A theoretical study of He$_2$ICl van der Waals cluster

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The structure, energetics, and dynamics of He$_2$ICl complex in its ground state are studied by means of ab initio electronic structure and quantum-mechanical calculations. Interaction energies for selected He$_2$ICl configurations are calculated at the coupled-cluster [CCSD(T)] level of theory using a large-core pseudopotential for the I atom and the aug-cc-pVTZ and aug-cc-pV5Z basis sets for the Cl and He atoms, respectively. The surface is characterized around its lower five minima and the minimum energy pathways through them. The global minimum of the potential corresponds to a "police-nightstick (1)" configuration, the second one to a linear, the next one to tetrahedral configuration, and the following two to "bifork" and "police-nightstick (2)" structures, with well depths of −99.12, −97.42, −88.32, −85.84, and −78.54 cm$^{-1}$, respectively. An analytical form based on the sum of the three-body parametrized HeIICl interactions plus the He–He interaction is found to represent very well the tetra-atomic CSSD(T) results. The present potential expression is employed to perform variational five-dimensional quantum-mechanical calculations to study the vibrational bound states of the van der Waals He$_2$ICl complex. Results for total angular momentum $J=0$ provide the binding energy $D_0$ and the corresponding vibrationally averaged structure for different isomers of the cluster. Comparison of these results with recent experimental observations further justifies the potential used in this work. © 2006 American Institute of Physics.

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I. INTRODUCTION

Small rare gas-dihalogen van der Waals (vdW) complexes have proven to be ideal systems for studying the nature of long-range intermolecular forces, photodissociation dynamics, and energy transfer mechanisms. During the last decades, with the development of experimental techniques, such as supersonic beam expansion, and by performing more accurate ab initio electronic structure calculations, we are able to study the structure and dynamics of such complexes in detail.\textsuperscript{1,2} Considerable attention has been paid both by theory and experiment to the structure and interactions of systems with a single rare gas atom, i.e, of Rg-XY complexes where Rg is He, Ne, or Ar atom and X, Y= F, Cl, Br, or I. In particular, the assignment of the two-band structure of the $B\rightarrow X$ excitation spectrum turned out to be interesting and several theoretical studies have been carried out to explore it.\textsuperscript{3-5} A necessary condition for understanding the vibrational dynamics and for interpreting the spectra is an accurate description of the potential energy surfaces involved. Up to now accurate potentials for triatomic systems have been obtained either by fitting the potential parameters to experimental data obtained from high resolution spectroscopic methods\textsuperscript{6-10} or by performing state-of-the-art electronic structure calculations.\textsuperscript{11-18} For all Rg-XY cases studied, both experimental and theoretical studies support a double-minima topology for the ground state potential, corresponding to linear- and T-shaped configurations.\textsuperscript{4,19-22}

Studies of larger species are more complex and the difficulty in evaluating their potential surfaces increases with the cluster size. Janda and co-workers\textsuperscript{23-25} were the first to obtain rotationally resolved excitation spectrum of complexes containing more than one rare gas atom. An interesting example is their experimental studies on Rg$_2$Cl$_2$ clusters, where difficulties in fitting the observed excitation spectrum by means of rigid rotor analysis led them to conclude that He$_2$Cl$_2$ is an extremely floppy, liquidlike cluster without any average structure and the dynamics of He$_2$Cl$_2$ complexes will be quite different from their Ne$_2$Cl$_2$Ar$_r$ and Cl$_2$ analogs. Similar conclusions have been reported by several theoretical studies performing quantum Monte Carlo\textsuperscript{26} or variational\textsuperscript{27,28} calculations, where the importance of performing exact calculations for such liquidlike systems is emphasized. In all the above mentioned dynamical studies for the tetra-atomic Rg$_2$Cl$_2$ systems, pairwise atom-atom potential energy surfaces (PESs) have been employed. Even though the atom-atom potentials have been widely used, they have not been able to reproduce the high anisotropy of van der Waals complexes and to describe accurately enough all details of their dynamics.

The construction of ab initio potential energy surfaces for polyatomic molecular systems (including heavy atoms in our case) is a computationally prohibitive task. Thus, given the high quality ab initio PESs calculated for triatomic species, attempts are made using pairwise three-body interaction potentials to represent PESs of larger Rg$_2$XY complexes. Ab initio results have been presented for He$_2$Br$_2$ system, indicating that pairwise atom-atom interactions are not able to describe the complex, while a sum of three-body He–Br$_2$ terms,\textsuperscript{17} plus the He–He interaction can accurately represent the interaction energies for this cluster.\textsuperscript{29} Such surfaces are of
particular interest in the study of both the solvent properties of superfluid helium\textsuperscript{30} and the relaxation dynamics of impurities embedded in helium droplets. Rotational and infrared spectroscopic studies for helium droplets doped with a variety of molecules are currently conducted in order to answer new and challenging questions on the role of the “quantum environment.”\textsuperscript{31–35} In this sense, our current studies on the interaction of helium with dihalogen molecules for the case of two helium atoms serve to bridge the gap between the small cluster and the large cluster limits.

In the present study the validity of the pairwise additivity of the three-body potentials for the He\textsubscript{2}ICl is investigated. Comparison with the He\textsubscript{2}Br\textsubscript{2} complex will allow us to evaluate the effect of changing the dihalogen upon the vDW bond. The electric dipole moment of ICl molecule and the larger bond length of ICl, \( R_1 \), and compared to experiment. Finally, a summary is given in Sec. V.

**II. AB INITIO CALCULATIONS**

The \textit{ab initio} calculations are performed using the Gaussian 98 package.\textsuperscript{36} Computations are carried out at the CCSD(T) level of theory. The He\textsubscript{2}−ICl system is described using the \((r, R_1, R_2, \theta_1, \theta_2, \gamma)\) coordinate system. \( r \) is the bond length of ICl, \( R_1 \) and \( R_2 \) are the intermolecular distances of each He atom from the center of mass of I−Cl, \( \theta_1 \) is the angle between the \( R_1 \) and \( r \) vectors, while \( \theta_2 \) is the one between \( R_2 \) and \( r \), and \( \gamma \) is the angle between the \( R_1 \) and \( R_2 \) vectors (see Fig. 1).

The supermolecular approach is used for the determination of the intermolecular energies, \( \Delta E \):

\[
\Delta E = E_{\text{He}_2\text{ICl}} - E_{\text{BSSE}} - 2E_{\text{He}} - E_{\text{ICl}},
\]

where \( E_{\text{He}_2\text{ICl}} \), \( E_{\text{He}} \), and \( E_{\text{ICl}} \) are the energies of He\textsubscript{2}−ICl, He, and ICl, respectively. The correction, \( E_{\text{BSSE}} \), for the basis-set superposition error is calculated using the standard counterpoise method.\textsuperscript{37}

We performed CCSD(T) calculations for several configurations fixing the ICl bond length at its equilibrium value \( r_e=2.321 \text{ Å} \).\textsuperscript{38} For the present calculation we used for I atom the Stuttgart-Dresden-Bonn (SDB) large-core energy-consistent pseudopotential\textsuperscript{39} in conjunction with the augmented correlation consistent triple zeta (SDB-aug-cc-pVTZ) valence basis set.\textsuperscript{40} This basis set is of cc-pVTZ quality and has been optimized for use with the SDB pseudopotential. For the Cl atom we employed the aug-cc-pVTZ basis set while for the He atoms we used the aug-cc-pV5Z from EMSL library.\textsuperscript{41} In all calculations here 6\( d \) and 10\( f \) Cartesian functions are used.

<table>
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<th>( R_1 )</th>
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<th>Police nightstick (1)</th>
<th>Tetrahedral</th>
<th>Police nightstick (2)</th>
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<tr>
<td>8.0</td>
<td>−34.24</td>
<td>8.0</td>
<td>−33.60</td>
<td>8.0</td>
</tr>
</tbody>
</table>

**FIG. 1.** Schematic representation of coordinate system for He\textsubscript{2}ICl complex.
The results for the CCSD(T) supermolecular interaction energies at selected geometries are listed in Table I, while the geometries for the five optimal structures are shown in Fig. 2. According to the CCSD(T) results the linear configuration [see Fig. 2(b)] has the lowest energy $-79.58 \text{ cm}^{-1}$ with $R_1 = 3.922$ and $R_2 = 5.152$ Å. The next equilibrium structure is found at energy $-78.99 \text{ cm}^{-1}$ and corresponds to a “police-nightstick (1)” configuration [see Fig. 2(a)] with one helium in a near T-shaped orientation ($\theta_2 = 110.6^\circ$), while the second one is located in side of the iodine atom ($R_1 = 3.924$ and $R_2 = 3.858$ Å). In turn, a tetrahedral configuration [see Fig. 2(c)] with $R = 4.123$ Å, $\theta = 110.6^\circ$, and the He–He–distance $2.9506$ Å is located at energy of $-74.58 \text{ cm}^{-1}$. A “bifork” configuration [see Fig. 2(d)] with one helium atom at linear $\theta_1 = 0^\circ$ and the other one at $\theta_2 = 39.73^\circ$ with $R_1$ and $R_2$ to be $3.863$ and $4.537$ Å, respectively, at energy of $-67.59 \text{ cm}^{-1}$ is the fourth minimum, and the last one corresponding to a “police-nightstick (2)” configuration [see Fig. 2(e)] with one helium in the near T-shaped position and the other one in the side of Cl ($R_1 = 5.151$ and $R_2 = 3.858$ Å) is found at energy of $-67.18 \text{ cm}^{-1}$.

For weakly bound systems it has been demonstrated that an efficient way to saturate the dispersion energy is the use of midbond functions. In particular, studies on triatomic dispersion-bound complexes have shown an improvement of $\approx 5\%$ in the interactions energies. Thus, in order to investigate the role of using bond functions in tetra-atomic He$_2$XY clusters and to account for their effect in the interaction energies of the complex, test runs are carried out for specific configurations around the optimal structures, namely, linear, police nightstick, tetrahedral, and bifork (see Fig. 2 and Table II). We choose the same set of bond functions that has been employed in the study of the triatomic He–ICl system, namely, $(3s3p2d2f1g)$. As for a polyatomic vdW system the location for such midbond functions is not clearly defined, and calculations are carried out in order to evaluate their influence in the interaction energies for the different configurations. For the linear and police-nightstick structures we compare results obtained by placing two sets of the $(3s3p2d2f1g)$ functions, each of them at the midpoints of the two $R_1$ and $R_2$ bonds and at the middle of the He–I and Cl–He distances, respectively. Very small differences, accounting $0.02 \text{ cm}^{-1}$, are obtained in the CCSD(T) interaction energies for these structures (see values in square brackets in Table II). For the tetrahedral and bifork configurations calculations are performed by using one or two sets of the $(3s3p2d2f1g)$ functions. The one set of midbond functions is placed at the middle of the intermolecular distance $R$ for both tetrahedral and bifork structures, while the two sets of midbond functions are located, as for the linear and police-nightstick configurations at the midpoints of the two $R_1$ and $R_2$ bonds (see Fig. 2). As it was expected, CCSD(T) interaction energies obtained using two sets of midbond functions are lower, by about $3 \text{ cm}^{-1}$, compared with the ones from the one set calculations.

The MP4(SDTQ) and CCSD(T) results for all the above mentioned cluster structures, with and without the use of bond functions, are presented in Table II for different intermolecular distances. Similar differences in the interaction energies are obtained at both levels of theory, and the improvement in the interaction energies by using bond functions is calculated to be more than $10\%$, around the equilibrium geometries. In particular, the importance of midpoint functions is larger for structures containing linear He–I configuration than He–Cl one; as a major dispersion component comes from the He–I interaction, e.g., for the police-nightstick (1), a difference of $22.21 \text{ cm}^{-1}$ is obtained in the CCSD(T) interaction energy, due to the absence of midpoint functions, while for the police-nightstick (2) this difference accounts $11.36 \text{ cm}^{-1}$. However, as a single point CCSD(T)+bf calculation requires an additional computational cost, five times more compared with a CCSD(T) one, we choose to perform such calculations for selected points of the He$_2$ICl PES.

Thus, CCSD(T)+bf calculations are carried out around the above mentioned configurations, and the computed optimal energies and geometries for He$_2$ICl are as follows: the police-nightstick (1) ($R_1 = 3.863$ and $R_2 = 3.821$ Å, $\theta_1 = 110.6^\circ$) is found at energy of $-99.12 \text{ cm}^{-1}$, the linear ($R_1 = 3.860$ and $R_2 = 5.151$ Å) with energy $-97.43 \text{ cm}^{-1}$, the tetrahedral ($R = 4.079$ Å, $\theta = 110.6^\circ$, and He–He distance $2.9504$ Å) at energy of $-88.32 \text{ cm}^{-1}$, the bifork ($R_1 = 3.863$ and $R_2 = 4.482$ Å, $\theta_2 = 39.73^\circ$) at energy of $-85.84 \text{ cm}^{-1}$, and police-nightstick (2) ($R_1 = 5.152$ and $R_2 = 3.821$ Å) at $-78.54 \text{ cm}^{-1}$. As can be seen, the police-nightstick (1) configuration is energetically favored (by only about $1.69 \text{ cm}^{-1}$) as compared to linear one. The difference is very sensitive to
TABLE II. MP4(SDTQ)/CCSD(T) interaction energies for the He$_2$ICl obtained with and without bond functions at the indicated configurations. bf stands for the (3s3p2d2/1g) set of bond functions. Values in square brackets are obtained for different locations of the bf (see in the text), while values in parentheses are computed using one set of bf. Energies in cm$^{-1}$ and distances in Å.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$R_1/R_2$</th>
<th>MP4(SDTQ)/CCSD(T)</th>
<th>MP4(SDTQ)+bf/CCSD(T)+bf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Police</td>
<td>3.70/3.70</td>
<td>−68.39/−67.82</td>
<td>−93.15/−92.64</td>
</tr>
<tr>
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<td>−98.63/−98.85/−98.26</td>
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<td>−78.44/−78.15</td>
<td>−96.35/−96.10</td>
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<tr>
<td>$\theta_1=110.6^\circ$</td>
<td>4.20/4.20</td>
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<td>−87.24/−87.09</td>
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<tr>
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<td>4.90/4.90</td>
<td>−64.46/−67.88</td>
<td>−89.79/−88.29</td>
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<tr>
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<td>−98.21/−98.28/−97.05</td>
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<td>$\theta_1=110.6^\circ$</td>
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<td>$\theta_1=110.6^\circ$</td>
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<tr>
<td></td>
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<tr>
<td>Bifork</td>
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<tr>
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<tr>
<td></td>
<td>⋯/4.70</td>
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<td>⋯</td>
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TABLE III. Summary of the supermolecular calculations of the nonadditive effects around the lower five equilibrium He$_2$ICl structures. Results for each method without/with bond functions are presented. Energies in cm$^{-1}$ and distances in Å.

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<th>HF</th>
<th>MP2</th>
<th>MP3</th>
<th>MP4(SDTQ)</th>
<th>MP4(SDTQ)+bf</th>
<th>CCSD (CCSD(T))</th>
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</tbody>
</table>
the basis set used, due to the importance of the dispersion energy of the complex. It is necessary to saturate this component in order to correctly predict the ordering of the minima, which is achieved in our case by supplementing the basis set with two sets of midbond functions. We should note that interaction energies as well as equilibrium distances of the above structures are very close to the ones obtained by CCSD(T)+bf calculations for the three optimized geometries of the triatomic HeICl complex. In particular, the interaction energies and equilibrium $R_e$ distances have been predicted to be 58.62 cm$^{-1}$ and 3.86 Å for the linear well, 38.96 cm$^{-1}$ and 3.82 Å for the near T shaped ($\theta=110.9^\circ$), and 38.03 cm$^{-1}$ and 5.12 Å for the antilinear one. These results are compared very well with experimental data on HeICl (Ref. 22) and their quality has been also demonstrated by dynamical simulations for the $B−X$ excitation spectrum.

In order to extract information on nonadditive interactions in He$_2$ICl we examine the above tetra-atomic equilibrium structures based on the $ab$ initio calculations by partitioning the interaction energy into components, as given in Ref. 46. Therefore, we show in Table III the summary of supramolecular calculations of the entire nonadditivity in the different He$_2$ICl equilibrium structures using the results of the Møller-Plesset perturbation theory (MPPT) up to fourth order along with the ones of the CCSD(T) method. As can be seen in Table III, the use of bond functions clearly affects the interaction energies of the complex at the MP2 level, where the second-order dispersion term appears in the analysis of the contents of the two- and three-body supramolecular interaction energies. In turn, the total three-body interaction for different intermolecular configurations around the lower five equilibrium geometries computed through the MP3 amounts to $−70.45/−89.11$, $−70.26/−85.88$, $−64.64/−76.53$, $−60.99/−75.92$, and $−58.56/−68.32$ cm$^{-1}$, respectively. These energies neglect completely the effects of intramonomer correlation on three-body dispersion. The major effect of the intrasystem correlation on dispersion appears in MP4 level and is specially sensitive to the presence of triple excitations. For all configurations studied the MP4(SDQ) calculations reduce this effect to $−66.37/−65.69$, $−64.15/−79.91$, $−61.01/−73.04$, $−56.87/−72.16$, and $−53.73/−63.34$ cm$^{-1}$, respectively, while the inclusion of triples enhances both the interaction energies as well as equilibrium distances of the complexes studied appear to have linear global minimum. In contrast, for heteropolar ones, the location of their global minimum depends from the energy difference balance of the corresponding three triatomic potential wells. Such findings indicate a similar nature of binding in triatomic and tetraatomic complexes of such type, and thus information on intermolecular interactions available for triatomic species might serve to study larger systems.

### III. ANALYTICAL REPRESENTATION OF THE PES

We used one functional form for the He$_2$−ICl potential energy function based on the sum of three-body HeICl interactions and the He−He one, which has been used in previous tetra-atomic calculations for the He$_2$−Br$_2$.

$$V(r_e,R_1,R_2,\theta_1,\theta_2,\gamma) = \sum_i V_{HeICl}(r_e,R_i,\theta_i) + V_{HeHe}(R_1,R_2,\gamma),$$

(2)

where the corresponding $V_{HeICl}(r_e,R_i,\theta_i)$ terms with $i=1$ and 2 are the CCSD(T) parametrized potential of the HeICl complex and $V_{HeHe}(R_1,R_2,\gamma)$ term is the potential function for He$_2$ given in Ref. 48.

Configuration energies are determined by optimizing different structures with respect to atomic positions using the functional expressions given in Eq. (2). In Fig. 3 we plot the potential curves obtained and compare them with the tetraatomic CCSD(T)/CCSD(T)+bf $ab$ initio results. We should note that triatomic HeICl CCSD(T)/CCSD(T)+bf calculations were performed employing the same above mentioned basis sets. In Fig. 3 open circles indicate the CCSD(T) $ab$ initio values, while crosses represent the sum of the three-body CCSD(T) HeICl interaction potential at the same points. Solid lines are for the potential curves obtained using the three-body CCSD(T)+bf HeICl interaction potential from Ref. 22 and filled circles are for the CCSD(T)+bf $ab$ initio data. Figure 3(a) corresponds to police-nightstick (1) structures [see Fig. 2(a)] and represents the potential energy
curves as a function of the distance $R_1$ between the center of mass of ICl and one He atom. In Figs. 3(b) and 3(c) representations of the potential energy curve are given for linear and distorted tetrahedral structures, respectively, as a function of $R_2$ distance. At the end, Fig. 3(d) corresponds to police-nightstick (2) configurations. As can be seen, the model potential based on the sum of the three-body CCSD(T) HeICl interactions with and without bond functions plus the He–He interaction reproduce very well the corresponding ab initio data with an average absolute deviation of 1.1 cm$^{-1}$ for the CCSD(T)+bf values. Once we check the validity of the analytical form using the triatomic CCSD(T) and CCSD(T)+bf interactions we decide for our later calculations to employ the CCSD(T)+bf HeICl parameterized potential given in Ref. 22, that includes an additional set of bond functions in the middle of the triatomic van der Waals bond.

Figure 4 shows two-dimensional contour plots of the $V(r_1,R_1,R_2,\theta_1,\theta_2,\gamma)$ surface in XY or ZX Cartesian plane. The equipotential curves are shown for He moving around a triatomic HeICl molecule fixed at specific linear [see Fig. 4(a)] and T-shaped [see Figs. 4(b) and 4(c)] configurations. In this case the lowest five wells of the potential are found at energies of 97.72, 96.67, 86.38, 85.64, and 77.40 cm$^{-1}$, for the police-nightstick (1), collinear, bifork, tetrahedral, and police-nightstick (2) structures, respectively. The equilibrium distances and angles are at $R_1^e=3.860$ Å, $R_2^e=3.811$ Å, and $\theta_1=110.4^\circ$ for the police nightstick (1), $R_1^e=3.861$ and $R_2^e=5.124$ Å for the linear one, $R_1^e=3.863$ Å, $R_2^e=4.458$ Å, $\theta_1=0^\circ$, and $\theta_2=39.73^\circ$ for the bifork, $R_1^e=4.087$ Å and $\theta=110.5^\circ$ for the tetrahedral well, and $R_1^e=5.121$ Å, $R_2^e=3.817$ Å, and $\theta_2=110.75^\circ$ for the police-nightstick (2). These results compare very well with the values obtained from the ab initio CCSD(T)+bf interaction energies and structures calculations. Both studies predict a police-nightstick (1) structure as the global minimum, with the linear one, to lie above by only 1.0–1.7 cm$^{-1}$, as local minimum of the He$_2$ICl surface, together with the next three equilibrium structures. One can see that the analytical form predicts the bifork configuration to be energetically favored by 0.76 cm$^{-1}$, compared to the tetrahedral one. This ordering of the minima is opposite to that found by the ab initio CCSD(T)+bf calculations, and such small differences are due to accidental accumulation of errors involved in the parameterization procedure of the HeICl potential surface. In particular, ab initio CCSD(T)+bf calculations are performed at the two different HeICl geometries corresponding to the

FIG. 3. Comparison of potential values for (a) police-nightstick (1), (b) linear, (c) tetrahedral, and (d) police-nightstick (2) configurations He–ICl. Solid lines are for the sum of three-body CCSD(T)+bf HeICl interaction potentials, while the CCSD(T)/CCSD(T)+bf ab initio values are indicated by open and filled circles, respectively. The sum of three-body CCSD(T) HeICl terms is also indicated by crosses.

FIG. 4. Contour plots of the He$_2$ICl potential energy surface, $V(r_1,R_1,R_2,\theta_1,\theta_2,\gamma)$, Eq. (2) in the XY [(a) and (b)] or ZX [(c)] plane. The ICl distance is fixed at 2.321 Å along the Z axis, while the geometry of the triatomic molecule is fixed to a linear configuration with $R_1=3.86$ Å (a) and to a near T-shaped configuration with $R_1=3.82$ Å, $\theta_1=110.6^\circ$ [(b) and (c)]. Contour intervals are of 5 cm$^{-1}$ and for energies from $-70$ to $-95$ cm$^{-1}$ (a), $-55$ to $-90$ cm$^{-1}$ (b), and $-45$ to $-85$ cm$^{-1}$ (c).
bifork and tetrahedral structures. By comparing them with the values of the HeICl parametrized potential terms used in the Eq. (2), total errors of 0.624 and $-1.93 \text{ cm}^{-1}$ are obtained in the interaction energies for the bifork and tetrahedral minima, respectively. The major error of 0.96 cm$^{-1}$ is found for the HeICl geometries with angle value close to one of the near-T-shaped well of the molecule. Taking into account these deviations the order of the two minima changes, in accord now with the ab initio CCSD(T) results, and with the values of $-85.76$ and $-87.55 \text{ cm}^{-1}$ for the tetrahedral and bifork configurations, respectively. We should stress that similar analysis carried out for the other three potential minima shows no change in their ordering. However, an energetic distance of about 2.0 cm$^{-1}$, that is closer to the $ab\ initio$ CCSD(T) data, is obtained between the police-nightstick (1) and linear minima.

One-dimensional representations of the potential are shown in Fig. 5, where minimum energy paths are plotted as a function of the angle $\gamma$ for planar [see Fig. 5(a)] and nonplanar with $\theta_1=\theta_2=110.6^\circ$ [see Fig. 5(b)] configurations. The isomerization barrier between the police nightstick (1) $\leftrightarrow$ linear wells is found at energy of $-81.46 \text{ cm}^{-1}$ and an angle $\theta_2$ of 139.75$^\circ$, while the one between police nightstick (1) $\leftrightarrow$ bifork at energy of $-75.24 \text{ cm}^{-1}$ and $\theta_2=64.43^\circ$. In Fig. 6 we plot at indicated geometries, selected along to a minimum energy path [HeICl molecule is fixed at linear configuration, $\theta_1=0^\circ$ and $R_1=3.86$ Å (see Fig. 2), while the $R_2$ distance is optimized for each $\theta_2$ value], the ab initio CCSD(T) values and compare them with the corresponding $V(r_e,R_1,R_2,\theta_1,\theta_2,\gamma)$ ones, given by the Eq. (2) using CCSD(T) and CCSD(T)+bf three-body HeICl interactions. The above data and their comparison with MP4(SDTQ) values are available in an EPAPS document. As can be seen, the differences obtained in the CCSD(T) results are fully justified due to the different basis sets used, whether or not including bond functions, in the ab initio calculations of the triatomic and tetra-atomic complexes, respectively. Note that MP4(SDTQ)/CCSD(T) and MP4(SDTQ)+bf/CCSD(T)+bf results are within the difference of 10% in the interaction energies, attributed from the test runs to the use of bond functions (see Table I).

IV. BOUND STATE CALCULATIONS

The Hamiltonian operator in the coordinate system shown in Fig. 1 has the form:

$$
\hat{H} = \frac{\hbar^2}{2\mu_1}\left(\frac{\partial^2}{\partial R_1^2} + \frac{2}{R_1} \frac{\partial}{\partial R_1} - \frac{\partial^2}{\partial R_2^2} + \frac{2}{R_2} \frac{\partial}{\partial R_2}\right) + \frac{j^2}{2\mu_2 r_e^2} + \frac{\hat{I}_1^2}{2 \mu_1 R_1^2} + \frac{\hat{I}_2^2}{2 \mu_2 R_2^2} - \frac{\hbar^2}{m_I + m_{Cl}} \nabla_1 \nabla_2 + V(r,R_1,R_2),
$$

(3)

where $\mu_1^{-1}=\mu_2^{-1}=(m_{He}^{-1}+(m_{I}+m_{Cl})^{-1}$ and $\mu_1^{-1}=m_1^{-1}+m_{Cl}^{-1}$ are the reduced masses, $m_{He}=4.0026$ amu, $m_{I}=126.904 473$ amu, and $m_{Cl}=34.968 852 721$ amu are the atomic masses of $^4\text{He}$, $^{127}\text{I}$, and $^{35}\text{Cl}$ isotopes, and $\hat{I}_1$, $\hat{I}_2$, and $\hat{j}$ are the angular momenta associated with the vectors $\mathbf{R}_1$, $\mathbf{R}_2$, and $\mathbf{r}$, respectively, leading to a total angular momentum $\hat{J}=\hat{I}_1+\hat{I}_2+\hat{j}=\hat{L}+\hat{j}$. $\mathbf{r}$ is fixed at the equilibrium I–Cl bond length ($r_c$), and the potential for He$_2$ICl complex is given by the expansion in Eq. (2).

For a total angular momentum $J$, the Hamiltonian of Eq. (3) is represented in a set of basis functions consisting of linear combinations of products of bidimensional radial functions by angular functions, which incorporate the whole symmetry of the system. For the $R_1$ and $R_2$ coordinates numerical $\{\ell_i(R_i)\}$ with $i=1,2$ and $n=1,\ldots,N_R$ functions are used. We evaluate them as follows: First, the two-dimensional Schrödinger equation is solved in $(R,\theta;r_c)$ variables for a triatomic He–ICl system at total angular momentum zero. The employed PES was the CCSD(T) ab initio surface given in Ref. 22, and a discrete variable representation (DVR) basis set is used. It consists of functions given by

![FIG. 5. Minimum energy path, $V_e$ in cm$^{-1}$ as a function of angle $\gamma$, for planar (a) and nonplanar configurations.](image)

![FIG. 6. ab initio CCSD(T) interaction energies (open circles) and potential values obtained using the sum of three-body (3B) CCSD(T) HeICl terms (crosses)](image)
the NR calculation. were enough to achieve convergence in the variational calculation above is represented as linear combinations of the /H2O849−28.03 cm−1 contributions are orthonormalized through a Gram-Schmidt procedure, and constitute the radial basis set, \( \{ \xi_n(R_i) \} \), for the tetra-atomic calculations.

For the angular basis functions, we consider the following linear combinations, which are eigenfunctions of the parity of total nuclear coordinates inversion \( \rho \),

\[
\mathcal{F}_{l_1,l_2|\Omega}^{(JM)} = \sqrt{ \frac{1}{2(1 + \delta_{l_1 l_2})} } [\mathcal{W}_{l_1,l_2|\Omega}]^M + p(-1)^{l_1 + l_2 + l_4} \mathcal{W}_{l_1,l_2|\Omega},
\]

with

\[
\mathcal{W}_{l_1,l_2|\Omega} = \sqrt{ \frac{2J + 1}{4\pi} } D_{M1}^{J'}(\phi, \theta, \Omega) \mathcal{Y}_{l_1,l_2}^{M} (R_1, R_2),
\]

\( M \) is the projection of \( J \) on the space-fixed (SF) \( z \) axis, \( \Omega \) its projection on the body-fixed (BF) \( z \) axis, which is chosen here along the \( r \) vector. The \( D_{M1}^{J'} \) are Wigner matrices and \( \mathcal{Y}_{l_1,l_2}^{M} \) are angular functions in the coupled BF representation.

In turn, taking into account the fact that in the case of He2ICl the Hamiltonian is also invariant under \( R_1 \rightarrow R_2 \), inversion, a well-defined parity, \( p_{l_1 l_2} \), basis set is built up as follows:

\[
\Phi^{(JM)p_{l_1 l_2}}_{l_1,l_2|\Omega} = \sqrt{ \frac{1}{2(1 + \delta_{l_1 l_2})} } [\mathcal{W}_{l_1,l_2|\Omega}]^{M} + p_{l_1 l_2}(-1)^{l_1 + l_2 + l_4} \mathcal{W}_{l_1,l_2|\Omega},
\]

where \( \Phi^{(JM)p_{l_1 l_2}}_{l_1,l_2|\Omega} = \phi_{nm}^{(p_{l_1 l_2})} \mathcal{F}_{l_1,l_2|\Omega}^{(JM)} \) and \( \phi_{nm}(R_1, R_2) = \xi_n(R_1) \xi_m(R_2) / R_1 R_2 \).

For the evaluation of the Hamiltonian matrix elements, the numerical set of the radial basis functions \( \{ \xi_n(R_i) \} \) mentioned above is represented as linear combinations of the \( f_i \) DVR functions, \( \xi_n(R_i) = \sum_{i=1}^{N} c_i \xi_i(R_i) = \sum_{i} \xi_i(R_i) f_i(R_i) = \sum_{i} \xi_i(R_i) f_i(R_i) \).

In our calculations at \( J=0, N_R=5 \) radial numerical functions, represented at 50 DVR points over the range of 2.5–8 Å, for each \( R_1 \) and \( R_2 \) coordinates are used. In turn, values of \( L=j=0–12 \) with \( m_{l_1} = m_{l_2} = 12 \) for even \( (p_{l_1 l_2} = (-1)^{l_1 + l_2 + l_4} + 1 \) and \( p = (-1)^{l_1 + l_2 + l_4} \) parity symmetries were enough to achieve convergence in the variational calculation.

The five lowest vibrational states of He2ICl are found at energies of \(-33.51, -31.60, -30.46, -29.19, \) and \(-28.03 \text{ cm}^{-1} \) (see Table IV and Fig. 5). In Fig. 5, together with the minimum energy path, we plot the angular probability density of the angle \( \gamma \) for the \( n=0 \) (solid line), \( n=1 \) (dotted line) \( n=4 \) (dashed-dotted line) [see Fig. 5(a)], \( n=2 \) (dashed line), and \( n=3 \) (long-dashed line) [see Fig. 5(b)] eigenfunctions, while in Fig. 7 the radial \( R_{i=1,2} \) and angular \( \theta_{i=1,2} \) distributions for these states are shown. As can be seen, the \( n=0 \) state is localized in the police-nightstick (1) well and its distributions show peaks at \( \theta_{1,2}=10.26^\circ, 109.83^\circ, R_{1,2}=4.197 \text{ Å, and } \gamma=109.9^\circ \). The \( n=1 \) state corresponds to linear configurations, with maxima at \( \theta_{1,2}=9.60^\circ \) and \( 105.13^\circ/166.05^\circ \), and at \( R_{1,2}=4.170 \text{ and } 5.328 \text{ Å, and only one peak at } \gamma=164.46^\circ \) [see Fig. 5(a)], while the \( n=2 \) and \( n=3 \) states exhibit tetrahedral structures with maximum values at \( \theta_{1,2}=109.87^\circ \) and \( 109.56^\circ, R_{1,2}=4.188 \text{ and } 4.193 \text{ Å, respectively. The } n=2 \text{ presents a broad distribution in } \gamma, \text{ except small peak at } \gamma=60^\circ, \text{ where the He–He attractive interaction is maximum, while the } n=3 \text{ state has one more peak at } \gamma=134^\circ. \text{ We should also note that around } \gamma=0 \there is a forbidden area, where the two helium atoms are collided [see Fig. 5(b)]. At the end the \( n=4 \) state is mainly localized in the police-nightstick (2) well, with peaks at \( \theta_{1,2}=109.58^\circ \) and \( 166.01^\circ, R_{1,2}=4.169 \text{ and } 5.312 \text{ Å, and } \gamma=67.17^\circ. \text{ Here, we should stress that the analysis of the above vibrational wave functions shows that the tetrahedral configuration is favored over the bifork configuration despite the reverse ordering of the minima predicted by the analytical form. This is due to the greater volume of the well in the}

![Fig. 7. Radial (a) and angular (b) probability densities for the lowest five vDW levels of He2ICl for J=0 calculated using the V(r,R1,R2,R3,θ1,θ2) PES. Solid line is for n=0 (police nightstick (1)), dotted line for n=1 (linear), dashed line for n=2 (tetrahedral), long-dashed line for n=3 (tetrahedral), and dotted-dashed line for n=4 (police nightstick (2)) states.](http://jcp.aip.org/jcp/copyright.jsp)
former case. The radial expectation values for each of the above structures, $R_i^0$ with $i=1,2$, obtained by averaging $R_i$ over the corresponding distributions, are listed in Table IV. To our knowledge, for the first time such results on the vibrationally averaged structures of He$_2$ICl are presented. In contrast with previous studies, based on ab initio calculations we propose different structural models, such as police nightstick or linear, in order to fit the rotationally resolved excitation spectrum of He$_2$Cl$_2$ or similar species. In addition, recent experimental observations have shown the existence of two different isomers for He$_2$ICl complex. The police nightstick has been found to be the most strongly bound one, while a second one has been assigned to a distorted tetrahedral structure, with both He atoms in the near T-shaped well. Unfortunately, more experimental data are not yet available. Our CCSD(T) results support the police-nightstick (1) structure as the most stable one in agreement with experimental observations. As it can be seen, the energy differences between the above mentioned isomers are small, with the larger one to account for 1.91 cm$^{-1}$ between the police nightstick (1) and linear isomer, while the smaller value (1.14 cm$^{-1}$) corresponds to the difference of the linear and tetrahedral ones (see EPAPS document). In turn, we should note that the lack of the $r$ dependence in the potential form might influence their relative stability. It has been shown that for the triatomic vdW complexes of He atom with homopolar/heteropolar halogens, the energy difference between the linear and T-shaped wells increases when the $r$ bond is lengthened, and such behavior should be reflected in the properties of the corresponding tetra-atomic complexes. However, in order to justify our assertions for such tetra-atomic species, further experimental data are needed for He$_2$ICl or similar clusters, and their comparison with our results would finally contribute to evaluate the present CCSD(T) potential.

V. SUMMARY AND CONCLUSIONS

A ground potential energy surface is presented for the He$_2$ICl complex, where the ICl molecule is frozen at its equilibrium bond length. CCSD(T) calculations are carried out at selected configurations and the existence of five different minima, namely, police nightstick (1), linear, bifork, tetrahedral, and police nightstick (2), is found for the He$_2$ICl. The ordering of the minima is confirmed by single point calculations in larger basis sets, including midbond functions and also using both MP4(SDQ) and CCSD(T) levels of theory, with the the police-nightstick (1) structure to be energetically more favored than the linear one. An analytical expression based on a sum of three-body HeICl CCSD(T)+bfs potentials and He−He interaction is used to represent the tetra-atomic CCSD(T) ab initio data. A very good agreement is found between the analytical potential values and the computed CCSD(T) interaction energies for the He$_2$ICl system. Further, by analyzing the behavior of individual components of the interaction energy, and by comparing with the He$_2$Br$_2$ case, we were able to rationalize the trends within the He$_2$XY family and to relate them to the properties of He−XY trimers. Accurate PESs for small molecules interacting with He atoms continue to be in demand since these molecules are probes of superfluidity in He nanodroplets. Thus, we propose such analytical form to accurately describe the intermolecular interactions for He$_2$-dihalogen complexes. This finding may also contribute to fit the rotationally resolved excitation spectrum of He$_2$Cl$_2$ or similar species, where the traditional tetrahedral structural models, based on atom-atom pairwise potentials, have failed.

The above surface is used to perform variational bound state calculations, and vdW energy levels and eigenfunctions for $J=0$ are evaluated for He$_2$ICl. Radial and angular distributions are computed for the five lower vibrational vdW states. All of them are well localized in configuration space, with an exception of the broad angular $\gamma$ distributions for the $n=2$ and $n=3$ states. The ground state corresponds to police-nightstick (1) isomer, while the linear isomer lies above in energy by only 1.91 cm$^{-1}$. The next two excited vdW levels are assigned to tetrahedral configurations and the fifth one to a police-nightstick (2) isomer. The binding energies and the average structures for these species are determined to be $D_0=33.51$ cm$^{-1}$ with $R_{0,1}^0=4.38$ Å, $D_0=31.60$ cm$^{-1}$ with $R_{0,2}^0=4.86$ Å, $D_0=30.46$ cm$^{-1}$ with $R=4.38$ Å, and $D_0=28.03$ cm$^{-1}$ with $R_{0,2}^0=4.87$ Å, respectively. For the first time results on energetics and vibrationally averaged structures of He$_2$ICl are presented. Comparison of these results with recent experimental predictions attributes to evaluate the quality of the present surface, at least in an area nearby the different isomeric configurations, and to justify our predictions on their relative stability.

Whether the properties of the weak bonding in such systems can be predicted by the sum of atom-diatom interactions deserve further investigation. Such model might be applicable to a broad class of R$_2$XY vdW clusters. In the present study, the importance of introducing a heteropolar dihalogen, as well as changing the reduced mass of the complex, is evaluated. However, it is particularly interesting to investigate the intermolecular interactions and structural properties of similar clusters consisting of heavier R$_2$ atoms, e.g., argon, where the Ar–Ar interaction is stronger. Thus additional interactions terms should be included for representing the global PES. Further, calculation and analysis of bound states for $J>0$ are also useful, as it could be indicative for infrared experimental studies. Extension of the present work in these lines is in progress.

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47 See EPAPS Document No. E-JCPSA6-124-017623 for the MP4(SDTQ)/CCSD(T) ab initio interaction energies and the potential values obtained from Eq. (2). This document can be reached via a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).
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