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Rovibrational energy transfer in the He-C₃ collision: Potential energy surface and bound states

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We present a four-dimensional potential energy surface (PES) for the collision of C₃ with He. Ab initio calculations were carried out at the coupled-cluster level with single and double excitations and a perturbative treatment of triple excitations, using a quadruple-zeta basis set and mid-bond functions. The global minimum of the potential energy is found to be −26.9 cm⁻¹ and corresponds to an almost T-shaped structure of the van der Waals complex along with a slightly bent configuration of C₃. This PES is used to determine the rovibrational energy levels of the He-C₃ complex using the Close Coupling level (RB-CC). The calculated dissociation energies are −9.56 cm⁻¹ and −9.73 cm⁻¹, respectively at the RMA and RB-CC levels. This is the first theoretical prediction of the bound levels of the He-C₃ complex with the bending motion. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4866839]

I. INTRODUCTION

Since their first detection in dense intermolecular clouds in the 1970s,¹ the carbon chains are expected to play an important role in the chemistry of interstellar and circumstellar clouds. It is especially interesting to estimate the abundance of the small pure carbon molecules, such as C₂, C₃, and C₅, because they are supposed to be the building blocks for other more complex interstellar molecules. Pure carbon chains have no permanent dipole moment but can be detected in dense and cold interstellar clouds through their infrared active low-energy bending vibrations as suggested by Van Orden.² In the present study we focus our interest on the carbon trimer C₃. Its emission spectrum near 4050 Å was observed³,⁴ first in comets as early as 1881, and it was identified⁵ in the laboratory in 1951. Since then, C₃ has been observed in several regions of the interstellar medium (ISM): in the atmospheres of cool stars,⁶ in circumstellar shell,⁷ and in diffuse interstellar clouds.⁸ Recently, Cernicharo et al.⁹ have detected nine lines of the bending mode of C₃ in Sagittarius B2 and IRC +10216. Mookerjea et al.¹⁰ observed several rovibrational transitions between the vibrational ground state and the low-energy bending mode in stars forming cores. In the dense ISM the presence of C₃ was proven using its mid- and far-infrared vibrational transitions.⁷,⁹,¹¹ C₃ was also identified in the diffuse interstellar medium, first by Maier et al.⁵ and later in several other studies¹²,¹³ along different lines of sight.

The detection of C₃ in the ISM has motivated many experimental¹⁴–¹⁸ and theoretical¹⁹–²² studies dedicated to the spectroscopy of this molecule. Contradicting measurements and theoretical calculations have alternatively reported a linear or nonlinear equilibrium geometry for C₃. Van Orden and Saykally²³ reviewed all previous works and proposed a linear structure with a very flat bending potential. They also discussed the barrier to linearity which is observed when the anti-symmetrical stretching is excited. A very small barrier to linearity (0.3 cm⁻¹) is observed in the semi-empirical potential energy surface (PES) obtained by Špirko et al.²¹ from a fit to experimental data. In contrast, the high-level coupled-cluster with single and double excitations and a perturbative treatment of triple excitations (CCSD(T)) calculations of Mladenović et al.²⁰ resulted in a linear equilibrium geometry. While we cannot still conclude whether C₃ is a linear or a quasi-linear molecule (i.e., a molecule with a barrier to linearity much smaller than the bending frequency), a good quantitative agreement has been obtained with the experimental energy levels.²⁰,²¹

The interaction of C₃ with He and Ar has been investigated by Zhang et al.²⁴–²⁶ They observed the ground and first electronic excited states of the Ar-C₃ van der Waals complex by laser-induced fluorescence. They carried out CCSD(T) calculations which predict that the equilibrium structure of Ar-C₃ and He-C₃ are nearly T-shaped, and they calculated the intermolecular vibrational levels. For He-C₃, they build a 2D PES with C₃ linear and a second one with C₃ bent with an angle of 160°. Another 2D PES with C₃ linear was also reported by Ben Abdallah et al.²⁷

When the local thermal equilibrium (LTE) conditions do not apply, the determination of the abundance of C₃ requires a study of its (de-)excitation resulting from collisions. In molecular clouds, the most abundant collider is usually H₂, followed by He. Such calculations are usually performed within the rigid monomer approximation (RMA). However, it must be noted that the bending frequency of C₃ is small²⁸ (63.4 cm⁻¹), and therefore a significant coupling of the vibrational bending with the intermonomer vibrational modes can be expected. The small bending frequency of C₃ brings a supplementary

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interest to the investigation of collision with He, as it could be seen as a case study of rovibrational energy transfer induced by collision.

We have recently developed the theory of rovibrational energy transfer for atoms colliding with a linear triatomic molecule and applied it to the HCN-He systems.\(^ {29,30}\) In this previous study,\(^ {30}\) denoted hereafter as Paper I, the coupling between rotation and vibrational bending was treated exactly within the rigid bender approximation at the Close Coupling level (RB-CC). Using this approach, we found that for the HCN-He collision, the pure rotational transitions could be computed accurately using a vibrationally averaged PES, similarly as was done in the investigations of CH\(_2\)-He\(^ {31}\) or even with the simple RMA. But for transitions involving two different bending levels, the use of the RB-CC approach was needed. In order to apply the latter approach to the C\(_3\)-He inelastic collision, we will first focus, in the present work, on the development of a four-dimensional PES for the C\(_3\)-He system, which takes into account the bending motion. A first use of this PES to determine the bound states energies of the C\(_3\)-He complex will also be presented.

The paper is organised as follows. In Sec. II, we summarise the \textit{ab initio} calculations and detail the analytical form of the PES while the bound states calculations are presented in Sec. III. Finally, we present and discuss the results of this study in Sec. IV.

II. \textit{AB INITIO} CALCULATIONS AND ANALYTICAL FORM OF THE PES

A. \textit{Ab initio} calculations

The coordinate system used in this work is presented in Fig. 1. The center of coordinates is the center of mass of the C\(_3\) molecule and \(R\) is the distance between this center of mass and the He atom. The bending angle of the C\(_3\) molecule is \(\gamma\), and the rotation of He is defined by \(\theta\) while the azimuthal angle is \(\varphi\). The C–C diatomic distance has been fixed to its experimental value\(^ {23}\) in the ground state of C\(_3\), \(r = 2.413\) \(a_0\).

The interaction potential is symmetric under the transformations \(\theta \leftrightarrow \pi - \theta\) and \(\varphi \leftrightarrow -\varphi\). For the calculation of the \textit{ab initio} points, these symmetries allow us to reduce the range of \(\theta\) to \([0,\pi/2]\) and the range of \(\varphi\) to \([0,\pi]\).

![Fig. 1. Body-fixed coordinates. The linear C\(_3\) molecule is along the \(z\)-axis, and the bent C\(_3\) molecule is in the plane \(xy\). The angle \(\varphi\) is indefinite when \(\gamma = 180^\circ\).](image)

Within the supermolecular approach, the potential energies of C\(_3\) with He have been calculated with the coupled-cluster method with single and double excitations and a perturbative treatment of triple excitations (CCSD(T)). The interaction energy was corrected at all geometries for the basis set superposition error (BSSE) with the counterpoise procedure of Boys and Bernardi.\(^ {32}\) A comparison of the interaction energies calculated with basis sets of triple, quadruple, and quintuple-zeta quality is shown in Table I, with or without an additional set of bond functions centred at mid-distance between the He atom and the C\(_3\) center of mass. The interaction energy, calculated at a configuration close to the equilibrium geometry, is quite stable in respect of the size of the basis set and the use of bond functions. For the largest basis set, it is safe to assume that the convergence of the one-electron basis is close to the complete basis set limit. Considering the computational cost associated with the various basis sets, we have chosen the quadruple zeta basis set with bond functions.

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The potential energy has been computed for 12 values of the bending angle from 180\(^\circ\) to 80\(^\circ\). The radial grid included 34 points ranging from 4.1 \(a_0\) to 22.7 \(a_0\). The angular grids were spaced uniformly in steps of 10\(^\circ\) for \(\theta\) in the range \([0, 90]^\circ\) and steps of 30\(^\circ\) for \(\varphi\) in the range \([0, 180]^\circ\). The total number of points was 26 526. All calculations have been carried out with the MOLPRO package.\(^ {33}\)

The potential energy of the isolated C\(_3\) molecule has been computed using the same \textit{ab initio} method and basis set as we used for the C\(_3\)-He system. We computed the \textit{ab initio} energy for 43 bending angles in the range from 50\(^\circ\) to 180\(^\circ\). These energies were fitted to a linear combination of seven Legendre polynomials.

B. Analytical representation of the PES

The interaction potential is expanded as the sum of a short-range function \(V^S\) and a long-range function \(V^L\) with the expansion coefficients defined by the switching function \(S\):

\[
V_{\text{int}}(R, \theta, \varphi, \gamma) = S(R)V^S(R, \theta, \varphi, \gamma) + (1 - S(R))V^L(R, \theta, \varphi, \gamma),
\]

\[
S(R) = \frac{1}{2}[1 - \tanh (A_0(R - R_0))].
\]

The \(V^S\) and \(V^L\) functions are in turn the sum of two terms. The first term represents the interaction energy in the case \(\gamma = \pi\). Thus, it has no dependence in \(\gamma\) and \(\varphi\). The second term
is different from zero only for \(\gamma < \pi\). It can be seen as the difference between the interaction energy at some \(\gamma < \pi\) and the interaction energy at \(\gamma = \pi\), both at the same value of \(\theta\) and \(R\).

\[
V^S(R, \theta, \varphi, \gamma) = \sum_{l=0}^{12} F_l^s(R) \bar{P}_l(\cos \theta) + \sum_{l=0}^{13} \sum_{m=0}^{\min(l,4)} G^S_{lm}(R, \gamma) \bar{P}_l(\cos \theta) \cos(m\varphi),
\]

(3)

\[
V^L(R, \theta, \varphi, \gamma) = \sum_{l=0}^{4} F_l^l(R) \bar{P}_l(\cos \theta) + \sum_{l=0}^{4} \sum_{m=0}^{\min(l,2)} G^L_{lm}(R, \gamma) \bar{P}_l(\cos \theta) \cos(m\varphi),
\]

(4)

Due to the symmetry properties of the interaction potential (vide supra), the sum over \(l\) in the first term of right-hand side of Eqs. (3) and (4) is restricted to even value and in the second term, the summation over \(l\) and \(m\) is restricted to even value of \(l-m\). \(\bar{P}_l\) are normalized Legendre polynomials and \(\bar{P}_m\) are normalized associated Legendre polynomials,

\[
F_l^s(R) = e^{-\alpha_1 R} \sum_{n=0}^{11} R^n A_{ln},
\]

(5)

\[
F_l^l(R) = \frac{t_k(\beta_1 R)}{R^k} C_{lk},
\]

(6)

\[
G^S_{lm}(R, \gamma) = e^{-\alpha_1 R} \sum_{j=0}^{5} Q^S_{lj}(\gamma) \sum_{n=0}^{10} B_{lmnj} R^n,
\]

(7)

\[
G^L_{lm}(R, \gamma) = \frac{3}{8} \sum_{j=0}^{3} Q^S_{lj}(\gamma) \sum_{k=6}^{8} D_{lmkj} \frac{t_k(\beta_2 R)}{R^k},
\]

(8)

where \(t_k\) is the Tang-Toennes damping function:

\[
t_k(x) = 1 - e^{-x} \sum_{i=1}^{k} \frac{x^i}{i!}.
\]

The functions \(Q^S_{lj}(\gamma)\) were chosen for all values of \(m\), with the exception of \(m = 1\), as

\[
Q^S_{lj}(\gamma) = \frac{1 + P_{2j+1}(\cos \gamma)}{2}
\]

(10)

and for \(m = 1\),

\[
Q^L_{lj}(\gamma) = \sin(\gamma).
\]

(11)

In a first step, we fitted the linear case (\(\gamma = \pi\)), using the first term in Eqs. (3) and (4). In a second step, the difference between the linear potential and the ab initio points was fitted for each value of \(\gamma\) and \(R\) using the second term of (3) and (4). These angular coefficients were interpolated using the functions (10) and (11). Finally, we fitted the radial part to get the coefficients \(B_{lmnj}\) and \(D_{lmkj}\).

The nonlinear parameters \(R_0, A, \alpha_1, \beta_1, \alpha_2, \) and \(\beta_2\) were set to the values \(R_0 = 5.2 \text{ Å}, A_0 = 5.6 \text{ Å}^{-1}, \alpha_1 = 4.8 \text{ Å}^{-1}, \beta_1 = 2.0 \text{ Å}^{-1}, \alpha_2 = 2.2 \text{ Å}^{-1}, \) and \(\beta_2 = 2.8 \text{ Å}^{-1}\). These values were determined by the trial and error method.

The ab initio grid was computed only for \(\gamma \geq 80^\circ\) and the extrapolation was done just until \(\gamma = 75^\circ\). The rigid bender approximation used for C3 is expected to be reliable only for the ground state and the first excited bending states. Considering that the potential energy of the C3 molecule at \(\gamma = 75^\circ\) is about 5400 cm\(^{-1}\) and the vibrational frequency of the bending mode \(v_2\) is around 63 cm\(^{-1}\), there is no need to represent the interaction energy for \(\gamma \leq 75^\circ\). Therefore we used this value as a cut-off limit. Beyond this limit, the interaction energy was set equal to its value at \(\gamma = 75^\circ\). A similar procedure has been previously used\(^{29}\) in the study of HCN in collision with He without any drawback.

### III. Bound States Calculations

Two kinds of calculations were performed: the first one considering C3 as a linear rigid molecule, i.e., using the RMA, and the second one modelling C3 by a rigid bender, i.e., using the RB-CC method. In both cases we used the coupled-channel bound state method introduced long ago by Johnson\(^{34}\) and adapted to the log-derivative and R-matrix propagators, respectively, by Hutson\(^{35}\) and Danby.\(^{36}\) This method was already used in our study dedicated to the HCN-He system.\(^{29}\) In the RMA approach, the rotational constant of the C3 molecule\(^{23}\) was taken equal to 0.43 cm\(^{-1}\). A modified version of our scattering code based on the log-derivative propagator, was used following the recommendations of Hutson.\(^{35}\) The calculations were performed for two values of the propagator step size (0.05 \(\omega_0\) and 0.1 \(\omega_0\), and the values of the bound state energies were obtained from a Richardson extrapolation.\(^{35}\) We tested the convergence of the bound state energies of the He-C3 complex as a function of the size of the rotational basis set of C3. As the nuclear spin of the carbon atom is zero, ten even values of the rotational quantum number were included in the basis set describing C3 and the maximum propagation distance was set to 50 \(\omega_0\).

The RB-CC approach presented in Paper I had to be adapted to take into account the exchange symmetry of the C atoms inside C3 as the rigid bender Hamiltonian used in this previous work cannot be used for symmetric triatomics. We use instead the symmetric Hamiltonian developed by Carter \textit{et al.}\(^{37}\) Fig. 1 shows the coordinates used in this study for the C3 molecule. The x-axis is the bisector of the bending angle \(\gamma\), while the molecule is lying in the \(xz\) plane.

The symmetric form of the Hamiltonian developed by Carter \textit{et al.}\(^{37}\) is written as usual as a sum of a vibrational,
a rovibrational, and a potential term
\[ H = H_v + H_r + V(\gamma). \] (12)

The vibrational term \( H_v \) developed by Carter and Handy\(^{29}\) is unchanged and its expression can be found in our previous work.\(^{29}\) The rigid bender approximation of the rovibrational term \( H_r \) takes the following form:
\[ H_r = \frac{3}{4mR_1^2} \cos^2(\gamma/2) \Pi_z^2 + \frac{1}{4mR_1^2} \sin^2(\gamma/2) \Pi_z^2 \]
\[ + \frac{1}{2mR_1^2} \left( 1 + \frac{\cos \gamma}{2} \right) \Pi_y^2, \] (13)
where \( R_1 \) is the C–C equilibrium distance and \( m \) is the mass of the carbon atom while \( \Pi_x \), \( \Pi_y \), and \( \Pi_z \) are the projections over the molecule-fixed axes of the total angular momentum \( J \) of \( C_3 \). As in our previous work, we use the following symmetrised rovibrational basis set to diagonalise the Hamiltonian \( H \):
\[ |jn\tilde{K}M, p\rangle = |jn\tilde{K}M\rangle + (-1)^p |jn - \tilde{K}M\rangle, \] (14)
where \( M \) and \( K \) are the projections of \( J \) over the space-fixed \( z \)-axis and the body-fixed \( z \)-axis, respectively. \( \tilde{K} \) is the absolute value of \( K \), and \( p \) is equal to 0 or 1. Furthermore we have
\[ |jn\tilde{K}M\rangle = \tilde{P}_n^K(\cos \gamma)|jKM\rangle, \] (15)
where
\[ |jKM\rangle = \sqrt{\frac{2J+1}{4\pi}} D_{JM,K}^{*}(\alpha, \beta, \gamma) \] (16)
is a symmetric top wavefunction while \( \tilde{P}_n^K(\cos \gamma) \) is a normalized associated Legendre polynomial describing the bending vibration. From the expression of \( H_r \) we see that a value of \( K \) can only be coupled with \( K' = K, K \pm 2 \). In other words, each rovibrational state is associated with a given parity of \( K \). The calculation of the rovibrational wavefunctions is performed for a given value of \( J \) and \( p \) which means for a given parity as
\[ \Pi|jn\tilde{K}M, p\rangle = (-1)^{J+|p|} |jn\tilde{K}M\rangle, \] (17)
We can further take advantage of the symmetry of the total wavefunction under the exchange of the bosonic \( C \) nuclei\(^{39}\) which implies that the rovibrational wavefunction has to be symmetric too. The exchange of the carbon nuclei, as shown in Fig. 1, can be obtained by a rotation along the \( x \)-axis or equivalently by an inversion of the coordinates of the carbon nuclei followed by a rotation along the \( z \)-axis,
\[ C_2^x\Pi|j\tilde{K}M, p\rangle = (-)^{|p|+K} |j\tilde{K}M, p\rangle. \] (18)
This means that \( J + p + \tilde{K} \) has to be even. As each rovibrational state is associated with a given parity of \( K \), we get immediately that for non-zero value of \( J \) one rovibrational state in two is missing, as illustrated, for example, by Gendriesch et al.\(^{18}\)

Finally, the eigenvalues and eigenfunctions of \( H \) have been used in the calculations of the bound states of the \( \text{He}-C_3 \) complex with the RB-CC method. All the details of the RB-CC close coupling equations can be found in Paper I. We included in the calculations six bending eigenfunctions of \( C_3 \) and ten rotational eigenfunctions for each bending functions. The propagator step size was the same as for the RMA calculations.

IV. RESULTS AND DISCUSSION

A. Features of the potential energy surface

The quality of the fit was checked by using the root means square (RMS) of the differences between the \textit{ab initio} and the interpolated energies. For this analysis, we have divided the grid of points in two regions. As we focus on the collision dynamics at low temperature, we can define the limit between the two regions by \( \gamma = 120^\circ \). For such a bending angle, the energy of the isolated \( C_3 \) molecule is around 300 cm\(^{-1}\). Thus the region defined by \( \gamma < 120^\circ \) may be represented with less accuracy. In the region \( \gamma \geq 120^\circ \), for the negative interaction energies \( E \) the RMS is 0.09 cm\(^{-1}\), for 0 cm\(^{-1}\) \( \leq E \leq 100 \) cm\(^{-1}\) the RMS is 0.77 cm\(^{-1}\), and for 100 cm\(^{-1}\) \( \leq E \leq 5000 \) cm\(^{-1}\) the RMS is equal to 13.17 cm\(^{-1}\). The second part of the grid (\( \gamma < 120^\circ \)) has a RMS of 0.31, 2.68, and 35.46 cm\(^{-1}\), respectively. We have also checked the quality of the fit of the bending potential of the isolated \( C_3 \) molecule. The RMS for \( E < 500 \) cm\(^{-1}\) is 1.89 cm\(^{-1}\), and for higher energies the relative error is less than 5.4%.

We found that the isolated \( C_3 \) molecule has a linear structure at equilibrium, with a flat potential energy which extends from \( \gamma = 180^\circ \) until about 160°.

Figs. 2 and 3 show contour plots of the interaction energy for selected values of \( \gamma \) with \( \varphi = 180^\circ \) and \( \varphi = 0^\circ \), respectively. For a linear configuration of \( C_3 \), the minimum interaction energy with \( \text{He} \) is \( -26.73 \) cm\(^{-1}\) at \( \theta = 6.82^\circ \) and \( \varphi = 120^\circ \). Symmetry, there is a second minimum at \( \theta = 98.6^\circ \). The barrier to the \( \theta = 90^\circ \) structure is 0.07 cm\(^{-1}\). This double minimum structure disappears when \( \gamma \) decreases as it can be observed in Fig. 2 for \( \varphi = 180^\circ \). Conversely, the double minimum is more pronounced for \( \varphi = 0^\circ \) as seen

![FIG. 2. Contour plot of the interaction energy for selected values of \( \gamma \) and for \( \varphi = 180^\circ \). Negative contour lines (blue) are equally spaced by 4 cm\(^{-1}\). The lowest positive contour lines (red) show the 4 cm\(^{-1}\) energy and there is a factor of 2 in energy between successive positive contour lines (red).](https://example.com/fig2.png)
in Fig. 3. These results are close to the previous ones obtained with the 2D PESs which are similar to a cut of our 4D PES at $\gamma = 180^\circ$. Ben Abdallah et al.\cite{27} reported a T-shaped equilibrium structure with an energy of $-25.87$ cm$^{-1}$ while Zhang et al.\cite{28} noticed that the T-shaped structure is slightly distorted, with $R = 6.78$ a$_0$ and an energy of $-25.54$ cm$^{-1}$. These small differences are easily explained by the use of slightly different distance between the carbon atoms and different basis set (both previous 2D PES were build with the aug-cc-pVTZ basis set with bond functions).

For $R$ close to the equilibrium value, we can see in Figs. 2 and 3 that the interaction potential is strongly anisotropic. This is the consequence of the repulsion between He and the terminal carbon atoms, while the equilibrium structure is almost T-shaped. By comparing the different panels of Fig. 2, we observe that the long range energy is hardly changed while the short range energy varies strongly with $\gamma$. Consequently, the minimum of the interaction energy varies significantly with $\gamma$. Fig. 4 shows that the minimum of the interaction energy occurs when C$_3$ is bent. The global minimum of the interaction potential is $-36.3$ cm$^{-1}$ and corresponds to $\gamma = 120^\circ$, $R = 6.57$ a$_0$, $\theta = 90^\circ$, and $\phi = 180^\circ$. Thus, the interaction with He tends to displace the C$_3$ molecule from its linear equilibrium structure, therefore inducing a coupling between the internal bending motion and the intermonomer motions. But this coupling is weak. Indeed, if we consider the total potential energy, i.e., the sum of the He-C$_3$ interaction energy and the bending energy of C$_3$, then the global minimum has the geometry $\gamma = 176.7^\circ$, $R = 6.77$ a$_0$, $\theta = 84.1^\circ$, and $\phi = 180^\circ$, with the energy $-26.93$ cm$^{-1}$. The structure of this last minimum is close to the equilibrium structure found for $\gamma = 180^\circ$.

By the definition of the coordinates, there is no dependence of the interaction energy with $\psi$ when $\gamma = 180^\circ$. But for smaller values of $\gamma$, this dependence becomes significant. Fig. 5 shows the contour plot of the interaction energy in function of $\theta$ and $\phi$, with $R$ and $\gamma$ having the values found for the global minimum.

### B. Bound states

In Table II, we report some of the lowest rovibrational energies obtained for the rigid bender C$_3$ molecule by

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<td>2</td>
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*TABLE II. The rovibrational energies of the rigid bender C$_3$ molecule. The experimental values are shown in parenthesis.*

FIG. 3. Contour plot of the interaction energy for selected values of $\gamma$ and for $\phi = 0^\circ$. The contour lines have the same spacing as in Fig. 2.

FIG. 4. Interaction energy versus the bending angle of C$_3$. All other coordinates $R$, $\theta$, and $\phi$ are relaxed.

FIG. 5. Contour plot of the interaction energy for $\gamma = 120^\circ$ and $R = 6.57$ a$_0$. The contour lines have the same spacing as in Fig. 2.
TABLE III. Bound levels of the C₃-He complex.

<table>
<thead>
<tr>
<th>State</th>
<th>RMA</th>
<th>RB-CC</th>
<th>State</th>
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<th>RC-CC</th>
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<td>Energy (cm⁻¹)</td>
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<td>ε</td>
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</table>

diagonalising the Hamiltonian \( H \) (Eq. (12)), along with the corresponding vibrational quantum number \( \nu \), the total angular quantum number \( j \) and its projection \( K \), and the value of the parameter \( p \). As can be seen in this table, the rigid bender energies differ from the experimental values by less than 5%. This qualitative agreement indicates that the rigid bender model is a reliable approximation, at least for the lowest states.

The bound state energies of the He-C₃ complex, calculated with the RMA and RB-CC methods, are presented in Table III. The total angular momentum \( J \) and the parity \( \varepsilon \) are also reported. The energies computed using the RMA are found to be above those obtained using the RB-CC with only one exception at \( J = 4 \). This general behaviour can be explained by two factors. First, the RMA rotational constant used for C₃ differs from the one obtained from the rigid bender calculations. Second, the minimum of the He-C₃ interaction potential is not in the linear configuration of C₃ as seen in Fig. 4. For \( J = 4 \), with the RB-CC method, we also found two more bound levels than with the RMA method.

The maximum value of the total angular momentum \( J \) leading to bound states is 6 using both methods. Since the \( \nu = 0 \rightarrow \nu = 1 \) excitation energy of C₃ is larger than the well depth of the interaction potential, all the He-C₃ bound levels correspond to the bending quantum number of C₃ \( \nu = 0 \). The dissociation energy computed using the RMA is 9.56 cm⁻¹ while it is 9.73 cm⁻¹ with the RB-CC method. The corresponding zero-point energies (ZPEs) are 17.37 cm⁻¹ and 17.20 cm⁻¹. A similar value of 17.95 cm⁻¹ was reported by Zhang et al. Therefore, the ZPE is above 152.77.24.10 On: Wed, 16 Apr 2014 15:26:26

that the RMA approach is a good approximation to compute the bound levels of an atom-triatom van der Waals complex, even for a very floppy molecule like C₃.

Zhang et al. calculated only the vibrational bound states for \( J = 0 \) and with C₃ strictly linear. They reported three levels at \(-7.59 \text{ cm}^{-1}, -4.43 \text{ cm}^{-1}, \) and \(-2.1 \text{ cm}^{-1} \), while we report only two levels in Table III. This discrepancy arises from symmetry consideration. Owing to the nuclear spin of carbon atoms, the rovibrational wavefunctions of He-C₃ have to be symmetric under the exchange of the terminal carbon atoms. This implies that the latter wavefunctions are symmetric under the transformation \( \theta \mapsto \pi - \theta \), which is true only for the first and the last level reported by Zhang et al. The energies of these two levels are in qualitative agreement with the data shown in Table III.

V. CONCLUSION

We presented the first four-dimensional analytical representation of the PES for the C₃-He complex, including the bending motion of the C₃ molecule. This surface is based on supermolecular \textit{ab initio} calculations using a quadruple zeta basis set with mid-bond functions and BSSE correction. The total PES has a global minimum of \(-26.93 \text{ cm}^{-1} \) at \( \gamma = 176.7^\circ, R = 6.77 \text{ a}_0, \theta = 84.1^\circ, \) and \( \varphi = 180^\circ \). The bound states calculations for the C₃-He complex were performed both at the RMA and at the RB-CC levels. The dissociation energy computed using the RMA is 9.56 cm⁻¹ while it is 9.73 cm⁻¹ at the RB-CC level. The agreement between these two values shows that the RMA approach is valid for this system, mainly because the interaction potential is too shallow to couple excited bending states of C₃, and also because the coupling between the inter- and intra-monomer motions is weak. More bound levels of lower energy were found however at the RB-CC level as a consequence of the nonlinear geometry of C₃ associated with the minimum of the interaction potential. Future work dedicated to the rovibrational energy transfer in He-C₃ collisions will be presented shortly but we can...
however already expect that pure rotational transitions should be calculated correctly at the RMA level.

ACKNOWLEDGMENTS

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4P. Swings, Rev. Mod. Phys. 14, 190 (1942).