On the use of explicitly correlated treatment methods for the generation of accurate polyatomic –He/H2 interaction potential energy surfaces: The case of C3–He complex and generalization


Citation: The Journal of Chemical Physics 141, 044308 (2014); doi: 10.1063/1.4890729
View online: http://dx.doi.org/10.1063/1.4890729
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I. INTRODUCTION

Small carbon clusters, Cₙ, play an important role in our environment, as precursors of soot and large carbon molecules, including aromatic species and fullerences, and also in Astrochemistry. The tricarbon cluster, C₃,¹ is considered as the most abundant chain in the interstellar medium (ISM). Its first spectroscopic observation in one astrophysical source was reported over a century ago when Huggins investigated the spectra of a comet tail and identified the emission of C₃ through the ₁^A Σ⁺ band. In 1988, the same emission was observed in cold carbon stars and supergiant circumstellar shells.² Because of its importance, considerable theoretical and experimental work was devoted to C₃ in the ground (₁^X Σ⁺) and electronically excited (₁^A Π_u, ₃^A Π_u, ₅^B Π_g, ₁^B Π_u, ₁^Y Π_u) states.³⁻⁵ The ₁^A Π_u, ₁^Y Π_u system has been extensively studied in laboratory.²⁻⁶⁻⁸ The first electronically excited state ₁^A Π_u, which lies ~3 eV over the ground state, presents a linear geometry and exhibits large Renner-Teller effects.⁹ In the singlet manifold, ₁^Σ⁺ represents the next higher electronically excited state. The ₁^Σ⁺, ₁^X Σ⁺ pattern was observed and studied by Chang and Graham in the 1980s,¹⁰ which was confirmed by a recent vacuum ultraviolet spectroscopy study on the matrix-isolated C₃ molecule.¹¹ The observation of this band is difficult because of the strong interaction with the ₁^A Π_u state and because of interactions with the triplet manifold. Two metastable triplet states, ₃^A Π_u and ₃^B Π_g, have been detected in matrix and gas phase.¹¹,¹² The ₃^B Π_g state is less known, even though gas phase ₅^B Π_g ₃^A Π_u vibronic transitions have been observed.¹³,¹⁴ However, as has been shown in experimental matrix isolated studies of C₃,¹¹,¹₂,¹₅ both manifolds interact mutually. For interpretation, several potential energy surfaces (PESs)⁵,¹⁶⁻¹⁸ were generated for the ground and excited states of C₃. In whole, this huge amount of experimental and theoretical investigations led to accurate characterization and to a reliable set of spectroscopic data for C₃(₁^X Σ⁺). They also showed that this molecule presents a pronounced floppy character.
More recently, the Herschel mission and ALMA telescopes have specific observations for $C_3$. These observations provided and still provide huge amount of data in the far-infrared and submillimeter energy domains for this molecule. The accurate analysis of this highly resolved spectra needs, in addition to high quality spectroscopic studies, the computations of cross sections for the excitation and de-excitation of $C_3(\tilde{X}^1\Sigma_g^+)$ by collisions with the abundant H$_2$ molecule. For simplicity, H$_2$ is replaced here by He, sure less abundant, but presenting similar electronic structure. For many systems, the similarity of collisional properties computed with He and para-H$_2$ has been demonstrated (see, for instance, Refs. 19, 20. Rate constants for rotational (de-)excitation of $C_3(\tilde{X}^1\Sigma_g^+)$ by He ($^1S$) were computed for the first time, in 2008, by Ben Abdallah et al.,$^{21}$ after incorporation of a 2D interaction PES into full close-coupling quantum scattering calculations within the rigid monomer approximation (RMA). The 2D-PES was generated at the CCSD(T)/aug-cc-pVTZ + 3s3p2d1f/bond functions (denoted hereafter as 2D-BA) and it was developed over R (distance between this center of mass and the He atom, Figure 1) and $\theta$ (defining the rotation of He around $C_3$, Figure 1) Jacobi coordinates, where the $C_3$ molecule was kept fixed to its structure at the ground vibrational state ($r_0 = 1.2772$ Å, $^{22,23}$ i.e., linear $C_3$ bond distances). The collision rates were obtained for low-temperatures ($T \leq 15$ K) avoiding hence to reach the first bending anharmonic level of C$_3$ (located at very low energy, 63 cm$^{-1}$).

In 2009, Zhang et al.$^{24}$ provided two 2D-PESs of C$_3$–He complex both of them computed at the MP4 and CCSD(T) levels. These 2D PESs were mapped along the $R$, $\theta$ Jacobi coordinates. $C_3$ structure was frozen to be either linear (CCC = 180°) or bent (CCC = 160°). Thus, they found that the two global minima correspond to a slightly distorted T-shaped configuration. Using these 2D PESs, these authors derived the rovibrational levels of C$_3$–He complex. Very recently, Denis-Alpizar et al.$^{25}$ built a 4D-PES over the $R$, $\theta$ Jacobi coordinates and also over the azimuthal angle ($\phi$) and the bending angle ($\gamma$) of the C$_3$ molecule (Figure 1). The intramonomer C–C distances were kept fixed to their $r_0$ experimental value in C$_3(\tilde{X}^1\Sigma_g^+)$. The electronic computations were carried out using the standard coupled-cluster technique with single and double excitations and a perturbative treatment of triple excitations (CCSD(T)) in connection with the aug-cc-pVQZ basis set and mid-bond functions. These larger computations confirm the near T-shaped structure of the C$_3$–He. These 4D-PES was used for the deduction of C$_3$–He bound states including excitations for the C$_3$ bending motion. In the following, we will refer to this PES as 4D-DA.

In this paper, we use the explicitly correlated coupled cluster methodology (CCSD(T)-F12) to generate two vdW surfaces corresponding to the ground electronic states: one 2D-PES for linear-C$_3$ ($C=C=C = 180^\circ$) interacting with He and one 4D-PES for the C$_3$–He system over the van der Waals (vdW) inter monomer coordinates and the internal bending coordinate. Both PESs correlate to the C$_3(\tilde{X}^1\Sigma_g^+) +$ He($^1S$) in the asymptote region. For the 2D-PES (4D-PES), we use a similar coordinate system and an analytical fitting procedure than Ben Abdallah et al.$^{21}$ and Denis-Alpizar et al.$^{25}$ which allows direct comparison of our explicitly correlated PESs with those deduced using the standard coupled cluster techniques. After dynamical computations, we also compare the pattern of bound rovibrational levels of this complex derived using both sets of PESs and the cross sections for the (de-)excitation of C$_3$ by He. This is the first time where the use of explicitly correlated methods for the generation of multidimensional potentials for vdW systems depending on both intra- and intermolecular degrees of freedom. As has been recently established for C$_4$–He, HCl–He, and CO$_2$–CO$_2$ complexes,$^{26–28}$ an overall agreement together with a strong reduction on computational time and disk occupancy are found when CCSD(T)-F12 in connection with the aug-cc-pVTZ basis set is used. Hence, it represents the selected method for mapping of multidimensional PESs of polyatomic – He/H$_2$ vdW interacting systems.

**II. GENERATION OF THE 2D AND 4D PES AND ANALYTICAL FITS**

The electronic structure computations were performed with the MOLPRO (version 2012) program suite$^{29}$ in the C$_1$ point group. They were carried out with the explicitly-correlated (CCSD(T)-F12) method in connection with the augmented correlation-consistent aug-cc-pVTZ basis set. We followed the methodology established by Hochlaf and co-workers for the computations of accurate interaction potentials for vdW systems depending on both intra- and intermolecular degrees of freedom. As has been recently established for C$_4$–He, HCl–He, and CO$_2$–CO$_2$ complexes,$^{26–28}$ an overall agreement together with a strong reduction on computational time and disk occupancy are found when CCSD(T)-F12 in connection with the aug-cc-pVTZ basis set is used. Hence, it represents the selected method for mapping of multidimensional PESs of polyatomic – He/H$_2$ vdW interacting systems.

![Figure 1. Coordinate system of the C$_3$–He complex. The linear C$_3$ molecule is along the Z axis, and the bent C$_3$ molecule is in the plane XZ.](image-url)
TABLE I. Comparison between present and previous minima characteristics for selected C₃–He configurations. Distances (R) are in bohr, angles (θ, φ, and γ) are in degrees and potentials (V) are in cm⁻¹.

<table>
<thead>
<tr>
<th>Method/basis set</th>
<th>Linear C₃ (γ = 180°)</th>
<th>Bent C₃ (γ = 160°)</th>
<th>Bent C₃ (γ = 120°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R</td>
<td>θ</td>
<td>V</td>
</tr>
<tr>
<td>CCSD(T)-F12/aug-cc-pVTZ</td>
<td>6.78</td>
<td>83.5</td>
<td>−27.91</td>
</tr>
<tr>
<td>CCSD(T)/aug-cc-pVQZ + mid-bond functions</td>
<td>6.82</td>
<td>81.4</td>
<td>−26.73</td>
</tr>
<tr>
<td>CCSD(T)/aug-cc-pVTZ + 3s3p2dΓ</td>
<td>6.75</td>
<td>90</td>
<td>−25.87</td>
</tr>
<tr>
<td>MP4/Cc-pVTZ and He:aug-cc-pVTZ</td>
<td>6.65</td>
<td>90</td>
<td>−31.29</td>
</tr>
<tr>
<td>CCSD(T)/aug-cc-pVTZ/3s3p2d</td>
<td>6.78</td>
<td>90</td>
<td>−25.54</td>
</tr>
</tbody>
</table>

*4D-F12 PES. This work.
*4D-DA PES. Reference 25.
*4D-BA PES. Reference 21.
*4D PES. Reference 24.

needed to correct for the non-size-consistency of CCSD(T)-F12 caused by the inclusion of triples, since CCSD-F12 itself is size-consistent. Therefore, the total energies were shifted up by their corresponding values for R = 100 bohrs (of ~4.5 cm⁻¹). This forces hence the PES to decay to zero in the asymptotic region.

When determining the interaction potentials (V(R, θ, φ, γ)), we took into account the basis set superposition error (BSSE) using the Boys and Bernardi counterpoise correction formula:

\[
V(R, \theta, \phi, \gamma) = \frac{E_{C_3 - He}(R, \theta, \phi, \gamma) - E_{C_3}(R, \theta, \phi) - E_{He}(R, \theta, \phi)}{E_{He}(R, \theta, \phi)},
\]

where \( E_{C_3 - He}(R, \theta, \phi, \gamma) \) can be computed in full basis set of the C₃–He complex. Close to the C₃–He equilibrium, the contribution of the BSSE to the interaction energy was about 1%–2%.

More than 24 700 total energies were carried out for different nuclear configurations covering the equilibrium geometry and the regions of the interactions of He with C₃. The θ angle was varied from 0° to 90° by step of 10°, and φ from 0° to 180° by step of 30°. The grids on γ and R were not uniform. Indeed, γ was fixed to values from 30° to 180° by step of 10°. γ was also fixed to 175° to account for the quasilinear behavior of C₃ along this coordinate. For R coordinate, we considered 29 values (R = 4.1, 4.2, 4.3, 4.4, 4.4, 4.5, 4.6, 4.8, 5.0, 5.2, 5.6, 6.0, 6.5, 7.0, 7.5, 8.0, 9.0, 10.0, 11.0, 12.0, 13.0, 14.0, 15.0, 16.0, 17.0, 18.0, 19.0, 20.0, 22.0, and 100, in bohrs).

Later on, the CCSD(T)-F12/aug-cc-pVTZ total energies were used to deduce a 2D (denoted hereafter as 2D-F12) and 4D (denoted as 4D-F12) analytical representations for C₃–He. For 2D-F12, we followed the methodology of Ben Abdallah et al. This was developed over the R and θ Jacobi coordinates where the γ was kept fixed to 180° and 0° (linear C₃). For 4D-F12, we used the fitted procedure described by Denis-Alpizar et al. Briefly, V(R,θ,γ,φ) is deduced as the contribution of short- and long-range terms. Both of them are developed over normalized associated Legendre polynomials depending on θ and Fourier expansion functions depending on φ. The coefficients of this expansion are function of R and γ. The switch between the short and long range terms is ensured by a switching function, S, which is a function of R. Further details can be found in Ref. 25.

For both fits, the mean difference between the analytic fit and the \textit{ab initio} interaction energies was less than 3.8% over the corresponding entire grid. This mean relative error should only be slightly underestimated. Indeed, several precautions were taken in order to avoid regions of the grid (at very long ranges and at the limit between attractive and repulsive regions at short range) where the potential is zero. Both expansions can be sent upon request.

III. RESULTS AND DISCUSSION

Table I presents the complex properties corresponding to the linear (γ = 180°) and bent structures (γ = 160° and 120°) deduced from 2D-BA, 4D-DA, 4D-F12, as well as, those derived from the 2D-PES of Zhang et al. Figures 2 and 3 display two-dimensional cuts of the C₃–He 4D-F12 PES together with the corresponding 2D cuts deduced from 4D-DA PES. These cuts are done over the R Jacobi distance and intra- and the inter-monomer bending coordinates. At first glance, both sets of contour plots are similar. For linear C₃, 2D-DA, our 2D-F12 and the one derived from 4D-DA PESs are similar. In addition, the anisotropy of the PES along the R, θ, φ, and γ already noticed by Denis-Alpizar et al. is well reproduced by the CCSD(T)-F12/aug-cc-pVTZ method. In the following, we will concentrate on the small deviations observed between 4D-F12 and 4D-DA.

For linear C₃ configuration (γ = 180°), the minimum of the 4D-F12 PES is −27.91 cm⁻¹ and corresponds to θ = 83.5° and R = 6.78 a₀. In the 4D-DA PES, the minimum of −26.73 cm⁻¹ is located at R = 6.82 a₀ and θ = 81.4°. In both cases, the barrier between the two symmetric minima is very small: it has been computed to be 0.03 cm⁻¹ with CCSD(T)-F12/aug-cc-pVTZ, while it was found to be 0.07 cm⁻¹ with the standard coupled cluster approach. It is worth noting that these values are in the order of the RMS. Nevertheless the \textit{ab initio} points confirm that the minimum is not exactly for θ = 90°. For γ = 180°, Zhang et al. computed a relatively deep potential by using MP4, which is rather doubtful. This was corrected well in their CCSD(T) treatment which is consistent with the present findings.

As expected, both PESs show similar behaviors along the inter-monomer coordinates and along the γ C₃ internal
bending. For $\gamma = 180^\circ$, 4D-F12 is $\sim 1.2$ cm$^{-1}$ deeper. This result unnoticed in the CCSD(T) surfaces, derives from the fact that explicitly correlated methods account better for electron correlation. Generally, CCSD(T)-F12/aug-cc-pVTZ results are viewed to be as accurate as those computed using CCSD(T)/aug-cc-pV5Z. This makes the system dissociation energy (from the first calculation of the bound levels) 0.4 cm$^{-1}$ deeper with respect to Denis-Alpiza et al. calculation (see below). Explicitly correlated treatment leads also to near T-shape equilibrium structure for the $C_3$–He complex very
close to the one found by these authors. Indeed, we compute $R = 6.59$ bohrs, $\theta = 90^\circ$, $\gamma = 120^\circ$, and $\phi = 180^\circ$ at equilibrium that compare quite well with their equilibrium geometry, i.e., $R = 6.57$ bohrs, $\theta = 90^\circ$, $\gamma = 120^\circ$, and $\phi = 180^\circ$. The 4D-F12 potential depth is $-37.1 \text{ cm}^{-1}$, which is slightly deeper than the depth of the 4D-DA PES ($-36.3 \text{ cm}^{-1}$). Hence, both PESs are similar, whereas the computational time (CPU time) using explicitly correlated method is reduced by $\sim 2$ orders of magnitude and the disk occupancy is reduced by a factor of $\sim 40$.

**IV. APPLICATIONS**

**A. Bound states computations**

The calculations of the bound levels were done using the atom-rigid bender close coupling (RB-CC) approach presented recently by Stoecklin et al.\textsuperscript{42} We took advantage of the fact that the bound states calculations differ from the scattering calculations only in the boundary conditions. A modification in our scattering code based on the log-derivative propagator following the recommendations of Hutson and Thornley\textsuperscript{43} was introduced to compute the ro-vibrational levels of C\textsubscript{3}–He complex using the 4D-DA PES. The details of these calculations were described in Ref. 25. Let us recall here only some of the essential features. For instance, we computed the rovibrational energies and wavefunctions of the rigid bender C\textsubscript{3} molecule using the symmetry adapted Hamiltonian developed by Carter et al.\textsuperscript{44} The close coupling equations were written considering the bending-rotation interaction. The calculations using the 4D-F12 PES were performed for two values of the propagator step size (0.05 bohr and 0.1 bohr), and the values of the bound state...
energies were obtained from a Richardson extrapolation. We included in the calculations six bending eigenfunctions of C₃ and ten rotational eigenfunctions for each bending function. The maximum propagation distance was set to be 50 bohrs.

Table II presents the bound state energies of the He–C₃ complex. The total angular momentum J and the parity ε are also reported. We give also the values reported by Denis-Alpizar et al.²⁵ using the RB-CC and those of Zhang et al.²⁴ considering the C₃ as a linear rigid molecule. The maximum value of the total angular momentum J leading to bound states is 6. Since the ν₂ = 0  → ν₂ = 1 excitation energy of C₃ (≈63 cm⁻¹) is larger than the depth well of the interaction potential, all the He–C₃ bound levels correspond to the bending quantum number of C₃ ν₂ = 0. This PES supports 27 bound levels and the dissociation energy (Dₑ) is 10.14 cm⁻¹, which is 0.41 cm⁻¹ higher than the calculated Dₑ from the 4D-DA PES. In fact, all our values are smaller than the computed ones using the 4D-DA PES, since our PES is expected to consider more correlation. The difference of the number of levels for J = 0 between our calculations and those of Zhang et al.²⁴ arises from symmetry restraints as Denis-Alpizar et al.²⁵ have discussed.

### Table II. Energies (E in cm⁻¹) of the bound states of C₃–He complex. J and p are the rotational quantum numbers and the parity of the levels, respectively. See Ref. 25 for more details.

<table>
<thead>
<tr>
<th>J</th>
<th>p</th>
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<th>Eᵇ</th>
<th>Eᵇ</th>
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<td>6</td>
<td>−</td>
<td>−1.95</td>
<td>−1.64</td>
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</tbody>
</table>

²⁴ 4D-F12 PES. This work.
²⁵ 4D-DA PES of Ref. 25.
²⁶ 2D-PES of Ref. 24.

### B. Cross sections calculations

The analytical representations of the 2D-PESs were used for computing the cross sections corresponding to the low energy collision rotational excitations of C₃ by He. These computations have been performed using the CC approach. Since CC is numerically exact, the results reflect the quality of the PESs incorporated into these calculations. Figure 4 presents the inelastic cross sections for the J = 2  → 0 transitions computed using 2D-BA and 2D-F12. Mostly, nor obvious neither significant differences exist between the two sets of data signature of the agreement between the cross sections obtained using both PESs.

In order to check the effect of the differences between the 4D-F12 PES and the surface of Denis-Alpizar et al.
(4D-DA) on the dynamics of the He–C₃ collision, we performed dynamics calculations using the Rigid Bender Close Coupling method (RBCC). This method allows treating exactly the coupling between bending and rotation within the rigid bender approximation. All the details of the calculations can be found in a paper dedicated to the dynamics of this system under publication. The collisional cross sections are represented in Figure 5 for the transitions starting from the initial fundamental rotational and bending level of C₃. As can be seen on this figure the results of the dynamics obtained using the two models of PES are almost identical for collision energies larger than 1 cm⁻¹ which are of interest in astrochemistry.

V. CONCLUSIONS AND PERSPECTIVES

Generally, the comparison of the multidimensional PESs generated using the CCSD(T)-F12/aug-cc-pVTZ approach and the standard CCSD(T) method shows that we achieve similar accuracy over the intermonomer vdW coordinate. This method describes also correctly the region of the PESs involving the intra-monomer coordinate. Accordingly, the evolution of the potential along these coordinates is well accounted for in addition to the possible potential couplings. Nevertheless, the computational time (CPU) and disk space are reduced by up to two orders of magnitude when using CCSD(T)-F12 instead of standard CCSD(T).

In recent works, we showed that CCSD(T)-F12/aug-cc-pVTZ is the method of choice for the generation of 1D and 2D intermonomer long range potentials and 4D intermonomer polyatomic complexes. Here, we go beyond these findings and a generalization is done. Indeed and through the comparison of the CCSD(T)-F12/aug-cc-pVTZ 4D-PES of C₃–He complex to the PESs generated using standard methodologies, we show that the use of explicitly correlated method leads to accurate mapping of the multi-dimensional PESs of polyatomic molecular systems, including the long range Jacobi and intermonomer coordinates and more interestingly the intramonomer degrees of freedom. As previously, a strong reduction of computational cost is observed. Hence, CCSD(T)-F12/aug-cc-pVTZ should be viewed as the key method for the generation of multi-dimensional polyatomic –He/H₂ potential energy surfaces for reactive and non-reactive collisions between polyatomic molecules (e.g., prebiotic molecules) with He or H₂, where several thousands (even millions) of energies for non-equivalent nuclear configurations are needed.

ACKNOWLEDGMENTS

This study was undertaken, while M.H. was a Visiting Professor at King Saud University. The support of the Visiting Professor Program at King Saud University is hereby gratefully acknowledged. O.D.-A., T.S., and P.H. thank a support from the Agence Nationale de la Recherche, Contract Nos. ANR-12-BS05-0011-01 and ANR-HYDRIDES. The authors acknowledge Marie Curie International Research Staff Exchange Scheme Fellowship within the 7th European Community Framework Program under Grant No. PIRSES-GA-2012-31754 and the COST Action CM1002 CODECS.

7. See http://webbook.nist.gov for other previous experimental determinations.