

Diabatic diffusion Monte Carlo calculations of the energy and structure of the Cl_2He_n ($n = 1-10$) clusters

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Abstract

The diffusion Monte Carlo method is applied to study the ground van der Waals (vdW) states of $\text{Cl}_2\text{-He}_n$ clusters with $n = 1-10$. This approach assumes a diabatic separation of the Cl_2 stretch vibration. Analysis of the calculated energies and probability density distributions shows that the He atoms arrange in equivalent positions, forming a ring perpendicular to the Cl–Cl inter-nuclear axis. The relatively large amplitude of the vdW modes prevents repulsions between the rare gas atoms in this configuration. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Cluster systems composed of several rare gas atoms weakly bound to a molecule acting as a chromophore have attracted much attention in last years [1–9]. A gradual increase in the cluster size makes it possible to bridge the gas-phase limit and the condensed-matter regime. This allows one to investigate fundamental statements such as: the mechanisms of energy transfer from the electronically or vibrationally excited chemical bond (or bonds) to the solvent; the influence of the weak solvation interactions on the molecule dissociation; and the effect of caging and recombination of the chemical impurity induced by the solvent [8,9].

Complexes with a halogen diatomic molecule bound to one or more rare gas atoms have been extensively investigated by means of frequency-domain experiments [1–4]. The pioneering experiments of Levy and co-workers on $\text{I}_2\text{-He}_n$ ($n = 1-3$) [10] and $\text{I}_2\text{-Ne}_n$ ($n = 1-7$) [11] led to the measurement of

binding energies, pre-dissociation line-widths, and spectral band shifts in order to explore the structure, possible co-ordination effects, and energy transfer mechanisms in these systems. The dynamics of complexes with diatomic molecules different from I_2 , like $\text{Br}_2\text{-Ne}_n$ ($n = 1-3$) [12], ICl-Ne_n ($n = 1-3$) [13], $\text{Cl}_2\text{-Ne}_n$ ($n = 1-3$) [14] and $\text{Cl}_2\text{-He}_n$ ($n = 1-2$) [15], were also investigated. In addition, a number of theoretical works has been reported in literature for several cluster sizes [16–32].

From the theoretical point of view, one of the most relevant aspects in the study of the dynamics of vdW clusters is the proper characterization of the initial state. The use of variational methods provides accurate initial states (within the accuracy of the potentials employed), which correspond with the conditions of the systems prepared experimentally, and make the theoretical results comparable with the experimental data. In general, however, such methods are computationally feasible only for triatomic and tetraatomic complexes [30], becoming intractable for larger systems if the full dimensionality is included.

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Table 1
Morse potential parameters used in this work

	D (cm ⁻¹)	α (Å ⁻¹)	R _{eq} (Å)
Cl–Cl	3176.4	2.345	2.435
Cl–He	16.2	1.5	3.8
He–He	7.61	2.126	2.963

Diffusion Monte Carlo (DMC) techniques appear as an alternative to calculate the ground state of relatively large aggregates within a quantum framework [33–42]. The main limitation of the DMC approach is that it is designed essentially for the calculation of nodeless ground-state wave functions, although some extensions of the method have been suggested in order to get excited levels [39–41].

In this work, the dependence of the energetics and the structure of the Cl₂He_n clusters ($n = 1–10$) with increase in size is studied by means of a diabatic version of the DMC method (called diabatic diffusion Monte Carlo, DDMC). The DDMC essentially consists of separating diabatically the Cl₂ vibration, leading to a cluster wave function which is a product of a Cl₂ vibrational wave function times a ground state wave function for the vdW modes (calculated with DMC). The DDMC method incorporates vibrational excitation in the Cl₂ subunit, which is not possible with the conventional DMC. The DDMC method was successfully tested against diabatic variational calculations for the Cl₂–He and Cl₂–He₂ systems [32].

The organization of the paper is as follows. In Section 2, the DDMC approach used in this work is described. In Section 3, the results are shown and discussed. Finally, in Section 4 some conclusions are drawn.

2. Theory

2.1. Potential-energy surface

For a cluster BC–X_n, the potential-energy surface (PES) used in the calculation is represented as

$$V = V_{\text{BC}} + \sum_i V_{\text{BC}-X_i} + \sum_{ij} \sum_{i<j} V_{X_i-X_j}. \quad (1)$$

The term V_{BC} is the interaction potential of the

diatomic molecule (BC = Cl₂) in the B electronic state, described by a Morse function with the parameters reported in Ref. [44]. The term $V_{\text{BC}-X_i}$ represents the vdW interaction between the BC molecule and each rare gas atom, expressed as the sum of atom–atom interactions,

$$V_{\text{BC}-X_i} = V_{\text{B}-X_i} + V_{\text{C}-X_i}, \quad (2)$$

where both $V_{\text{B}-X_i}$ and $V_{\text{C}-X_i}$ are also described by Morse potentials. In this case, the Morse parameters were taken from Ref. [43]. A Morse potential was also used for the X_i–X_j interaction (X_i, X_j = He) whose parameters were obtained by fitting the more complicated analytical form of Aziz and Slaman [45]. All the potential parameters are listed in Table 1.

2.2. Diabatic diffusion Monte Carlo method

The starting point of the DMC method is the time-dependent Schrödinger equation which for a system of N particles of masses m_i ($i = 1, \dots, N$) is

$$i\hbar \frac{\partial \Psi}{\partial t} = - \sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2 \Psi + V\Psi. \quad (3)$$

By using the transformation $\tau = it$, Eq. (3) can be converted into a diffusion equation

$$\hbar \frac{\partial \Psi}{\partial \tau} = \sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2 \Psi + V\Psi. \quad (4)$$

The corresponding solution of this diffusion equation is

$$\Psi(\tau) = \sum_n c_n \psi_n e^{-\tau E_n/\hbar}, \quad (5)$$

that can also be obtained from the formal solution of the time-dependent Schrödinger equation, by using the above mentioned transformation of time, where E_n and ψ_n are the eigenenergy and eigenfunction of the Hamiltonian. By choosing the zero of energy, such that all the eigenvalues are positive, the wave function will decay to zero at large values of τ , and the ground state E_0 will be represented by the longest lasting transient. In this way, if we redefine the zero of energy, the function will become

$$\Psi(\tau) = \sum_n c_n \psi_n e^{-\tau(E_n - E_{\text{REF}})/\hbar}. \quad (6)$$

At sufficiently large τ , the coefficients of all states with energies larger than E_{REF} will vanish, and the coefficients of those states lower than E_{REF} will grow exponentially. Thus, if E_{REF} is the energy of the ground state, the corresponding function will be proportional to the ground state wave function, $\Psi(\tau \rightarrow \infty) \propto \psi_0$. This is the basis of the DMC method. The random-walk method, as described by Anderson [33,34], is an efficient way to solve the diffusion equation (Eq. (4)), and this is the procedure followed in this work.

In the determination of energies and probability density distributions of vdW clusters, the DMC method for rigid bodies developed by Buch [39] provides a good approximation. In this approach, a decoupling of the high frequency intra-molecular vibrations from the low frequency intermolecular vibrations is performed. In order to study a quasi-bound state corresponding to the vibrational excitation of the diatomic molecule, two possibilities emerge. First, is to use an effective Cl_2 distance associated to the vibrational level of interest within a rigid body DMC approximation [39]. The second possibility, which is more accurate, is to carry out a diabatic separation of the diatomic vibrational motion. In this case, the wave function of the isolated diatomic molecule is obtained for a certain quantum level ν , which is then used to obtain the corresponding rotational constant and an averaged PES. The diabatic separation (called vibrational diabatic approximation, VDA) is justified because of the frequency mismatch between the diatomic vibration and the vdW modes. The VDA usually provides very good estimation for resonance positions of $\text{BC}(\nu)\text{-X}_n$ clusters, in particular, for complexes between He and Cl_2 with not too high values of the inter-halogen vibrational excitation. The kinetic energy of the BC-X_n system can be written as:

$$T = - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 - \frac{\hbar^2}{2m_{\text{BC}}} \nabla_{\text{BC}}^2 - \frac{\hbar^2}{2\mu} \nabla_r^2, \quad (7)$$

where the first term gives the motion of the rare gas atoms (X) of mass m_i , the second one describes the motion of the center of mass of BC, and the last one the internal diatomic motion. By averaging the

vibrational BC wave function, the Hamiltonian becomes:

$$H_\nu = \langle \chi_\nu | H | \chi_\nu \rangle = - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 - \frac{\hbar^2}{2m_{\text{BC}}} \nabla_{\text{BC}}^2 + \langle \chi_\nu | \frac{\hbar^2}{2\mu r^2} | \chi_\nu \rangle \mathbf{j}^2 + E_\nu + \sum_i \langle \chi_\nu | V_{\text{BC},X_i} | \chi_\nu \rangle + \sum_{ij} \sum_{i < j} V_{X_i, X_j}, \quad (8)$$

where $i = 1, \dots, n$ and χ_ν is the eigenfunction of the isolated non-rotating halogen molecule, satisfying the equation

$$\left[\frac{-\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + V_{\text{BC}}(r) \right] \chi_\nu(r) = E_\nu \chi_\nu(r), \quad (9)$$

and ∇_i^2 and ∇_{BC}^2 are Laplacian operators associated to the vector locating rare gas i and the vector locating the center of mass of BC (in Cartesian co-ordinates), respectively. In Eq. (8), $\mu = m_{\text{B}}m_{\text{C}}/m_{\text{BC}}$, $m_{\text{BC}} = m_{\text{B}} + m_{\text{C}}$ and m_{B} , m_{C} and m_i are the masses of B, C and X_i , respectively. Finally, \mathbf{r} is the vector joining B and C (r is its modulus) and j is the angular momentum associated to \mathbf{r} . It can be seen that H_ν is formally the Hamiltonian for a rigid BC interacting with n atoms X. The DMC method for rigid bodies can be straightforwardly applied by using the corresponding effective rotational constant ($B_\nu = \langle \chi_\nu | \hbar^2 / 2\mu r^2 | \chi_\nu \rangle$) and interaction potentials $\langle \chi_\nu | V_{\text{BC},X_i} | \chi_\nu \rangle$.

3. Results and discussion

The ground vdW state of the clusters Cl_2He_n ($n = 1\text{--}10$) that corresponds to the $\nu = 13$ Cl_2 (B) vibrational excitation are investigated in this work. In order to compute the quadrature $\langle \chi_\nu | V_{\text{BC},X_i} | \chi_\nu \rangle$ of Eq. (8), it is computationally more efficient to expand the r dependence of the interaction potential BC-X_i in a Taylor series around an effective Cl_2 distance r . An expansion up to the fourth order is used in the calculation. The distribution functions and energies of the clusters are calculated by using a modified version of the original code written by Sandler and Buch [40] for DMC calculations with rigid bodies. In the present calculation, three seeds are employed to initiate the random walk procedure. The time step is of the

Table 2

Ground vdW energies of the Cl_2He_n clusters (referred to the vibrational energy of the Cl_2 (B) in the $\nu = 13$ level)

	E_{vdW} (cm^{-1})	E_{vdW}/n (cm^{-1})
He– Cl_2	–12.55	–12.55
He ₂ – Cl_2	–25.05	–12.52
He ₃ – Cl_2	–37.6	–12.53
He ₄ – Cl_2	–50.3	–12.57
He ₅ – Cl_2	–62.9	–12.58
He ₆ – Cl_2	–75.5	–12.58
He ₇ – Cl_2	–88.15	–12.59
He ₈ – Cl_2	–100.25	–12.53
He ₉ – Cl_2	–113.3	–12.58
He ₁₀ – Cl_2	–125.75	–12.58

order of 7 fs, and the maximum number of steps is 10 000. The initial number of replicates [34] used was 5000.

The ground vdW energies that corresponds to the ten cluster sizes studied are presented in Table 2 (second column). The results show that the stability of the cluster increases with increasing size in the range $n = 1$ –10. It is interesting to analyze the behavior of the vdW energy per rare gas atom, E_{vdW}/n which is shown in the third column of Table 2. The trend found is that the quantity E_{vdW}/n remains nearly constant and close to the value corresponding to the triatomic Cl_2He cluster. The above results indicate that the rare gas atoms arrange in such a way that the stabilization of the cluster is due to the Cl_2 – He_i interactions, while the contribution of the He–He interactions is very small. This is not surprising taking into account that the He–He bonding energy is rather negligible (about 0.001 cm^{-1}).

In order to obtain more information about the structural details of the cluster arrangement, the distribution functions were analyzed. In Fig. 1, histograms of the probability density are displayed versus the distance R between each He atom and the center of mass of Cl_2 , for several cluster sizes, $n = 1, 3, 6, 9$. Actually, each $P_n(R)$ distribution of Fig. 1 is obtained as an average of the distributions associated with each rare gas atom in the cluster,

$$P_n(R) = \frac{1}{n} \sum_{i=1}^n P(R_i), \quad (10)$$

where the individual probability densities $P(R_i)$ are

calculated by integrating the Monte Carlo wave function (squared modulus) over all the co-ordinates except R_i . Probability density distributions of the angles θ_i are calculated in a similar way, with θ_i being defined such that $z_i = R_i \cos(\theta_i)$, where z_i is the Cartesian component of the i th He atom, and the z -axis coincides with the Cl–Cl inter-nuclear axis. After averaging all the rare gas atoms present in the cluster, the distributions shown in Fig. 2 for different sizes are obtained.

The main feature of the probability density distributions is that they are similar (both in the R and θ co-ordinates) for all the cluster sizes studied. Moreover, the distributions of the clusters with $n > 1$ do not differ much from that associated with the smallest Cl_2He aggregate, which is consistent with the behavior found for the vdW energy of the clusters with increasing size. The mean R -value remains almost unchanged for small aggregates, 4.09 and 4.08 Å for $n = 1$ and $n = 3$, respectively. However, a slight tendency for larger clusters can be realized, obtaining values of 4.15 Å ($n = 6$) and 4.19 Å ($n = 9$). These results indicate that in the size range up to $n = 10$, the He atoms behave within Cl_2He_n clusters like particles independent from one another, essentially interacting only with the diatomic subunit.

The peak at $\theta = \pi/2$ of the probability distributions of Fig. 2 shows that the most likely arrangement of the He atoms in different clusters forms a “belt” around Cl_2 , placed in a plane which is perpendicular to the diatomic axis. The relatively large amplitude of the bending mode allows the rare gas atoms to move outside of this perpendicular plane, avoiding repulsions between them. Similar mean quadratic deviation for each of this distribution corroborates the floppiness of all the clusters without any distinction in size.

In a previous study on Cl_2He_n clusters (with slightly different potential and ground vibrational Cl_2 level) [42], it was stated that six equivalent He atoms form the first ring around Cl_2 . The results of the present work show that at least ten equivalent He atoms can be placed in the first ring around the diatomic subunit. We find that inclusion of the bending modes of these clusters become crucial in determining, with reasonable accuracy, the size and structure of the different shell arrangements of the rare gas atoms around the diatomic molecule.

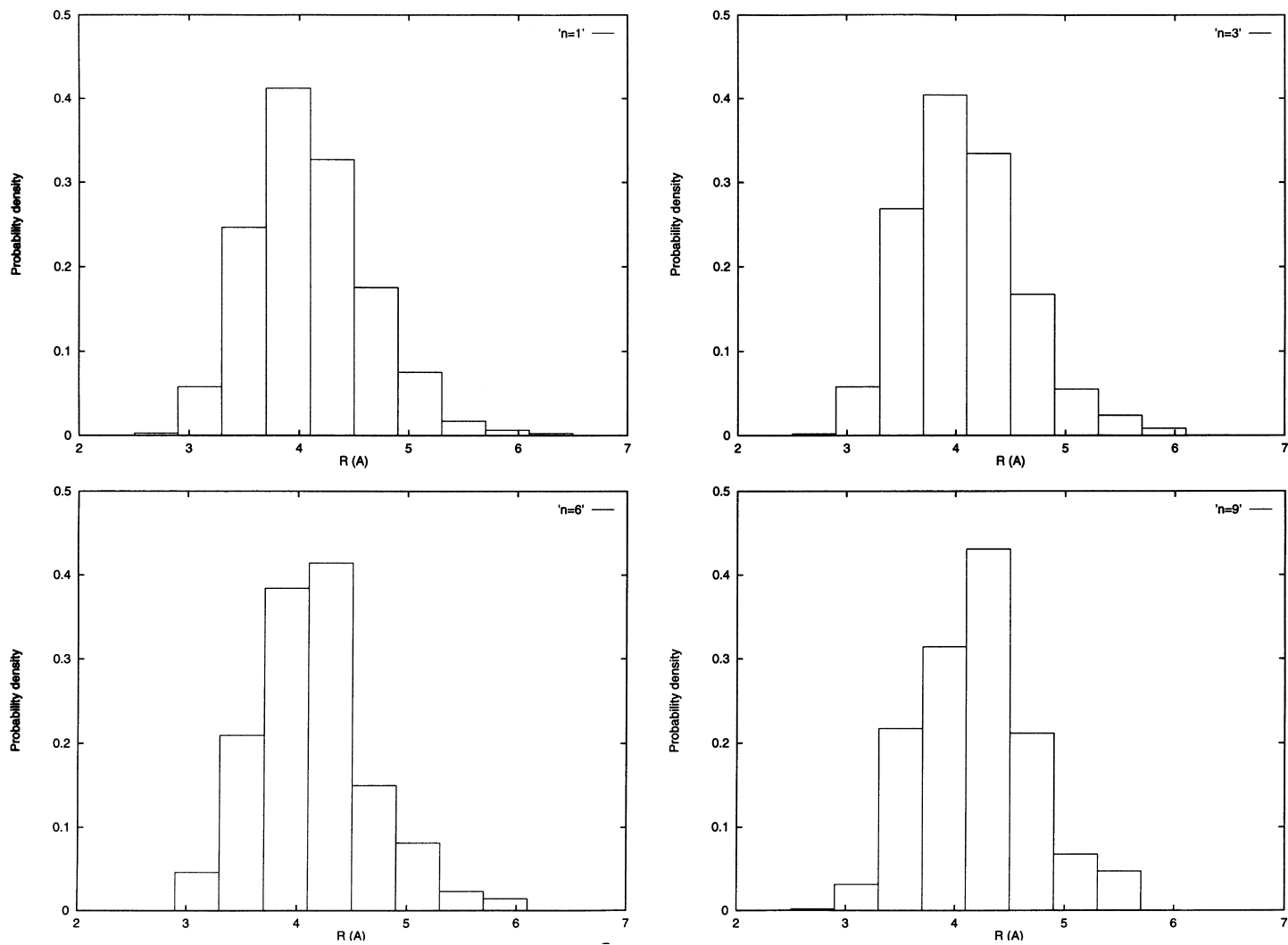


Fig. 1. Probability density associated with the vdW co-ordinate R of the He atom for the clusters Cl_2He_n , with $n = 1, 3, 6$ and 9 .

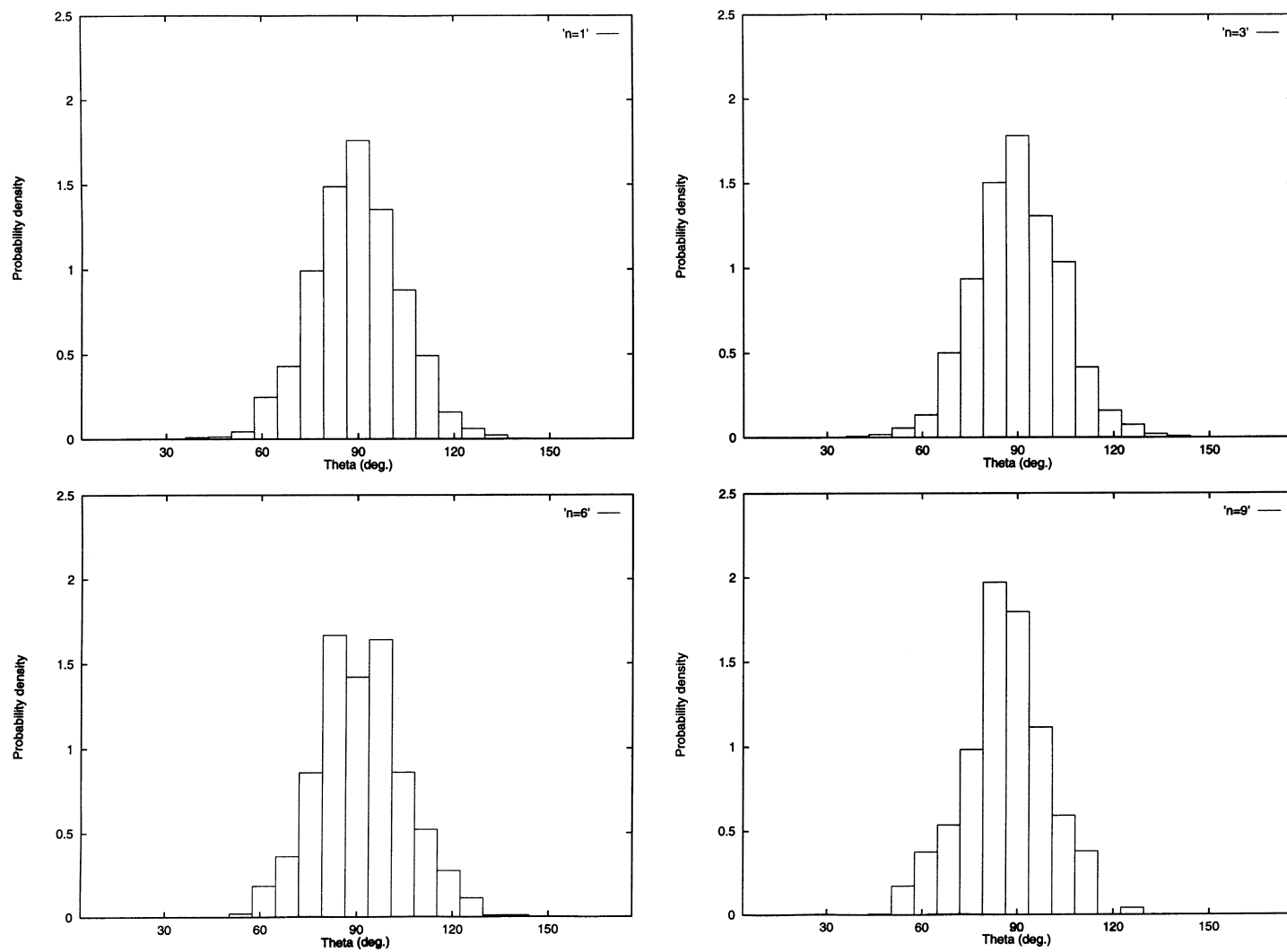


Fig. 2. Probability density associated with the vdW co-ordinate θ of the He atom for the clusters Cl_2He_n with $n = 1, 3, 6$ and 9 .

4. Conclusions

The energy and structure of the ground vdW state of the clusters Cl_2He_n ($n = 1-10$) were investigated with a diabatic diffusion Monte Carlo method. This approach assumes a diabatic separation of the Cl_2 vibration, allowing the incorporation of the excitation in this mode, which is not possible with ordinary diffusion Monte Carlo methods. This is necessary, if the Monte Carlo wave function of the cluster is used as the initial state in a simulation of a dynamical process where the diatomic molecule is vibrationally excited (for instance, vibrational pre-dissociation of the cluster).

The vdW energies obtained with the DDMC approach for the Cl_2He_n clusters show a trend in stabilization with increasing size, up to $n = 10$. This stabilization is only due to the interactions between the different He atoms and the Cl_2 molecule. Each He seems to ignore the presence of the remaining He particles in the cluster, and the effect of the He–He interactions in the total energy of the aggregate is negligible.

The above interpretation is further confirmed by the probability density distributions associated with the rare gas atoms, which are not found significantly different from the $n = 1$ result when the cluster size is increased. The picture emerging from the distributions shows that at least 10 equivalent He atoms can arrange in a “belt” perpendicular to the Cl_2 axis, at half the Cl–Cl distance. The belt is rather broad due to the large amplitude bending motions of the rare gas atoms, which makes it possible to minimize the He–He repulsions as the cluster size grows. Further calculations for clusters with $n > 10$ should be both interesting and desirable in order to establish the size limit of the first co-ordination shell of He atoms around Cl_2 .

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