Comparative investigation of pure and mixed rare gas atoms on coronene molecules

Rocío Rodríguez-Cantano, Massimiliano Bartolomei, Marta I. Hernández,
José Campos-Martínez, Tomás González-Lezana*, and Pablo Villarreal
Instituto de Física Fundamental, IFF-CSIC, Serrano 123, 28006 Madrid, Spain

Ricardo Pérez de Tudela
Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany

Fernando Pirani
Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, 06123 Perugia, Italy

Javier Hernández-Rojas and José Bretón
Departamento de Física and IUdEA, Universidad de La Laguna, 38205 Tenerife, Spain
(Dated: September 29, 2016; to submit to Journal of Chemical Physics)

Clusters formed by the combination of rare gas (RG) atoms of He, Ne, Ar and Kr on coronene have been investigated by means of a basin-hopping algorithm and path integral Monte Carlo calculations at $T = 2$ K. Energies and geometries have been obtained and the role played by the specific RG-RG and RG-coronene interactions on the final results is analysed in detail. Signatures of diffuse behaviour of the He atoms on the surface of the coronene are in contrast with the localization of the heavier species, Ar and Kr. The observed coexistence of various geometries for Ne suggests the motion of the RG atoms on the multi-well potential energy surface landscape offered by the coronene. Therefore, the investigation of different clusters enables a comparative analysis of localized versus non-localized features. Mixed Ar-He-coronene clusters have been also considered as well as the competition of the RG atoms to occupy the docking sites on the molecule is discussed. All the obtained information is crucial to assess the behavior of coronene, a prototypical polycyclic aromatic hydrocarbon clustering with RG atoms at a temperature close to that of interstellar medium, which arises from the critical balance of the interactions involved.

PACS numbers:

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) have been largely investigated as possible responsible sources of unidentified absorption lines from diffuse interstellar bands [1–4]. This hypothesis has encouraged spectroscopists to improve the technical approaches to record spectra under better defined and more astrophysically relevant conditions. One of the most commonly employed methods in experimental investigations of PAH has comprised the use of rare gas (RG) matrices to condensate the PAH onto an optical window at a cryogenic temperature [5–7]. The special physical environment provided by these inert guests ensures a good approach to simulate the isolation and low rotational excitation exhibited by molecules in the interstellar medium [8].

Analogously, formation of RG clusters adsorbed on a PAH substrate has been also subject of great interest [2, 9–36]. One of the most frequently treated issues on these studies regards the structure of the cluster surrounding the molecular impurity. The precise position of the RG atoms with respect to the PAH molecule and its effect on the observed spectra has been discussed before [18, 37]. The existence, for a given number of RG atoms, of a manifold of nearly energetically equivalent species which may be identified in the experimental spectra at

slightly different absorption frequencies and the presence of multiwell potential energy surfaces for the movement of those atoms constitute a rich landscape of investigation.

The analysis of spectral shifts, for instance, provides useful information about the location of the atoms. The large difference observed between the shifts of the (1,1) configurations of ultracold ($T = 0.4$ K) He₂-anthracene with helium atoms above and below the PAH plane, with respect to the (2,0) arrangement, with both atoms at the same side, was explained by the effect of the He-He repulsion [37]. Thus, in the (2,0) structure, the two He atoms at the exterior region of the anthracene molecule, give a larger contribution to the spectral shift. Analogous different spectral shifts for He_N-anthracene clusters, with $N = 1 - 6$, were assigned to either one-sided or two-sided structures in Ref. [29]. Violation of the usually accepted additivity of spectral shifts per added atom is attributed to occupation of geometrically inequivalent locations for the RG atoms [35]. In the study of vibrations and binding energies of Kr_N-carbazole clusters, microscopic red shift of the Kr₂-carbazole was found to be about twice that of Kr-carbazole [36]. This feature was explained assuming that the second RG atom is symmetrically located with respect to the first one, according to a (1,1) geometry. Evidences of the existence of different stable conformers for Ar_N-benzene clusters [32, 38, 39] have been accompanied by the investigation of the corresponding isomer dynamics when the system explores one or another configuration [40]. Red-shifted absorption bands were assigned to Ar_N-perylene aggregates with

*Electronic mail: t.gonzalez.lezana@csic.es

different stabilization energies [41]. In fact processes such as melting of clusters have been related to these multistate isomerization observed in RG-PAH systems [42, 43].

Line splittings have been also interpreted in terms of the position of the RG atoms on the PAH molecule. In particular, in order to explain the hole-burning spectra of tetracene in helium droplets [26], models with two nearly equivalent sites occupied by localized atoms or with tunneling of 1-2 atoms through the barrier in the double-well potential on the surface of the tetracene were invoked. The tunneling-type motion of the Ar atom exploring the different minima exhibited by its interaction with tetracene analysed in Ref. [18] was also connected with splitting in the corresponding spectrum. It is then clear that the influence of the RG environment on the recorded spectra from the embedded molecules still constitutes the subject of interesting discussions [9, 16, 18, 24–28, 37, 44–46].

Several investigations have considered atoms of different RG attached to the same PAH [11, 18, 27, 34, 35, 47, 48]. The distinct atom-atom interaction potential was found to play a crucial role to explain the structures adopted by Ar_7 , Ne_7 and Kr_7 on the basal plane of graphite according with the Monte Carlo (MC) calculation performed in Ref. [11]. Six atoms were found surrounding another one on the central hollow with interparticle distances which were close to the equilibrium distance of the corresponding RG-RG potential. Larger clusters with the same number of atoms, $N = 19$, formed with combinations of Ne and Ar on a model surface were studied by means of a simulated annealing MC method [47]. Lowest energy structures of both pure (Ne_{19} and Ar_{19}) and alloy ($\text{Ne}_9\text{Ar}_{10}$ and $\text{Ne}_{12}\text{Ar}_7$) systems were analysed. In the mixed clusters, the Ar atoms form a central core with bond lengths within 1 % difference with respect to the equilibrium internuclear distances of the dimer in the gas phase, surrounded by Ne atoms maximizing the number of unlike bonds. These structures were result of the differences of the existing interactions rather than size effects.

The helium environment was found to promote novel structures in heterogeneous clusters formed with the addition of more RG atoms on the PAH surface which are usually not stable in the gas phase. The interest of these investigations relies on discovering whether or not the helium solvation shell is affected by the presence of strongly bound heavier RG atoms which might hinder collective excitations. The addition of Ar atoms to tetracene molecules in helium droplets of Ref. [48] yielded new features in the measured spectra. The process of attachment of one Ar atom to the PAH molecule was regarded as the corresponding substitution of one He atom by the new RG atom in the vicinity of the tetracene substrate, with a subsequent spectral red shift with respect to that observed with the exclusive presence of helium. In fact the absence of zero phonon lines observed when Ar atoms are attached to the complexes was attributed to hindered tunnelling of helium when one of the two equivalent sides involved is blocked with an atom of the heavier RG. The pick up sequence into the helium droplet of both Ar atoms and the tetracene molecule was studied in detailed by Pörtner *et al.* [49]. Noticeable differences were observed between the spectra measured with embedding of the tetracene to the droplet prior

to the Ar atoms and vice versa. The authors suggested in their analysis a possible competition between helium and argon atoms to occupy favourable docking sites on the molecular substrate. Redshifted peaks in the electronic spectra of argon-coronene clusters inside helium nanodroplets were interpreted in terms of the location of the Ar atoms in the spectroscopic study by Birer *et al.* [31]. A similar investigation was performed recording the laser-induced fluorescence spectra of tetracene complexes in ^4He droplets with increasing pressures of Ne [50]. The obtained broad spectrum was interpreted as result of the existence of numerous Ne_N -tetracene species and blue-shifted bands, not seen for the case of Ar. An experimental investigation of s-tetrazine plus a few percent of Ar in a helium carrier concluded that the addition of the heavier RG eliminates the He complexes on the molecular substrate and produces spectral signatures assigned to Ar-tetrazine complexes [33].

In our previous investigation on coronene-doped helium clusters [51] we carried out classical and quantum mechanical (QM) calculations to study energies and structures of He_N -coronene aggregates with N up to 69. A detailed analysis of the positions adopted by the surrounding atoms when adsorbed on the molecular substrate at $T = 2$ K provided relevant information about thermal and QM effects. Conclusions regarding the stability of clusters with specific values of N were confirmed also for coronene cations in the experimental work performed by Kurzthaler *et al.* [46]. In this paper we extend our study considering the attachment of atoms of different RG such as Ne, Ar and Kr. In addition to well defined RG-RG interactions, the recently obtained and internally consistent formulation at the intermolecular potential for all RG-coronene dimers [52] has been exploited. All these conditions are crucial to establish energy, structure, relative stability and the temperature dependence of possible isomerization processes for each type of cluster. Specifically, both pure RG-coronene and mixed ($\text{Ar}_{N_1}\text{He}_{N_2}$)-coronene clusters have been investigated by means of a path integral MC (PIMC) method [51]. The structure of this work is the following: Details of the theoretical approaches and potential energy surfaces are given, respectively, in Sections II and III; results are presented in Section IV and discussed in Section V. Finally conclusions are presented in Section VI.

II. THEORY

A. Path integral Monte Carlo method

Theoretical details regarding the PIMC approach employed here have been given elsewhere before [53–57]. Briefly, the density matrix at a temperature T is replaced by the product of M density matrices at higher temperatures MT :

$$\rho(\mathcal{R}_0, \mathcal{R}_M; \beta) = \int d\mathcal{R}_1 \dots d\mathcal{R}_{M-1} \prod_{\ell=0}^{M-1} \rho(\mathcal{R}_\ell, \mathcal{R}_{\ell+1}; \eta), \quad (1)$$

where $\beta = 1/k_B T$, with k_B being the Boltzmann constant and $\eta = \beta/M$. $\mathcal{R}_\ell$ is the vector which collects the $3N$ positions

of the N RG atoms: $\mathcal{R}_\ell \equiv \{\mathbf{r}_1^\ell, \dots, \mathbf{r}_N^\ell\}$, being $\mathbf{r}_i^\ell$ the position vector of the i -th RG atom at the time *slice* or *imaginary* time ℓ . The center of mass (CM) of the non-rotating coronene molecule, with a much larger mass than the RG, is supposed fixed to the origin of coordinates. Under such assumptions the total Hamiltonian $\hat{H}$ is written as follows:

$$\hat{H} = \sum_{i=1}^N \frac{-\hbar^2}{2m_{\alpha(i)}} \nabla_i^2 + V(\mathcal{R}) \quad (2)$$

where $\alpha(i)$ stands for the type of RG (He, Ne, Ar and Kr) within the cluster. In the most general case, $N = N_1 + N_2$, where N_1 and N_2 refer to atoms of two different RG ($N_2 = 0$ if we consider pure clusters); $m_{\alpha(i)}$ is the RG atom mass, $\hbar$ is the Planck constant, and

$$V(\mathcal{R}) = \sum_{i=1}^N V_{\alpha(i)\text{-cor}}(\mathbf{r}_i) + \sum_{i<j}^N V_{\alpha(i)\alpha(j)}(r_{ij}) \quad (3)$$

is the total potential where the first term corresponds to the pairwise RG-coronene interaction and the last term refers to the interaction potential between the two $\alpha(i)$ and $\alpha(j)$ RG atoms and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ the distance separating them.

The internal energy can be obtained by means of the estimators proposed in Refs. [58, 59] as:

$$\langle E(T) \rangle = \frac{3N}{2\beta} - \left\langle \frac{1}{2M} \sum_{\ell=0}^{M-1} \sum_{i=1}^N (\mathbf{r}_i^\ell - \mathbf{r}_i^C) \cdot \mathbf{F}_i^\ell - \frac{1}{M} \sum_{\ell=0}^{M-1} V(\mathcal{R}_\ell) \right\rangle, \quad (4)$$

where $\mathbf{r}_i^C = M^{-1} \sum_{\ell=0}^{M-1} \mathbf{r}_i^\ell$ defines the centroid of the M beads of the i th-particle. The first term in Eq. (4) accounts for the classical kinetic energy and the second one is a quantum correction where $\mathbf{F}_i^\ell$ is the force experienced by the i -particle on the ℓ slice and the third term describes the interaction between each pair of particles on that ℓ slice. Finally, the integration is carried out via a Metropolis MC algorithm, as an average over a number of paths $\{\mathcal{R}_0, \mathcal{R}_1, \dots, \mathcal{R}_M\}$ sampled according to a probability density proportional to the factorised product of M density matrices of Eq. (1).

The PIMC calculation was performed at $T = 2$ K as in our previous study on helium-coronene clusters. The MC simulation involves between $10^6 - 10^8$ steps and, in order to guarantee the ergodicity of the sampling algorithm, we employ a combined procedure consisting on: (i) staging involving 8 beads in each movement and (ii) a classical displacement of all beads describing a particular atom as a whole every 10^5 steps. As in previous applications of the PIMC method, the final average energy is obtained by extrapolation to the $M \rightarrow \infty$ case following a parabolic law [57, 60–62].

B. Basin-hopping method

Putative global energy minima of RG_N -coronene clusters with $N < 65$ were located using the basin-hopping (BH)

scheme [63], which is also known as the ‘‘Monte Carlo plus energy minimization’’ approach of Li and Scheraga [64]. This unbiased method transforms the PES into a collection of basins and explore them by hopping between local minima. This technique has been used successfully for both neutral [63, 65, 66] and charged atomic and molecular clusters [67–73], along with many other applications [74]. A total of five runs of 2×10^4 BH steps each were performed for $N < 30$, and five runs of 7×10^4 steps for the other clusters sizes. For the larger clusters, some differences in the predicted lowest-energy minimum were found in each run. The optimization temperature was chosen between $k_B T = 1.5$ and 3.5 meV.

III. POTENTIAL ENERGY SURFACE

Following our previous study on coronene-doped helium clusters [51] the PES employed in this work is constructed as a sum of the pairwise potentials describing both the RG-RG and RG-coronene interactions.

A. Rare Gas-Rare Gas Interaction

For the interaction between pairs of RG atoms we have employed improved Lennard-Jones (ILJ) functions with the only exception of the He-He case, which is described by means of the potential developed by Aziz and Slaman [75] for a better comparison with our earlier calculation [51]. For internal consistence with the other of RG pair interactions under consideration we have followed the general expression [76]:

$$V(\tilde{r}) = \frac{\epsilon}{n(\tilde{r}) - 6} \left[6\tilde{r}^{-n(\tilde{r})} - n(\tilde{r})\tilde{r}^{-6} \right], \quad (5)$$

where ϵ corresponds to the potential well depth and $\tilde{r}$ is the reduced interatomic distance r/r_m and the $n(\tilde{r})$ term is written as follows:

$$n(\tilde{r}) = \beta + 4\tilde{r}^2, \quad (6)$$

with β related with the hardness of the interacting pair. Eq. (5) corresponds to the case of a neutral system and values for these parameters in all cases here considered are shown in Table I. These values have been tested and fine tuned exploiting a combined analysis of high resolution scattering data, spectroscopic results and gaseous transport coefficients. In Ref. [77] two potential models have been adopted for He-Ar. For internal consistence with the other RG pairs, the potential parameters referred to the model having the well shape coincident with that of ILJ functions has been selected.

A comparison between the RG-RG potentials is shown in Figure 1. Differences are manifested in increasing well depths and equilibrium distances as the atom mass gets larger. The pair He-Ar presents an interaction potential which displays an even shallower well than the Ne-Ne potential and the equilibrium distance is in between this case and the Ar-Ar one.

TABLE I: Parameters for the ILJ potentials describing the interaction between RG atoms: Well depth ϵ in meV and equilibrium distance r_m in Å. ^a Taken from Ref. [76] and ^b from Ref. [77].

System	ϵ	r_m	β
Ne-Ne ^a	3.660	3.094	9
Ar-Ar ^a	12.370	3.757	9
Kr-Kr ^a	17.300	4.010	9
He-Ar ^b	2.669	3.483	9

He-He interaction is clearly the weakest of those considered in this study. Note also that respect to He-He, the well depth in He-Ar, Ne-Ne, Ar-Ar and Kr-Kr are a factor 2.8, 3.9, 13.1 and 18 deeper, respectively.

FIG. 1: Pairwise potentials for the He-He from Ref. [75], and Ne-Ne, Ar-Ar, Kr-Kr and He-Ar interactions described by the ILJ models of Eq. 5 and with values of the parameters from Table I.

B. Rare Gas-Coronene Interaction

The potentials describing the interaction between the coronene molecule and the corresponding RG atom have been taken from Ref. [52]. Similarly to our previous study of He-coronene clusters [51], the $V_{\text{RG-cor}}(\mathbf{r}_i)$ interaction is expressed following an optimized atom-bond pairwise additive scheme [78, 79]:

$$V_{\text{RG-cor}} = \sum_l V^l(R_l, \theta_l). \quad (7)$$

where l runs for all atom-atom bonds in the coronene structure, the different V^l potential terms depend both on the distance R_l between the atom and the C-C and C-H bond reference point, and on θ_l , the Jacobi angle describing the orientation of the atom relative to the bond axis. These V^l potentials are further parameterised according to the ILJ function shown

as in Eq. 5 [76], with both ϵ and reduced distance depending on the θ_l angle as given by [79]:

$$\epsilon_l(\theta_l) = \epsilon_l^\perp \sin^2 \theta_l + \epsilon_l^\parallel \cos^2 \theta_l, \quad (8)$$

$$R_{ml}(\theta_l) = R_{ml}^\perp \sin^2 \theta_l + R_{ml}^\parallel \cos^2 \theta_l, \quad (9)$$

so that $\epsilon_l^\perp$, $\epsilon_l^\parallel$, $R_{ml}^\perp$ and $R_{ml}^\parallel$ are, respectively, well depths and equilibrium distances for the perpendicular and parallel approaches of the atom to the bond. The corresponding $n(\tilde{r}_l)$ function, with $\tilde{r}_l = R_l/R_{ml}(\theta_l)$, is defined according to Eq. (6). Optimized values for these parameters [52] after a fine-tune comparison with high level electronic structure calculations [80, 81] are shown in Table II.

FIG. 2: RG-coronene optimized atom-bond potentials employed in this work for the central hollow position.

In Figure 2 we present a comparison for the different RG of the potential along an axis z perpendicular to the molecular plane and passing through the center of the central hexagon (central hollow). Analysis of other approaches of the RG atom to the coronene reveals a similar trend where energies are, for all RGs, slightly less negative for the top and bridge positions. Both equilibrium distances and especially well depth are found to increase with the mass of the RG atom. This is consistent with the increase of the RG atomic polarizability which is the basic physical property controlling strength and range of the interaction. Specifically, respect to the He-coronene, the well depth in Ne-coronene, Ar-coronene and Kr-coronene becomes a factor 2, 5.7 and 7 times larger, respectively.

TABLE II: Parameters of the different RG-(C-C) and RG-(C-H) pair potentials for the RG-Coronene PES from Ref. [52] employed in this work. Units for distances R are Å, energies ϵ are measured in meV and β is a dimensionless parameter.

atom-bond pair	$R_m^\perp$	$R_m^\parallel$	$\epsilon^\perp$	$\epsilon^\parallel$	β
He-CC	3.589	3.936	0.721	0.866	8.5
Ne-CC	3.643	3.995	1.297	1.809	8.5
Ar-CC	3.851	4.147	3.553	5.207	8.5
Kr-CC	3.974	4.249	4.250	5.906	8.5
He-CH	3.234	3.584	1.364	0.924	9.0
Ne-CH	3.316	3.655	2.544	1.782	9.0
Ar-CH	3.641	3.851	4.814	3.981	9.0
Kr-CH	3.782	3.987	5.667	4.781	9.0

IV. RESULTS

A. Pure clusters

We started our study with clusters formed with only one kind of RG atoms on the molecular substrate. Total energies E obtained by means of both the BH and PIMC approaches for Ne_N -coronene, Ar_N -coronene and Kr_N -coronene clusters are shown in Figure 3 for $N = 1 - 10$. For all cases the energies become more negative as the size of the cluster increases as expected with a more pronounced dependence with N for Ar and Kr. Both BH and PIMC results for each RG display similar behaviour with increasing differences between the QM and classical values of E as N gets larger. For Ne, the relative error between BH and PIMC results, $|(E^{\text{BH}} - E^{\text{PIMC}})/E^{\text{PIMC}}|$, increases from 14 % for $N = 1$ to 25 % for $N = 10$. The BH calculation becomes quite accurate for the heavier atoms and, in particular, the error for Kr reduces to about 3-5%.

FIG. 3: Total (top right side) and evaporation energy (bottom left side) of the Ne_N -coronene, Ar_N -coronene and Kr_N -coronene clusters for $N=1-10$ obtained by means of the BH (empty circles) and PIMC (full squares) methods.

Figure 3 also includes the evaporation energy, E_{evap} , values

TABLE III: Energy per atom (in meV) for Ne-, Ar- and Kr-coronene clusters obtained by means of the BH and PIMC methods. (n_a, n_b) configurations in the PIMC calculation are specified. * correspond to those Ne_N -coronene clusters where the BH minimum energy structure and PIMC results are different. See text for details.

	Ne		Ar		Kr		
N	$E_{\text{atom}}^{\text{BH}}$	$E_{\text{atom}}^{\text{PIMC}}$	$E_{\text{atom}}^{\text{BH}}$	$E_{\text{atom}}^{\text{PIMC}}$	$E_{\text{atom}}^{\text{BH}}$	$E_{\text{atom}}^{\text{PIMC}}$	(n_a, n_b)
1	-27.83	-24.49	-80.08	-76.20	-98.59	-95.70	(1,0)
2	-27.86	-24.51	-80.32	-76.43	-99.00	-96.10	(1,1)
3	-29.14	-24.40	-83.18	-77.29	-103.03	-98.45	(3,0)
4	-29.32	-24.47	-82.67	-77.27	-102.35	-98.19	(3,1)*
5	-29.06	-24.16	-81.68	-76.24	-101.23	-97.00	(3,2)*
6	-29.20	-24.46	-83.61	-77.71	-103.74	-99.15	(3,3)
7	-29.56	-24.20	-82.31	-76.15	-102.31	-97.53	(4,3)*
8	-29.39	-24.00	-81.37	-74.99	-101.29	-96.36	(4,4)
9	-29.22	-23.60	-80.28	-73.78	-99.87	-94.85	(5,4)
10	-29.50	-23.55	-80.65	-73.91	-100.46	-95.25	(7,3)

defined as $E_N - E_{N-1}$ for $N > 1$, and Table III contains results for the energy per atom E_{atom} obtained by means of the two theoretical methods. Numerical values for energies shown in Figure 3 can be actually calculated from these E_{atom} . The (n_a, n_b) configurations shown in Table III refer to the number of atoms at each side of the coronene molecular plane. Despite present PIMC simulations have not been necessarily initiated from minimum energy configurations, agreement with the optimised structures obtained with the BH algorithm is observed in almost all cases. The only exception (marked with * in Table III) are found for the $N = 4, 5$ and 7 in the Ne_N -coronene clusters. For those cases the BH minimum energy structures are not $(3, 1)$, $(3, 2)$ and $(4, 3)$, respectively, but rather $(4, 0)$, $(4, 1)$ and $(7, 0)$, respectively.

The E_{evap} display an oscillating behaviour with N with noticeable minima at $N = 3, 6$ and 10 for the heavier RGs, which are nicely described by both the PIMC and the BH approaches. As we will discuss below by means of the analysis of the probability density functions [51], this stability with respect to the corresponding $N-1$ and $N+1$ neighbours is related with the position of the atoms on the molecular substrate.

A comparison for He_5 -coronene, Ne_5 -coronene, Ar_5 -coronene and Kr_5 -coronene is shown in Figure 4, where probabilities on each side for the corresponding $(3, 2)$ structures are in separated panels. One of the most remarkable features is the different degree of localization depending both on specific details of the potential energy surface and on the mass of each system. On one extreme, He displays largely diffuse distributions on both sides (top panels in Figure 4), with vaguely defined maxima and a probability cloud extended over the available sites on the coronene surface. When the mass is increased to the case of Ne, the distributions (second panels) start to display more localized maxima but the coexistence of equivalent configurations suggests the capability of the atoms to hop between neighbour potential wells. Much more defined maxima are observed for the cases of Ar and Kr (shown in the last two rows of Figure 4) which provide examples of how the PIMC

FIG. 4: Probability density functions from top to bottom for He_5 -coronene, Ne_5 -coronene, Ar_5 -coronene and Kr_5 -coronene clusters obtained with the PIMC method at $T = 2$ K. Left and right side corresponds to the two sides of the coronene molecular plane. Color scale goes from blue for the lowest probability to red for the maxima.

simulation barely modifies its initial configuration. Ar and Kr atoms remain separated by interparticle distances which are almost identical to the equilibrium distances of their respective Ar-Ar and Kr-Kr interaction potentials (see Figure 1).

Results for larger clusters formed with $N = 10$ atoms of either He, Ne, Ar or Kr, show the atoms according to a (7, 3) structure as shown in Figure 5. Identical results than in the $N = 5$ case are found for the side with three atoms (right panels). The configuration with seven atoms (left panels of Figure 5) varies with the RG atom. The structure comprises an atom occupying the central hollow and the other six on surrounding positions. For He and Ne, those correspond to the external ring of hexagons. As expected, whereas the He atoms present a distribution of blurred maxima, for Ne, the peakings are more clearly defined. The precise positions of the solvating atoms seem to be ruled by the Ne-Ne equilibrium distance, $3.09 \text{ \AA}$ [76], since all pairs of closest Ne atoms are separated $\sim 3.11 \text{ \AA}$. As the mass increases we observe that the external RG atoms are displaced to further positions with respect to the center, moving to the dimples formed by the sequence H-C-C-C-H at the border of the molecule along a 30° -shift of the line which interconnects each outer atom with the central one from the location seen for Ne clusters. This displacement is mainly motivated by the fact that the RG pair tends to place on the most stable position on the coronene surface keeping the

FIG. 5: Same as Figures 4 for $N = 10$. The equilibrium structure found in all cases is (7, 3).

interparticle separation as close as possible to the equilibrium distance of the corresponding interaction (shown in Figure 1). Thus for example, the Kr atoms of the probability densities of Figure 5 are $\sim 3.95 \text{ \AA}$ apart, near to the corresponding minimum r_m of $4.01 \text{ \AA}$ as shown in Table I. A similar good agreement is observed between the distance ($\sim 3.71 \text{ \AA}$) which separates each external Ar atom and the central one (see left panel in third row of Figure 5) and the corresponding equilibrium Ar-Ar distance in Table I ($3.76 \text{ \AA}$). The slightly smaller Ar-Ar and Kr-Kr mean distances when the atoms are bound to coronene can be explained by a confinement effect due to the molecular substrate. On the other hand, quantum effects leading to an increase of the excluded volume must be at the origin of the slight increase of the Ne-Ne average distance as compared with the equilibrium distance [82].

B. Mixed Clusters

Our analysis also comprises the study of mixed RG atoms, in particular Ar and He, covering the PAH surface. It is interesting to investigate the competition between both types of atoms for the most stable positions on the coronene and the role that the distinct interparticle interactions may play in the final overall structure of the doped clusters. Thus different $\text{Ar}_{N_1}\text{He}_{N_2}$ -coronene clusters have been studied and the energies and structures have been calculated by means of the BH and PIMC methods of Section II.

Table IV shows the energies of a series of Ar-He mixed clusters ($n_a^{\text{Ar}}, n_b^{\text{He}} | n_b^{\text{Ar}}, n_a^{\text{He}}$) on the coronene surface. In particular combinations of $N_1 = 2, 14$ and 26 Ar atoms with $N_2 = 1, 12, 14, 24, 26$ and 38 He atoms have been investigated. PIMC simulations from initial configurations with equally-weighted number of atoms at both sides of the coronene plane, $n_a^{\text{Ar}} \sim n_b^{\text{Ar}}$ and $n_a^{\text{He}} \sim n_b^{\text{He}}$, have been compared with classical minimum energy structures obtained by the BH approach. Both methods yield similar results in most of the cases, especially for the largest clusters (see $\text{Ar}_{14}\text{-He}_{N_2}\text{-coronene}$ in Table IV). Those cases in which the configuration for the QM calculation does not coincide with the global minimum structure predicted by the BH optimization, are characterised, however, by small energy differences between the corresponding minima. Thus for example there are only 10^{-2} meV separating the (2, 2 | 0, 4) configuration (the most stable according with the BH algorithm) and the (1, 3 | 1, 3) structure (used in the PIMC calculation), with -248.10 meV and -248.00 meV, respectively, for $\text{Ar}_2\text{He}_6\text{-coronene}$. The energy difference between BH minima becomes only slightly larger for $\text{Ar}_2\text{He}_{24}\text{-coronene}$: 0.5 meV between (2, 11 | 0, 13) (-465.60 meV) and (1, 12 | 1, 12) (-464.90 meV). For $\text{Ar}_2\text{He}_{12}$, on the contrary, the equal distribution of the He atoms at both sides of the molecular plane seems not to be among the most stable classically probable.

One of the most noticeable features observed in the PIMC calculations is that atoms of the heaviest counterpart, Ar, dominate when the docking sites on the coronene are chosen. Thus the resulting probability density distributions for the Ar atoms are identical to those obtained for pure clusters with the same number N_1 . Distributions for $\text{Ar}_2\text{He}_{N_2}\text{-coronene}$ (not presented here) show that the two Ar atoms are located following a (1, 1) configuration with each one occupying the hollow position of the central C-hexagon as they do in the equilibrium geometry of a pure $\text{Ar}_2\text{-coronene}$. Analogously, for $N_1 = 14$, the 7 Ar atoms found at each side of the molecular plane are located exactly like those in the (7, 3) structure of $\text{Ar}_{10}\text{-coronene}$ (see Figure 5). Then the lighter He atoms do not compete with the Ar atoms to occupy the docking sites. This result is even found for those cases in which the PIMC simulation is started with the He atoms already on the surface of the coronene and Ar is added afterwards. He atoms occupying for instance the hollow at the centre of the molecule are removed by an Ar counterpart as the simulation evolves towards the most energetically stable configuration.

Therefore the positions adopted by the He atoms in these mixed clusters reveal remarkable differences with respect to the case of pure $\text{He}_N\text{-coronene}$ clusters. The smallest possible size corresponds to the addition of one single He atom when a pair of Ar units are already present. Helium thus finds its natural first option, the central hollow on the central hexagon, already occupied and explores some other position over the external side of the outer hexagons. As a result the minimum energy distribution calculated by means of the BH algorithm (left side of Figure 6) shows the He atom on a peripheral position over the external hexagons. The distance between the He atom and the Ar atom on the same side of the coronene (3.36 Å) is close to the equilibrium Ar-He dis-

FIG. 6: Minimum energy geometry obtained with the BH algorithm (left) for the Ar_2He -coronene cluster with Ar atoms (blue) at the central hollow positions on both sides (note that one is below the surface) and He (grey) on a peripheral location; (right) The PIMC distribution of the He atom at $T = 2$ K.

tance, 3.48 Å, in the ILJ potential employed in this study (see table I). The PIMC simulation on the other hand yields probability density distributions for the helium component (see right side of Figure 6) which can be interpreted as result of a delocalized He atom which explores almost the entire ring centered on the central Ar atom. This apparent freedom of movement decreases noticeably with the addition of more He atoms. In particular when $N_2 = 12$ the PIMC calculation (not shown here) with an equal share of atoms at both side of the molecule, reveals that besides each Ar atom, the He atoms become localized at the H-C-C-C-H dimples of the border of the coronene.

A possible way to investigate the differences of the behaviour of the He atoms on the coronene surface due to the presence of heavier Ar atoms is the comparison with the situation of pure He-coronene clusters. Thus for example, Figure 7 shows the probability density functions for the case of 24 He atoms within pure helium-coronene clusters (top panel) and for systems also containing 2 (middle panel) and 14 Ar atoms (bottom panel) obtained by means of the PIMC method at $T = 2$ K. Whereas for the pure cluster the distribution of the He atoms exhibits maximum peaks over all hollows inside the carbon hexagons and the above mentioned C-structure dimples, the presence of Ar atoms in the central hexagons in the mixed cluster forces helium to find vacancies at more external positions on the coronene surface. In particular, according to the result shown on the middle panel of Figure 7, atoms on the external ring of hexagons move further away from the center of the molecule, consistent with the enlargement of interparticle distance when the pair changes from He-He to He-Ar. Those He atoms which in the pure cluster occupy the dimples remain unchanged and signatures of probability at even more outside locations are observed. When the number of the heavier Ar atoms is even larger, the migration of He is even more remarkable. Bottom panel of Figure 7 shows how all the he-

FIG. 7: Helium probability density distributions for the He_{24} -coronene (top panel), $\text{Ar}_2\text{He}_{24}$ -coronene (middle panel) and $\text{Ar}_{14}\text{He}_{24}$ -coronene clusters (bottom panel) at $T = 2$ K.

lium content of $\text{Ar}_{14}\text{He}_{24}$ -coronene is mainly located outside the molecular surface.

V. DISCUSSION

Present results show that some of the RG atoms certainly have the possibility to explore different equivalent locations on the coronene surface. For He, the resulting probability density distributions show diffuse maxima, a feature which can be interpreted as an indication of a continuous movement around the different potential energy minima offered by the coronene surface. When the mass increases and the interaction becomes stronger the probability to explore adjacent minima diminishes. Ne seems to be an intermediate case between the extremely diffuse character observed for He and the localization experienced by both Ar and Kr atoms. Thus, in most of the cases, distributions obtained for Ne-coronene clusters exhibit well defined maximum peaks in some of the various equivalent conformers that the symmetry of the C-hexagons allows. Signatures of coexistence of energetically equivalent configurations on PAH molecules have been also previously reported in MC calculations of Ar atoms on carbazole [10]. In that work the two most stable configurations of Ar_4 -carbazole, with only a 12 cm^{-1} (1.5 meV) energy difference, comprise equivalent structures with minor displacements of the RG atoms to positions in the vicinity of the original locations which are explored as the temperature increases.

A similar result for the case of $N = 5$ Ar atoms led the authors to mention the possibility of finding both ordered rigid structures and disordered configurations as a consequence of a surface-decoupling process. Under these circumstances the adcluster were found to lose the original orientational ordering with respect to the host molecule and become free to undergo large-amplitude movements on its surface.

These movements of the RG atoms on the surface of the PAH have been usually related to tunneling-type motion along the multiwell potential energy landscape which characterise the interaction with the substrate [18], and are responsible for the onset of multiply structured probability density functions. As commented in the introduction, line-splittings have been interpreted in terms of the occupation of nearly equivalent sites and coexistence of isoenergetic isomers [26]. In principle, one would think that the movement of the atoms on the surface simply depends on the mass of the RG atoms, with more rigid and localized structures for the heavier cases, but harmonic zero point energy calculations for RG_3 -coronene, reveals a non-monotonically decrease from He to Kr (19.8 meV, 13.6 meV, 15.9 meV and 12.0 meV, for He, Ne, Ar and Kr, respectively) as one would expect from a purely mass dependent feature. In turn, these results show that potential energy surfaces exhibit different curvature around the minimum in each case. Furthermore, barriers between adjacent potential wells are found below the PIMC energies, and therefore, tunnelling should play a minor role to rule the movements of atoms which are, on the contrary, subject to intrinsic differences between isomerization pathways for each RG-coronene potential.

The dependence of the final structure adopted by the atoms on the surface on the precise nature of the corresponding pairwise potentials is manifested by the above discussed results. In particular, the tendency to keep an interparticle separation similar to the corresponding RG-RG equilibrium distance has been also seen in a MC calculation of different clusters on model surfaces [11]. Similar results to those shown in Figure 5 for the 7 atoms on one side the coronene for the $N = 10$ clusters were reported in Ref. [11], where the enlargement of the Ar–Ar and Kr–Kr separation on the surface with respect to Ne produces identical differences between the location of the atoms of each element on the surface.

The analysis of the BH results of the explored minima reveals that the equilibrium geometry comprises a subtle balance between the different interactions within the cluster. Having Ar atoms at the same side of the coronene yields a noticeable contribution coming from the Ar–Ar interaction (~ 12 meV for each pair) in comparison with those configurations in which Ar atoms are separated by the molecular plane. In turn, when atoms of this heavier RG occupy both hollows inside the central carbon ring, the contribution of the RG-coronene interaction plays a substantial role on the final energy. Both He–He and He–Ar contributions start to be substantially important when the number of atoms become large. Therefore, in spite of Ar–coronene interaction constitutes the main proportion to the final value, the precise total energy is thus the result of a fine compromise on the specific position of the atoms solvating the PAH and their corresponding interactions among

TABLE IV: Energies (in meV) for the $\text{Ar}_{N_1}\text{He}_{N_2}$ -coronene clusters obtained by means of the BH and PIMC approaches. Corresponding configurations of both Ar and He atoms above and below the molecular plane ($n_a^{\text{Ar}}, n_a^{\text{He}} | n_b^{\text{Ar}}, n_b^{\text{He}}$) are also specified. See text for details. (*) Two He atoms are in the plane of the coronene.

	$N_1 = 2$		$N_1 = 14$		$N_1 = 26$	
N_2	PIMC	BH	PIMC	BH	PIMC	BH
1	-160.0 (1, 1 1, 0)	-174.4 (1, 1 1, 0)	-1017.0 (7, 1 7, 0)	-1126.3 (7, 1 7, 0)	-1686.5 (13, 1 13, 0)	-1970.5 (13, 1 13, 0)
12	-233.9 (1, 6 1, 6)	-332.8 (1, 7 1, 5)	-1047.7 (7, 6 7, 6)	-1265.2 (7, 6 7, 6)	-1742.8 (13, 6 13, 6)	-2112.1 (14, 7 12, 5)
14	-233.8 (1, 7 1, 7)	-361.5 (1, 7 1, 7)	-1080.1 (7, 7 7, 7)	-1286.8 (7, 8 7, 6)	-1760.1 (13, 7 13, 7)	-2134.4 (14, 4 12, 10)
24	-267.2 (1, 12 1, 12)	-465.6 (2, 11 0, 13)	-1118.4 (7, 12 7, 12)	-1396.9 (7, 12 7, 12)	—	—
26	-272.7 (1, 13 1, 13)	-485.8 (2, 12 0, 14)	-1126.7 (7, 13 7, 13)	-1418.9 (7, 13 7, 13)	-1802.4 (13, 13 13, 13)	-2264.6 (14, 13 12, 13)
38	-300.0 (1, 19 1, 19)	-597.3 (2, 19 0, 19)	-1153.6 (7, 19 7, 19)	-1537.8 (7, 19 7, 19)*	-1830.4 (13, 19 13, 19)	-2391.3 (14, 18 12, 20)

them.

In their electronic spectroscopy experiment on argon-coronene complexes inside He droplets, Birer *et al.* [31] observed two redshifted peaks in the $S_1 \leftarrow S_0$ spectrum which were assigned to clusters where one Ar atom was localized on the outer rings or over the central hollow, respectively. A third peak appeared with increasing Ar pressure which was subsequently attributed to the presence of two Ar atoms, although nothing could be stated regarding the precise position on the coronene plane. Our PIMC results conclude however that the most stable configuration for clusters with either 1 or 2 Ar atoms involves occupying the central hollow of the coronene at both sides of the molecular plane. This feature is further supported by the fact that *ab initio* calculations consistent with Ref. [52], predict that the potential minimum at this central position is about 10 meV deeper than the local minima at the surrounding hollows. It is possible than the empirical functional form employed in Ref. [31], in principle adequate for benzene, might lead to incorrect results when applied to coronene. The overall interaction is expected to decrease at the outer hollows where the Ar atom is closer to the C-H bonds, less polarizable than the aromatic C-C ones [83]. Results reported by Birer *et al.*, on the other hand, are at odds with one of the main findings of this work which shows that Ar atoms are usually located in mixed clusters with helium, as in the case of pure Ar_N -coronene, with interparticle Ar–Ar distances close to the corresponding equilibrium configuration.

VI. CONCLUSIONS

The energetics and structure of coronene clusters formed with rare gas atoms such as He, Ne, Ar and Kr have been in-

vestigated by means of a classical optimization procedure and PIMC calculations at $T = 2$ K. A comparative analysis of how the different RG-RG and RG-coronene interactions play a role in the final structure of the atoms on the molecule has been performed. In particular, the equilibrium distance between the atom pairs has been found to rule the separation of the solvating atoms on the coronene surface. Differences between masses of the RG atoms and their corresponding interaction with the PAH yield to different degrees of localization, with noticeably signatures of diffuse peaks for the probability density functions in the case of the lightest atom, He, and rigid peaks for the two heavier cases, Ar and Kr. In addition, the co-existence of equivalent geometries displayed by the RG atoms on the surface is clearly manifested in the case of Ne. Mixed clusters formed by combination of He and Ar atoms have been also treated in detail in order to understand the competition established between the different RG to occupy the docking locations offered by the potential energy surface of the RG-coronene interaction.

VII. ACKNOWLEDGEMENTS

This work has been supported by MICINN Grant No. FIS2011-29596-C02-01, FIS2013-48275-C2-1-P and FIS2014-51993-P. RR-C acknowledges funding from the Grant No. JAE-Pre-2010-01277. J. H.-R. and J. B. acknowledge the financial support from Ministerio de Economía y Competitividad under Grants No. FIS2013-41532-P. FP acknowledges Dipartimento di Chimica, Biologia e Biotecnologie di Perugia for financial support.

-
- [1] T. P. Snow, V. Le Page, Y. Keheyan, and V. M. Bierbaum, *Nature* **391**, 259 (1997).
 - [2] H. Knorke, J. Langer, J. Oomens, and O. Dopfer, *Astrophys. J. Lett.* **706**, L66 (2009).
 - [3] A. Leger and J. L. Puget, *Astron. Astrophys.* **137**, L5 (1984).
 - [4] E. K. Campbell, M. Holtz, D. Gerlich, and J. P. Maier, *Nature*

523, 322 (2015).

- [5] J. Oomens, in *PAHs and the Universe*, edited by C. Joblin and A. G. G. M. Tielens (2011), vol. 46 of , pp. 61–73.
- [6] I. Garkusha, J. Fulara, P. J. Sarre, and J. P. Maier, *J. Phys. Chem. A* **115**, 10972 (2011).
- [7] M. Steglich, C. Jäger, G. Rouillé, F. Huisken, H. Mutschke, and

- T. Henning, *Astroph. J. Lett.* **712**, L16 (2010).
- [8] C. Joblin, L. d'Hendecourt, A. Leger, and D. Défourneau, *Astron. Astrophys.* **281**, 923 (1994).
- [9] H. D. Whitley, J. L. DuBois, and K. B. Whaley, *J. Chem. Phys.* **131**, 124514 (2009).
- [10] S. Leutwyler and J. Boesiger, *Chem. Rev.* **90**, 489 (1990).
- [11] N. Y. Matos and G. E. López, *J. Chem. Phys.* **109**, 1141 (1998).
- [12] B. K. Agrawal, *Phys. Rev. B* **23**, 1778 (1981).
- [13] S. Leutwyler, A. Schmelzer, and R. Meyer, *J. Chem. Phys.* **79**, 4385 (1983).
- [14] S. Leutwyler and J. Jortner, *J. Phys. Chem.* **91**, 5558 (1987).
- [15] Y. Kwon and K. B. Whaley, *J. Chem. Phys.* **114**, 3163 (2001).
- [16] P. Huang, H. Whitley, and K. Whaley, *J. Low Temp. Phys.* **134**, 263 (2004).
- [17] A. Heidenreich, U. Even, and J. Jortner, *J. Chem. Phys.* **115**, 10175 (2001).
- [18] M. J. Ondrechen, Z. Berkovitch-Yellin, and J. Jortner, *J. Am. Chem. Soc.* **103**, 6586 (1981).
- [19] M. L. Klein, S. O'Shea, and Y. Ozaki, *J. Phys. Chem.* **88**, 1420 (1984).
- [20] A. Ambrosetti and P. L. Silvestrelli, *J. Phys. Chem. C* **115**, 3695 (2011).
- [21] J. Kysilka, M. Rubeš, L. Grajciar, P. Nachtigall, and O. Bludský, *J. Phys. Chem. A* **115**, 11387 (2011).
- [22] L. Sheng, Y. Ono, and T. Taketsugu, *J. Phys. Chem. C* **114**, 3544 (2010).
- [23] S. Bouzón Capelo, B. Fernández, H. Koch, and P. M. Felker, *J. Phys. Chem. A* **113**, 5212 (2009).
- [24] M. Hartmann, A. Lindinger, J. Peter Toennies, and A. F. Vilesov, *Phys. Chem. Chem. Phys.* **4**, 4839 (2002).
- [25] A. Lindinger, J. P. Toennies, and A. F. Vilesov, *Phys. Chem. Chem. Phys.* **3**, 2581 (2001).
- [26] M. Hartmann, A. Lindinger, J. P. Toennies, and A. F. Vilesov, *J. Phys. Chem. A* **105**, 6369 (2001).
- [27] S. Leutwyler, *J. Chem. Phys.* **81**, 5480 (1984).
- [28] S. Krasnokutski, G. Rouill, and F. Huysken, *Chem. Phys. Lett.* **406**, 386 (2005).
- [29] U. Even, J. Jortner, D. Noy, N. Lavie, and C. Cossart-Magos, *J. Chem. Phys.* **112**, 8068 (2000).
- [30] E. Shalev, N. BenHorin, U. Even, and J. Jortner, *J. Chem. Phys.* **95**, 3147 (1991).
- [31] O. Birer, P. Moreschini, and K. K. Lehmann, *Phys. Chem. Chem. Phys.* **10**, 1648 (2008).
- [32] M. Schmidt, M. Mons, J. L. Calvé, P. Millié, and C. Cossart-Magos, *Chem. Phys. Lett.* **183**, 69 (1991).
- [33] R. E. Smalley, L. Wharton, D. H. Levy, and D. W. Chandler, *J. Chem. Phys.* **68**, 2487 (1978).
- [34] A. Amirav, U. Even, and J. Jortner, *J. Chem. Phys.* **74**, 3745 (1981).
- [35] A. Amirav, U. Even, and J. Jortner, *J. Chem. Phys.* **75**, 2489 (1981).
- [36] J. Boesiger and S. Leutwyler, *Chem. Phys. Lett.* **126**, 238 (1986).
- [37] U. Even, I. Al-Hroub, and J. Jortner, *J. Chem. Phys.* **115**, 2069 (2001).
- [38] M. Albertí, M. Castro, A. Laganà, F. Pirani, M. Porrini, and D. Cappelletti, *Chem. Phys. Lett.* **392**, 514 (2004).
- [39] M. Schmidt, M. Mons, and J. L. Calvé, *Chem. Phys. Lett.* **177**, 371 (1991).
- [40] J. Vacek, P. Hobza, and J. Jortner, *J. Phys. Chem. A* **102**, 8268 (1998).
- [41] M. M. Dextader, I. M. Gulis, S. A. Schwartz, and M. R. Topp, *Chem. Phys. Lett.* **112**, 483 (1984).
- [42] U. Even, N. Ben-Horin, and J. Jortner, *Phys. Rev. Lett.* **62**, 140 (1989).
- [43] J. Bösigler and S. Leutwyler, *Phys. Rev. Lett.* **59**, 1895 (1987).
- [44] P. Huang and K. B. Whaley, *Phys. Rev. B* **67**, 155419 (2003).
- [45] H. D. Whitley, J. L. DuBois, and K. B. Whaley, *J. Phys. Chem. A* **115**, 7220 (2011).
- [46] T. Kurzhäler, B. Rasul, M. Kuhn, A. Lindinger, P. Scheier, and A. M. Ellis, *J. Chem. Phys.* **145**, 064305 (2016).
- [47] M. Ocasio and G. E. López, *J. Chem. Phys.* **112**, 3339 (2000).
- [48] M. Hartmann, A. Lindinger, J. Toennies, and A. F. Vilesov, *Chem. Phys.* **239**, 139 (1998).
- [49] N. Pörtner, A. F. Vilesov, and M. Havenith, *Chem. Phys. Lett.* **343**, 281 (2001).
- [50] A. Lindinger, J. P. Toennies, and A. F. Vilesov, *Chem. Phys. Lett.* **429**, 1 (2006).
- [51] R. Rodríguez-Cantano, R. Pérez de Tudela, M. Bartolomei, M. I. Hernández, J. Campos-Martínez, T. González-Lezana, P. Villarreal, J. Hernández-Rojas, and J. Bretón, *J. Chem. Phys.* **143**, 224306 (2015).
- [52] M. Bartolomei, E. Carmona-Novillo, M. I. Hernández, J. Campos-Martínez, and F. Pirani, *J. Phys. Chem. C* **117**, 10512 (2013).
- [53] D. M. Ceperley, *Rev. Mod. Phys.* **67**, 279 (1995).
- [54] Y. Kwon, D. M. Ceperley, and K. B. Whaley, *J. Chem. Phys.* **104**, 2341 (1996).
- [55] R. Rodríguez-Cantano, D. López-Durán, R. Pérez de Tudela, T. González-Lezana, G. Delgado-Barrio, P. Villarreal, and F. A. Gianturco, *Comp. Theor. Chem.* **990**, 106 (2012).
- [56] R. Rodríguez-Cantano, R. Pérez de Tudela, D. López-Durán, T. González-Lezana, F. A. Gianturco, G. Delgado-Barrio, and P. Villarreal, *Eur. Phys. J. D* **67**, 119 (2013).
- [57] R. Rodríguez-Cantano, T. González-Lezana, P. Villarreal, and F. A. Gianturco, *J. Chem. Phys.* (2015).
- [58] M. F. Herman, E. J. Bruskin, and B. J. Berne, *J. Chem. Phys.* **76**, 5150 (1982).
- [59] K. R. Glaesemann and L. E. Fried, *J. Chem. Phys.* **116**, 5951 (2002).
- [60] R. Pérez de Tudela, D. López-Durán, T. González-Lezana, G. Delgado-Barrio, P. Villarreal, F. A. Gianturco, and E. Yurtsever, *J. Phys. Chem. A* **115**, 6892 (2011).
- [61] J. E. Cuervo and P.-N. Roy, *J. Chem. Phys.* **125**, 124314 (2006).
- [62] N. Blinov, X. Song, and P.-N. Roy, *J. Chem. Phys.* **120**, 5916 (2004).
- [63] D. J. Wales and J. P. K. Doye, *J. Phys. Chem. A* **101**, 5111 (1997).
- [64] Z. Li and H. A. Scheraga, *Proc. Natl. Acad. Sci. U.S.A* **84**, 6611 (1987).
- [65] J. Hernández-Rojas, F. Calvo, J. Bretón, and J. Gomez Llorente, *J. Phys. Chem. C* **116**, 17019 (2012).
- [66] S. Acosta-Gutiérrez, J. Bretón, J. M. G. Llorente, and J. Hernández-Rojas, *J. Chem. Phys.* **137**, 074306 (2012).
- [67] T. James, D. J. Wales, and J. Hernández-Rojas, *Chem. Phys. Lett.* **415**, 302 (2005).
- [68] J. Hernández-Rojas, J. Bretón, J. M. Gomez Llorente, and D. J. Wales, *J. Phys. Chem. B* **110**, 13357 (2006).
- [69] J. P. K. Doye and D. J. Wales, *Phys. Rev. B* **59**, 2292 (1999).
- [70] J. Hernández-Rojas and D. J. Wales, *J. Chem. Phys.* **119**, 7800 (2003).
- [71] J. Hernández-Rojas, J. Bretón, J. M. Gomez Llorente, and D. J. Wales, *J. Chem. Phys.* **121**, 12315 (2004).
- [72] J. Hernández-Rojas, J. Bretón, J. G. Llorente, and D. Wales, *Chem. Phys. Lett.* **410**, 404 (2005).
- [73] J. Hernández-Rojas, F. Calvo, F. Rabilloud, J. Bretón, and J. M. Gomez Llorente, *J. Phys. Chem. A* **114**, 7267 (2010).
- [74] D. J. Wales, *Energy Landscapes* (Cambridge University Press, (1989)).

- Cambridge, 2003).
- [75] R. A. Aziz and M. J. Slaman, *J. Chem. Phys.* **94**, 8047 (1991).
 - [76] F. Pirani, S. Brizi, L. Roncaratti, P. Casavecchia, D. Cappelletti, and F. Vecchiocattivi, *Phys. Chem. Chem. Phys.* **10**, 5489 (2008).
 - [77] L. J. Danielson and M. Keil, *J. Chem. Phys.* **88**, 851 (1988).
 - [78] F. Pirani, D. Cappelletti, and G. Liuti, *Chem. Phys. Lett.* **350**, 286 (2001).
 - [79] F. Pirani, M. Albertí, A. Castro, M. M. Teixidor, and D. Cappelletti, *Chem. Phys. Lett.* **394**, 37 (2004).
 - [80] M. Pitonák and A. Hesselmann, *J. Chem. Theory Comput.* **6**, 168 (2010).
 - [81] A. Hesselmann, G. Jansen, and M. Schütz, *J. Chem. Phys.* **122**, 014103 (2005).
 - [82] R. Rodríguez-Cantano, R. Pérez de Tudela, M. Bartolomei, M. I. Hernández, J. Campos-Martínez, T. González-Lezana, P. Villarreal, J. Hernández-Rojas, and J. Bretón, *J. Phys. Chem. A* **120**, 5370 (2016).
 - [83] K. G. Denbigh, *Trans. Faraday Soc.* **36**, 936 (1940).