Interaction of Helium Rydberg State Molecules with Dense Helium
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ABSTRACT: The interaction potentials of the He₂⁺ excimer, in the a'Σ_u⁻, b'Π_u, c'Σ_u⁺, and d'Σ_g electronic states with a ground state helium atom are presented. The symmetry of the interaction potentials closely follows the excimer Rydberg electron density with pronounced short-range minima appearing along the nodal planes of the Rydberg orbital. In such cases, a combination of the electrostatic short-range attraction combined with Pauli repulsion leads to the appearance of unusual long-range maxima in the potentials. Bosonic density functional calculations show that the a'Σ_u⁻ state excimer resides in a localized solvation bubble in dense helium at 4.5 K, with radii varying from 12.7 Å at 0.1 MPa to 10.8 Å at 2.4 MPa. The calculated a'Σ_u⁻ → b'Π_u pressure-induced fluorescence band shifts are in good agreement with experimental results determined by application of corona discharge. The magnitude of the spectral shifts indicate that the observed He₂⁺ molecules emit from dense helium whereas the corresponding fluorescence signal from the discharge zone appears quenched. This implies that fluorescence spectroscopy involving this electronic transition can only be used to probe the state of the surrounding medium rather than the discharge zone itself.

INTRODUCTION
Many studies have been published on the conduction of dielectric liquids, e.g., refs 1−5 and references therein. It is, however, still difficult to predict the behavior of these liquids in high electric fields, in particular, breakdown characteristics, without having to recourse to numerous and expensive experimental investigations.6 The electric breakdown of liquids consists of a complex sequence of correlated events7−10 and the investigation of such processes requires the application of high electric fields, which can be achieved, for example, by corona discharge in the liquid. The corona discharge method is technically simple and can be used to interrogate mechanistic aspects of liquid breakdown. It has been determined that the initial localized discharge in the liquid phase is linked to ionization and excitation processes of the medium, which is subsequently followed by liquid heating and cavity formation.11 However, salient physical parameters of the discharge zone, such as the density and temperature as well as the ionization coefficient of the liquid, are still largely unknown. The lack of this information is an obstacle for realistically modeling the discharge event. In gases, a good understanding of the discharge phenomena was obtained by using spectroscopic diagnostic techniques to measure the relevant discharge parameters.12−14 These parameters were deduced from a detailed spectral analysis of the light emitted by the discharge. However, the application of the same technique in dielectric liquids is facing difficulties due to the high density present inside the discharge cavity.

In addition to possible fluorescence quenching, the influence of impurities, such as water and other polar molecules, become increasingly pronounced at higher densities. Moreover, the organic dielectric liquids that are currently employed to study the electric breakdown process undergo fragmentation due to the discharge, which further complicates the data analysis.15−17 An effective way to study electric discharge events and extract relevant parameters in the liquid phase is to characterize such phenomena in a chemically inert monatomic fluid. To this end, liquid helium is an attractive candidate as it possesses rich fluorescence spectroscopy and contains practically no contaminants. The present work assesses the suitability of fluorescence spectroscopy to determine the physical parameters associated with corona discharge in dense helium, as a function of pressure and temperature.

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**EXPERIMENT**

The experimental setup, as described in greater detail in ref 18, consists of a helium cryostat that allows measurements to be taken from ambient temperatures down to 4.2 K. Briefly, a beryllium copper cell equipped with sapphire windows was attached to the cryostat cold head, which allowed optical measurements up to 10 MPa pressure. The temperature inside the cell was measured with a germanium sensor (LakeShore GR-200A-2500) with an accuracy of ±0.5 mK and pressure by a capacitance manometer (MKS Instruments Micro Baratron model 980B-33PCB2GK).

The cell was first evacuated using a turbo molecular pump down to $10^{-7}$ Pa and then filled with ultra pure helium (N60 !/Air Liquide; impurity concentration of less than 0.1 ppm of O2). Prior to entering the cell, helium gas was passed through a series of liquid nitrogen immersed traps, which were filled with a mixture of molecular sieves (3–10 Å) and activated charcoal, with the latter prepared under vacuum for 3 days at 350 °C.

The point electrode placed inside the cell was made of electrolytically etched 1 mm diameter tungsten wire. Etching reduced the tip diameter to 0.45–2.5 μm, which was determined by an electron microscope (Jeol JSM 5600LV). The plane electrode was made of copper and located 8 mm away from the point electrode. All electrodes were insulated with Macor ceramic. The point electrode was either negatively or positively polarized by a stabilized high voltage dc power supply (Spellman RHSR/20PN60). The positive and negative corona discharges were driven by positive or negative point electrode polarity, respectively. The current (0.1–1 μA in the liquid phase) and voltage characteristics were measured by using a Tektronix TDS540 oscilloscope and a Keithley 610C ammeter. The corona discharge in this geometry is axially symmetric and appears as a luminous spherical discharge zone (ionization region) localized near the point electrode. The light originating from this zone was collected by two quartz lenses (ionization region) localized near the point electrode. The light was then directed to a spectrograph (Acton Research Corporation 300i) equipped with gratings 150 g/mm, 1200 g/mm blazed at 750 nm, and 1200 g/mm blazed at 300 nm). A liquid nitrogen cooled charge coupled device (CCD; Princeton Instruments model 2D-CCDTKB-UV/AR) was placed at the exit plane of the spectrograph. The noise level of this CCD detector was determined by the read-out noise as the dark current was less than 1 e/pixel/h at 153 K. The wavelength and the intensity response of the detection system was calibrated by using low pressure helium (Lot Oriel SS.SPEC.He.10.0) and tungsten ribbon lamps. Line broadening due to the instrument response (1200 g/mm grating) was estimated from the 706 nm helium line at 183 K.

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**THEORY**

**Excimer-Atom Pair Potentials.** Triplet state potential energy curves were calculated to assess the interaction of the He$^+$ excimer in the presence of a third, impinging, helium atom in the ground, $^3S$, electronic state. Henceforth, the triatomic potentials will be denoted by the diatomic excimer state at the asymptotic separation limit with respect to the third atom. The ground state potential, $a(^3\Sigma_g)$, was calculated by the coupled-cluster based, CC3 approach, which employed iterative, partial triple excitations. A restricted open shell Hartree–Fock calculation served as the reference for the CC3 wave function. Excited state energies for the $b(^3\Pi_g)$, $c(^3\Sigma_u)$, and $d(^3\Sigma_u)$ excimer states were determined using the equation-of-motion CC3 approach (EOM-CC3). Basis set superposition error (BSSE) was addressed by counterpoise correction, which was allowable as the EOM-CC3 approach is size consistent. All pair potential calculations were performed using the Psi4 software package, version 0.3.

The two basis sets employed to calculate the He$^+$–He triplet potentials have previously shown to be capable of providing sufficient accuracy to match absorption and emission spectra from atomic, and diatomic helium Rydberg states. The smaller basis set, denoted in ref 24 and this study as ‘&&’, was originally developed by Sunil et al. and was subsequently modified to increase accuracy. The larger basis, denoted in ref 23, and in this study as ‘&&’, was originally developed by Deguilhem and Gadek, and was subsequently parsed to increase functionality. To avoid a linear dependency in the fully uncontracted basis set && from ref 23, a diffuse $p$-Gaussian with exponent 0.006 was eliminated and the two $f$ basis functions were dropped to reduce the computational time. The parameters for basis set &&, as used in this study, are specified in Table 1.

<p>| Table 1. Uncontracted Gaussian Basis Set Exponents for Basis Set &amp;&amp; |
|------------------|------|--------|----------|</p>
<table>
<thead>
<tr>
<th>s</th>
<th>p</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>50000, 10000, 2000, 1000, 500, 100, 50, 20, 10, 5, 2, 1</td>
<td>0.5, 0.2, 0.1</td>
<td>0.05, 0.025, 0.012</td>
</tr>
<tr>
<td>1.0, 0.5, 0.2, 0.1, 0.055, 0.05, 0.025</td>
<td>0.011, 0.006</td>
<td></td>
</tr>
</tbody>
</table>

For closure, the excimer–helium pair potentials were calculated for both linear and perpendicular (T) orientations of the He$^+$ quantization axis with respect to position of the third, $^3S$, He atom. Calculations for both orientations employed the C$_{2v}$ point group. The T-orientation calculation included consideration of both, nondegenerate, $^3b$-states with $\pi$ highest occupied molecular orbital (HOMO) of the excimer aligned (B$_t$) and oriented perpendicular (A$_t$) to the impinging ground state He atom. The helium atoms in the excimer were centered about the origin and separated from each other by the equilibrium bond distance of 1.05 Å.

**Bosonic Density Functional Theory Calculations.** To model the distribution of liquid helium around He$^+$ molecular excimers, the Orsay–Trento (OT) density functional theory (DFT) method was employed, which includes static thermal corrections up to 3.0 K. Since the calculations were carried out in imaginary time, the backflow functional of OT was not included. Furthermore, the effect of the kinetic energy correlation term in OT appeared negligible and was therefore not considered. This basic form of OT functional has been shown to be able to model solvation of several types of impurities, e.g., electron, halogen anions, and Ba$^+$ cations. Impurities that exhibit strong binding with helium typically require inclusion of the density cutoff functional, but the He$^+$–He potentials employed do not possess such binding, with the exception of short-range pocket present for some excimer states. This excimer–liquid interaction is incorporated in the calculations as an external potential, which involves integration over the zero-point density of the excimer.

The OT-DFT calculation numerically solves the coupled nonlinear Schrödinger equations for the excimer and superfluid...
helium\textsuperscript{29–32} in three-dimensional space by employing the Crank–Nicolson method combined with the operator splitting technique.\textsuperscript{35–38} In this work, a 256 × 256 × 256 Cartesian grid with a 1.0 bohr spatial step length was employed for both grids representing the liquid order parameter and the He\textsuperscript{2} zero-point wave function. The ground state solution for the system was obtained by propagating the equations in imaginary time.\textsuperscript{35,36} A time step of 20 fs (5 fs for real time dynamics calculations) and 200 iterations were sufficient to reach convergence. This criterion was selected by observing the changes in both the liquid density around the excimer as well as the evolution of the OT energy density.

The linear dipolar fluorescence spectrum between two states, e.g., He\textsuperscript{2} \textsuperscript{3}d → \textsuperscript{3}b\textsubscript{1}, can be obtained from the time-dependent response of first order polarization, \( P^{(1)}(t) \), through Fourier transformation.\textsuperscript{39} Unfortunately, this function depends on the true many-body wave function of the helium bath and therefore it cannot be directly obtained from OT-DFT. In this work, we have employed the approach developed in our earlier work\textsuperscript{18,40,41}, which allows approximate evaluation of first order polarization at excitation angular frequency \( \omega \):

\[
P^{(1)}(t) \propto i \int_0^t \exp \left( -\frac{i}{\hbar} \int_0^t E_{\text{ext}}(t') \, dt'' - i \omega t' \right) \, dt' + \text{CC}
\]

where CC stands for the complex conjugate of the preceding term and \( E_{\text{ext}}(t) \) is the energy gap determined by the excimer–bath interaction energies for the ground (g) and excited (e) electronic states:

\[
E_{\text{ext}}(t) = \int \int \rho_e'(R, 0) V_e(|R - r|) \rho_g'(r, 0) \, d^3r \, d^3R - \int \int \rho_e'(R, t) V_e(|R - r|) \rho_g'(r, t) \, d^3r \, d^3R
\]

where \( V_e \) is the excited state pair potential (e.g., He\textsuperscript{2} \textsuperscript{3}d–He), \( V_g \) is the ground state pair potential (e.g., He\textsuperscript{2} \textsuperscript{3}b–He), and \( \rho_{e/g} \) correspond to He\textsuperscript{2} and liquid helium densities around the excited and ground state excimer, respectively. Note that only the second term in eq 2, which requires real time propagation of the system, is responsible for dynamic line broadening.

For He\textsuperscript{2} \textsuperscript{3}d → \textsuperscript{3}b fluorescence, the experimental linewidths are only available at low pressures and hence the calculated lineshift is the most important quantity that can be compared directly with experiments. Eq 1 does not include electronic dephasing, which can be included phenomenologically by a decaying exponential function:\textsuperscript{41}

\[
P^{(1)}(t) = e^{-t/\tau} P^{(1)}(t)
\]

Here \( \tau \) represents the dephasing time constant. In practice, the value of \( \tau \) controls the time that the final state dynamics contributes to the line shape. For small values of \( \tau \), a structureless broad line is obtained whereas discrete lines may appear with larger \( \tau \) values.\textsuperscript{40,41} The fluorescence spectrum is finally obtained by Fourier transforming eq 3. To simplify eq 1, we have approximated the fluorescence spectrum by calculation of the power spectrum of eq 2. Finally, we note that all the triatomic state potentials correlated with the \textsuperscript{3}b state appear essentially flat at distances relevant to \textsuperscript{3}d state excimer solution. According to eq 2, only the upper state potential (i.e., He\textsuperscript{2} \textsuperscript{3}d–He) contributes to the fluorescence band shift provided that \( \tau \) remains sufficiently small. For long \( \tau \), the bound regions of He\textsuperscript{2} \textsuperscript{3}b–He potentials could provide additional line broadening and shift.

**RESULTS AND DISCUSSION**

He\textsuperscript{2}–He Pair Potentials. The triplet state eigenenergies of an isolated He\textsuperscript{2} excimer are perturbed by the presence of an additional helium atom, as demonstrated in Figures 1 and 2.

![Figure 1.](image1.png)  
**Figure 1.** Overview of low-lying \( ^3 \text{A}_1 \) states of He\textsuperscript{2}–He in the \( C_{2v} \) point group. The He\textsuperscript{2} excimer (bond length fixed at 1.05 Å) was oriented as indicated: aligned (linear) or perpendicular (T) with respect to the asymptotically impinging He\textsuperscript{2} \textsuperscript{3}d atom. The data were obtained from EOM-CC3 calculation employing basis set *.

![Figure 2.](image2.png)  
**Figure 2.** Overview of low-lying \( ^3 \text{B}_1 \) states of He\textsuperscript{2}–He in the \( C_{2v} \) point group. The He\textsuperscript{2} excimer (bond length fixed at 1.05 Å) was oriented as indicated: aligned (linear) or perpendicular (T) with respect to the asymptotically impinging He\textsuperscript{2} \textsuperscript{3}d atom. For completeness, a second \textsuperscript{3}b state in the T-orientation is shown, which possesses an \( A_1 \) symmetry (dotted line). The data were calculated using EOM-CC3 calculation employing basis set *.

The excimer–atom potential profiles can be qualitatively rationalized by the electron density of the Rydberg orbital.\textsuperscript{42} The symmetry of the valence states of He\textsuperscript{2}–He in the \( C_{2v} \) point group are determined by the symmetry of the Rydberg orbital on the excimer. This holds, since the unpaired valence electron in He\textsuperscript{2} \textsuperscript{3}d exists on the \( 1\sigma_g \) orbital, which belongs to the \( A_1 \) irreducible representation in \( C_{2v} \). As such, the symmetry of the Rydberg electron in He\textsuperscript{2} \textsuperscript{3}d denotes the symmetry of the molecule due to direct product rules and the fact that the third, impinging, He atom is a complete shell, i.e., the impinging atom itself has an \( A_1 \) symmetry.

The following discussion delineates the triatomic, He\textsuperscript{2}–He potentials, shown in Figures 1 and 2, with respect to the
corresponding excimer states. As the $^3\text{a}$ Rydberg orbital is nearly isotropic, only minor differences are present in the respective pair potentials between the linear and T-orientations (cf. Figure 3). As previously determined, the linear potential is slightly more repulsive than the T-potential. Although the $^3\text{a}$ state potentials are largely repulsive, they exhibit a small long-range minimum, ca. 1 cm$^{-1}$, situated around 7.3 Å (see Table 2). The calculated minimum distances of the $^3\text{a}$-state are shorter by more than 0.5 Å and have deeper binding of up to more than 0.5 cm$^{-1}$.

Figure 3. He$^\text{fi}$$^3\text{a}$—He potentials from EOM-CC3/basis ** calculation. Linear and T-orientations are represented by (**) and (**), respectively.

Table 2. Survey of He$^\text{fi}$ $^3\text{a}$—He Triplet State Potentials in C$_2\text{v}$ for the Linear (L) and T-Orientations (T)*

<table>
<thead>
<tr>
<th>state</th>
<th>sym</th>
<th>$r_1$ (Å)</th>
<th>$D_1$ (cm$^{-1}$)</th>
<th>$r_2$ (Å)</th>
<th>$E_b$ (cm$^{-1}$)</th>
<th>$D'_2$ (cm$^{-1}$)</th>
<th>$E$ (10$^5$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\text{d}$ L</td>
<td>A$_1$</td>
<td>2.1</td>
<td>725</td>
<td>5.8</td>
<td>94.9</td>
<td>15.0</td>
<td>0.07</td>
</tr>
<tr>
<td>$^3\text{d}$ T</td>
<td>B$_1$</td>
<td>2.4</td>
<td>394</td>
<td>5.8</td>
<td>79.4</td>
<td>15.0</td>
<td>0.05</td>
</tr>
<tr>
<td>$^3\text{c}$ L</td>
<td>A$_1$</td>
<td>1.9</td>
<td>980</td>
<td>2.5</td>
<td>2805</td>
<td>10.0</td>
<td>0.43</td>
</tr>
<tr>
<td>$^3\text{c}$ T</td>
<td>A$_1$</td>
<td>2.4</td>
<td>395</td>
<td>2.5</td>
<td>2805</td>
<td>10.0</td>
<td>0.43</td>
</tr>
<tr>
<td>$^3\text{b}$ L</td>
<td>B$_1$</td>
<td>2.2</td>
<td>594</td>
<td>2.5</td>
<td>2805</td>
<td>10.0</td>
<td>0.43</td>
</tr>
<tr>
<td>$^3\text{b}$ T</td>
<td>A$_2$</td>
<td>2.1</td>
<td>535</td>
<td>2.5</td>
<td>2805</td>
<td>10.0</td>
<td>0.43</td>
</tr>
<tr>
<td>$^3\text{a}$ L</td>
<td>A$_1$</td>
<td>7.4</td>
<td>0.98</td>
<td>2.5</td>
<td>2805</td>
<td>10.0</td>
<td>0.43</td>
</tr>
<tr>
<td>$^3\text{a}$ T</td>
<td>B$_1$</td>
<td>7.2</td>
<td>0.93</td>
<td>2.5</td>
<td>2805</td>
<td>10.0</td>
<td>0.43</td>
</tr>
</tbody>
</table>

*Potentials calculated by EOM-CC3 with basis ** except for italicized values indicating potentials calculated with basis *. Terms $r_2$ and $D_2$ denote equilibrium separation and binding energy respectively, and $r_2$ and $E_b$ indicate the barrier position and height with respect to the asymptote. The prime values: $r_{2}'$ and $D_{2}'$ pertain to a second minima, and the excitation energy, $E$, is the excimer excitation energy calculated with respect to the asymptotic limit of the $^3\text{a}$ state.

decreased electron density along the nodal plane of the Rydberg molecular orbital “belt,” i.e., the xz-plane in Figure 4a, results in decreased short-range repulsion between the excimer and the atom. Thus, the belt approaches encounter reduced repulsion with respect to the “head-on”, T-orientation, approach along the y-axis. These belt state potentials also contain deep, short-range binding, due to deshielding of the He$_2$ excimer core, at 2.1 and 2.2 Å with binding energies of 535 and 594 cm$^{-1}$, respectively. The “head-on” T-orientation with B$_1$ symmetry is largely repulsive, with a shallow binding of less than 1 cm$^{-1}$ at 8.2 Å. The $^3\text{b}$ belt states did not possess any equivalent long-range minima.

As with the case of the $^3\text{b}$ state, the $^3\text{c}$ ($^3\Sigma^+_u$) state is also defined by a Rydberg HOMO that resembles an atomic p-orbital, Figure 4b. The potential defined by the linear excimer orientation (see Figure 1), contains a very shallow minimum of 0.4 cm$^{-1}$ at 10 Å and a gradual repulsive wall starting at ca. 5 Å, which is similar in appearance to the “head-on”, T-orientation of the B$_2$, $^3\text{b}$ state potential. Proceeding inward on the linear $^3\text{c}$ potential, a deep short-range pocket exists at 1.9 Å due to the presence of a radial node, which is visible in Figure 4b. The outer and inner minima are separated by a 2805 cm$^{-1}$ energy barrier centered at 2.5 Å. As shown in Figure 1, the T-orientation of the $^3\text{c}$ state possesses the general form of the “belt” potentials of the $^3\text{b}$ state and has a minimum of 395 cm$^{-1}$.

Figure 4. HOMO canonical molecular Rydberg orbitals of He$^\text{fi}$ in the $^3\text{b}$ - and $^3\text{c}$-states, placed (a) left and (b) right, respectively. The position of the nuclei, represented as filled circles vertically centered about the origin (along z-axis), are colored white for the b-state and black for the c-state. See also refs 24 and 42 for natural Rydberg orbital and electron density contour plots of additional states.
at 2.4 Å, which is bound by a hard repulsive wall at short distances.

The \( ^3d \) state possesses a nearly isotropic s-type Rydberg orbital. An extremely small long-range binding was calculated at 15 Å of 0.07 and 0.05 cm\(^{-1}\) for the T- and linear orientations, respectively. More prominently, a radial node in the HOMO results in an energy barrier at 5.8 Å of 79 and 95 cm\(^{-1}\) for the linear and T-orientations, respectively. A deep pocket exists for both orientations between the barrier and the hard inner repulsive wall. The inner minimum of the linear geometry is located at 2.1 Å with a depth of 725 cm\(^{-1}\) and for the geometries 2.4 Å and 394 cm\(^{-1}\). The He\(^2\)\(^*\)(\( ^3d \))–He potential, which is mainly responsible for the experimentally observed \( ^3d \) \( \rightarrow \) \( ^3b \) fluorescence band shift (see Figure 5), appears similar to

![Image](image_url)

**Figure 5.** Experimentally observed pressure dependence of He\(^2\)\(^*\) excimer \( ^3d \) \( \rightarrow \) \( ^3b \) fluorescence band in dense helium at 4.5 K. Notice the pronounced blue shift and the gradual disappearance of the rotational structure starting at 0.1 MPa. The applied current was 0.3 \( \mu \text{A} \) and the following discharge voltages correspond to the pressures cited in the legend: \( P = 0.1 \text{ MPa} \), \( V = -3.5 \text{ kV} \); \( P = 0.5 \text{ MPa} \), \( V = -5.8 \text{ kV} \); \( P = 1 \text{ MPa} \), \( V = -5.7 \text{ kV} \); \( P = 1.4 \text{ MPa} \), \( V = -5.8 \text{ kV} \); \( P = 1.6 \text{ MPa} \), \( V = 6 \text{ kV} \).

To complement this spectroscopic data, electron mobility between the electrodes was also determined to assess the relative density of the system. As the previously cited studies have shown, the mobility decreases rapidly when transitioning from the gas to the liquid phase. Figure 7 displays the observed fluorescence spectra and discharge currents of both He\(^2\)\(^*\) and He* obtained at two relatively similar pressures: 5.1 and 5.5 bar, which are both located in the supercritical fluid region of the phase diagram. Note that the current is directly proportional to the electron mobility between the two electrodes.

![Image](image_url)

**Figure 6.** Magnified view of He\(^2\)\(^*\)(\( ^3d \))–He potentials from CC3-EOM/basis \(*\)* calculations. Both linear (\( ^\) and T-shape (\( \square \)) approaches are plotted. For comparison, the He*\(^*\)(3s)–He potential (\( \times \)) from ref 18 is also shown.

![Image](image_url)

**Figure 7.** Fluorescence band shift for He\(^2\)\(^*\)(\( ^3d \)) \( \rightarrow \) \( ^3b \) at ca. 640 nm (left) and He* 3s \( (^5S) \rightarrow 2p \ (^{1P}) \) at 706 nm (right) at 14 K. The solid lines correspond to a pressure of 5.1 bar, 30 \( \mu \text{A} \) current, and a discharge voltage of \(-2.635 \text{ kV}\). The dotted lines correspond to a pressure of 5.5 bar, 2 \( \mu \text{A} \) current and a discharge voltage of \(-3.445 \text{ kV}\).
However, the existing reference data shows a rather weak dependence of density on pressure near this \((P, T)\) point, which cannot alone account for the observed rapid changes. By solely considering the \(\text{He}^*_n\) fluorescence spectrum, one could suggest that the local surrounding of the excimer is not in complete thermodynamic equilibrium, which could cause more pronounced variations in the local density as a function of pressure and the experimentally observed abrupt change in the blue shift of the fluorescence band. However, the electron mobility is determined by helium present throughout in the region between the two electrodes, and hence it is not sensitive to such local density variations. Therefore, a more plausible explanation for this behavior is the formation of a localized state ("pre-bubble state"),\(^{24,31}\) which takes place at the same \((P, T)\) for both \(\text{He}^*_n\) and the electron.\(^{24,31}\) In this case, \(\text{He}^*_n\) is either not yet localized or the fluorescence shift cannot be observed, as the \(\text{He}^*_n(3s)\)–\(\text{He}\) potential has more abrupt long-range behavior than the corresponding \(\text{He}^*_n\) potential (see Figure 6). Note that the volume occupied by \(\text{He}^*_n(3s)\) \((R = 12.6 \, \text{Å} \text{ at } 4.5 \, \text{K})\) in liquid helium is smaller than both \(\text{He}^*_n(3d)\) \((R = 13.2 \, \text{Å} \text{ at } 4.5 \, \text{K})\) and the electron \((R \approx 15.2 \, \text{Å} \text{ at } 0 \, \text{K})\) at 0.5 MPa pressure.\(^{24,31}\) Provided that the order of this size estimate is also valid in less dense helium, \(\text{He}^*_n\) should not localize as easily as the other two species.

**OT-DFT Lineshape Calculations.** To model the pressure induced broadening of \(\text{He}^*_n(3d) \rightarrow (b)\) fluorescence spectrum, the corresponding pair potentials between the excimer and ground state helium atom are required. A summary of the previously discussed \textit{ab initio} potentials in the region relevant for the fluorescence line broadening are shown in Figures 6 and 8. The static liquid density profiles around freely rotating \(3d\) state \(\text{He}^*_n\) excimer, i.e., the spherically averaged potential, from the OT-DFT calculations at 3.0 K are shown in Figure 9 at the specified pressures. To mimic the conditions of the experiment at 4.5 K, bulk liquid densities corresponding to this temperature were employed in the calculations.\(^{32}\)

The bubble radii, as defined by the half-bulk-density position, vary between 12.7 Å (0.1 MPa) and 10.8 Å (2.4 MPa) at 4.5 K, depending on the pressure. This implies that the \(3d\) state excimer bubble is much less compressible than the electron bubble.\(^{31}\) The oscillatory liquid density structure appearing at the gas–liquid interface is related to the \(\text{He}^*_n(3d)\)–\(\text{He}\) correlations present in the OT functional. Note that the inclusion of the OT kinetic energy correlation functional would slightly increase these interfacial oscillations. While such oscillations do not influence the spectroscopic observables, they can, for example, increase the apparent hydrodynamic size of the excimer when it collides with the thermal excitations of the liquid. Furthermore, in the superfluid phase, the period of these oscillations correlates with the roton minimum of the dispersion relation, which suggests that they could be interpreted as localized rotons at the solvation bubble interface. At higher pressures, these oscillations become more pronounced due to the increasingly repulsive potential pressing against the liquid. Note that a presence of a bound external potential would also result in similar oscillatory liquid structure.

The solvation energy of the \(3d\) state excimer depends on the external pressure through the variation of the liquid density around it. To first approximation, the fluorescence band shift is dictated by the difference between the solvation energies of the initial \((3d)\) and final \((b)\) states evaluated with the initial state liquid density around the excimer. According to eq 2, the rapid resolution dynamics toward the final state equilibrium configuration may also contribute to the dynamic lineshift as well as the overall line shape. However, based on the initial liquid density around the \(3d\) state, the interaction with the \(b\) state is negligible as evidenced by the calculated \textit{ab initio} potentials (compare potentials in Figures 6 and 8). Thus, the fluorescence band shift should track the solvation energy of the initial state as a function of pressure. Since the initial \(3d\) state is purely repulsive, a monotonic blue shift of the fluorescence band position is expected with increasing pressure. This general trend is reflected by the experimental data shown in Figure 10.

![Figure 9. OT-DFT liquid helium density profiles around \(\text{He}^*_n\) excimer in the \(3d\)-state at 4.5 K calculated with the CC3-EOM/basis ** potentials. Note that the OT-DFT functional is evaluated at 3.0 K but the liquid density corresponding to 4.5 K is employed in the calculations. An orientationally averaged \(\text{He}^*_n(3d)\)–\(\text{He}\) potential, cf. Figure 6, is shown for reference: dotted line and right ordinate.](image-url)
calculations with experiments. Within the typically applicable range, $r = 100–300$ fs, the calculated $^3d \rightarrow ^3b$ band blue shift appeared independent of the dephasing time (see eq 3). Furthermore, the full width at half-maximum of the excimer zero-point density distribution was approximately 1 Å, which had no impact on the calculated fluorescence line shift. The results from the calculated rotational band shifts are shown in Figure 10, along with the experimental data obtained at 4.5 K. The calculations reproduce the general blue shift trend but shows some deviation that increases toward the higher pressures. This deviation appears similar to that observed previously for the pressure dependence of the atomic He*(3s) $\rightarrow$ He*(2p) transition. Since this pronounced blue shift is a direct consequence of the shallow long-range repulsion in the He*($^3d$)–He pair potential (cf. Figure 6), the observed difference may be ascribed to a limitation in the accuracy of the calculated repulsive interaction. Other possible sources include many body effects contributing to the overall excimer–liquid interaction and the difference in the temperatures used in OT-DFT functional (3.0 K) vs experiment (4.5 K). Note that the thermal OT-DFT model has not yet been extended beyond the applied temperature in this work. To summarize, the present spectroscopic data can be used to directly interrogate the $^3d$ state excimer solvation energy as a function of pressure and temperature. Within the applied pressure range at 4.5 K, both He* and He*18 emit from bubble states, which require sufficiently high helium density to form. The good agreement observed between the OT-DFT simulations and the experimental fluorescence data suggests that both He* and He* emit from a liquid environment at 4.5 K ($P > 0.15$ MPa) rather than directly from the hot gaseous discharge zone.

Finally, we note the possibility of filling the bound short-range pocket of the $^3d$ state potential with helium (see Figures 1 and 2). If the applied pressure or temperature would be sufficiently high, the surrounding ground state helium atoms could reach over the long-range barrier (see Figure 6) to fill the pocket. Since this part of the He*($^3d$)–He potential is strongly bound and the lower $^3b$ state is no longer flat in that region, the fluorescence band corresponding to this transition would experience very strong red shift and broadening. From the experimental point of view, this would effectively lead to quenching of the fluorescence signal. By including the high-density cutoff functional in OT-DFT the maximum number of helium atoms that can localize in the well around a freely rotating $^3d$ state excimer is approximately 17. On the basis of the discussion above, the present experiments carried out at 4.5 K observe the He* $^3d \rightarrow ^3b$ fluorescence band that originates exclusively from excimers that are solvated in the bulk portion of the liquid. This is a consequence of the fluorescence quenching that takes place in the high temperature discharge zone where high kinetic energy helium atoms are able to cross over the $^3d$ state barrier. For this reason, the current experiments observe only the minority of excimers that are formed outside the discharge zone in the bulk liquid. Note that a similar situation appears for the fluorescence that originates from the atomic He*(3s) state (cf. Figure 6)). To conclude, due to the high temperature and pressure in the discharge zone, fluorescence originating from both He* ($^3d$) and He* (3s) states become effectively quenched. This implies that spectroscopic experiments involving these initial electronic states can only be used to probe the state of the surrounding dense helium rather than the discharge zone itself. The electron impact process responsible for the formation of He* and He* species outside the discharge zone is discussed in detail in ref 18.

CONCLUSIONS

We have computed the interaction of molecular excimers, He*18, in its various triplet electronic states with a ground state helium atom. The symmetry of these pair potentials is dictated by the Rydberg electron density due to the Pauli repulsion with the closed shell He atom. When nodal planes are present in the Rydberg orbital, the charge–induced dipole interaction with the exposed He* core produces deeply bound minima at short distances, which may result, for example, in fluorescence quenching when populated. Because of the long-range repulsive $^3d$ state potential, the experimentally observed He* ($^3d$) $\rightarrow$ He*($^3b$) fluorescence band at 4.5 K exhibits a similar spectral blue shift with increasing pressure as the previously studied atomic He*(3s) $\rightarrow$ He*(2p) line. The accuracy of the presented ab initio potentials was assessed by performing OT-DFT calculations to model the $^3d \rightarrow ^3b$ fluorescence line shift. The theory slightly overestimated the blue shift but, in general, produced satisfactory agreement with the experiments. The small difference may originate either from the application of a simplified theory to model the surrounding helium bath or the presence of reduced helium density around the excimers created by corona discharge. By combining both spectroscopic and mobility data, a transition from gas phase to localized bubble state was observed to take place at a temperature of 14 K and pressure of 0.5 MPa for both He* and the electron. The magnitude of the spectral shifts at 4.5 K indicate that observed He* molecules emit from dense helium (i.e., bulk liquid when $P > 0.15$ MPa) rather than the gaseous high temperature discharge zone. This rather surprising observation can be explained by fluorescence quenching in this zone where high kinetic energy helium atoms are able to penetrate the short-range bound pocket around the $^3d$ state. In general, this implies that spectroscopy involving the previously discussed electronic transitions can only be used to probe the state of the surrounding medium rather than the discharge zone itself.
**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b08412.

Tables 1–4, containing calculated triplet interaction potentials (PDF)

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Notes
The authors declare no competing financial interest.

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