Monolayer transition metal dichalcogenides (TMDs) exhibit strongly bound exciton complexes [1–7] even at room temperature due to enhanced electron-hole interaction resulting from strong out-of-plane quantum confinement [8], large in-plane carrier effective mass [9,10], and small dielectric constant [9,11]. To be able to externally control their binding energy will provide an unprecedented opportunity to design novel exciton-based devices. Owing to the ultrathin nature of the monolayer, a change in the surrounding dielectric medium is expected to provide a direct way to achieve this through screening of the electron-hole Coulomb interaction [12–20]. However, despite such expected change in the binding energy of the exciton complexes, several studies [1,18,19,21–24] report that the photoluminescence (PL) emission peak position of the $1s$ exciton remains practically unaltered, irrespective of the surrounding dielectric environment. This apparently bemusing result is generally understood as a consequence of strong quasiparticle band-gap renormalization resulting from screened many-body interaction [18,19,23]. The change in the electron-hole interaction strength of the $1s$ exciton bound state in the presence of different dielectric media is almost equal to the change in the electron-electron interactions. Such compensation makes it challenging to experimentally validate the predicted effect of the dielectric environment on the binding energy of excitons using optical studies in an unambiguous way [1,18–24]. While a few indirect approaches, including combinations of photoluminescence studies [18,19] with first-principles calculations [17–19,25] and scanning tunneling spectroscopy [19,26,27], have been reported in the recent past, direct evidence of binding energy modulation in monolayer TMDs by changing the surrounding dielectric media is still lacking. Also, a generalization of the compensation effect between band-gap renormalization and binding energy change for higher energy exciton states remains unclear.

In this work, by using low-temperature PL spectra of monolayer MoSe$_2$ embedded in different dielectric environments, we observe that unlike the unchanged PL emission peak position of the $1s$ exciton state, the higher energy ($2s$, $3s$, $4s$, $5s$) exciton states show monotonically increasing peak shifts in response to changed surroundings. Further, the charged trion binding energy is also found to exhibit a strong shift. The experimental observations are explained by a screening model with spatially distributed charge. The results confirm that a change in the surrounding dielectric medium induces a strong quasiparticle band-gap modification in conjunction with a strong binding energy modulation of different exciton complexes. While the $1s$ exciton binding energy change is almost exactly equal in magnitude to the quasiparticle band-gap change, the higher energy exciton states exhibit larger percentage change in binding energy.

The origin of a reduction in binding energy in the presence of a surrounding medium of higher dielectric constant can be conceptually understood as a consequence of the proximity of an image charge, as schematically illustrated in Fig. 1(a). The additional repulsive force due to the image charge effectively weakens the strong in-plane electron-hole Coulomb attraction, in turn reducing the binding energy of various excitonic bound states. Monolayer flakes of MoSe$_2$ are mechanically exfoliated on clean Si substrate, covered with 300 nm SiO$_2$. In some of the samples, 10-nm-thick Al$_2$O$_3$ film was deposited by using electron beam evaporation at a chamber pressure of $2 \times 10^{-6}$ mbar. Figure 1(b) shows the acquired PL spectra of MoSe$_2$/SiO$_2$ (sample M1) and Al$_2$O$_3$/MoSe$_2$/SiO$_2$ (sample M2) stacks at $T = 8$ K. The $1s$ state of the neutral $A$ exciton ($A_{1s}^0$) and the corresponding charged trion ($A_{1s}^-$) peaks (only negatively charged trions are considered due to slight n-type doping of the sample) are found to be at similar energies in both the samples. To confirm this observation further, we measure the PL emission of monolayer MoSe$_2$ at room temperature, embedded in five different dielectric surroundings. The PL spectra showing the $A_{1s}^0$ peak is presented in Fig. 1(c), confirming a negligible peak shift ($\approx 10$ meV). While the
enhanced electrostatic screening due to the surrounding dielectric medium reduces the exciton binding energy ($\Delta E_b$), at the same time, this screens and modifies the electron-electron interaction term in the many-body Hamiltonian as well. This results in a reduction ($\Delta E_s$) in the quasiparticle band gap. The nontunability of the $A_{1s}^0$ peak for different dielectric environments suggests that the change in energy of this state due to these two effects are equal and opposite, almost entirely compensating for each other for the $1s$ exciton, as schematically illustrated in the left panel of Fig. 1(d). However, on moving to states with increasing principal quantum number ($n$), $\Delta E_b$ reduces gradually, whereas $\Delta E_s$ remains the same, and hence such exact compensation is not expected. This possibility allows for a direct observation of PL peak shift for these higher energy states with a change in dielectric environment, as explained in the middle and right panels of Fig. 1(d).

Information regarding the higher energy states is obtained by careful observation of the PL spectrum of sample M1 at different temperatures, as shown in Figs. 2(a)–2(d). We identify four peaks by fitting the experimental data in the energy range of 1.75–2.0 eV. The small peak (in purple) around 30 meV below the prominent $B_{1s}^0$ peak (in green) is attributed to the $B_{1s}$ trion peak. Note that the $A_{1s}$ trion peak intensity is much stronger than the $A_{1s}^0$ exciton peak, while the $B_{1s}$ trion is significantly weaker than the $B_{1s}^0$ exciton peak. This difference can be explained from the origin of lowest energy bright and dark trion states, as schematically illustrated in Figs. 2(e) and 2(f). The availability of the second electron in the spin split lower conduction band required to form the $B_{1s}$ trion is bottlenecked as most of these electrons are consumed to form the more favorable $A$ exciton and trion. In addition, the dipole allowed bright trion $B_{1s,D}$ which contributes to the PL signal, is at higher energy compared to the dark trion $B_{1s,D}$ and hence forms with lower probability. On the other hand, for the $A$ trions, their energy positions get interchanged, making the $A_{1s,D}$ bright trion a more favorable trion state than the dark trion $A_{1s,D}$. This also explains the observation of enhanced intensity of the $B_{1s}$ peak at higher temperature as shown in Figs. 2(a)–2(d) as the fractional contribution of bright trions increases with temperature.

The conspicuous peak around 1.8 eV is assigned to the $A_{2s}^0$ exciton. A 2$s$ exciton peak at similar energy has been reported for monolayer MoSe$_2$ in a recent reflectance experiment [28]. We also observe the existence of another higher energy peak due to the $A_{3s}^0$ exciton around 1.9 eV.

In the bottom panel of Fig. 3(a), the peak positions of $A_{2s}^0$ to $A_{5s}^0$, and the $B_{1s}^0$ and $B_{2s}$ states for sample M2 are shown.
FIG. 2. (a)–(d) The experimental PL data for sample M1 (in gray) in the energy range 1.75–2.00 eV, measured at sample temperatures ranging from 8 to 35 K. Four peaks are obtained from fitting the data, namely, $A_0^2$ exciton (orange), $A_0^3$ exciton (pink), $B_{1s}^-$ trion (purple), and $B_0^1$ exciton (green). The $B_{1s}^-$ trion peak, about 30 meV below $B_0^1$, shows a slight increase in intensity with temperature. (e) Schematic of lowest energy bright (left panel) and dark (right panel) $A$ trion states. The dotted and solid lines in the conduction band (valence band) correspond to spin-up (down) and spin-down (up) states of electrons (hole) in monolayer MoSe$_2$. The bright state $A_{1s, B}$ is at lower energy than the dark $B_{1s, D}$ trion state. (f) The lowest energy bright (left panel) and dark (right panel) $B$ trion states suggest that the bright $B_{1s, B}$ state is at higher energy than the dark $B_{1s, D}$ trion state. This explains the slight increase in $B_{1s, B}$ intensity with temperature in (a)–(d).

overall peak intensities in this sample are weaker than sample M1, but are clearly distinguishable. From the peak positions, we estimate a strong redshift of 50.3 and 104.1 meV in the $A_0^2$ and $A_0^3$ peaks, respectively, due to the addition of a top Al$_2$O$_3$ coating at $T = 8$ K. The higher energy peaks become difficult to distinguish beyond $T = 35$ K. Figure 3(b) shows a comparison between the $A_0^1$ PL emission peak positions for both samples, measured at different temperatures and suggests that the nontunability of its energy is temperature independent. In Fig. 3(c), the temperature-dependent $A_0^2$ and $A_0^3$ transition energies confirm strong redshift of PL peaks in sample M2 at various temperatures. The Bohr radius of these higher energy states is significantly larger compared to the $1s$ exciton. Consequently, the magnitude of change in binding energy becomes increasingly weak with higher $n$ in the presence of Al$_2$O$_3$ coating. This leaves the band-gap renormalization effect partially uncompensated, explaining the redshift [Fig. 1(d)].

To have a quantitative understanding, we compute the effective potential due to a hole by solving Poisson’s equation for the five-layer dielectric structure schematically shown in

FIG. 3. (a) PL peak positions for higher energy $A$ exciton states ($A_0^2$ to $A_0^3$) in sample M2 (bottom panel). For reference, spectrum from sample M1 is shown in the top panel. Clear redshifts for the $A_0^2$ and $A_0^3$ peaks are observed in M2 compared with M1. The $B_{1s}^-$ trion peak close to the $B_0^1$ peak for both samples is also discernible. (b) The $A_0^3$ exciton peak is almost similar for samples M1 and M2 at various measurement temperatures. (c) The $A_0^1$, $A_0^3$, PL peak positions for M1 and M2 at different temperatures testify to the strong PL peak shift for higher energy exciton states.
for both the stacks as first few bound states). The binding energies and shape of the wave functions of σ and sponding charge density and the in-plane potential profiles are automatically taken care of the image force effects arising from Fig. 4(a). The solution of Poisson’s equation in the potential profile for this distributed hole charge [29]. To account for the finite spread of the carrier wave function, the point charge is replaced by a Gaussian distribution in the plane (x, y) of the monolayer, modulated by the square of the wave function of the first eigenstate in a square quantum well in the out-of-plane (z) direction, and is given by

$$\rho(x, y, z) = \frac{q}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{x^2 + y^2}{2\sigma^2}\right) \cos^2\left(\frac{\pi z}{t}\right).$$

The thickness (t) of the monolayer is taken to be 6.5 Å. The solution of Poisson’s equation provides the converged potential profile V for this distributed hole charge [29]. The energy eigenvalues E and wave functions $\psi(x, y)$ of the exciton bound states are obtained by numerically solving the two-dimensional time-independent Schrödinger equation in the x-y plane [30]:

$$-\frac{\hbar^2}{2\mu_{ex}}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - qV(x, y)\psi(x, y) = E\psi(x, y).$$

The in-plane spread $\sigma$ is used as a single fitting parameter, and $\sigma = 22.5$ Å (both for samples M1 and M2) provides the best fitting with the experimental data in Fig. 5. The corresponding charge density and the in-plane potential profiles are shown in Figs. 4(b) and 4(c) (see Supplemental Material [31] for the binding energies and shape of the wave functions of first few bound states).

We estimate the quasiparticle band-gap energy (continuum) for both the stacks as $E_g = A_{1s}^0$ (experiment) + $E_g^b$(model). The calculated PL emission energies are plotted as a function of n in Fig. 5 for both samples, and are in good agreement with the experimental peak positions. The difference between the computed continuum levels in the samples immediately leads to an estimation of $\Delta E_{2s} \approx 246$ meV due to quasiparticle band-gap renormalization. The estimated reduction in the $A_{1s}^0$ exciton binding energy due to the addition of a top Al2O3 coating is 58.6%. The corresponding reductions for $A_{1s}^0$ and $A_{1s}^0$ excitons are 72.8% and 75.85%, respectively. The measured PL peak position and estimated binding energy of different states are tabulated in Table I.

In Table I, we have also shown the measured $A_{1s}^-$ trion binding energy: $\Delta_{1s}^- = A_{1s}^- - A_{1s}^0$, which also exhibits 15.1% reduction in sample M2. Note that $\Delta_{1s}^-$ being estimated from the separation between two PL peaks does not involve the quasiparticle band gap, and provides independent direct evidence of the modulation of binding energy in the presence of larger dielectric screening.

In conclusion, we explored the role of environment screening on two-dimensional monolayers by increasing the mismatch between quasiparticle band-gap renormalization and exciton binding energy modification for exciton states with higher quantum number. The proposed technique allows us to unambiguously estimate all the necessary information about the excitonic series and quasiparticle band-gap change in two-dimensional monolayers embedded in different dielectric media. Our results clearly demonstrate the prominent effect of substrate and environment induced screening in two-dimensional (2D) systems, making this effect crucial to be taken into account while analyzing results in existing devices based on 2D materials. For example, the band structure of the 2D material in the region underneath the contact material or in the presence of a gate dielectric is expected to be modified locally as a result of this effect, and is expected to play an important role in determining the device performance. A similar revisit will also be required in analyzing the performance of 2D material based photodetectors as this screening induced unintentionally created built-in field at the source junction will support efficient electron-hole separation. Finally, planar heterojunctions in two-dimensional crystals are generally
difficult to achieve due to stringent growth conditions. The results described in this work open up the possibility of another class of two-dimensional planar heterostructure devices by only spatially modifying the substrate or top dielectric constant.

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**TABLE I.** Binding energy of different excitonic states at $T = 8$ K in samples M1 and M2.

<table>
<thead>
<tr>
<th>Type of exciton complex</th>
<th>MoSe$_2$/SiO$_2$</th>
<th>Al$_2$O$_3$/MoSe$_2$/SiO$_2$</th>
<th>Change in binding energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1s}$</td>
<td>420(±0.37)</td>
<td>174</td>
<td>58.6%</td>
</tr>
<tr>
<td>$A_{2s}$</td>
<td>276(±0.93)</td>
<td>75 (±0.021)</td>
<td>72.8%</td>
</tr>
<tr>
<td>$A_{3s}$</td>
<td>188 (±0.02)</td>
<td>45.4 (±0.038)</td>
<td>75.85%</td>
</tr>
<tr>
<td>$A_{4s}$</td>
<td>117$^a$</td>
<td>16.8 (±0.025)</td>
<td>85.64%</td>
</tr>
<tr>
<td>$A_{5s}$</td>
<td>74$^a$</td>
<td>10.3 (±0.053)</td>
<td>86%</td>
</tr>
<tr>
<td>$A_{1t}$</td>
<td>32.3</td>
<td>27.4</td>
<td>15.1%</td>
</tr>
</tbody>
</table>

$^a$ Model predicted.