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Theoretical investigation of the He–I₂(E3Πg) ion-pair state: *Ab initio* intermolecular potential and vibrational levels

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We present a theoretical study on the potential energy surface and vibrational bound states of the E electronic excited state of the HeI₂ van der Waals system. The interaction energies are computed using accurate *ab initio* methods and large basis sets. Relativistic small-core effective core potentials in conjunction with a quintuple-zeta quality basis set are employed for the heavy iodine atoms in multireference configuration interaction calculations for the 3A′ and 3A″ states. For the representation of the potential energy surface we used a general interpolation technique for constructing potential surfaces from *ab initio* data based on the reproducing kernel Hilbert space method. The surface presents global and local minima for T-shaped configurations with well-depths of 33.2 and 4.6 cm⁻¹, respectively. Vibrational energies and states are computed through variational quantum mechanical calculations. We found that the binding energy of the HeI₂(E) T-shaped isomer is 16.85 cm⁻¹, in excellent agreement with recent experimental measurements. In lieu of more experimental data we also report our predictions on higher vibrational levels and we analyze the influence of the underlying surface on them. This is the first attempt to represent the potential surface of such a highly excited electronic state of a van der Waals complex, and it demonstrates the capability of the *ab initio* technology to provide accurate results for carrying out reliable studies to model experimental data.

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I. INTRODUCTION

Research on van der Waals (vdW) complexes has a long and rich history mainly due to their protagonist role in the study of energy transfer mechanisms and weak intermolecular forces.1 Progress in both experimental techniques and computational methods during the last years has contributed to an improved understanding of these “simple” molecular entities (see Refs. 2–8 and references therein).

Rare gas (Rg) dihalogen systems (XY) represent an interesting class of vdW complexes with the He–I₂ system being the first to be studied experimentally by the Levy group through laser excited fluorescence spectroscopy as early as 1976.9 At that time the He–I₂(X1Σg⁻) system was predicted to have a C₂v (T-shaped) configuration characterized by a perpendicular distance R₀ = 4.47 ± 0.13 Å (Ref. 10) and a binding energy, D₀, initially estimated at 18.8 ± 0.6 cm⁻¹ (Ref. 11) but later revised to D₀ = 17.6 ± 1.0 cm⁻¹.12 The most recent experimental binding energy, reported by the Loomis group,13 amounts to 16.6 ± 0.6 cm⁻¹ for the C₂v conformer and 16.3 ± 0.6 cm⁻¹ for the linear conformer. The double minimum topology of the potential energy surface (PES), an interesting feature per se, was a known experimental fact from the studies on Ar–I₂ (Refs. 14 and 15) and Ne–I₂ (Ref. 16) by the groups of Klemperer and Heaven. From a theoretical perspective, *ab initio* high level calculations have also predicted the existence of a double-minimum topology for such systems.17–21 In the light of the latest experimental data by the Loomis group,13 we recently revisited the He–I₂(X) vdW complex.22 Our estimates of 15.72 cm⁻¹ (linear) and 15.51 cm⁻¹ (T-shaped) for the binding energy are very close to each other and to the most recent experimental values.

In all these experimental studies10–13 electronic excited states of the HeI₂ are involved, such as the B(3Πg⁻) and E(3Πg+) states, thus for any direct comparison between theoretical simulations and experimental measurements the knowledge of the underlying intermolecular interactions is mandatory. Information on these excited electronic states of such complexes based on *ab initio* computations is rather limited, and only recently calculations on the B state of some vdW systems, such as HCl₂, HeBr₂, NeCl₂, and HeI₂, have been reported.23–26

Concerning the He–I₂(B) system, we reported PES based on high level variational and coupled-cluster (CC) calculations that incorporate scalar relativity, while the spin–orbit (SO) coupling effects were considered indirectly by averaging the 3A′ and 3A″ surfaces.26 A C₂v structure was found, bound by 12.33 cm⁻¹ with a vibrationally averaged R₀ = 4.58 Å, in excellent agreement with the corresponding experimental findings of 12.8 ± 0.6 cm⁻¹ and 4.79 ± 0.22 Å.13

Unfortunately, no theoretical results are available today for higher excited electronic states of either HeI₂ or any other similar Rg-XY vdW complex. As we mentioned above the E state of He–I₂(E 0′⁺) vdW complex is involved in the experimental setup, although not experimentally studied until
The electronic configuration of the ground $2p$ state of the I atom is $[\text{Ar}]3d^{10}4s^24p^64d^{10}5s^25p^5$. The $[\text{Ar}+3d^{10}]$ electrons are described by the relativistic ECP28MD effective core potential,\textsuperscript{33} while for the $4s^24p^64d^{10}5s^25p^5$ electrons the aug-cc-pVQZ-PP basis set\textsuperscript{13} is employed generally contracted to [8s8p6d4f3g2h]. The accuracy of small-core ECP and associated basis sets for the $I_2$ states correlating to the $I^3(P)+I^3(P)$, $I^3(P)+I^2(P)$, $I^2(P)+I^2(P)$, and $I^2(P)+I^1(S)$ asymptotes have been recently investigated.\textsuperscript{26,28} For the He atom, the aug-cc-pVQZ basis set is used generally contracted to [5s4p3d2f].\textsuperscript{34} Overall, the description of the triatomic system is achieved through $139 \times 2 + 46 = 324$ spherical Gaussian functions.

The approach of the He ($1^S$) atom to the $I_2(3^3\Pi_1)$ state results in two PES of $3^3A'$ and $3^3A''$ symmetry, the Renner–Teller companions of the He$I_2(3^3\Pi)$ linear configuration. Jacobi coordinates $(r, R, \theta)$ are employed for the description of the PES of the He$I_2$ complex, where $R$ is the intermolecular distance of the He atom from the center of mass of $I_2$, $r$ is the bond length of iodine, and $\theta$ is the angle defined by the $R$ and $r$ vectors. We constructed potential energy curves of both $3^3A'$ and $3^3A''$ symmetry for $\theta$ angles ranging from $\theta = 0^\circ$ (C$_{\infty h}$) to $\theta = 90^\circ$ (C$_{2v}$) with a step of $10^\circ$. At each $\theta$ value we calculated the interaction energy at $R$ distances ranging from 3 to 30 Å. The $(r-I)$ interatomic distance has been kept frozen at its equilibrium $r_e = 3.5931$ Å value.\textsuperscript{28} The total grid in $r \times R \times \theta$ ($= r_e \times [3, 30 \text{ Å}] \times [0^\circ, 90^\circ]$) consists in calculating the interaction energy of $\sim 1300$ points in the configuration space.

Due to the multireference equilibrium character of the $I_2$ E state\textsuperscript{28} we have employed a complete active space self-consistent field (CASSCF) zeroth order wavefunction that describes properly the triatomic system at every point of its configuration space. Dynamical correlation was extracted by single and double replacements out of the reference wavefunction (CASSCF+1+2 = MRCI), while the internally contraction scheme as implemented in the MOLPRO 2006 package\textsuperscript{35} was used in order to keep the CI spaces at manageable levels. The He–$I_2(E)$ $3^3A'$ corresponds to the 6th root of the MRCI matrix, while the $3^3A''$ one to its 5th root. This is due to the fact that there are six lower lying molecular states resulting from the interaction of He with $I_2$ states of triplet spin character originating from the ground state atomic I fragments, i.e., $3(^1\Sigma_u^+, ^1\Sigma_g-, ^3\Pi_g, ^3\Pi_u, ^1\Delta)$, that under C$_2$ symmetry split into five $3^3A'$ and four $3^3A''$ states. Size non-extensivity errors were accounted for by the multireference analog of the Davidson correction, denoted as +Q in what follows.\textsuperscript{36} The active space of our zeroth order wavefunction contains, in addition to the plain valence shell, four orbitals of Rydberg character. The resulting MRCI space contains $23.7 \times 10^6$ configuration functions (CF) internally contracted to $\approx 136 \times 10^6$ CF under C$_2$ symmetry restrictions. Size non-extensivity errors amount to $35(2)\text{ mE}_{\text{h}}$ at the MRCI(+Q) level of theory.

In the presence of SO coupling, the two $3^3A'$ and $3^3A''$ states of He–$I_2(E)$ are mixed. The SO splitting of the three $I_2(E^3\Pi_1)$ states, namely, $3^3\Pi_g$, $3^3\Pi_u$, and $3^1\Pi_u$, is $3–4$ orders of magnitude larger than the minute difference of the $3^3A'$ and $3^3A''$ states. Thus, when these states are interacting with a He atom the SO coupling effect can be approximated by the semi-sum of the adiabatic $3^3A'$ and $3^3A''$ potentials, their difference being negligible. Although no explicit SO calcul-
lations have been performed here for He–I2(E), one can see based on MRCI and MRCI+SO results of the diatomic I2 and He–I2(B) molecules,26,28 as well as on previous studies of similar triatomic complexes,23,37–41 that this is indeed an excellent approximation. Therefore, the interaction potential for the E3Π0′ state approximately modified by spin–orbit coupling is given by the average of the 3A′ and 3A″ potentials, 

\[ V_E = \frac{V_{3A'} + V_{3A''}}{2}. \]

### B. Representation of the potential energy surface

For the representation of the PES, we used an interpolation process within the reproducing kernel space (RKHS) method by Ho and Rabitz.45 It consists in expressing the interaction energy as

\[ V_E(R, \theta; r_e) = \sum_{m=1}^{N_m} \sum_{j=1}^{N_j} v_{ij} q_1^m(R_i, R) q_2(y_j, y), \quad (1) \]

where \( y = \cos \theta \), \( N_m \) and \( N_j \) is the number of the calculated \( ab \) \textit{initio} points in \( R \) and \( \theta \) coordinates, respectively. The \( q_1^m \) and \( q_2 \) are the one-dimensional reproducing kernel functions for the distance-like, \( R \), and angle-like, \( \theta \), variables, respectively, given by

\[ q_1^m(x, x') = n^2 x_{>}(m+1) B(m+1, n) \]

\[ \times F_1 \left( -n + 1, m + 1; n + m + 1; \frac{x}{x_{<}} \right), \quad (2) \]

\[ q_2(y, y') = \sum_{l} \frac{(2l + 1)}{2} P_l(y) P_l(y') \quad (3) \]

with, \( x_{<} \) and \( x_{>} \) are the largest and smallest value of the \( x \) and \( x' \), respectively. The superscripts \( n \) and \( m \) refer to the order of smoothness of the function, and its asymptotic behavior at large distances, \( B \) is the beta function, \( i \) \( F_1 \) is the Gauss hyper-geometric function. The \( P_l \) are the Legendre polynomials with \( l = 0, 2, 4, 6, 8, 10, 12, 14, 16, \) and 18 in the present case. The linear coefficients, \( v_{ij} \), are obtained as solutions of Eq. (1), where \( V(R_i, \theta_j; r_e) \) is the average value of the calculated MRCI+Q interaction energies of \( 3A' \) and \( 3A'' \) symmetry at the \( (R_i, \theta_j; r_e) \) grid point, with \( i = 1-N_m \) and \( j = 1-N_j \).

### C. Bound state calculations

As it has already stated the \( 3A' \) and \( 3A'' \) states are coupled via the SO coupling operator, and an effective Hamiltonian including the SO term should have been employed (see Refs. 37–39) for dynamics calculations. However, in the atom-diatom case, and following the formalism described in Refs. 37 and 38 for a diatom in the \( 3 \Pi_{0} \) state, the matrix elements of the interaction potential can be represented by the semi-sum of the adiabatic potentials, and a spin-free closed-shell-type rovibrational Hamiltonian is employed here, as in previous studies of such systems,13,23,26,46 to study the nuclear dynamics. The two-dimensional operator in the Jacobi coordinate system reads

\[ \hat{H} = -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2\mu_1 R^2} + \frac{\hbar^2}{2\mu_2 r_e^2} + V_E(R, \theta; r_e), \quad (4) \]

where, \( \hat{I} \) and \( \hat{J} \) are the angular momentum operators associated with the vectors \( R \) and \( r_e \), respectively, leading to a total angular momentum \( \hat{J} = \hat{l} + \hat{j} \), \( \frac{1}{\mu_1} = \frac{1}{m_{He}} \), \( \mu_1 = \frac{1}{m_I} + \frac{1}{m_e} \), \( m_{He} = 4.002600 \), \( m_I = 126.904473 \) amu, and \( V_E(R, \theta; r_e) \) is given by Eq. (1). The \( r(1-I) \) interatomic distance is fixed at the equilibrium value of \( r_e = 3.5931 \) Å. The bound vDW levels and corresponding wavefunctions are calculated variationally by diagonalizing the two-dimensional Hamiltonian matrix.

As previously done in similar vDW systems,22,43,44 the corresponding Hamiltonian (see Eq. (4)) is represented in a space composed of products of radial and angular basis functions. For the \( R \) coordinate, a basis set of 160 discrete variable representation functions over the range \( 3 \leq R \leq 15 \) Å, is used based on the particle in a box eigenfunctions,45 while for the \( \theta \) coordinate the orthonormalized Legendre polynomials \( P_j(\cos \theta) \) with \( j \) values ranging from 0 to 79, for the diatomic rotation are employed. In this way, a convergence of 0.001 cm\(^{-1}\) is achieved in bound state calculations for the ten lowest vDW vibrational \((J = 0)\) levels of He–I2(E).

### III. RESULTS AND DISCUSSION

In Table I, we list total energies, equilibrium distances, well-depths with respect to the corresponding dissociation channels and adiabatic excitation energies for the ground X, valence B and ion-pair E states. At the MRCI+Q level of theory, the E state is located at 44482 cm\(^{-1}\) above the global potential minimum of the ground X state (as calculated at the CCSD(T) level). By comparing the \( T_E^{3} \) of HeI2 with the one of I2 at 41547 cm\(^{-1}\),28 we obtain a difference of 3025 cm\(^{-1}\) due to the different (CCSD(T) and MRCI+Q) methods employed here for the X and E states. Also from CCSD(T) calculations we estimated the excitation energy of the B state, \( T_B^{3} = 12534 \) cm\(^{-1}\). These values do not include the SO

<p>| TABLE I. Total energies ( E ) (in a.u.), equilibrium distances ( R_e ) (in Å), dissociation energies ( D_e ) (in cm(^{-1})), and energy gaps ( T ) (in cm(^{-1})) for the indicated electronic states of the HeI2 vDW complex. These values are obtained by CCSD(T), for the ground X and excited valence B states, and MRCI+Q, for the E state, calculations using the ECP28MDF/AVSZ-PP/AVQZ basis sets. For the B and E states we used the averaged value of the ( 3A' ) and ( 3A'' ) states. Comparison with previous calculations (in parenthesis) is also presented. |
|---|---|---|---|</p>
<table>
<thead>
<tr>
<th>Config.</th>
<th>X state</th>
<th>B state</th>
<th>E state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>T-shaped</td>
<td>T-shaped</td>
<td>T-shaped</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>( E )</td>
<td>( -592.61674 )</td>
<td>( -596.61670 )</td>
<td>( -592.55963 )</td>
</tr>
<tr>
<td>( R_e )</td>
<td>( 4.88 ) (4.83 ( a ))</td>
<td>( 3.83 ) (3.82 ( a ))</td>
<td>( 3.97 ) (3.96 ( b ))</td>
</tr>
<tr>
<td>( D_e )</td>
<td>( 37.75 ) (38.92 ( a ))</td>
<td>( 39.63 ) (39.48 ( b ))</td>
<td>( 33.14 )</td>
</tr>
<tr>
<td>( T_e )</td>
<td>0</td>
<td>( ... )</td>
<td>( 20.50 )</td>
</tr>
</tbody>
</table>

\( a \) From RCCSD(T)/ECP28MDF/AV(Q)/5Z-PP/AV(Q)/5Z calculations extrapolated at the CBS(85) limit, see Ref. 22.

\( b \) From UCCSD(T)/ECP28MDF/AVSZ-PP/AV(Q)/5Z calculations, see Ref. 26.
effects, of about 3065 cm\(^{-1}\) from previous MRCI+SO calculations of the B state.\(^{26}\)

Figure 1 shows the interaction potentials of \(^3A'\) and \(^3A''\) symmetries at the MRCI+Q level of theory, as a function of \(R\) for four selected \(\theta\) values, \(\theta = 0^\circ\) (\(C_{\infty v}\)), 30\(^\circ\), 60\(^\circ\), and \(\theta = 90^\circ\) (\(C_{2v}\)) (see left panel). In the right panel of Fig. 1, we display the minimum energy path for both \(^3A'\) and \(^3A''\) potentials as a function of \(\theta\) by optimizing at each angle the \(R\) coordinate.

In Figure 2, we present a valence bond diagram of the ion-pair \(\text{I}_2(\Pi_g)\) state interacting with the He atom at \(C_2\) symmetry. As the He atom approaches the \(\text{I}_2\) molecule, the system lowers its symmetry from \(D_{\infty h}\) to \(C_2\), and consequently the electronic wavefunction does not display the \(g\) symmetry anymore but at \(\theta = 90^\circ\) (\(C_{2v}\)) the two I atoms are identical. At linear configurations the two states are degenerate. When \(\theta \neq 90^\circ\) a charge asymmetry shows up between the two I atoms with the positive end located on the I atom that is closer to He. This leads to a more attractive interaction when the symmetry defining electron is perpendicular to the molecular plane, i.e., at \(^3A''\) symmetry and \(\theta \sim 70^\circ\) (see Fig. 1). As we move on at smaller angle values the interaction energy drops to \(\sim 10\) cm\(^{-1}\). In all cases, the interaction energy for the \(^3A''\) symmetry is larger than that for the \(^3A'\) one, since the symmetry defining electron is off the way of the He atom (see Fig. 1). In general, the two states show distinct topologies. For example, the \(^3A'\) has a minimum for the T-shaped configuration with a well-depth of 33.4 cm\(^{-1}\), and two shallow ones around 25\(^\circ\) and 155\(^\circ\), respectively, at an energy of \(-12.9\) cm\(^{-1}\), while the \(^3A''\) one has a symmetric double minimum at 70\(^\circ\) and 110\(^\circ\) with well-depths of 42.0 cm\(^{-1}\), while the T-shaped structure at \(-32.9\) cm\(^{-1}\) corresponds to a saddle point connecting them. A common feature of both states is the presence of a local minimum at all angles and at large \(R\) distances (see Fig. 1, right panel). The computed MRCI and MRCI+Q interaction energies for the \(^3A'\) and \(^3A''\) states of the \(\text{HeI}_2(\Sigma)\) for each \(\theta\) and \(R\) values are listed in the supplementary material.\(^{46}\)

In Fig. 1 (see right panel), we also plot the minimum energy path of their averaged value, \(\frac{1}{2}(A' + A'')\). One can see that the T-shaped configuration is the global minimum with \(D_r = 33.2\) cm\(^{-1}\), while the linear one at energy of \(-11.2\) cm\(^{-1}\) is a saddle point. Further, we should mention a rather wide plateau for angles between 25\(^\circ\) and 60\(^\circ\) that reflects the region of major differences between the two states.

Given the complicated topology, with the presence of multiple minima along the \(R\) coordinate, the representation of the PES using an analytical form, such as in the previous studies of similar vdW clusters, is not a straightforward task. Therefore, we consider that a more efficient way for constructing a smooth potential surface from the \textit{ab initio} data could be to employ the general interpolation method based on the RKHS and the inverse problem theory,\(^{42}\) as described above (see Sec. II B).

In Figure 3, we present a three-dimensional plot of the RKHS PES, Eq. (1), \(V(R, \theta; r_e = 3.5931 \text{ Å})\) in the \((\theta, R)\) plane, while in Figs. 4 and 5 we display the minimum energy path along the \(\theta\) coordinate, and the potential curves at the indicated \(\theta\) values as a function of the distance \(R\), respectively. In Table II, we list the main characteristics of the present surface, and we compare them with the ones available from the DIM-PT1 (diatomics-in-molecule first-order perturbation theory) approach.\(^{32}\) The MRCI+Q/RKHS PES predicts the global minimum at an energy of \(-33.18\) cm\(^{-1}\) with \(R = 4.10\) Å and \(\theta = 90^\circ\). One can see that both MRCI+Q

FIG. 1. MRCI+Q interaction energies of the \(^3A'\) (dashed lines) and \(^3A''\) (solid lines) states as a function of \(R\) at the indicated \(\theta\) angles (left panel), and MRCI+Q minimum energy path of \(^3A'\), \(^3A''\) and their averaged values as a function of \(\theta\) (right panel).

FIG. 2. Schematic valence bond description of the He...I\(_2(\Pi_g)\) system.
and DIM-PT1 surfaces predict the global minimum at a T-shaped configuration, with the linear geometry corresponding to a saddle point. However, the DIM-PT1 PES clearly overestimates the well-depth of the global minimum by ~20 cm⁻¹, while the energy of the linear saddle point differences by only 3 cm⁻¹.

The major new feature of the MRCI+Q PES (see Fig. 4), as compared to the previous ab initio PESs of the X and B HeI₂ states, is the existence of local minima at 7.7 Å (θ = 90°) and at 9.3 Å (θ = 0°) at −4.6 cm⁻¹ and −3.7 cm⁻¹, respectively. The barrier between the global and local minima are at R = 6.6 Å and energy of −3.9 cm⁻¹, and R = 7.8 Å and energy of −2.3 cm⁻¹ for the T-shaped and linear configurations, respectively. We should mention that this shallow minimum at large R values, between 8.0 and 9.5 Å with energies ranging from −5.5 to −3.5 cm⁻¹, is present at all θ values for both 3A' and 3A'' symmetries (see Fig. 1). Its existence should be due to the electronic ion-pair character of the I₂ E state since it is absent in both the X and B PES of the He–I₂ vdW complex. As it can be seen in Figs. 3 and 4, the surface presents a plateau for angles between 30° and 60°, showing a larger anisotropy around the T-shaped well as compared to the PESs of the X and B states of this complex.

The accuracy of the RKHS interpolation is checked by comparing with additional MRCI+Q ab initio points not included in the interpolation scheme. In Table III, we list for some selected configurations of them along the minimum energy path, the RKHS potential value, together with the MRCI+Q interaction energy and the difference between them. In total, we obtained an averaged deviation of 0.1 cm⁻¹ for the RKHS PES with respect to the MRCI+Q energies.

Using the RKHS PES, we performed nuclear bound state calculations, as described in Sec. II C. The energies of the ten lowest vibrational levels of He–I₂(E) vdW complex are listed in Table IV, while their corresponding angular and radial distributions are displayed in Figs. 4 and 5, respectively. Our calculations predict these states at energies of −16.85 (even), −10.68 (odd), −7.74 (even), −6.46 (odd), −5.05 (even), −3.56 (odd), −2.78 (even), −2.23 (even), −1.71 (odd), and −1.40 (even) cm⁻¹, with even/odd symmetry with respect to the diatomic f₁ rotation. As can be seen in Fig. 4 the n² = 0 is strictly localized at a θ = 90° configuration, while the n² = 6 vdW level presents its maximum probability also at C₂v structure with some delocalization near linear geometries. The first excited vibrational level is localized around θ = 70° and 110°, while the n² = 2, 3, 4, and 5 vibrational levels present an “interesting” oscillating pattern, spreading over the whole range of θ, and with their corresponding probability maxima located at ~55°, 40°, 30°, and 20° θ values, respectively, while their secondary maxima converge towards T-shaped nuclear arrangements. The two most excited vibrational levels, n² = 8 and 9, present a highly fluxional behavior rendering a floppy character to the corresponding states. The radial distributions provide also interesting comments (see Fig. 5). The ground vdW level is located at R₀ = 4.4 Å, while the corresponding values of the n² = 1–5 levels increase monotonically up to ~6 Å (n² = 5). As we move on to higher energies the radial distributions acquire double maxima at both small and large R values due to the double minima character of the underlying PES.
This is more pronounced for the \( n^l = 8 \) and \( n^l = 9 \) levels. The \( n^l = 6 \) level has also a highly irregular \( R \) distribution, since it is mostly located in the shallow well at large \( R \) for \( \theta = 90^\circ \), as we can see from its angular distribution.

The only available experimental results on the He–I\(_2\) E state was published by the Loomis group\(^{13}\) and are limited to the binding energies of the three lowest levels \( n^l = 0, 1, \) and 2 of the He–I\(_2\)(E, \( v^l = 1 \)) at 16.7 ± 0.6, 14.1 ± 0.6, and 10.7 ± 0.6 cm\(^{-1}\), respectively (see Table IV). Moreover, the experiment predicts a T-shaped isomer for the E state of the HeI\(_2\), and we can see its calculated structure and binding energy are in excellent accord with the experimental measurements. However, for the next two, \( n^l = 1 \) and 2, vibrational levels we find (see Table IV) differences of 3.4 and 3.0 cm\(^{-1}\), respectively, compared with the ones obtained from the RKHS PES. At a first glance, these deviations can be attributed to the errors in the \textit{ab initio} calculations, approximations for including the spin-orbit effects, and thus in the construction of the PES, which was not able to reproduce correctly the anharmonicity of the potential well.

### Table II

<table>
<thead>
<tr>
<th>He–I(_2)(E)</th>
<th>( \theta = 90^\circ )</th>
<th>( \theta = 0^\circ )</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Global (Local) minimum</td>
<td>Saddle points</td>
</tr>
<tr>
<td>( D_e )</td>
<td>( D_0 )</td>
<td>( R_e )</td>
</tr>
<tr>
<td>This work</td>
<td>33.178 (4.62)</td>
<td>16.85</td>
</tr>
<tr>
<td>DIM-PT1 value(^{32})</td>
<td>52.7</td>
<td>\ldots</td>
</tr>
<tr>
<td>Experimental value(^{13})</td>
<td>\ldots</td>
<td>16.7±0.6</td>
</tr>
</tbody>
</table>

\(^{a}\text{Linear saddle points energies and geometries.}\)

see that the \( n^l = 1 \) level is predicted by the RKHS PES to be at almost the same energy, just a difference of 0.02 cm\(^{-1}\), with the \( n^l = 2 \) level of the experimental observations. Thus, we should further analyze the experimental conditions and the corresponding assignment in order to gain some insights into the underlying dynamics and possible reasoning for the disagreement obtained with the data of the present intermolecular PES. The recorded two-color, pump-probe spectra show three features (see Fig. 4 in Ref. 13) at total excitation energies of around 41456, 41458.5, and 41463.5 cm\(^{-1}\), respectively. The pump laser was fixed in the \( n^l = 0 \), and 3 features of the I\(_2\) B–X, 23–0 region, the probe laser scanned the I\(_2\) E–B, 1–23 region, and these peaks have been assigned\(^{13}\) to transitions from the \( n^l = 0 \) or 3 levels of the He–I\(_2\)(B, \( v^l = 23 \)) \( \rightarrow \) He–I\(_2\)(E, \( v^l = 1 \)) with \( n^l = 0, 1, \) and 2 (see Table IV).

In Figure 6, we show the angular distributions and energies of the involved vibrational levels for each electronic state as they are predicted in the present and previous theoretical studies,\(^{22,26}\) together with the experimentally assigned transitions.

Based on theoretical calculations of the vibrational levels for each electronic state, and taking into account the Franck-Condon factors, one can see that the transition from the \( n^l = 0 \) \( \rightarrow n^l = 0 \) corresponds to the highest relative intensity feature, in agreement with the experiment. It turns out, that a possible proposed scenario, based on the available theoretical information for the next two observed features, could attribute them to transitions from the \( n^l = 1 \rightarrow n^l = 1 \) and \( n^l = 0 \rightarrow n^l = 1 \) states, which are shifted in energy by 2.09 and 6.17 cm\(^{-1}\), respectively. These values are in excellent accord (see Table IV) with the experimental reported energy shifts;\(^{13}\) however, we should stress that in the experimental setup only the \( n^l = 0 \) or 3 states are involved, and thus the theoretical assignment of the second peak is rather questionable. Further, we should mention that the \( n^l = 1 \) state was the only vibrational level of the B state that has not been detected from the experiment, while all the other vibrational states have been obtained,\(^{13}\) and this might be an argument for further investigation. Also, as we pointed out above, in the experimental setup the X, B, and E states of the HeI\(_2\) are involved, and one can see that for the X state the linear and T-shaped \( n^l = 0, 1, \) and 2 states are very close in energy (see Fig. 6), with a difference of 0.3 (in reverse ordering) and 0.2 cm\(^{-1}\) based on the experimental and theoretical predictions,\(^{13,22}\) respectively. In any case, we should say that the present theoretical estimates are for zero temperature, while experimental measurements have been recorded.
TABLE IV. Theoretical and experimental energies (in cm⁻¹) for the bound vibrational vdW levels of HeI₂(E), together with theoretical and experimental values for the energy shifts of the indicated E ← B transitions.

<table>
<thead>
<tr>
<th>n'</th>
<th>This work (2D)</th>
<th>Expt. ¹³</th>
<th>This work/Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RKHS PES</td>
<td>He + I₂(E, v₁ = 1)</td>
<td>(E,vᵢ = rₑ) ← (B,vᵢ' = 20)(E,vᵢ = 1) ← (B,vᵢ' = 23)</td>
</tr>
<tr>
<td>0</td>
<td>-16.85</td>
<td>-16.7 ± 0.6</td>
<td>(0.0',e) ← (0.1',o)/0 or 3 = 0.0/0</td>
</tr>
<tr>
<td>1</td>
<td>-10.68</td>
<td>-14.1 ± 0.6</td>
<td>(1.0',o) ← (1.1',e)/1 or 3 = 2.09/2.6 ± 0.6</td>
</tr>
<tr>
<td>2</td>
<td>-7.74</td>
<td>-10.7 ± 0.6</td>
<td>(1.0',o) ← (0.1',e)/2 or 3 = 6.176 ± 0.6</td>
</tr>
<tr>
<td>3</td>
<td>-6.46</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>4</td>
<td>-5.05</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>5</td>
<td>-3.56</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>6</td>
<td>-2.78</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>7</td>
<td>-2.23</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>8</td>
<td>-1.71</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>9</td>
<td>-1.40</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

at a low temperature regime (T ≤ 1 K), where rovibrational states with J' < 9 were significantly populated,¹³ and does not facilitate detailed comparisons.

Unfortunately, no more experimental and/or theoretical data are up to now available in order to justify our assertion, and thus to further evaluate the present surface.

IV. CONCLUSIONS

We present for the first time high level ab initio results on the electronic excited E state of the HeI₂ vdW system based on large MRCl+Q calculations in conjunction with ECP and large basis sets. Interaction energies were calculated at a frozen r = rₑ distance for the I₂ moiety for a grid of several points in the R and θ coordinates for values between 3.0 and 30.0 Å and 0° and 90°, respectively, for the 3A' and 3A'' states which correlate with the 3Π_ACCEPTING ion-pair state of I₂. The surface is approximated by the semi-sum of the spin-free 3A' and 3A'' interaction potentials. Given the complicated morphology of this ion-pair character PES, an interpolation scheme based on the RKHS method has been adopted for its representation. The surface presents a global minimum for the T-shaped configuration with a well-depth of 33.18 cm⁻¹, a local one at energy of −4.62 cm⁻¹, saddle points for linear structures and a wide plateau for intermediate bending geometries.

Variational bound state calculations were performed for the RKHS PES and the lowest ten bound vibrational states of the HeI₂(E) cluster were determined. The binding energy, D₀, is calculated to be 16.85 cm⁻¹, with the corresponding wavefunction being located at the T-shaped structure. These findings are in excellent agreement with the available experimental data on the n’ = 0 level of the He..I₂(E, vᵢ = 1) from a two-color, pump-probe spectra recorder in the I₂ B–X, 23–0, and E–B, 1–23 regions. The next two vibrational levels are calculated at energies of −10.68 and −7.74 cm⁻¹, while the experimental ones have been set to −14.1 ± 0.6 and −10.7 ± 0.6, respectively. Higher vibrational states are also obtained, and we found that their probability distributions clearly reflect the large anisotropy of the underlying PES. Based on the theoretical predictions for all three (X, B, and E) involved electronic states of HeI₂, we discussed different possible scenarios in order to analyze our results in comparison with the experimental assignments for these energy levels aiming in this way to understand the source of the disagreement. We may conclude that both experimental conditions and theoretical treatments do not facilitate a detailed comparison, so additional observations and calculations are in order.

FIG. 6. Vibrational energies and corresponding angular distributions for the three electronic states, ground X, valence B, and ion-pair E, as calculated in the present and previous theoretical studies,²²,²⁶ being involved in the experimental spectra,¹⁵ of the HeI₂ molecule. The inter y axes correspond to the interaction potential energies for each state, while the outer y axis indicates the total excitation energy. T_B and T_E indicate the adiabatic excitation energies for the B and E states, respectively, (see Table I). Transitions corresponding to the experimental and theoretical assignments are also shown (see Table IV).

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The study of electronically excited vdW systems presents a challenge for the theory of intermolecular interactions, and here we demonstrate to what extent ab initio computations can reach. We found that highly electronic excited interaction energies for such vdW systems can be determined, providing a reliable and accurate description for the E state PES of the He$_2$, that in combination with the ground X and electronic excited B state of the complex, is useful to model experimental data related to potential minima and also predict higher vibrational vdW states. However, for a further evaluation of the surface it is clear that more experimental data are required, together with the corresponding theoretical simulations.

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See supplementary material at http://dx.doi.org/10.1063/1.4733983 for the computed interaction energies.