDs from other emitters. Of specific interest is parasitic emitters that are often observed in single-molecule experiments. In order to identify these emitters, some control experiments on the GQD-free polystyrene matrix have been performed. They allow us to record luminescence spectra of single parasitic emitters (see Fig. S3). In particular, we show that their vibronic signatures differ strongly from those of the GQDs. We thus demonstrate that the vibronic signature unambiguously allows for identification of GQDs (see the [supplementary material](#), Figs. S3

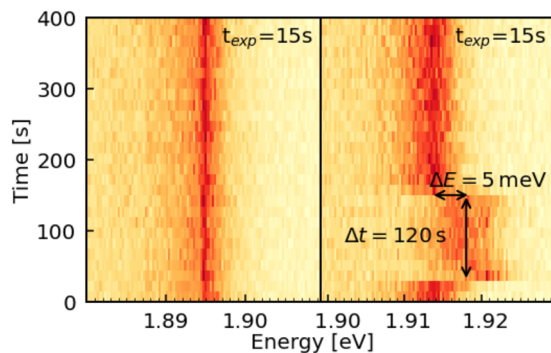


FIG. 3. Photoluminescence spectra as a function of time of two different single GQDs recorded at 7 K. Integration time per spectrum $t_{\text{exp}} = 15$ s.

and S4). In addition, it is worth mentioning that looking at the vibration frequencies of parasitic emitters, we found that they correspond very well to the ones reported previously (see Fig. S5).^{23,24}

Finally, we address the question of the luminescence stability of GQDs at low temperature. Figure 3 shows PL time traces for two different GQDs for a recording time of 400 s and integration time of 15 s. First, the left panel of Fig. 3 shows an example of a very stable GQD with a standard deviation of the maximum energy below the resolution of our setup. The right panel of Fig. 3 displays the time trace of a single GQD undergoing a sudden spectral jump of $\Delta E \sim 5$ meV. This is a global spectral jump with almost no influence on the energy of the vibronic replicas with respect to the zero-phonon line (see Fig. S6). This suggests that such spectral jumps are related to charge fluctuations in the local environment of the GQD, leading to a global shift of the vibronic transitions through quantum confined Stark effect.²⁵

III. CONCLUSION

In conclusion, we report on the investigation of the photo-physics of single graphene quantum dots at cryogenic temperatures. Some vibronic replicas have been observed and identified as being specific to graphene GQDs. In particular, breathing modes at low frequency related to the structure and symmetry of the GQD have been identified. Finally, we show that the emission of GQDs can be very stable even at low temperature. Reaching the lifetime limited linewidth may be desirable for some applications of GQDs as quantum emitters. Therefore, their inclusion in other types of matrices such as Sh'polskii matrices or anthracene nanocrystals is planned.

IV. EXPERIMENTAL DETAILS

A. Synthesis

GQDs were synthesized via bottom-up chemistry via a previously reported synthetic route.^{10,26} GQDs were characterized mainly by Matrix Assisted Laser Desorption Ionization-Time of Flight (MALDI-TOF) mass spectrometry. The GQD batch used here is the same as in the work of Liu *et al.*¹¹

B. Sample preparation

Stock solutions of GQDs with a target concentration of 3×10^{-5} mol l⁻¹ were obtained by dispersing grains of GQD powder in 1,2,4-trichlorobenzene (TCB) and by stirring for 24 h at room temperature after sonicating the solution for a few seconds (Elma, Elmasonic P). Absorption measurements were performed on stock solutions. Stock solutions and diluted solutions were stored in a glovebox under inert Ar atmosphere between sample-preparation sessions.

Samples for single-molecule experiments were obtained by mixing one volume of the diluted GQD solution with one volume of a solution of polystyrene in TCB (at 10% in wt.). The solution was spin-coated on a solid immersion lens (SIL) for 180 s at 2000 rpm. Before the spin-coating procedure, the SIL was subjected to a 5 min plasma cleaning. The sample was dried on a hot plate by heating to 90 °C for 1 h in air.

C. Optical measurements

Single-molecule measurements were performed using a home-built micro-PL setup. Samples were placed in a cryostat (Montana Instruments Cryostation), enabling temperature control down to 7 K combined with a home-built vacuum chamber hosting the microscope objective. The chamber is appended to the sample room, allowing the use of a high NA microscope objective with a low working distance. The sample position was controlled using xyz low-temperature nanopositioners (attocube). The excitation source was a continuous-wave diode laser at 594 nm (Cobolt Mambo 100). The excitation beam was focused onto the sample using a microscope objective (NA = 0.8, Olympus LMPLFLN 100x). The typical laser power measured before the microscope objective is of the order of 1–2 μ W. Samples were scanned using a steering mirror (FSM-300, Newport) conjugated to the microscope objective via a 4f system. Luminescence from the sample was collected through the same objective with the excitation beam filtered by a dichroic mirror (zt 594 RDC, Chroma) and long-pass filters (FELH0600, Thorlabs). Collected luminescence was focused and filtered by a pinhole (50 μ m) and then directed into a spectrometer (SP-2350, Princeton Instruments) coupled with a LN-cooled CCD camera (PyLoN:100BR eXcelon, Princeton Instruments) or into two silicon-based avalanche photodiodes (SPCM-AQR-13, PerkinElmer) mounted in the Hanbury Brown and Twiss configuration. Second-order photon correlation measurements were performed using a time-correlated single-photon counting module (Time Tagger 20, Swabian Instruments).

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for the additional data: results of vibrational mode calculations; analysis of the data dispersions; spectra of parasitic emitters and comparison of their vibronic replicas with the ones of GQDs and with the literature; and modification of the spectra after a spectral jump.

ACKNOWLEDGMENTS

J.-S.L. and L.R. thank Bruno Vivan for the design of the vacuum chamber. This work has been financially supported by the

FLAG-ERA Grant OPERA by Grant Nos. DFG 437130745 and ANR-19-GRF1-0002-01 and by the ANR-DFG NLE Grant GRANAO by Grant Nos. DFG 431450789 and ANR-19-CE09-0031-01 by a public grant overseen by the French National Research Agency (ANR) as a part of the “Investissements d’Avenir” program (Labex NanoSaclay, Reference No. ANR-10-LABX-0035). Computational resources were provided by the Consortium des Équipements de Calcul Intensif (CÉCI), funded by the Fonds de la Recherche Scientifiques de Belgique (F.R.S.-FNRS) under Grant No. 2.5020.11, as well as the Tier-1 supercomputer of the Fédération Wallonie-Bruxelles, the infrastructure funded by the Walloon Region under Grant Agreement No. n1117545. D.B. is a FNRS Research Director.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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