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ABSTRACT
Lattice defects and dielectric environment play a crucial role for 2D materials. Gas molecules can get physisorbed easily on the surface through van der Waals forces and can modify dramatically their electronic and optical properties. In this work, we investigate the impact of the physisorbed gas molecules on the optical properties of MoSe₂ monolayers by means of low-temperature photoluminescence (PL). More specifically, we focus on the physics of excitons localized by gas molecules. The associated PL peak is observed to show a systematic and large red-shift with temperature and a blue-shift with laser irradiation. Both energy shifts are explained in terms of thermal instability of the localization in combination with hopping effects. Finally, a model is presented, which can reproduce the experimental data with excellent agreement.

In recent years, a lot of scientific research has been conducted to understand the electronic and optical properties of transition metal dichalcogenide (TMD) monolayers (MoS₂, WSe₂...). The interest in these materials is closely connected with the atomic vertical scale of these semiconductors. This geometrical property made the scientific community face new interesting physics and at the same time new technological opportunities and challenges.

An effect related to the extreme surface-to-volume ratio is the huge influence of physisorption and chemisorption of gas molecules on the optical and electronic properties. This efficient interaction can be exploited to engineer the materials for related applications, for instance, chemical treatment for enhancing and tuning photoluminescence (PL) emission as well as gas sensing and biosensing using modulations in electronic and optical responses as fingerprints for physisorbed gas molecules. In this context, PL offers an elegant, low-power consuming, and contactless tool.

Furthermore, physisorption is strongly connected with other prominent effects on TMD monolayers, i.e., photo-annealing and photo-doping. Regarding optical properties, it has been shown that the exposure to low-intensity visible laser light changes drastically the optical response of the material. On one hand, these effects can be used for technological applications such as reversible optical control of the doping.

Even if the effects of physisorption are well-documented in literature, discussions and comprehension of the physics of such effects on localized excitons are still missing. For this purpose, we present here a systematic experimental study on the impact of gas molecules present in air on optical properties of a MoSe₂ monolayer via low-temperature PL. We follow the temperature evolution of the localized excitons related to gas molecules (GM-LX). We observe a large red-shift, and we present a model that can reproduce the data with excellent agreement. Within the same approach, we analyze the evolution of the GM-LX peak for different laser irradiation doses, where a blue-shift of the peak is observed with increasing irradiation doses. We suggest that both the red-shift and the blue-shift can be explained by hopping between localized states. Finally, we also introduce an effective temperature particularly important at low temperature in order to describe the disorder potential induced by the physisorbed gas molecules.

We focus our attention on a MoSe₂ monolayer, that is, a paradigmatic compound of TMDs. Nevertheless, in comparison with other W-based TMD monolayers, it shows cleaner optical spectra, a condition that allows us to isolate more easily the effects of the physisorbed gas molecules. Moreover, the possibility to use MoSe₂ monolayers...
as gas sensors both electronically and optically via PL has been recently demonstrated experimentally. Such works make this material promising for technology.

Our measurements were carried out using a micro-PL setup with a microscope cryostat. The cryostat is a cold finger, and the sample is kept in vacuum ($10^{-6}$ mbar at $T = 300$ K). We used a cw frequency-doubled Nd:YAG laser as an excitation pump at a wavelength of $\lambda = 532$ nm. The spot diameter on the sample is approximately 3 $\mu$m, therefore, it is smaller than the monolayer flake but still large enough in order to minimize the power density. A nitrogen-cooled Si-CCD deep-depletion camera was used to detect the PL emission, which is dispersed in a spectrometer.

The samples were prepared by means of mechanical exfoliation from a CVD-grown crystal from 2D Semiconductors and transferred via a PDMS foil onto a SiO$_2$ (100 nm)/undoped-Si substrate. During preparation and between measurement series, the samples were exposed to ambient conditions. Gas molecules, in particular, H$_2$O and O$_2$, will be physisorbed and chemisorbed at the surface, remaining there even when the samples are placed in vacuum in the cryostat. For comparison, we show also PL data from an encapsulated MoSe$_2$ monolayer in hexagonal Boron Nitride (hBN). The hBN encapsulated MoSe$_2$ stacks are fabricated by using the dry transfer technique as described previously by Wang et al. By using this polymer assisted fabrication technique, we ensured a clean interface between monolayer MoSe$_2$ and top hBN.

In Fig. 1(a), a typical scenario of low-temperature PL spectra of MoSe$_2$ monolayers is depicted. The excitation power is kept very low (100 nW) for all three spectra. The PL spectrum on top is taken from a freshly exfoliated sample. The PL is dominated by a broad peak at a photon energy of around 1.6 eV, that is, the GM-LX peak. The resonance of the free exciton is also visible at 1.65 eV.

After few seconds of laser-irradiation at a wavelength of 532 nm and a power density of 0.5 kW cm$^{-2}$, the localized exciton peak almost disappears and the trion peak dominates the spectrum, an effect, that is, completely reversible in air. This fact means that the low-energy peak is related to adsorption of gas molecules on the MoSe$_2$ surface, and more specifically, it points toward physisorption rather than chemisorption even if we cannot conclude that chemisorption does not play any role. Moreover, intrinsic defects in the monolayer—for instance, Se vacancies—do not affect strongly the PL emission properties, except for the fact that intrinsic defects increase the probability that a gas molecule is physisorbed. The PL yield of the nonirradiated sample is around ten times higher than that for the sample after irradiation due to the giant oscillator strength of the localized excitons, as is typical in semiconductors.

The appearance of the trion peak is the evidence for the increased number of available free carriers in the flake. There is a double origin: both the desorption of physisorbed and chemisorbed polar and nonpolar gas molecules (O$_2$ or H$_2$O) and a laser-induced spatial separation of carriers trapped into the substrate can generate a gating. Consequently, using extremely low excitation power, it is possible to avoid any modification in the physical properties of a freshly exfoliated sample. In this condition, we studied the temperature dependence of air gas molecule localized excitons physisorbed on the monolayer surface.

In Fig. 2, the low-temperature PL spectra for different temperatures are shown. At low temperature, most of the PL emission comes from the localized states. The exciton peak is barely visible. With increasing temperature, the localized exciton peak drops in intensity and the exciton and the trion peaks appear. Nevertheless, the PL spectra are dominated until 80 K by localized exciton emission. The shape...
of the GM-LX peak does not change much with temperature, but there is a pronounced red-shift and broadening.

In order to fit the lineshapes of the PL peaks, we have used a standard model for localized excitons.\textsuperscript{33–35} This model takes into account an exponential sub-bandgap tail of states and a finite temperature that accounts for the thermal probability to escape from a localization center:

$$P(E) = \frac{I(T) \exp \left( \frac{E}{E_u} \right)}{1 + \exp \left( \frac{E - E_{LX}(T)}{k_B T_{\text{eff}}(T)} \right)}$$

where $P$ is the PL intensity for every photon energy $E$, $I$ is a normalization factor, $E_u$ is the depth of the bandgap tail (Urbach energy), $T$ is the lattice temperature, $T_{\text{eff}}$ is an effective temperature, and $E_{LX}$ almost corresponds to the peak energy position at the maximum $E_{\text{max}} = E_{LX} + k_B T_{\text{eff}} \ln \left( \frac{k_B T_{\text{eff}}}{E_{LX}} \right)$. The Urbach-like part of this function is responsible for the low-energy side of the GM-LX peak in the fit, while the Fermi-Dirac-like part is responsible for the high energy side. The effective temperature determines the slope of the exponential decay on the high-energy side of the GM-LX peak. For higher temperatures where the exciton and trion peaks are more pronounced, we used this fitting function plus a Gaussian centered at the exciton and trion resonances.

The fact that the GM-LX peak shows such a smooth distribution means that the density of physisorbed molecules is very high: it is possible that there is a full covering of gas molecules on top of the surface.\textsuperscript{13}

The agreement of this fitting function with the data is excellent in spite of the small number of parameters as shown in Figs. 3(a) and 3(b) at $T = 6$ K and $T = 80$ K, respectively. However, even for the lowest temperature, we obtain, from the fit, effective temperature values above 100 K [see Fig. 4(a)].

Before going into details regarding the latter observation, we comment on the Urbach energy $E_u$.\textsuperscript{36} From our data, it is found that $E_u$ is independent of temperature—with our range of uncertainties—and has a value around 30 meV. An indication of this is already visible in the normalized spectra in Fig. 2, where the exponential low-energy tail of the spectra does not change its shape with temperature. Furthermore, we note that applying a Gaussian distribution or a Franz-Keldysh tail for the sub-bandgap density of states results in worse agreement with the measured data (not shown).\textsuperscript{37–39}

In Fig. 4(a), the dependence of the effective temperature obtained as a fitting parameter on the lattice temperature is shown. According to Marianer and Shklovskii,\textsuperscript{40} the effective temperature can be interpreted as a Pythagorean sum of the lattice temperature and an induced temperature $T_0$ at zero Kelvin:

$$T_{\text{eff}}(T) = \sqrt{z(T^2 + T_0^2)}$$

where $z$ is a fitting parameter that in the ideal case should be identical to 1. As it is clear from Fig. 4(a), the agreement with the experimental data is excellent; however, we get $z = 2.0 \pm 0.1$. 

![FIG. 2. Low-temperature PL spectra for different temperatures normalized with respect to the GM-LX peak. Curves are shifted vertically for clarity.](image1)

![FIG. 3. Low-temperature PL spectra and fit functions (red) at $T = 6$ K and $T = 80$ K.](image2)

![FIG. 4. (Top) The dependence of the effective temperature on lattice temperature with the fit according to Eq. (2). (Bottom) The temperature dependence of the GM-LX peak energy.](image3)
From the fit, we also get $T_0 = 101 \pm 4$ K that corresponds to the energy of 9 meV [Fig. 4(a)]. We interpret this value as the quadratic deviation of the inhomogeneous potential distribution in the monolayer induced by physisorbed gas molecules. We note that even non-polar gas molecules can introduce locally a disorder potential. The induced strong inhomogeneity of potential has the effect of smearing the sharp edge of the Fermi-Dirac part of Eq. (1). We considered the possible effect of higher carrier temperature with respect to the lattice temperature, but we had to rule out this interpretation since we have used an extremely low excitation power.

The energy $E_{LX}$ has a clear temperature dependence [Fig. 4(b)]. In this figure, we already subtracted the contribution of the red-shift due to the renormalization of the bandgap using the Varshni formula,\(^\text{114}\) that is, anyway, almost one order of magnitude less than the observed red-shift in this temperature range.

The red-shift of the localized exciton peak with temperature is clearly not only due to the red-shift of the renormalization of the bandgap but also due to another physical effect. This effect could be related to hopping between localized states.\(^\text{44,43}\) Hopping between defects means that a localized exciton can anyway travel across the flake through hopping between different defects via emission of acoustic and optical phonons.\(^\text{44}\) Furthermore, the exciton prefers to hop into a favorable lower energy state (infrared side). This phenomenon results in a redistribution of the PL spectral intensities toward lower energies.

Increasing the temperature also means increasing the probability for hopping (mobility of a localized exciton) that translates in a red-shift of the localized exciton peak. This effect has already been shown for different semiconductors with reduced dimensions like dilute nitride quantum wells\(^\text{12}\) and quantum dots.\(^\text{46}\)

An analytical model that quantifies the red-shift with temperature due to the hopping effect has been developed by Baranovskii et al.\(^\text{47}\) for an exponential sub-bandgap density of states. The peak energy can be approximated by $E_{LX} = E_{\text{LX}}^0 - k_B T \ln \left( \nu_0 \tau_0 \right)$, where $\nu_0$ is the attempt-to-escape rate from a defect and $\tau_0$ is the lifetime of a localized exciton at $T = 0$ K. From the linear fit in Fig. 4(b), we get $\ln \left( \nu_0 \tau_0 \right) = 8.1$. Typically, $\nu_0$ is of the order of $10^{13}$ s\(^{-1}\),\(^\text{12}\) and therefore, we get a localized exciton lifetime of the order of 5 ns, that is, in good agreement with experimental data.\(^\text{46}\)

Using the same ansatz, we present our analysis of the effects of laser irradiation on the GM-LX peak. The spectra are measured using again low excitation power (100 nW) after different irradiation doses. The trend that we observe is depicted in Fig. 5(a). Again, the exponential tail does not change that much up to hundreds of microwatts of excitation power, while the effective temperature decreases and the GM-LX energy shows a blue-shift. According to the previous interpretation, the blue-shift is due to a transfer of population rather than an energetic redistribution of defect states. More specifically, the hopping probability drops due to the lower amount of gas molecules available as localization sites on the surface after the annealing. Consistently, the effective temperature decreases because the disorder potential induced by the gas molecules is smaller.

Above an irradiation power of 1 mW, we start to observe a decrease in the trion peak PL intensity (not shown) which is a consequence of an irreversible decrease in the crystal quality. Also, the shape GM-LX peak starts to change.

In Fig. 5(b), the energy shift of the GM-LX with increasing dose of laser exposure is depicted. At a fixed irradiation exposure, we observe a monotonic blue-shift of the peak that saturates in a time scale of minutes. This saturation behavior is usually attributed to the finite number of physisorbed gas molecules. For different power densities, the shift of the peak enters into an another regime: irradiating a monolayer with different average powers and keeping constant the product of irradiation time and power, the effects on the monolayer are very different.

In conclusion, we have performed a systematic investigation of excitons localized by physisorbed gas molecules (GM-LX) on the surface of MoSe\(_2\) monolayers. We corroborate previous results on other TMDs, showing photo-annealing, photo-doping, and reversibility in air for a MoSe\(_2\) monolayer. Successively, we focused on the physics of localized excitons, analyzing carefully the GM-LX peak in PL. This peak dominates the PL emission up to 80 K. In this range of temperatures, we observed a significant red-shift of the emission peak that we explain by a hopping effect between physisorbed gas molecules.
also find evidence of a strong inhomogeneous disorder potential in the monolayer induced by the physisorbed molecule that can be modeled by an effective temperature. Finally, we studied the effect of laser irradiation on GM-LX showing consistent results. With this work, we provide a basis to investigate further the interaction of physisorbed gas molecules and excitons in 2D semiconductors, a topic that is of clear interest both for the basic physics point of view and for technological applications.

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