Quantum effects on the stability of the He_5I_2 van der Waals conformers

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Abstract

We present 15-dimensional quantum multiconfiguration time-dependent Hartree calculations of the vibrational levels of the He_5I_2 van der Waals (vdW) complex employing an *ab initio*-based potential energy surface (PES). The energies and spatial features of such bound structures are analyzed, providing predictions on the structures and relative stabilities of its three lowest isomers. We found that the most stable isomer corresponds to all five He atoms encircling the I_2 molecule, indicating that in this case the anharmonic quantum effects do not stabilize the isomers involving a He atom in a linear configuration as reported previously for the smaller He_NI_2 systems. Such finding provides information on the overall structuring of the finite-size-solvent systems, highlighting the intriguing interplay between weak intermolecular interactions and quantum effects.

Keywords: weakly bounded doped systems, nuclear quantum treatments, microsolvation effects, Helium nanodroplets. ■

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INTRODUCTION

In the last decades weakly bounded complexes, such as the vdW clusters containing rare gas atoms, especially those with He, have become a fertile ground to study the molecular properties for both experimentalists^{1–14} and theoreticians.^{15–38} The richness of the undergoing mechanisms, as well as the development of both spectroscopical techniques and computational methodologies have made these systems a perfect scenario to study the nature of weak intermolecular forces, energy transfer mechanisms, as well as nanoconfined phenomena and solvation processes.

The advances in the computational capabilities along with the availability of observations from high resolution spectroscopic techniques urged to develop new methodological approximations to perform quantum calculations of such complexes with high accuracy. In this context, the increasing of the computational power have made affordable very precise calculations of their thermodynamical and spectroscopic properties of such complexes containing an increasing number of rare gas atoms.^{15–18,21,22,24–30,32,39} Finite-size clusters formed by the insertion of dopant neutral or charged species into initial He clusters of variable size have been the subject of recent studies, mainly due to the very flexible and low-T environment created by the He nanodrops that have allowed detailed spectroscopic studies of rather complex molecular species.^{40–46} Further, recent time resolved experiments of molecular rotation inside He droplets have revealed that moderately intense laser pulses can induce alignment of molecules, and a coherent collective rotation of a molecule and its solvation shell for short time.^{47,48} Such observations along with theoretical modeling have established a picture that molecules can rotate almost freely inside He droplets followed by a local solvation shell of He atoms, that open opportunities for real-time studies of non-equilibrium solute-solvent dynamics,^{42,44} and quantum thermalization of finite many-particle systems.⁴⁸

Computational studies using traditional first-principles electronic structure methods providing structures and frequencies are not appropriate for comparing with experimental observations for such weakly interacting and quantum nature systems. Even when an accurate representation of the potential interactions is available, it can only serve as a very useful starting point in studying on how quantum structures could be guided by the features of

such PES. The difficulty of moving to larger systems in the quantum nuclear dynamics calculations has opened different ways to address the computational problems associated with the growing dimensionality. On the one hand, the use of model potentials and approximate or thermodynamical methods offers the possibility to extend these studies to a large number of rare gas atoms, being of special interest, for example, to treat molecules embedded in Helium nanodroplets in the experiments of “quantum environment”.^{9,25,40,42,49–62} On the other hand, the ability of methods, like the multiconfiguration time-dependent Hartree (MCTDH),⁶³ to perform *exact* quantum dynamics calculations of multidimensional systems allows the computation of energy levels of small rare gas doped clusters with an increasing number of rare gas atoms. The results on the vibrational calculations of these systems should help to fill the gap between the well known small molecules and the large size clusters or nanodroplets.^{17,18,21–24,26,27,30,32,64}

In the case of the $\text{He}_N\text{-I}_2$ systems, quantum path integral Monte Carlo calculations have been carried out and thermal equilibrium structures and energies for complexes with $N=8$ up to $N=38$ have been reported,²⁵ while full dimensional quantum mechanical calculations determining the energy levels and probability distributions of the lowest isomers only for clusters up to $N = 4$ have been performed using the MCTDH method.¹⁷ It has been found that thermal effects, at typically low- T in He droplets, do not alter the classical solvation behavior of I_2 in small He clusters, while quantum effects clearly affect the microscopic behavior of such doped clusters. Quantum delocalization is important allowing to explain the stabilization of specific conformers in supersonic beam experiments.¹⁵

In this work we go one step further to study the $\text{He}_5\text{-I}_2$ vdW complex and present 15-dimensional (15D) MCTDH results of the structures and energetics of its more stable conformers. Recent studies of the $\text{He}_N\text{-I}_2$ complexes for $N=1,2,3,4$ have shown the near degeneracy of the different isomers with energy differences within 1 cm^{-1} , indicating the need of high accuracy methods, with energetical preference for isomers involving Helium atoms in the linear configurations.¹⁷ The data reported here highlight markable consequences on the overall quantum structures and their stability by the simple insertion of an extra He atom in small $\text{He}_N\text{-I}_2$ doped clusters.

The article is organized as follows: the next section describes the computational details

of the coordinate system together with the kinetic and potential energy operators used, as well as the details of the MCTDH calculations, such as the type, number, and grid of the primitive basis sets, the single particle functions and potentials. Following sections contain the presentation of the results obtained, a detailed discussion on the energetics and structures of the different He₅-I₂ isomers, and at the end some concluding remarks.

METHODOLOGY

Fig. 2 displays the satellite coordinates ($\mathbf{r}, \mathbf{R}_k$) used in this study, with the $\mathbf{r}$ vector pointing from one I atom to the other, while the $\mathbf{R}_k$ ($k=1,2,3,4$ or 5) are the vectors from the center of mass of the I₂ molecule to each of the five He atoms, with θ_k and ϕ_k being the polar and azimuthal angles.

The molecular Hamiltonian for zero total angular momentum ($J = 0$)^{27,32} is written as:

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + \frac{\mathbf{j}^2}{2mr^2} + \sum_{k=1}^5 \left(-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R_k^2} + \frac{\mathbf{l}_k^2}{2\mu R_k^2} \right) \\ & - \frac{\hbar^2}{2m_I} \sum_{k < l}^5 \nabla_k \cdot \nabla_l + V(\mathbf{r}, \mathbf{R}_{k=1-5}), \end{aligned} \quad (1)$$

where $\mathbf{j}$ and $\mathbf{l}_k$ are the angular momenta associated to the vectors $\mathbf{r}$ and $\mathbf{R}_k$, respectively, m and μ are the reduced masses of the I₂ and He-I₂, respectively, with 4.002602 and 126.904473 u the atomic He and I masses, respectively, while the kinetic energy coupling terms in the Hamiltonian ($-\frac{\hbar^2}{2m_I} \sum_{k < l} \nabla_k \cdot \nabla_l$), which are very small (less than 0.02 cm⁻¹) in these cases.²⁴ are neglected.

The potential $V(\mathbf{r}, \mathbf{R}_{k=1-5})$ term is represented as the sum of the three-body HeI₂ interactions plus the He-He and I-I ones,

$$V(\mathbf{r}, \mathbf{R}_k) = \sum_k^5 V_{\text{HeI}_2}(\mathbf{r}, \mathbf{R}_k) + \sum_{k < l}^5 V_{\text{He-He}}(\mathbf{R}_k, \mathbf{R}_l) + V_{\text{I}_2}(\mathbf{r}) \quad (2)$$

where the corresponding $V_{\text{HeI}_2}(\mathbf{r}, \mathbf{R}_k)$ terms are the CCSD(T) parameterized potential of the HeI₂ complex,²⁰ the $V_{\text{He-He}}(\mathbf{R}_k, \mathbf{R}_l)$ is the potential function for He₂ given in Ref.⁶⁵, and V_{I_2} is the ground state CCSD(T) potential of the diatomic I₂ molecule.²⁰ Such model

surfaces have been shown^{24,25} to describe reasonably well the topology of PESs of small and medium size He_NI_2 clusters, by comparison with *ab initio* data.

The body-fixed (BF) frame is chosen such that the Z axis is parallel to $\mathbf{r}$, and $\mathbf{R}_5$ is lying in the XZ -plane with a positive X direction (see Fig. 1). Then, the coordinates r , R_1 , R_2 , R_3 , R_4 and R_5 are the size of the corresponding vectors, θ_1 , θ_2 , θ_3 , θ_4 and θ_5 their polar angles, while ϕ_1 , ϕ_2 , ϕ_3 , ϕ_4 and ϕ_5 are the azimuthal angles. As a result of the above selection for the orientation of the $\mathbf{R}_5$ its ϕ_5 angle is zero, and the relative azimuthal angles are $\varphi_k = \phi_k - \phi_5$. The Hamiltonian operator, $\hat{H}$, for zero total angular momentum expressed in these coordinates is given in the supplementary information[†].

In turn, the Hamiltonian operator is expressed as a sum of products of single-particle operators, as it is required by MCTDH method, and the POTFIT approach^{66,67} is employed to expand the potential energy operator in the product form representation. The number of natural potentials in the POTFIT calculations for the V_{HeI_2} are 20/20 (in r/R , contracted in θ), and 150/10 (in $(R_k, \theta_k)/\phi_k$, contracted in one (R_k, θ_k) -mode) for the $V_{\text{He-He}}$ PESs. The root-mean-square (rms) error in the relative regions of each potential term is 0.001 and 0.1 cm^{-1} , respectively.

Table 1 lists the type, number and range of the primitive basis sets used in the MCTDH calculations for the He_5I_2 systems. For the r coordinate the sine *discrete variable representation* (DVR) basis (*sin*) was employed, for the $R_{k=1-5}$ the harmonic oscillator DVR basis (*HO*) is used, while for the angular θ_k and φ_k degrees of freedom the Legendre (*Leg*) and exponential (*exp*) DVR basis, respectively.

We employed the improved relaxation (IR) method, as implemented in the MCTDH package,^{63,68} to converge the ground and specific vibrational excited states. As we will see later on, the computation of excited states, even the lowest ones, is a computational demanding task, due to the states' degeneracy and the presence of close lying stationary points on the PES of the He_5I_2 cluster. Thus, particular attention has been paid to the number of single-particle functions (SPFs) and the choice of the mode combination scheme.

The number of SPFs for each combination mode, as well as the least populated orbital in the IR MCTDH calculations for the He_5I_2 are also given in Table 1. We should point out that the highly correlated R_k and θ_k coordinates are contracted to (R_k, θ_k) combination

modes. Also, one can see that for the r I-I distance, only one SPF was found enough to describe the lowest vdW states accurately. The populations of the highest (least populated) natural orbital is 10^{-3} for the He_5I_2 complex, respectively (see Table 1), and such values are accurate enough to converge the binding energy values within 0.001 cm^{-1} .

RESULTS AND DISCUSSION

We follow the ($\#T, \#L1, \#L2$) notation to label the number of He atoms in T-shaped ($\theta=90^\circ$) and linear (L1 for $\theta=0^\circ$ and L2 for $\theta=180^\circ$) potential wells, respectively. By minimizing the potential surface (see Eq. 2) and carrying out the corresponding frequency analysis, we found that the global minimum corresponds to the (5,0,0) configuration with energy of -226.46 cm^{-1} , while the lowest two local minima, the equivalent (4,1,0) and (4,0,1) structures, and the (3,1,1) one, are higher at energies -224.47 and -222.25 cm^{-1} , respectively.

Fig. 3 presents the corresponding structures of these minima and their energies. The minimum structure corresponds to a ring of five He atoms encircling the I_2 dopant, while the arrangements with one or two of these He atoms in the linear configurations lie very close in energy with differences of around 2 and 4 cm^{-1} , respectively. We should mention that many other stationary points of the surface have been located, although here we are only discussing those related to the lowest isomers of the cluster.

In Fig. 4 we show contour plot cuts of the PES (see Eq. 2). In these plots the system is formed from a fixed I_2 molecule at $r=2.666 \text{ \AA}$ along Z axis, and the four He atoms being at the (4,0,0), (3,1,0) and (2,1,1) equilibrium configurations (see upper, middle and lower panels, respectively), while the remaining He atom is moving in the ZX plane.

One can see that the PESs have a high anisotropy with several stationary points, including the global (5,0,0) and local minima (4,1,0) and (3,1,1) ones with the He atoms at the linear and T-shaped geometries, as well as others with the He atom being at a bending geometry with an angle θ around 40° , or with more He atoms in the linear well, although such configurations are found at higher energies.

Fig. 5 displays 1D representations of minimum energy paths of the PES as a function of θ_5 angle keeping fixed the remaining four He atoms at the (4,0,0) and (3,1,0) configurations

as shown in Fig. 4. One can see the global and some of the lowest local PES's minima, as well as the barriers between them, *e.g.* the barrier at -199.27 cm^{-1} (see black solid line) that connects the (5,0,0) with the two symmetric (4,1,0) and (4,0,1) minima, and the one at -197.17 cm^{-1} between the (4,1,0) and (3,1,1) minima (see black dashed line). Also, at energy of -206.85 cm^{-1} another type of potential minima with a He atom at a bent configuration of $\theta \approx 34^\circ$ is found.

As it can be seen there are various stationary points on the PES, very close in energy, that influence the vibrational dynamics of the system. This effect, alongside the high degeneracy of the He_5I_2 system, makes the convergence of its vibrational energy levels a hard and computationally demanding task. Thus, in order to overcome such difficulties in the convergence of the He_5I_2 states we used the IR method, where the relaxation procedure is accelerated by computing the MCTDH vector by diagonalization. In this way, the ground and specific excited vibrational states were converged by selecting the appropriate initial wave function, *e.g.* the lowest energy eigenvector, and the eigenvectors with the largest overlaps with the desired excited states.

We carried out such IR MCTDH calculations, and the results obtained are summarized in Table 2, together with the previously reported energies for smaller He_NI_2 clusters. As in all previously reported studies on such species, we found that the energy difference between the assigned isomers is very small. For the He_5I_2 case, the ground vibrational state corresponds to the (5,0,0) isomer with a binding energy of -80.14 cm^{-1} , while the following excited states at energies of -79.35 and -79.31 cm^{-1} are assigned to the (4,1,0) and (3,1,1) isomers, respectively.

In Figure 5 we show 1D plots of the angular probability density distributions of the three lowest vibrational the He_5I_2 states (see Table 2) corresponding to the (5,0,0), (4,1,0) and (3,1,1) isomers. One can see that all density functions presented are highly localized at the T-shaped ($\theta=90^\circ$) and linear ($\theta=0$ and 180°) angular configurations, so by examining them we can assign each state to a different isomer, *e.g.* the (5,0,0), (4,1,0) and (3,1,1) ones. We also checked the radial distributions of these states, and we found that they show peaks at around 4 and 5 Å, for the He atoms at the T-shaped or linear configurations, respectively. In Fig. 6 we display 3D probability distributions of these states in the ZX -plane, together with

the underlying potential energy curves. The He_4I_2 part of the cluster is kept fixed at specific configurations, while the fifth He atom is moving in the Cartesian plane, as mentioned above in Fig. 4. One can see that, the probability density for the (5,0,0) state is localized at the T-shaped potential well (see upper panel of the Fig. 6), while those of the (4,1,0) and (3,1,1) states show also lower peaks at the linear potential wells (see middle and lower panels of the Fig. 6, respectively), in accord with the 1D angular distributions given in Fig. 5.

In Table 2 we list the D_e , D_0 and ZPEs values for the most stable isomers of small $\text{He}_{N=1-5}\text{I}_2$ vdW clusters. In all cases, their binding energies are found to be very close to each other, indicating the need of the high accuracy full 15D calculations employed in the present study. We should note that for all isomers quantum ZPE effects count for more than 60% of the corresponding potential D_e values providing an indication of the high anharmonicity of these systems. Regarding the He_5I_2 conformers the reported ZPEs values show a slightly higher anharmonicity for the (5,0,0) isomer than the (4,1,0) and (3,1,1) ones involving one and two He atoms in the linear configurations, respectively, while for the smaller $N=1$ and 2 the linear isomers present higher ZPEs than the T-shaped ones. In Figure 7 we plot the energy difference between the two most stable isomers, as well as for the (N,0,0) and (N-1,1,0) isomers for each $\text{He}_{N=1-5}\text{I}_2$ cluster. One can see that for clusters up to 2 He atoms the most stable isomer corresponds to the linear global potential minimum structures, while for the $N=3$ and 4 clusters the most stable (2,1,0) and (2,1,1) conformers are localized to the local potential minima, although they are found to be very close in energy with the (3,0,0) and (4,0,0) states that are localized in the global minima of the PESs. In turn, a change in the stability ordering definitely occurs for the He_5I_2 isomers, with the (5,0,0) being the most stable, localized at the global T-shaped potential well, preserving in this way the order of the underlying potential energy minima. These findings highlight the importance of the quantum effects present in such weakly bounded doped systems, especially in the cold He droplets' environment.

CONCLUSIONS

The work presented in this study has been directed to investigate the isomers' stability of I_2 doped in a five He atoms cluster from full dimensional quantum calculations. The motivation has come from the strong interest in analyzing the modified structure behavior of such weakly interacting systems upon the presence of more He atoms surrounding the I_2 dopant. We employed a sum-of-potential approach to represent the overall interaction on the basis of three- and two-body *ab initio* CCSD(T)/CBS HeI_2 , and He-He and I-I terms, respectively. An accurate knowledge of the underlying potential can provide a very useful initial information on structures and solvation shells. However, given the quantum nature of such systems their overall cluster's structuring may be modified. Thus, taking advance of the capabilities of the MCTDH method, we performed quantum vibrational bound state calculations, to investigate the consequences on the corresponding quantum structures. In turn, the binding energies and structures of three different isomers of the He_5I_2 cluster have been determined from the MCTDH calculations. We found that a fully converged quantum treatment of the system is necessary to obtain the relative energy ordering between the (5,0,0), (4,1,0) and (3,1,1) isomers with energy differences below 1 cm^{-1} making these 15D computations really demanding. In this case, and contrary to the previous studies of the smaller finite-size vdW clusters the order of the calculated states is not reversed with respect to the classical order of the underlying PES showing that the inclusion of the fifth He atom stabilizes the (5,0,0) isomer with respect to those including one or two He atoms in the linear wells. This happens precisely due to the intriguing interplay between weak interactions and quantum effects.

The computational needs for such quantum treatments is really high at going to larger He-doped systems. However, we hope that the present work will provide a benchmark study for testing other approaches to deal with higher dimensional systems with an increasing number of particles. Such computations on molecules inside small He droplets could serve to studying microsolvation effects for modeling short-time solute-solvent dynamics.

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Figure 1: Minimum energy paths, lowest energy structures on the potential and angular probability density distributions of the most stable He_5I_2 isomers.

Figure 2: Schematic representation of the satellite coordinate system used for the he_5i_2 (see text).

Figure 3: Energies and structures for the global and local minima of the He_5I_2 PES (see text).

Figure 4: Contour plots of the He_5I_2 potential in the ZX -plane (see text). Contour are for energies from -225 cm^{-1} to -185 cm^{-1} with intervals of 5 cm^{-1} .

Figure 5: Minimum energy paths as a function of θ_5 angle keeping fixed the four He atoms at (4,0,0) (see solid black line) and (3,1,0) (see dashed black line) configurations with $\theta_{k=1,2,3}=90^\circ$ for the He_5I_2 . The probability density distributions of the three lowest vibrational states are also displayed, with the zero energy value of each state shifted to its eigenvalue (see text).

Figure 6: Probability density distributions of the ground (5,0,0) and excited (4,1,0) and (3,1,1) vibrational states of He_5I_2 . The underlying potential curves are also shown (see text).

Figure 7: Binding energy differences between (N,0,0) and (N-1,1,0) isomers (see black line), as well as between the two most stable ones at energies of E_0 and E_1 (see colored red line) as a function of the number N of He atoms surrounding the I_2 .

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Table 1: Primitive basis sets (type, number and range), number of SPFs for each combination mode and least populated orbital population of the MCTDH *improved relaxation* calculations.

Coordinate (DVR-type)	He ₅ I ₂
Primitive basis	
N_r (<i>sin</i>)	35
r-range (Å)	[2.2, 3.5]
$N_{R_{k=1-5}}$ (<i>HO</i>)	41
R-range (Å)	[2.96, 7.41]
$N_{\theta_{k=1-5}}$ (<i>Leg</i>)	21
θ -range (rad)	[0, π]
$N_{\varphi_{k=1-4}}$ (<i>exp</i>)	15
φ -range (rad)	[0, 2π]
SPFs	
N_r	1
$N_{R_{k=1-5}, \theta_{k=1-5}}$	3
$N_{\varphi_{k=1-4}}$	5
Least orbital population	10^{-3}

Table 2: Potential well-depths (D_e), binding energies (D_0) and zero point energies (ZPE) in cm^{-1} . The % value of the corresponding ZPEs are also presented, for the indicated He_NI_2 isomers from the MCTDH calculations. The results for the smaller $\text{He}_{N=1,2,3,4}\text{I}_2$ clusters¹⁷ are included for comparison purposes.

N	(#T,#L1,#L2)	D_e	D_0	ZPE (%)
5	(5,0,0)	226.46	80.14	146.32(64.6)
	(4,1,0)	224.47	79.35	145.12(63.6)
	(3,1,1)	222.25	79.31	142.94(63.6)
4	(4,0,0)	179.44	63.28	116.16(64.7)
	(3,1,0)	177.35	62.72	114.63(64.6)
	(2,1,1)	175.01	63.32	111.69(63.8)
3	(3,0,0)	132.47	47.54	82.75(64.1)
	(2,1,0)	130.30	47.55	84.93(63.5)
	(1,1,1)	128.17	47.26	80.91(63.1)
2	(0,1,1)	88.97	31.53	57.44(64.6)
	(1,1,0)	83.54	31.43	52.11(62.4)
	(2,0,0)	85.48	31.24	54.24(63.5)
1	(0,1,0)	44.30	15.72	28.58(64.5)
	(1,0,0)	38.92	15.51	23.41(60.1)