Ab initio study of He($^1S$)+Cl$_2$(X $^1\Sigma_g^-$, $^3\Pi_u$) potential energy surfaces

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The potential energy surface of the ground state He+Cl$_2$(X $^1\Sigma_g^-$) is calculated by using the perturbation theory of intermolecular forces and supermolecular Möller–Plesset perturbation theory approach. The potential energy surface of the first excited triplet He+Cl$_2$(X $^3\Pi_u$) was evaluated using the supermolecular unrestricted Möller–Plesset perturbation theory approach. In the ground state two stable isomers are found which correspond to the linear He–Cl–Cl structure (a primary minimum, $D_e$=45.1 cm$^{-1}$, $R_g$=4.25 Å) and to the T-shaped structure with He perpendicular to the molecular axis (a secondary minimum, $D_e$=40.8 cm$^{-1}$, $R_g$=3.5 Å). The small difference between these geometries is mainly due to the induction effect which is larger for the linear form. The results obtained for the T-shaped minimum are in good agreement with the excitation spectroscopy experiments which observed only the T-shaped form [Beneventi et al., J. Chem. Phys. 98, 178 (1993)]. In the lowest triplet states correlating with Cl$_2$(X $^3\Pi_u$), $^3A'$ and $^3A''$, the same two isomers correspond to minima. Now, however, the T-shaped form is lower in energy. The $^3A'$ and $^3A''$ states correspond to ($D_e$,$R_g$) of (19.9 cm$^{-1}$, 3.75 Å) and (30.3 cm$^{-1}$, 3.50 Å), respectively, whereas the linear form is characterized by (19.8 cm$^{-1}$, 5.0 Å). The binding energy for the T form in the lower $^3A''$ state is in good agreement with the experimental value of Beneventi et al.

I. INTRODUCTION

According to experimental findings, two different forms of rare-gas–halogen molecule complexes exist: a linear form and a T-shaped form. The linear form is adopted by the Ar–ClF$^1$ and Kr–ClF complexes$^2$ whereas the Rg–X$_2$ systems (where X stands for a halogen atom) were found to be T shaped, e.g., He–I$_2$, $^3$He–Cl$_2$, $^4$He–Br$_2$, $^6$Ne–Cl$_2$, $^6$Ne–Br$_2$, $^7$Ar–ClF$^8$ and Ar–Cl$_2$. Understanding the origin of these shapes as well as reliable characterization and modeling of the potential energy surfaces (PES) for such systems has proven to be a challenge for experimentalists and theoreticians alike.

The ab initio calculations for the Ar–ClF dimer$^9,10$ agreed with the experimental finding that the linear isomer should be stable.$^1$ However, the calculations predicted the linear form to be stable also in the Ar–Cl$_2$ case$^9,11$ while the experimental measurements, using excitation spectroscopy$^8$ and microwave spectroscopy$^{12}$ unambiguously detected only the T-shaped isomer. The energy difference between these two structures proved to be relatively small. Although the first estimates amounted to 30–36 cm$^{-1}$,$^9$ more extensive calculations recently provided a better estimate of about 15 cm$^{-1}$.$^9,11$ One plausible reason why only the T-shaped isomer is observed is, according to Tao and Klemperer,$^9$ that the zero-point energy of the linear form should be larger than that of the T-shaped form. In view of the small energy difference obtained in Ref. 11 it is conceivable that the T isomer of Ar–Cl$_2$ is stabilized by the smaller zero-point energy in this configuration.

Owing to Tao and Klemperer$^9$ and to our own recent results,$^{11}$ a better understanding of the discrepancy between theory and experiment in the Ar–Cl$_2$ case has been achieved. However, more detailed and quantitative study of the origin of the interaction and sources of anisotropy in the Rg–Cl$_2$ complexes is still needed.

The first question is whether in all Rg–Cl$_2$ complexes the T-shaped isomer is stable only because of the zero-point oscillations, or perhaps Ar–Cl$_2$ is an exception and some of the other complexes simply reveal a deeper well for the T structure. The best candidate to be different from Ar–Cl$_2$ is He–Cl$_2$ because a small difference between $L$ and $T$ forms in Ar–Cl$_2$ proved to be due to the induction effect$^{11}$ (the T-shaped isomer would be more stable than the linear if one neglected the induction contributions). The induction effect should be considerably reduced for He, due to its compact electron charge density and much smaller polarizability than Ar.

Another interesting issue is the stable structure of Rg–Cl$_2$ in the lowest triplet B excited state which correlates with the $^3B$(3$^3\Pi_{u}(a)$) state of Cl$_2$. This state is used in the excitation spectroscopy experiments to produce the ground state Rg–Cl$_2$ molecules. The experiment has proven that the
T-shaped isomer is stable. But is the excited state T-shaped due to the deeper well depth or again due to zero-point oscillations?

This paper addresses the above two issues in the particular case of the He–Cl₂ complex. The potential energy surfaces and their components are calculated ab initio for both the ground He+Cl₂(Σ⁺g) and excited He+Cl₂(Π₁g) states.

In the case of the ground state, the total interaction energy can be partitioned into fundamental components, such as electrostatic, exchange, induction and dispersion, by applying the combination of the supermolecular Möller–Plesset perturbation theory (MPPT) with the perturbation theory of intermolecular forces. Such an approach has proven successful in similar analyses of a number of other Ar-molecule van der Waals species.

In the case of the excited state we analyzed both the 3A' and 3A'' states which arise after removal of Π degeneracy for the $T$ and all skew shapes. We neglected the spin–orbit splitting which was assumed to be geometry independent.

The experience with supermolecular calculations of weak interactions between closed and open shell species is very limited. In the case of atom–diatom interactions one should mention two recently studied models, Ar–OH(²Π₂g, ³Σ₁g) and B(³P)–H₂(¹Σ₂g, ³Π₁g) which are relevant to our complex. These studies applied CI-type methods. In the present case we use unrestricted MPPT(UMPPT) which has been shown reliable and accurate previously, in the case of ³Π MgHe and ³Σ He₂.

II. METHOD AND DEFINITIONS

The supermolecular Möller–Plesset perturbation theory (MPPT) interaction energy corrections are derived as the difference between the values for the total energy of the dimer and the sum of the subsystem energies, in every order of perturbation theory

$$\Delta E^{(n)} = E^{(n)}_{AB} - E^{(n)}_{A} - E^{(n)}_{B}, \quad n = SCF, 2, 3, 4, \ldots$$

The sum of corrections through the $n$th order will be denoted $\Delta E^{(n)}$; thus, e.g., $\Delta E^{(3)}$ will symbolize the sum of $\Delta E^{(SCF)}$, $\Delta E^{(2)}$, and $\Delta E^{(3)}$.

Each individual $\Delta E^{(n)}$ correction can be interpreted in terms of intermolecular Möller–Plesset perturbation theory (I-MPPT) which encompasses all well-defined and meaningful contributions to the interaction energy such as electrostatic, induction, dispersion, and exchange, and may be expressed in the form of a double perturbation expansion. The I-MPPT interaction energy corrections are denoted $\epsilon^{(i)}$, where $i$ refers to the order of the intermolecular interaction operator and the intramolecular correlation operator, respectively (see Ref. 17 for more details).

A. Partitioning of $\Delta E^{SCF}$

$\Delta E^{SCF}$ can be dissected as follows (cf. Refs. 13–15 for more details):

$$\Delta E^{SCF} = \Delta E^{HL} + \Delta E_{def}^{SCF},$$

$$\Delta E^{HL} = \epsilon_{es}^{(10)} + \epsilon_{exch}^{HL},$$

where $\Delta E^{HL}$ and $\Delta E_{def}^{SCF}$ are the Heitler–London and SCF-deformation contributions, respectively. $\Delta E^{HL}$ is further divided into the electrostatic, $\epsilon_{es}$, and exchange, $\epsilon_{exch}$, components. The SCF deformation originates from mutual electric polarization restrained by the Pauli principle (quantum exchange effects). In this sense, the SCF deformation energy may be considered as quantum induction effect. Two exchangeless approximations to $\Delta E_{def}^{SCF}$ are also considered here, which are $\epsilon_{ind}^{(20)}$, and $\epsilon_{ind}^{(30)}$, and may be viewed as two representations of classic induction effect. The former describes the second-order induction effect at the uncoupled Hartree–Fock (UHF) level, and the latter at the coupled Hartree–Fock (CHF) level ("*" denotes inclusion of response effects).

B. Partitioning of $\Delta E^{(2)}$

$$\Delta E^{(2)} = \epsilon_{es}^{(12)} + \epsilon_{disp}^{(20)} + \Delta E_{def}^{(2)} + \Delta E_{exch}^{(2)},$$

$\epsilon_{es}^{(12)}$ denotes the second-order electrostatic correlation energy with response effects and $\epsilon_{disp}^{(20)}$ the second-order Hartree–Fock dispersion energy. $\Delta E_{def}^{(2)}$ and $\Delta E_{exch}^{(2)}$ stand for the second-order deformation correction and the second-order exchange correction, respectively. The latter encompasses the exchange–correlation effects related to electrostatic correlation and dispersion and can be approximated as follows (provided the deformation-correlation contribution is negligible): $\Delta E_{exch}^{(2)} = \Delta E^{(2)} - \epsilon_{disp}^{(20)} - \epsilon_{es}^{(12)}$.

C. Partitioning of $\Delta E^{(3)}$

$$\Delta E^{(3)} = \epsilon_{disp}^{(21)} + \epsilon_{disp}^{(30)} + \epsilon_{exch}^{(13)} + \Delta E_{def}^{(3)} + \Delta E_{exch}^{(3)},$$

$\epsilon_{exch}^{(13)}$ denotes the third-order electrostatic correlation energy with response effects. $\epsilon_{disp}^{(21)}$ represents the third-order Hartree–Fock dispersion energy, while $\epsilon_{disp}^{(30)}$ describes the first-order intracorrelation correction to the second-order dispersion energy. $\Delta E_{def}^{(3)}$ and $\Delta E_{exch}^{(3)}$ stand for the third-order deformation correction and the second-order exchange correction, respectively. The first term in Eq. (6) is the dominant component of the $\Delta E^{(3)}$ correction in Ar-molecule complexes.

D. Excited state case

The excited states of He–Cl₂ are open shell states which are calculated by means of UMPPT. The supermolecular energies are defined identically as in Eq. (1) by replacing the restricted Hartree–Fock and correlated energies by unrestricted ones. However, the decomposition into perturbation components is more involved and has not been done so far.

The fact that the UMPPT states are not pure spin states is not a serious problem as long as the contamination is small and identical for both the dimer and the monomer case. A typical problem is that not only may the UHF procedure have problems with convergence but may converge to a local minimum of different spin contamination for the dimer than for the monomers. Such an inconsistency may lead to nonsensical interaction energies. Applying a projected ap-
E. Calculations of interaction energies

Calculations of all the supermolecular $\Delta E$ values and perturbational interaction terms $d^{(ij)}$ are performed using the basis set of the entire complex, i.e., dimer-centered basis sets (DCBS). With reference to supermolecular quantities this procedure amounts to applying the counterpoise method of Boys and Bernardi. To assure the consistency of evaluation of the MPPT and I-MPPT interaction energy corrections of all the intermolecular perturbation terms, $d^{(ij)}$ must be derived in the DCBS as well.

In contrast to weak interactions between closed-shell states, the counterpoise procedure is not so clear-cut for interactions involving open-shell states. For example, calculation for the $\Pi$ symmetry Cl$_2$ monomers with ghost orbitals located as in the T-shaped geometry may provide an unphysical splitting into $A'$ and $A''$ states. The question is: shall we use separate monomer counterpoise states for separate $A'$ and $A''$ dimer states? Or, perhaps, the consistent treatment of monomers demands that we use the same monomer wave functions for both states. In either case the presence of ghost orbitals breaks the monomer symmetry. In addition, the splitting results in quasidegeneracy, the more serious the smaller BSSE. In this work we use the second approach (cf. also Esposti and Werner). Another solution has been suggested by Alexander. Nevertheless the problem is worth further studies.

F. Basis sets and geometries

The basis sets used throughout this study were based on the following choice: Cl: \{(14s,10p,4d,1f)/(7s,5p,2d,1f)\} medium-polarized basis set constructed in Ref. 32 according to the prescription of Sadlej, augmented with one $f$-symmetry orbital (exponent 0.15); the performance of this basis set for the Cl$_2$ molecule was discussed previously for Ar–Cl$_2$ (see Table 1 in Ref. 11).

For He the (10s,6p,2d)/(6s,4p,2d) basis set was used. The (10s6p)/(6s4p) part was taken from Gutowski et al. (this set was used there in the HeLi$^+$ case). The $d$-symmetry functions (exponents: 0.15293, 0.49871) were optimized for the dispersion term by Gutowski et al. This basis set, denoted $spdf$, was used to derive the PES.

Selected points on the PES were also calculated with a larger basis set, denoted $spdf(b-ext)$ which included a set of bond functions $[3s3p2d]$ of Tao and Pan. This set was originally designed for He$_2$ but has also proven very efficient in Ar$_2$ calculations as well as for other complexes with Ar. The role of bond functions has been investigated also in Refs. 35 and 38.

The definition of geometrical parameters of the He–Cl$_2$ complex is shown in Fig. 1. $R$ denotes the distance between the center of mass of the Cl$_2$ molecule and the He atom, and $\Theta$ corresponds to the angle between the $R$ vector and the Cl$_2$ bond axis. The interatomic separation in the ground $^{3}I^+\Sigma^+_g$ state of Cl$_2$ was fixed at 1.990 Å and in the $^3\Pi_u$ state at 2.400 Å. The excited Cl$_2$ molecule is in the lowest triplet state and thus accessible within the UMPPT framework. Moreover, this state is well isolated from the ground and other excited states so no curve crossing occurs. The spin contamination is very small and $S^2$ amounts to 2.0427. The optimization of geometry within the UMPPT calculation yielded $R_e=2.471 \pm 0.001$ Å, and the $ab initio$ estimate of 2.434 Å.

The calculations were carried out using GAUSSIAN 88 and GAUSSIAN 92 programs and the intermolecular perturbation theory package of Cybulski.

III. RESULTS AND DISCUSSION OF GROUND STATE OF HE–Cl$_2$(1$\Sigma^+_g$)

A. Features of total PES

The PES (Table I) reveals two minima: a global one for the linear configuration (at $\Theta=0.0^\circ$ and reflected by symme-
try at 180°) and a local one for the T configuration (Θ = 90.0°). The estimates of the equilibrium distances for the linear and T configurations at the MP4/spdf level are 4.25 and 3.50 Å, respectively (see Tables II and III). They are expected to be somewhat too large because the spdf basis set underestimates attraction.

In order to visualize the shape of the PES, the curves representing cuts across the PES (obtained at the MP2/spdf level of theory) at eight values of R: 3.0, 3.25, 3.50, 3.75, 4.0, 4.25, 4.50, and 4.75 Å, and for Θ from 0° to 180° are shown in Fig. 2 and Table I.

One can see that the T minimum region closely approaches the middle of the Cl–Cl bond and is located between steeply repulsive walls. These walls serve as a considerable barrier for internal rotation of the Cl₂ moiety around its center of mass. The linear minimum, although deeper in an absolute sense, occurs at larger R≈4.25 Å in a relatively flatter region of the PES. There, a barrier for the internal rotation of Cl₂ is only about 20 cm⁻¹. The barrier for the lowest energy path from L to T amounts to 20 cm⁻¹ and corresponds to a transition state at around R=4.5 Å and Θ=40°. All the above numerical values in Table I should be considered as approximate as the spdf basis set provides results that are not attractive enough by ~10% and additional unsaturation is caused by neglecting the higher order correlation effect.

The energetic characteristics of the two minima are presented in Tables II and III. To examine convergence with respect to the basis set effects, the analysis is performed for the spdf, and spdf(b-ext) basis sets. The best estimates of Dₓ at the global and local minima are 45.0 and 40.7 cm⁻¹, respectively, obtained with the spdf(b-ext) basis set. In Tables II and III one can see that the linear minimum persists as deeper than the T minimum at each level of theory [ΔE(2), ΔE(4), SCF+disp] and for each basis set [spdf, and spdf(b-ext)], and the difference at the MP4 level remains within the range of 3–5 cm⁻¹.

As expected, for both minima a major stabilizing factor is dispersion. What distinguishes them is the role of the induction effect. Indeed, the ratio ΔE_{def}/ΔE_{disp}(20) obtained using the spdf(b-ext) amounts to 9% for the linear structure and only 4% for T, which may be compared to 13% and 3%, respectively, in the Ar–Cl₂ case.¹¹ That is, the induction effect favors the linear structure of He–Cl₂, although not to the same degree as in the case of the complex with Ar (the compact electronic charge density of He yields less polarization effect than does Ar). Even stronger relative stabilization of the analogous linear minimum by induction has been observed previously for Ar–ClF¹⁰ and Ar–HCl.⁴³ For the collinear Ar–Cl–F configuration ΔE_{def}, compared with ΔE_{disp}(20), represents a larger contribution and amounts to 23% of the latter, whereas for the T configuration it amounts to only 3%. For the collinear hydrogen-bonded Ar–H–Cl configuration, the relative induction contribution is still larger, about 30% of the dispersion term.

To estimate the quality of our Dₓ values it is important to analyze the convergence of MPPT and the basis set effects. The convergence through the fourth order is similar to that for Ar–ClF¹⁰ and Ar–HCl⁴³ as well as other van der Waals complexes of argon.⁴⁴ That is, ΔE(2) provides a major attrac-

### Table III. Characteristics (in μH) of the minimum regions of the ground state He–Cl₂(Σ⁺) complex. Basis set was spdf unless stated otherwise.

<table>
<thead>
<tr>
<th>R (Å)</th>
<th>MP2</th>
<th>SCF+D</th>
<th>MP4</th>
<th>MP4*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T configuration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.25</td>
<td>-99.5</td>
<td>-180.0</td>
<td>-125.8</td>
<td>-125.8</td>
</tr>
<tr>
<td>3.50</td>
<td>-145.1</td>
<td>-180.0</td>
<td>-163.6</td>
<td>-185.7</td>
</tr>
<tr>
<td>3.75</td>
<td>-131.1</td>
<td>-147.4</td>
<td>-143.8</td>
<td>-143.8</td>
</tr>
<tr>
<td></td>
<td>Linear configuration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.00</td>
<td>-115.9</td>
<td>-183.1</td>
<td>-137.3</td>
<td>-137.3</td>
</tr>
<tr>
<td>4.25</td>
<td>-167.5</td>
<td>-193.5</td>
<td>-183.2</td>
<td>-205.5</td>
</tr>
<tr>
<td>4.50</td>
<td>-144.2</td>
<td>-153.8</td>
<td>-154.9</td>
<td>-154.9</td>
</tr>
</tbody>
</table>

* Basis set spdf(b-ext), i.e., spdf+bond(3s3p2d).
TABLE IV. \( \Theta \) dependence of the interaction energy contributions of the ground state He–Cl\(_2\)(\( \Sigma^+ \)) complex calculated with the \( spdf \) basis set (frozen-core approximation, \( R=4.25 \text{ Å} \), energies in \( \mu \text{H} \)).

<table>
<thead>
<tr>
<th>( \Theta ) (deg)</th>
<th>( \epsilon_{\text{exch}}^{(10)} )</th>
<th>( \epsilon_{\text{exch}}^{(9)} )</th>
<th>( \Delta E^{(10)} )</th>
<th>( \Delta E^{(9)} )</th>
<th>( \Delta E^{\text{SCF}} )</th>
<th>( \Delta E^{\text{SCF}} )</th>
<th>( \epsilon_{\text{disp}}^{(20)} )</th>
<th>( \epsilon_{\text{disp}}^{(20)} )</th>
<th>( \epsilon_{\text{disp}}^{(12)} )</th>
<th>( \Delta E^{\text{exch}} )</th>
<th>( \Delta E^{\text{exch}} )</th>
<th>( \Delta E^{(2)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-35.97</td>
<td>177.31</td>
<td>141.34</td>
<td>112.10</td>
<td>-29.24</td>
<td>-27.01</td>
<td>-305.60</td>
<td>-5.76</td>
<td>-279.66</td>
<td>31.70</td>
<td>-167.56</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>-41.16</td>
<td>210.18</td>
<td>169.02</td>
<td>142.07</td>
<td>-26.95</td>
<td>-21.90</td>
<td>-278.22</td>
<td>-6.29</td>
<td>-248.58</td>
<td>35.92</td>
<td>-106.51</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>-30.81</td>
<td>164.49</td>
<td>133.68</td>
<td>116.88</td>
<td>-16.80</td>
<td>-11.53</td>
<td>-205.29</td>
<td>-5.49</td>
<td>-179.37</td>
<td>31.41</td>
<td>-62.49</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>-11.74</td>
<td>64.23</td>
<td>32.49</td>
<td>46.39</td>
<td>-6.10</td>
<td>-3.89</td>
<td>-131.27</td>
<td>-2.88</td>
<td>-118.61</td>
<td>15.54</td>
<td>-72.22</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>-2.68</td>
<td>14.16</td>
<td>11.47</td>
<td>10.21</td>
<td>-1.26</td>
<td>-0.80</td>
<td>-91.59</td>
<td>-1.09</td>
<td>-87.83</td>
<td>4.85</td>
<td>-77.62</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>-1.71</td>
<td>8.69</td>
<td>6.98</td>
<td>6.24</td>
<td>-0.74</td>
<td>-0.48</td>
<td>-86.68</td>
<td>-0.86</td>
<td>-84.04</td>
<td>3.50</td>
<td>-77.80</td>
<td></td>
</tr>
</tbody>
</table>

FIG. 3. \( \Theta \) dependence of the SCF interaction energy and its components in the ground-state He–Cl\(_2\) complex \( (R=4.25 \text{ Å}) \).

FIG. 4. \( \Theta \) dependence of the correlated interaction energy components in the ground-state He–Cl\(_2\) complex \( (R=4.25 \text{ Å}) \).
atom may thus be considered a more sensitive probe of the electron distribution.\textsuperscript{46}

The details of the anisotropies of $\Delta E_{\text{def}}$ and $\epsilon_{\text{ind}}^{(20)}$ (not shown) are largely similar and the latter faithfully approximates the former.

The correlation components are shown in Fig. 4 along with the total interaction energy. One can see that $\Delta E(2)$ is actually determined by the dispersion term. $\epsilon_{\text{corr}}^{(2)}$ is practically negligible, while $\Delta E_{\text{exch}}$ is small. The $\Delta E(2)$ and $\epsilon_{\text{corr}}^{(2)}$ curves reveal minima at the CI ends and a maximum in the middle of the Cl-Cl bond. One notes that the dispersion term favors the linear configuration whereas the $T$ minimum occurs at the lowest value of the repulsive $\epsilon_{\text{exch}}$ term (see above and Fig. 3). The above description agrees with the findings for the Ar–Cl\textsubscript{2} case.\textsuperscript{51}

The total interaction energy $\Delta E(2)$, at $R$ fixed at 4.25 Å, shown in Fig. 4, gives us the shape of the PES in the region of the linear minimum. For angles close to the $T$ configuration, the curve corresponds to that portion of the PES which is related to distances substantially larger than the $T$ equilibrium distance ($R=3.5$ Å). In this region the PES looks like a wide plateau which lies above the $L$ minimum region. On closer look the plateau reveals small barriers at its borders, 40$^\circ$ and 140$^\circ$, and a tiny barrier in the middle. It should be noted that the border barriers occur for a wide range of intermolecular distances, as they separate the $L$-minimum valley from the $T$-minimum valley (see also Fig. 2).

For very large $R$ (not shown in the figures) the shape is determined by the dispersion component. That is, it has valleys at the CI ends whereas the plateau for the $T$ configuration transforms into a barrier.

\section*{IV. RESULTS AND DISCUSSION OF EXCITED $3\mathit{A'}$ AND $3\mathit{A''}$ STATES OF He–Cl\textsubscript{2}}

The He–Cl\textsubscript{2} clusters studied by pump–probe spectroscopy correlate with the long-lived Cl\textsubscript{2} $B\ 3\Pi_{0+}$, state.\textsuperscript{49,50} If we neglect spin–orbit coupling, this state corresponds to the lowest triplet state, $3\Pi_{1}$, with the dominant electronic configuration $(\sigma_{g})^{2}(\pi_{u})^{4}(\pi_{g})^{3}(\sigma_{u})^{1}$.\textsuperscript{39} The latter is a single excited configuration from the ground state configuration $(\sigma_{g})^{3}(\pi_{u})^{4}(\pi_{g})^{4}(\sigma_{u})^{0}$. Because of the presence of the He atom the symmetry of the complex is lower than that of Cl\textsubscript{2}, therefore, unless He–Cl\textsubscript{2} assumes a strictly linear geometry, two nondegenerate electronic states arise related to the original $3\Pi_{0}$ state of Cl\textsubscript{2}. More specifically, if the geometry of the complex is $C_{\text{a}}$, the $3\Pi_{u}$ state of Cl\textsubscript{2} correlates with the $3\Pi$ state of He–Cl\textsubscript{2}. If the geometry is $C_{2v}$, the $3\Pi_{u}$ state gives rise to $3\mathit{A'}$ and $3\mathit{B}$ states, which are, respectively, symmetric and antisymmetric with respect to the plane of the cluster. For the intermediate skew geometries of the $C_{2}$ symmetry, these two states are termed $3\mathit{A'}$ and $3\mathit{A''}$. The states are expected to be very close to each other since the perturbation exerted by He is small. In addition, when He rotates from the perpendicular T-shaped geometry toward the collinear structure these two states converge to become degenerate at the linear geometry. It is important to note here that we do not know how these two electronic states are involved in the experimentally produced excited $3\mathit{B}$ He–Cl\textsubscript{2} clusters.

Application of the UMPPT method to states which are so close must cause convergence problems (cf. Ref. 27). Below we describe how we obtained an almost complete scan of the PES for $3\mathit{A'}$ and a fragment of the $3\mathit{A''}$ PES related to the perpendicular configuration $3\mathit{A'}$: The convergence to the $3\mathit{A'}$ state was smooth for the $T$-shaped geometry. For the neighboring skewed geometries, convergence was only possible by initializing the SCF procedure with the vectors from the perpendicular geometry. Further geometries were converged by using vectors from some other converged nearby geometries. The reported points on the PES in the range of $\Theta=90^\circ$–$\Theta=40^\circ$ were obtained in this way. For $\Theta=20^\circ$ only two points ($R=4.75$ Å and $R=5.0$ Å) were obtained. For other $R$ distances we were not able to force convergence by using the vectors from neighboring geometries. It is plausible that the two states, $3\mathit{A'}$ and $3\mathit{A''}$, are already too close to each other in this geometry and the symmetry breaking prevented the procedure from converging.

In the collinear geometry where the $\Pi$ state degeneracy was exact, the convergence was smooth in the region of 4.25 Å–5.0 Å, provided that the initial guess was obtained by diagonalization of the core Hamiltonian. The points where the convergence failed are indicated by letter "e" in Table V.

In all the calculations described above the spin contamination of both the Cl\textsubscript{2} moiety (calculated within DCBS) and

\begin{table}[h]
\centering
\caption{Potential energy surface of the excited state $3\mathit{A'}$ He–Cl\textsubscript{2}($3\Pi_{1}$) complex from the UMP2/spdf level calculations in $\mu$H.}
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
$R$ (Å) & 0.0 & 20.0 & 40.0 & 60.0 & 80.0 & 90.0 \\
\hline
3.25 & & & & & 13.29 & \\
3.50 & 13.29 & & & & & \\
3.75 & & & & & & \\
4.00 & & & & & & \\
4.25 & 278.7 & & & & & \\
4.50 & 9.97 & & & & & \\
4.75 & & & & & & \\
5.00 & & & & & & \\
5.25 & & & & & & \\
5.50 & & & & & & \\
\hline
\end{tabular}
\end{table}

\textsuperscript{Convergence problems.}
in the dimer was very small. For the Cl₂ monomer \( S^2 \) was equal to 2.0427 for the MCBS and all DCBS calculations. For the dimer \( S^2 \) oscillated from 2.0423 to 2.0429. Occasionally the UHF procedure for the dimer converged to an unwanted local minimum. This was manifested by \( S^2 \) different from the above values and equal to 2.0197. It is important to stress that both the dimer and monomer must have practically the same spin contamination. Otherwise subtraction of the dimer and monomer energies becomes inconsistent and the interaction energies nonsensical.

For the dimer the ghost orbitals located in the \( 1s \) orbital. The resulting vectors were used to converge the remaining points. As in the \( A' \) state the spin contamination proved to be very small with \( S^2 \) equal to 2.0427. To evaluate the interaction energies, the same monomer energies (calculated with DCBS) were used as for the \( A' \) state. We also estimated that the difference between the DCBS energies for the ghost orbitals located in the \( A' \) and \( A'' \) symmetries did not exceed a few \( \mu \)H.

A. Features of total \( 3A' \) PES

The PES of the excited \( 3A' \) state reveals two minima: a global one for the \( T \) configuration (\( \Theta = 90.0^\circ \)) and a local one for the linear configuration (at \( \Theta = 0.0^\circ \) and reflected by symmetry at \( 180^\circ \)). The estimates of the equilibrium distances for the \( L \) and \( T \) configurations at the UMP2/spdf level are 5.0 and 3.75 Å, respectively. In contrast to the ground state, the \( T \)-shaped form constitutes a deeper minimum (see below).

In order to visualize the shape of the PES, the curves representing cuts across the PES (obtained at the UMP2/spdf level of theory) at eight values of \( R \) and for \( \Theta = 0^\circ \)–\( 180^\circ \) are shown in Fig. 5 and Table V. As noted above, at some points in Table V (the entries denoted \( c \)) we were unable to converge the UHF procedure.

One can see that the \( T \) minimum region relatively closely approaches the middle of the Cl–Cl bond and is located between steeply repulsive walls. These walls hinder the internal rotation of the Cl₂ moiety around its center of mass. In contrast to the ground state case, the \( T \) minimum is deeper than the \( L \) minimum. The linear minimum occurs at larger \( R = 5.0 \) Å, in a relatively flatter region of the PES. There, a barrier for the internal rotation of Cl₂ is only about 11.0 cm⁻¹. The barrier for the lowest energy path from \( T \) to \( L \) amounts to 6 cm⁻¹ and corresponds to a transition state at around \( R = 4.5 \) Å and \( \Theta = 40^\circ \).

To examine convergence with respect to the basis set extension we attempted to use the basis set augmented with bond functions, \( spdf(b-ext) \). For the linear isomer a reasonable lowering of 1 cm⁻¹ (which constitutes \( \sim 7\% \)) was obtained. Such lowering is compatible with the results for the ground state and is typical of other complexes. However, at the \( T \) configurations the bond functions resulted in breaking of symmetry and led to a dramatic and improbable lowering of 9 cm⁻¹, i.e., about 45%.

It is difficult to establish precisely the accuracy of the excited state results. First, the calculations are not as elaborate as for the ground state and the basis set lacked bond functions. Moreover, experience with van der Waals complexes in excited states is extremely limited and there is not much evidence which can guide us in this regard. Yet, the \textit{ab initio} calculations for model systems, \( 3\Sigma \) state of He₂ and \( 3\Pi \) state of MgHe, which used a similar strategy, provided \( D_e \) results which were too small by less than 10%. To be on the safe side we assume that our present results are at least semiquantitatively correct and certainly warrant further studies.

B. Sources of anisotropy of \( 3A' \) PES

For an open shell state we are not able to perform a similar decomposition of the interaction energy as for closed shell states. However, one can still analyze the major parts: the total SCF contribution and the total correlation contribu-
TABLE VI. \( \Theta \) dependence of the UMPPT interaction energy contributions in the \( ^3A' \) state of \( \text{He}-\text{Cl}_2(3\text{II}) \) complex in \( spdf \) basis set (frozen-core approximation; \( R=4.75 \text{ Å} \); energies in \( \mu \text{H} \)).

<table>
<thead>
<tr>
<th>( \Theta (\text{deg}) )</th>
<th>( \Delta E^{\text{SCF}} )</th>
<th>( \Delta E^{(3)} )</th>
<th>( \Delta E^{(2)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>109.34</td>
<td>-176.77</td>
<td>-67.43</td>
</tr>
<tr>
<td>20</td>
<td>71.37</td>
<td>-140.38</td>
<td>-69.02</td>
</tr>
<tr>
<td>40</td>
<td>26.23</td>
<td>-86.03</td>
<td>-59.80</td>
</tr>
<tr>
<td>60</td>
<td>9.40</td>
<td>-53.74</td>
<td>-44.34</td>
</tr>
<tr>
<td>80</td>
<td>7.39</td>
<td>-44.67</td>
<td>-37.28</td>
</tr>
<tr>
<td>90</td>
<td>7.22</td>
<td>-43.34</td>
<td>-36.12</td>
</tr>
</tbody>
</table>

TABLE VII. \( R \) dependence of the UMPPT interaction energy contributions for the T-shaped configuration in the \( ^3A' \) and \( ^3A'' \) excited states of \( \text{He}-\text{Cl}_2(3\text{II}) \) complex in \( spdf \) basis set (in \( \mu \text{H} \)).

<table>
<thead>
<tr>
<th>( R (\text{Å}) )</th>
<th>( \Delta E^{\text{SCF}} )</th>
<th>( \Delta E^{(3)} )</th>
<th>( \Delta E^{(2)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.25</td>
<td>529.52</td>
<td>-516.23</td>
<td>13.29</td>
</tr>
<tr>
<td>3.50</td>
<td>243.51</td>
<td>-321.84</td>
<td>-78.33</td>
</tr>
<tr>
<td>3.75</td>
<td>111.68</td>
<td>-203.43</td>
<td>-91.74</td>
</tr>
<tr>
<td>4.00</td>
<td>51.79</td>
<td>-131.57</td>
<td>-79.79</td>
</tr>
<tr>
<td>4.25</td>
<td>25.02</td>
<td>-87.82</td>
<td>-62.79</td>
</tr>
<tr>
<td>4.50</td>
<td>13.00</td>
<td>-60.75</td>
<td>-47.75</td>
</tr>
<tr>
<td>4.75</td>
<td>7.22</td>
<td>-43.34</td>
<td>-36.12</td>
</tr>
<tr>
<td>5.00</td>
<td>4.03</td>
<td>-31.49</td>
<td>-27.46</td>
</tr>
<tr>
<td>5.25</td>
<td>2.04</td>
<td>-23.07</td>
<td>-21.03</td>
</tr>
</tbody>
</table>

\*The CP-uncorrected result is 47.62 \( \mu \text{H} \).

\*The CP-uncorrected result is -660.50 \( \mu \text{H} \).

\*The CP-uncorrected result is -14.85 \( \mu \text{H} \).

\*The CP-uncorrected result is -688.68 \( \mu \text{H} \).
$A'$. First, the SCF energy is significantly reduced, and second, $\Delta E^{(3)}$ and $\Delta E^{(4)}$ are both attractive in the $A''$ state (while they cancel each other for the $A'$ state). Interestingly, the $\Delta E^{(2)}$ energies are very similar in both cases.

It is difficult to rationalize the difference in $\Delta E^{SCF}$ energies for the $A'$ and $A''$ states. Following Ref. 51 one could try to invoke the symmetry of overlapping orbitals to justify the difference in repulsion. However, all the orbitals which might make a difference [i.e., $\pi_{1s}(a_2,b_2)$ and $\sigma_{1s}(b_2)$] have zero overlap with the He $1s(a_1)$ orbital. Hence, the repulsive overlap-dependent part of $\Delta E^{SCF}_{exch}$ is expected to be similar for the $A'$ and $A''$ states. Therefore, it is plausible that the origin of the difference is in the attractive components $\epsilon_s^{\pi}$ or $\Delta E^{SCF}_{ad}$. We prefer to postpone further speculations until the perturbation analysis of the SCF energy for open-shell systems is implemented.

More puzzling facts are left unanswered. For example, are the $\Delta E^{(2)}$ terms almost equal in both cases? Perhaps, the dispersion energy, which dominates the excited state correlation energy is very isotropic. Much more difficult is rationalization of the reverse pattern of the third- and fourth-order terms in both states. It should be reiterated that the UMPPT convergence pattern in the $A''$ state is similar to the ground state and different from that in the $A'$ state.

Finally, we wish to comment on the value of the CP correction in these calculations. Table VII includes some values which are not CP corrected ($R=3.75$ Å, $\theta=90^\circ$). The uncorrected values are obviously nonsensical. The large magnitude of CP correction in this case is quite typical and results from the basis set which was chosen for the quality of interaction energy components and not to minimize BSSE. It should be stressed that the value of this correction should not be used to judge the quality of interaction energy.\(^{52}\)

V. CONCLUSIONS

A. Ground state of He–Cl$_2$

Our analysis of the ab initio PES of the ground state of the He–Cl$_2$ ($\Sigma_g^+$) complex indicates a global minimum for the collinear $L$ configuration and a local minimum for the T-shaped configuration. The estimates of $R_e$ and $D_e$ for these two minima are: (4.25 Å, 45.1 cm$^{-1}$) and (3.5 Å, 40.8 cm$^{-1}$). The obtained values of $D_e$ are expected to be in error by ±5%. According to our findings the $T$ configuration is confined by rather steep barriers to the bending motion, whereas in the $L$ configuration Cl$_2$ rotate nearly freely.

The experimental measurements of Beneventi et al.$^{46(c)}$ provide an estimate of $R_e$ and $D_e$ only for the $T$ configuration, $R_e$=3.56 Å and $D_e$=38.2 cm$^{-1}$, in good agreement with the present results. The $L$ configuration has so far eluded experimental detection. This is somewhat puzzling since the $L$ configuration is found to be slightly more stable. However, according to the estimates of Tao and Klemperer for Ar–Cl$_2$,$^9$ the zero-point energy may be different enough for these two isomers to make $D_e$ for the T-shape form larger. More likely, any complex as floppy as He–Cl$_2$ displays a complicated dynamics which should be treated in the way that goes beyond the simple harmonic approximation. The question as to which isomer is more stable should be resolved on dynamical grounds.

Our results shed new light also on the origin of anisotropy of the He–Cl$_2$ interaction. First, the electron distribution of the ground $\Sigma_g^+$ state Cl$_2$ may be visualized as a dumbbell. When He serves as a probe it can detect slight indentations at the Cl ends. In the previous study of Ar–Cl$_2$\(^{11}\) the Ar atom acting as a probe detected distinct flattening at the ends. Second, the induction energy favors the $L$ isomer. Indeed the HL+disp approximation predicts the T-shaped conformer to be more stable by about 1 cm$^{-1}$. The induction effect is relatively less important for the $L$ isomer than in the Ar–Cl$_2$ case (it amounts to 9% and 4% of the dispersion energy for the $L$ and $T$ forms, respectively, whereas for Ar–Cl$_2$ this contribution was 12% and 3%, respectively).

In this context, it is worthwhile to emphasize the role of the induction term in determining relative stability of different isomers of van der Waals complexes containing halogens. While this term never provides a quantitatively dominant portion of binding energy its anisotropy may significantly influence the energetic balance and the final geometry.

B. $^3A'$ and $^3A''$ states of He–Cl$_2$

Both states possess two minima, a global one for the $T$ structure and the local one for the linear geometry. This is in contrast to the ground state where the linear geometry corresponds to the deeper minimum. Of the two excited states $^3A''$ is deeper. The estimates of $D_e$ and $R_e$ for $^3A''$ are 30.3 cm$^{-1}$ and 3.50 Å. These values obtained at the UMP4 level are still basis-set unsaturated and $D_e$ may be viewed as a lower bound to the true values and $R_e$ is expected to be overestimated. Because of symmetry both states coincide at the linear geometry. The well depth parameters obtained at the UMP4 level for this minimum are $D_e$=18.9 cm$^{-1}$ and $R_e$=5.0 Å. Again, the $D_e$ value is expected to be underestimated.

Our results shed new light also on the origin of anisotropy of the He–Cl$_2$ interaction. In particular, the electron distribution of the $^3\Pi_e$ excited state Cl$_2$ may be visualized as a dumbbell. In contrast to the ground state, however, this dumbbell seems to be stretched, with a longer "waist," and of convex rather than concave shape at the Cl ends. This difference may be attributed to promotion of an electron from a $\pi$-symmetry orbital to a $\sigma$ orbital, thus enhancing the ellipsoidal shape of the electronic distribution. Unfortunately, at the present state of our decomposition scheme we were not able to separate the induction term to find out how its role has changed. Further studies of the excited state with complete dissection of the interaction energy are underway in this laboratory.

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