PHYSICAL REVIEW B **92**, 121408(R) (2015)

Cooperative lifetime reduction of single acene molecules attached to the surface of neon clusters

Markus Müller,[1] Sharareh Izadnia,[1] Sebastiaan M. Vlaming,[2] Alexander Eisfeld,[2] Aaron LaForge,[1,*] and Frank Stienkemeier[1]
[1]*Physics Department, University of Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg, Germany*
[2]*Max Planck Institute for the Physics of Complex Systems, Nöthnitzer Strasse 38, D-01187 Dresden, Germany*

(Received 24 November 2014; published 16 September 2015)

Tetracene and pentacene molecules attached to the surface of neon clusters have been spectroscopically investigated. The fluorescence spectra indicate that the molecules are immobilized on the surface and, to a large extent, do not form complexes. By varying the number of attached molecules, laser power, or neon cluster size, we find a systematic fluorescence lifetime reduction up to a factor of 20 indicating a cooperative coupling in our system. For averaged intermolecular distances greater than 33 Å, we attribute the reduction in fluorescence lifetime to Dicke superradiance, while for smaller intermolecular distances, nonradiative decay mechanisms cause additional lifetime reduction.

DOI: 10.1103/PhysRevB.92.121408 PACS number(s): 42.50.Nn, 33.70.Ca, 36.40.Gk, 79.60.Fr

The collective emission of coherent light is a fundamental process in quantum mechanics. The resulting radiation leads to effects such as lasing, self-amplified spontaneous emission in free electron lasers, and superfluorescence or superradiance. One particularly fascinating manifestation of superradiance is the process of *spontaneous* coherent emission of light by an ensemble of identical excited atoms, which was initially predicted by Dicke [1] and later experimentally confirmed [2]. Superradiance has been observed almost universally in weakly interacting systems such as hot dense gases [2], films [3], and Bose-Einstein condensates [4]. Furthermore possible applications such as remote sensing [5], ultrashort pulse generation [6], or highly coherent Raman lasing [7] make this a topic of broad interest.

In general, if there are many (noninteracting) atoms emitting incoherent light, the intensity of the radiation is simply proportional to the number of emitters. In the case of superradiance, the atomic/molecular dipoles of the excited sample radiate coherently [8] where the electric field of the emission becomes equal to the number of atoms/molecules N_m emitting radiation. This leads to an N_m^2 dependance of the radiation intensity and a reduction by N_m in the radiative lifetime.

In this Rapid Communication, we report the experimental observation of fluorescence lifetime reduction of tetracene (Tc) by directly tuning the number of cooperating molecules N_m confined on the surface of neon clusters. The doping process used allows one to create systems with one up to hundreds of molecules localized on the neon cluster surface with resulting intermolecular distances ranging from a few nanometers down to several Ångström.

Traditionally, investigation of superradiance of organic molecules has been performed on spatially extended systems like thin films, nanoaggregates or single crystals. Much interest on the superradiant properties of such organic semiconductors stems from their importance in application of organic electro-optical devices [3,9–11]. Typically in these systems, there is strong resonant dipole-dipole interaction between the molecules leading to delocalized exciton states, where a *single* excitation is shared by several molecules. For certain arrangements of the molecules (exemplified by so-called J aggregates) this state is considerably redshifted with respect to the single molecule transition and possesses the collective dipole strength of the participating molecules [3,10,12], i.e., it is superradiant. We will refer to this situation as single-exciton superradiance to contrast it from the more general case considered by Dicke. In particular, investigations on tetracene thin films, nanoaggregates, or single crystals revealed the existence of exciton delocalization providing single-exciton superradiance [13–15].

In contrast to the aforementioned experiments [3,10,13,14,16,17], cluster isolation offers the possibility to arrange a variable number of single molecules in a cold and weakly interacting environment. By this, we are able to explore the state of matter between the gas phase and the thin film or aggregate regime. The use of different neon cluster sizes in combination with variations in the number of attached molecules and the number of excited molecules allows us to access different regimes in a well-controlled manner. For the present study it is in particular worth mentioning that the size of the clusters and therefore the intermolecular distances can be chosen to be much smaller than the wavelength of the emitted light in contrast to typical gas-phase systems (e.g., [2,6]).

The experiment was performed at the molecular beam apparatus previously described in detail [18,19]. The neon cluster beam is created by supersonic expansion of cold (T_0), pressurized (P_0) gas through a pulsed 60 μm Even-Lavie nozzle [20] with pulse lengths around 30 μs at 1 kHz repetition rate. The pulsed nozzle is mounted onto a closed-cycle refrigerator allowing for expansion temperatures T_0 between 5 and 300 K. Neon cluster sizes are estimated by the use of scaling laws from Hagena [21–23] and confirmed using the titration method [24]. The width of the neon cluster size distribution is on the order of the mean cluster size. In the next vacuum chamber, the neon cluster beam passes a doping cell where the molecules are attached by inelastic collisions (pickup method) [25]. From neon cluster sizes and temperature-dependent molecular partial pressure [26,27] the mean number of attached molecules is calculated. The neon cluster temperature and the resulting temperature of the attached molecules are expected to be 10 ± 4 K [28,29] and constant over the entire doping range due to evaporative

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[*] aaron.laforge@physik.uni-freiburg.de

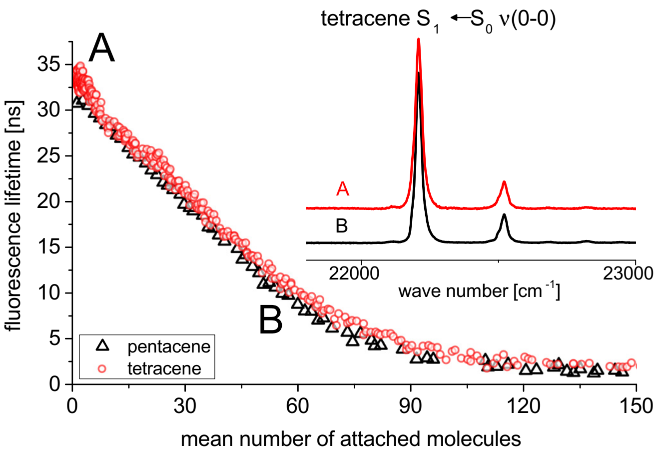

FIG. 1. (Color online) Fluorescence lifetime of Tc (red circles) and Pent (black triangles) on neon clusters with size $n \sim 122\,000$ as a function of the mean number of attached molecules. Laser excitation was performed on the pure electronic transition at 22 208 and 18 447 cm^{-1}, respectively, with laser pulse energy of 3.5 μJ. Inset: the LIF excitation spectra of Tc for ~1 (A) and ~50 (B) molecules on a neon cluster.

cooling of the neon cluster. The doped neon clusters then cross the beam of the excitation laser (Sirah Cobra dye laser pumped by a pulsed Nd:YLF laser Edgewave IS-IIIE) with Coumarin 2 or 157 as laser dye, covering the spectral ranges (~22 000–23 200 cm^{-1} and ~18 000–19 000 cm^{-1}) having a pulse duration of 9 ns. From the laser spot size (2 mm) and the neon cluster beam density, it is estimated to have about $\sim 10^4$ neon clusters in the interaction region. The resulting laser-induced fluorescence (LIF) is collected by a lens doublet and detected by a photomultiplier PMT (Hamamatsu R 5600U-01 or R 7400-04) placed perpendicular to both the neon cluster beam and the laser beam. For acquiring nonsaturated LIF spectra as well as the lifetime measurements, the pulse energy is attenuated to about 1–10 μJ. In the last chamber the doped neon cluster beam is analyzed and the overall neon flux is measured with a quadrupole mass spectrometer (EXTREL Max 1 000).

Previous spectroscopic studies comparing the helium nanodroplet isolation (HENDI) technique [30–32] and neon cluster isolation [19] revealed only weak interaction between the neon cluster and the attached molecule. From fluorescence spectra of the system, we have indication neither for the mobility of the attached molecules on the neon cluster nor for the agglomeration of the single molecules to complexes. In this work, tetracene and pentacene (Pent) were chosen due to previous results from HENDI spectroscopy [33] and the comparatively long fluorescence lifetime of the $S_1 \rightarrow S_0$ transition: 20(2) ns [34] for Tc in the gas-phase or 23(2) ns [35,36] for Pent in a cryogenic p-terphenyl matrix.

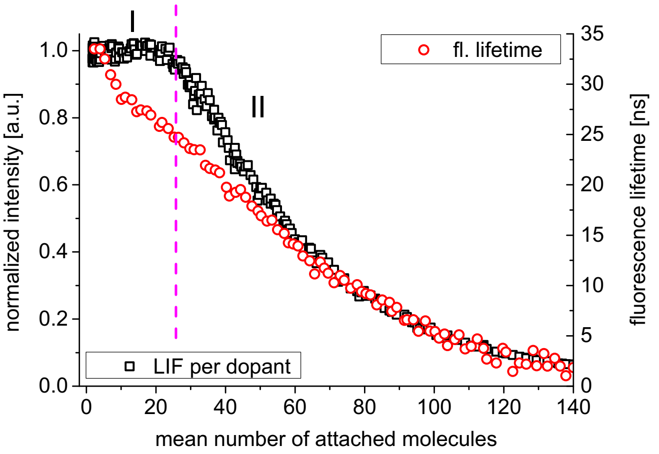

FIG. 2. (Color online) Normalized LIF intensity per molecule (black squares) and fluorescence lifetime (red circles) as functions of mean number of attached Tc molecules for a neon cluster size of ~122 000 atoms.

In Fig. 1, the fluorescence lifetime of the S$_1$ state of tetracene (red circles) and pentacene (black triangles) is plotted as a function of the mean number of attached molecules on neon clusters with mean size of $n \sim 122\,000$ (diameter ~173 Å). Laser excitation was performed on the pure electronic transition at 22 208 and 18 447 cm^{-1}, respectively, with a pulse energy of 3.5 μJ. For each data point, the time-resolved LIF intensity was recorded by averaging over at least 2 000 laser pulses. To extract the fluorescence lifetime τ_{fl}, the LIF time-trace was deconvoluted from the temporal laser pulse shape and fit to a single exponential decay function, providing satisfactory fitting and a resolution of less than 1 ns. The fluorescence lifetime for tetracene initially is 33(1) ns for ~1 molecule which is comparable to Tc in the gas phase [34] and embedded in helium droplets [37]. As the number of attached molecules is increased, we observe a dramatic reduction in the lifetime which asymptotically approaches 2 ns for doping levels of more than 90 molecules per neon cluster. Similar results were found for pentacene attached to the same neon cluster size, here the initial lifetime starts at 31(1) ns and evolves following the same curve progression as tetracene, also reaching a final lifetime of 2 ns for more than 90 molecules on the neon clusters.

To investigate if the observed reduction of the fluorescence lifetime is caused by complex formation or strong interaction between the molecules (leading, e.g., to J aggregates), LIF spectra at different doping levels have been recorded. The inset in Fig. 1 shows the LIF excitation spectra for only one tetracene molecule (A) and for ~50 tetracene molecules (B) on the neon cluster. As can be seen, both spectra are indistinguishable [38] showing that the tetracene molecules do not undergo strong interaction with each other via dipole-dipole coupling. This indicates that the lifetime reduction is not due to single-exciton superradiance [3,13,39], which is further supported by the excitation power dependence reported below.

For pentacene, our experimental results (e.g., fluorescence lifetime, cluster size dependence, laser power dependence) are very similar to that of tetracene. In light of this, the further discussion is restricted only to tetracene on neon clusters which we consider a model system showing a general trend of lifetime reduction for large molecules attached to rare-gas clusters.

To better understand the observed lifetime reduction, the normalized LIF intensity per molecule (black squares) along with the fluorescence lifetime (red circles) are plotted in Fig. 2 as functions of the mean number of attached molecules

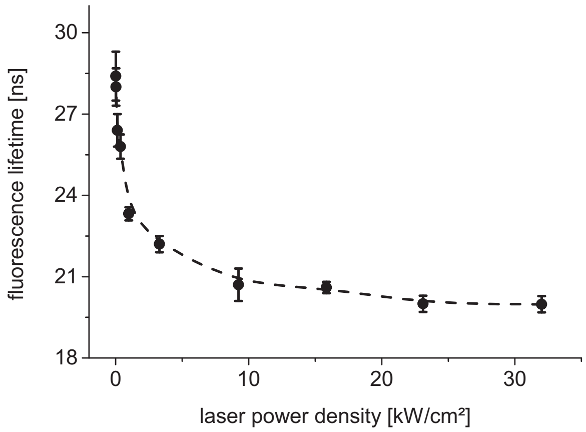

FIG. 3. Fluorescence lifetime as function of the power density of the excitation laser for 19 tetracene molecules attached to neon clusters with $n \sim 37\,000$ atoms.

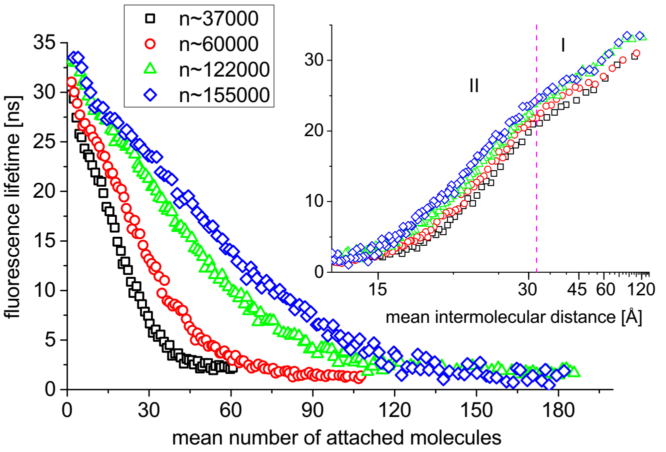

FIG. 4. (Color online) Fluorescence lifetime of Tc on neon clusters as a function of the mean number of attached molecules for neon cluster sizes $n \sim 37\,000$, 60 000, 122 000, and 155 000 atoms. Excitation is performed on the $S_1 \leftarrow S_0$ pure electronic transition at 22 208 cm^{-1} with laser pulse energy around 3.5 μ J. Inset: the fluorescence lifetime as a function of the mean intermolecular distance.

for a neon cluster size of about 122 000 atoms. For up to 25 molecules per neon cluster, one finds a constant value for the normalized LIF intensity per molecule, indicating that there is no change in the excited molecules due to nonradiative decay mechanisms. From this, we conclude that we have a constant quantum yield in this regime (labeled I in Fig. 2). At the same time a significant reduction in the fluorescence lifetime from 33 ns down to about 24 ns is observed, demonstrating enhanced radiative deexcitation.

A possible explanation for this lifetime shortening is Dicke superradiance. Here one expects that the fluorescence lifetime becomes shorter the more excitations there are initially in the system. To investigate if this is the case for our system, we measured the fluorescence lifetime for fixed cluster size and number of attached molecules as a function of excitation laser power. The result of such a measurement is shown in Fig. 3. Here, the laser power density is varied between 2 W/cm^2 and 5×10^4W/cm^2. The neon cluster size ($n \sim 37\,000$ atoms) and the mean number of attached molecules (∼19) was chosen such that the intermolecular distance falls within the region in Fig. 2 where we believe Dicke superradiance is the primary mechanism for lifetime shortening. Here, a clear significant lifetime reduction with increasing power density is observed. By this the number of excited molecules on a neon cluster has significant influence on the fluorescence lifetime consistent with Dicke superradiance. Additionally from the excitation power dependent LIF intensity we clearly see saturation of the transition indicating to have a significant portion of the molecules on the neon cluster being in a excited state.

Let us now turn our attention to region II of Fig. 2, where one has more than ∼25 molecules per cluster. Here the normalized LIF intensity per molecule (black squares) drastically decreases. For example, when more than 100 molecules are attached onto a neon cluster, the LIF intensity per molecule is reduced by 90%. The loss in LIF intensity is partially explained by destruction of the neon cluster beam during the doping process. That being said, additional nonradiative decay channels could also lead to a similar reduction in LIF intensity per molecule. Assuming the molecules are randomly distributed on the surface of the neon cluster, 25 molecules on a neon cluster of 122 000 atoms would give a mean distance of 33 Å between molecules. Although not shown in the paper, for all investigated neon cluster sizes, the LIF intensity per molecule remains constant when the corresponding intermolecular distances are greater than 33 Å, implying the quantum yield remains unchanged and thereby any observed lifetime reduction is strictly due to superradiance. Because the additional lifetime reduction occurs at relatively small intermolecular distance, one can assume the nonradiative decay channels arise from intermolecular interactions. To this end, by varying the neon cluster size and number of attached molecules, one can see the effect of the intermolecular distances on the fluorescence lifetime.

In Fig. 4, the fluorescence lifetime is plotted as a function of mean number of attached molecules for different mean neon cluster sizes ranging from 37 000 up to 155 000 atoms. For all neon cluster sizes, the initial lifetime for monomer doping is 33(1) ns. Similar to what was observed in Fig. 1, increasing the number of attached molecules leads to a strong reduction of the lifetimes down into the low nanosecond range. In general, we see a cluster size dependence such that the smaller the neon cluster, the steeper the reduction in fluorescence lifetime with increasing number of attached molecules. For example, for 30 molecules attached, the smallest neon clusters (n ∼ 37 000 atoms) give a fluorescent lifetime of about 6 ns while the largest neon clusters (n ∼ 155 000 atoms) give a lifetime of 24 ns where the mean intermolecular distance for the previous cases are 19.6 and 30.2 Å, respectively. The Dicke model itself cannot explain the observed cluster size dependent fluorescence lifetime reduction.

As such, nonradiative mechanisms are necessary to fully explain the results. In this case, Förster energy transfer combined with exciton-exciton annihilation [40–45] could lead to additional lifetime reduction. At a distance of 1 nm, the dipole-dipole interaction between two Tc molecules can still be on the order of a few wave numbers which leaves the spectra nearly unchanged but corresponds to subnanosecond transfer times. Furthermore, singlet fission could possibly contribute to reduced fluorescence lifetimes [46–48]. To our knowledge, singlet fission and exciton-exciton annihilation have, so far, not been reported in such low density systems of weakly interacting molecules as exhibited here. Therefore, molecules attached to the surface of rare-gas clusters could provide a technique for transitioning between interaction mechanisms in weakly bound systems in the gas phase (e.g., superradiance, interatomic Coulombic decay [49]) and condensed systems (exciton-exciton annihilation, singlet fission).

The fluorescence lifetime as a function of the calculated intermolecular distance is shown in the inset of Fig. 4. At about 33 Å, for all neon cluster sizes, one sees a change in the slope such that the lifetime reduction is further enhanced for smaller intermolecular distances. Since the intermolecular distance which separates regimes I and II (shown by the magenta dashed line in Figs. 2 and 4) appears constant with respect to neon cluster size, one can presume this distance to universally separate the purely superradiant regime from that where nonradiative mechanisms give rise to further lifetime reductions.

In conclusion, the use of rare-gas cluster isolation for molecular spectroscopy offers a method for directly controlling the number and/or the nearest neighbor distance of excited molecules in a cold and weakly interacting environment. Fluorescence lifetime reduction of up to a factor of 20 was observed for tetracene and pentacene molecules attached to neon clusters. Furthermore, the number of excited molecules on a neon cluster contributes to a significant fraction of the overall lifetime shortening. For intermolecular distances greater than 33 Å, constant quantum yield is observed, and here the lifetime reduction is due to Dicke superradiance. When intermolecular distances fall below 33 Å, additional lifetime reduction occurs due to the onset of nonradiative deexcitation which is supported by the cluster size dependence. As an outlook, one could use the cluster isolation technique to confine molecules to low intermolecular distances thereby studying the transition between dilute and condensed systems.

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