Molecular Dynamics Simulations of Site Geometries of Anthracene in an Argon Matrix†

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Received: November 8, 1999; In Final Form: January 21, 2000

Two different molecular dynamics-based models are compared with respect to their ability to predict the number and the distribution of trapping sites of a molecule in a rare-gas matrix. The two approaches are applied to the same problem: anthracene molecules trapped in an argon matrix. Both methods give a small number of trapping sites with similar structures, but the distributions of sites in each model are different. In all stable sites, the molecule was found to lie on either the {001} or the {111} plane of the crystalline argon. We propose a structure for the most stable site in which anthracene lies in the 6 substitutional site in the {001} plane.

1. Introduction

Matrix isolation has become a widely used method for the preparation of solid-state samples for high-resolution spectroscopy of polyatomic molecules. This technique had been developed originally for the study of highly reactive species that are stabilized due to the low chemical reactivity of the environment. However, the same environment also offers many advantages for the study of stable molecules. In the case of rare-gas matrixes, the perturbation of the molecular internal structure by the solvent is weak, leading to only small shifts in the vibrational and the electronic levels with respect to their values in the free molecule. Variations in the structure of the rare-gas matrix in the vicinity of the trapped molecule characterize different sites and lead to different spectral shifts.

Both organic substances and rare gases have been used as solvents in the study of electronic transitions of trapped polyatomic molecules. When molecules are trapped in glasses formed by frozen organic solvents, their spectra are characterized usually by inhomogeneously broad electronic spectra, which provide little spectroscopic information. However, incorporation of the guest molecule into a substitutional site of an organic host crystal can lead to very sharp spectroscopic lines. Nevertheless, finding a suitable host crystal is a difficult task; Shpol'skii matrixes (formed from frozen solutions of *n*-alkanes) are a rare exception to this rule.

When the concentration of the guest molecules is low enough, deposition of inert gas matrixes can lead to a small number of discrete electronic transitions, each accompanied by an independent set of narrow vibronic bands. The appearance of only a small number of sharp bands is associated with a local crystalline order around the trapped molecule, which can accommodate only a small number of stable sites. A recent example is the study of anthracene in argon.[1,2]

The number of trapping sites of anthracene in an argon matrix seems to depend on the deposition conditions, but two independent studies[1,2] reported only a small number of sites (3 or 11, respectively) for this relatively large polyatomic molecule. The low polarizability of argon (as compared to that of an organic solvent) results in only a small electron−phonon coupling; hence, the spectra are almost free of phonon sidebands that obscure much of the vibrational information in spectra measured in organic matrixes.

If the surrounding of the trapped molecule is characterized by crystalline order, it is reasonable to assume that a first approximation of most trapping sites can be achieved by removing several argon atoms from a perfect solid argon structure and inserting the guest molecule into the cavity. A distortion of the crystalline structure in the vicinity of the trapped molecule is expected but not a complete disappearance of order. Different sites of polyatomic molecules can thus be distinguished by their cavity size and by the orientation of this cavity with respect to the argon crystalline surfaces. Furthermore, it is likely that a particular spectral band is associated with a single trapping site. In contrast, trapping of molecules in organic glasses often leads to a quasi-continuous distribution of environments; hence, several sites can contribute to the same transition frequency.

At present, the geometry of the trapping site cannot be inferred from the spectral shifts. A theoretical description of the matrix and its detailed interaction with the trapped species is required to associate spectral lines with specific trapping sites. Such a description should be able to predict the following:

(1) The number, geometry, and relative stability of the possible sites.

(2) The relative population of these sites as a function of experimental conditions, such as temperature and deposition rates.

(3) The frequency shifts in the electronic and vibrational transitions of the molecule when trapped in each site.

In projects that aim at building such a model, the Jerusalem and Regensburg groups have developed two different approaches, both based on molecular dynamics calculations and each trying to address the first two requirements. The first approach[3,4] uses a computational procedure that mimics the

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† Part of the special issue "Marilyn Jacox Festschrift".

10.1021/jp993955g CCC: $19.00

TABLE 1. Parameters of Lennard−Jones Potentials

parameter	SDM[12]	RSM[13]
ϵ_{Ar-Ar} [cm^{-1}]	83.36	83.0
σ_{Ar-Ar} [Å]	3.40	3.45
ϵ_{Ar-C} [cm^{-1}]	35.03	40.4
σ_{Ar-C} [Å]	3.48	3.42
ϵ_{Ar-H} [cm^{-1}]	33.01	45.0
σ_{Ar-H} [Å]	3.208	3.205

experimental deposition of a rare-gas matrix on a cold template. This method will be called simulated deposition model (SDM) in the following text. The second approach[5] performs a random search in the configuration space for possible trapping sites and will be named the random search model (RSM). A comparison of the calculated results with the experimental data is hampered so far by the lack of a satisfactory theory for the calculation of solvent-induced spectral shifts. Such a theory is currently under development in our groups. Nevertheless, it is interesting to compare the results obtained by the two different approaches with regard to the number of trapping sites and their shapes and to assess the usefulness and consistency of these methods in predicting site structures and the probability of their formation. In this paper, we compare the application of the two approaches to the calculation of trapping sites of anthracene in an argon matrix.

2. Models and Details of Calculations

SDM and RSM have been described in detail elsewhere;[3,5] thus, only a short description will be given here, together with details that were not mentioned in previous reports. The interactions between atoms were calculated in both models using 6−12 Lennard−Jones (LJ) potentials of the form

$$V_{ij} = 4\epsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right)$$

In this equation, ϵ is the well-depth of the interaction between atoms i and j, σ is the contact distance, and r is the distance between the two atoms. The parameters used in the simulations are listed in Table 1. The cutoff parameter for the RSM was 13 Å for all interacting pairs, while SDM used 2.7 σ for the relevant pairs. The size of the unit cell was a fixed value of 5.32 Å in RSM, while SDM used the experimentally temperature-dependent size of the argon unit cell.[3] In RSM, an NVT ensemble was used, while an NVE one was used in SDM.

In both models, anthracene was treated as a rigid body, using the RATTLE algorithm[6] to impose the required constraints. The geometry of anthracene was obtained by an ab initio calculation with a MINI basis set.[7] The Velocity Verlet integrator[6] was used to solve Newton's equations of motion. The time step was set to 3 fs in the SDM method. RSM used a variable time step during the random search and a step of 2 fs for the relaxation runs.

2.1 RSM. RSM starts by forming either a cubic or a spherical cavity in the center of a cubic template of 8 × 8 × 8 cell units of an argon crystal. The length of the template is 42.56 Å, and the initial number of atoms is 2048. Atoms are removed from their ideal fcc positions to form a cavity that is larger than 20 Å in diameter, and the anthracene molecule is placed in the center of the cavity in a random orientation. The anthracene molecule is approximately 9 Å along its long axis and around 5 Å along its short axis, so that the cavity is large enough for a free translational and rotational motion of the guest molecule. At this first stage, all the argon atoms are fixed in their perfect fcc lattice positions, and only the guest molecule is allowed to move. Only the interactions between the guest and the host (argon) atoms are calculated.

While the guest molecule is allowed to move under the potential exerted on it by the surrounding atoms, argon atoms are forced to positions close to their lattice sites. The initially removed argon atoms are reinserted one by one into the cavity to an unoccupied lattice position, which is selected randomly. The energy of the system is calculated before and after the addition of a new argon atom, and the insertion is rejected if it introduces an increase in the potential energy that is larger than a threshold value. An initial threshold of 100 kJ/mol is used during most of the filling process. The insertions are performed at intervals of 500 fs; the anthracene molecule is allowed to move between insertions, exploring the remaining cavity for its most stable position. Toward the end of the filling process, the rate of rejections increases considerably. At this stage, following each consecutive rejection, the threshold value is increased in steps of 100 kJ/mol, up to a maximum value of 1000 kJ/mol. The procedure is repeated until 40 consecutive attempts to add an atom fail. The resulting structure (called a static site) provides a first approximation to the site geometry. This first stage is repeated until a large enough ensemble of static sites, typically several hundred, is collected. The collection of static sites is classified into groups of similar sites (see ref 5 for details).

In the second stage of the RSM, three-dimensional periodic boundary conditions are imposed on a representative structure of each group. The structure is allowed to relax by letting all atoms except those in the outermost layer of the template to move for 40 ps, at a temperature of 10 K. The system is then cooled to 0.01 K using a stochastic cooling procedure.[8] The energy and geometry of the system are calculated after the system has reached equilibrium.

The final stage involves the examination of the stability of the relaxed sites: configurations with very high potential energies are regarded as an artifact of the process of formation of the static sites and should therefore be discarded. The appearance of some unrealistically high energy sites seems to be unavoidable since a choice of a lower threshold results in overlooking most "tighter" sites. It was found that varying the final threshold value in the range of 500−1000 kJ/mol did not result in an appreciable change in the distribution of static sites. The stability of the sites is checked by running 20 ps NVE trajectories on the "inner" cluster of each of the relaxed structures. The extracted clusters are cubic and are composed of the anthracene molecule surrounded by the nearest two layers of argon atoms (at least 200 atoms). The starting temperature of the trajectory is 10 K, and no periodic boundaries are imposed on the cluster. A site is considered unstable if following the 20 ps run of its inner cluster any of the following occurs:

(1) Argon atoms have evaporated from the cluster.

(2) The temperature of the cluster has increased to more than 15 K.

(3) The Verlet order parameter[9] has dropped to 1/3 within the first 2−3 ps.

For comparison with SDM results, final energy calculations of the sites produced by the RSM method were performed on smaller subsystems originating from a 6 × 6 × 5 argon lattice. The SDM potential parameters (see Table 1) were used at this stage, thus allowing direct numerical comparison of the two methods.

2.2 SDM. SDM is based on mimicking the experimental deposition process: a template of 6 × 6 × 2 cell units is constructed using the experimental argon lattice parameters. The template is held at a variable deposition temperature, which is kept constant during the whole simulation by periodically scaling all the velocities (see ref 3 for details). The matrix is constructed by adding the guest molecule followed by additional solvent (argon) atoms to the system. Periodic boundary conditions are imposed on the x and y directions, and the added species are appended from the z direction onto the exposed {001} surface. The added species bears an initial velocity selected from a 300 K distribution and is placed in a random position (and orientation) at a distance just below the cutoff parameter. Affected by the potential, it then accelerates onto the surface, hits it, and eventually cools to the template's temperature. Most runs discussed in this paper were performed using the fast-cooling method[3] to avoid the effective annealing around the point of impact caused by the distribution the kinetic energy of the accelerated gas-phase atom. The system is allowed to equilibrate for 3 ps between each addition, and the deposition process continues until the total number of atoms is at least double the initial one. Throughout the deposition, all interactions are calculated, and all atoms are allowed to move.

The final structure of a site is obtained by annealing the system at 30 K, followed by cooling to 0.01 K and averaging the geometry for 15 ps. In the same process, the energy of the system is averaged as well, so that the relative stability of the different sites can be determined. The distortion of the matrix by the guest molecule is evaluated by comparing the position of the solvent atoms around the guest molecule with their positions in a perfect fcc lattice.

3. Results

A total of 357 runs were performed in the first stage of calculations of the RSM; each required between 15 and 30 min of CPU time on an IRIS INDIGO/R4000 workstation. Fifty different site geometries were identified among the initial runs, in which the anthracene molecule occupied a cavity of 6−13 missing argon atoms. The relaxation stage for each of those structures required 2 days of CPU time. Following the stability examination, only seven different site structures remained in which the anthracene replaced 6−8 argon atoms. Out of the initial 357 runs, 200 yielded stable sites, and the other 157 resulted in unstable ones.

Fifty-eight depositions were completed with the SDM, each using around 1.5 days of CPU time on an INDY/SGI workstation for each one. The deposition temperature of most runs was 5 K. The morphology of the exposed (topmost) surface was modified in more than two-thirds of the runs by depositing 50 argon atoms or more before the deposition of the anthracene molecule to check the effect of different surface structures exposed to the deposited molecule. SDM resulted in five different trapping sites of anthracene in argon, where the anthracene occupied a cavity of 6−8 argon atoms.

Table 2 lists the site structures obtained by the two simulation methods and their calculated relative energies. The sites are named by the number of argon atoms replaced by the anthracene molecule and by a letter signifying a different structure with the same nominal cavity size. DE is a dimensionless parameter that measures the relative stability of the sites relative to a perfect fcc lattice of argon atoms. Removal of any single argon atom causes destabilization; insertion of anthracene into the cavity leads to a more stable structure. Thus, in principle, a small trapping site is expected to be more stable than a larger one, since a smaller number of argon atoms are removed. In the case of anthracene, the smallest site is a 6 substitutional one—smaller ones cannot accommodate anthracene because of strong repulsive forces.

TABLE 2. Summary of Simulation Results

			RSM[a]	SDM	
site	Ar replaced	plane[b]	n[c]	n[c]	ΔE[d]
6a	6	001	65	37	−0.01
6b	6	111	69	3	0.74
7a	7	111	21	7	1.73
7b	7	111	11	1	1.80
7c	7	001	4	3	1.81
7d	7	001	3	2	2.42
8a	8	111	27	5	2.70

[a] Stable sites only. [b] Crystalline plane occupied by the anthracene molecule. [c] The number of runs that produced this site structure. [d] $\Delta E = [E(\text{fcc}) - E(\text{site})]/\langle E\rangle_{\text{Ar}}$, where E(site) is the site's energy, E(fcc) ($= (N_{\text{Ar}}\langle E\rangle_{\text{Ar}})$ is the stabilization energy of a full and perfect fcc argon lattice of the same size, and $\langle E\rangle_{\text{Ar}}$ is the average energy per argon atom in an argon crystal. The average energy per argon atom was calculated for each model under the same conditions used for the calculation of the site energies. Positive values reflect the net instability caused by the introduction of anthracene into the matrix.

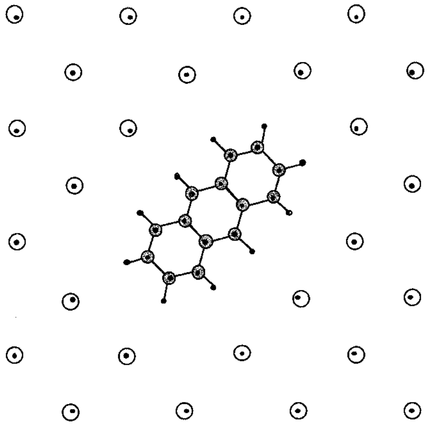

Figure 1. Overlaid structure of the 6 SS of anthracene in argon (6a) as produced by RSM (large circles) and SDM (small circles). Note that the anthracence molecule is located in a {001} plane of the crystalline argon.

As expected, the trapping sites differ from each other in the number of argon atoms missing from the full fcc lattice, in the lattice plane in which the anthracene molecule is lying, and in the displacement of the remaining argon atoms from their perfect fcc lattice position. Matching of site structures obtained by RSM and SDM was performed by overlapping all the atoms found within a cube of 20 Å centered on the center of mass of the anthracene molecule.

Inspection of the geometry of the obtained stable sites reveals that almost all of them belong to one of two large groups of structures: those in which the anthracene is lying in a {001} plane and those which position it in the {111} plane. Figure 1 shows the overlaid structure of the most stable site (6a) as obtained by RSM and SDM. The extent of agreement in the other six corresponding structures obtained by RSM and SDM is similar.

Since only a finite number of runs were performed using both models, we should consider the probability for overlooking a likely trapping site. We assume a probability P_i for the appearance of site i in each simulation run. Because of the two different approaches for the construction of trapping sites in the two models, site i may have a different probability to be formed by the RSM than by the SDM. The probability P_0 that the site i is not found in N simulation runs is given by

$$P_0 = (1 - P_i)^N$$

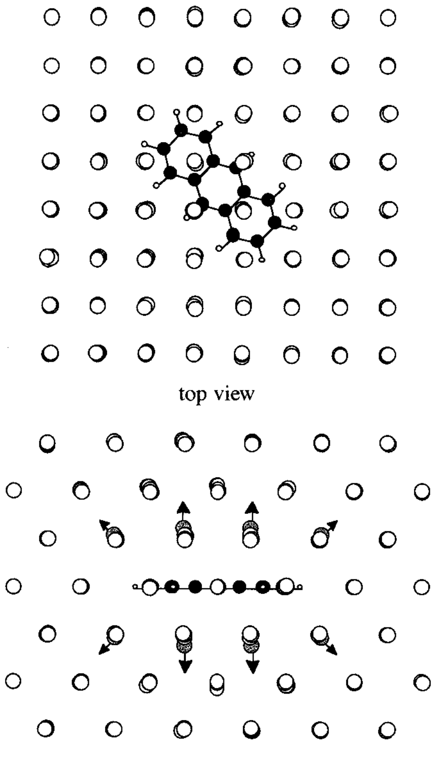

Figure 2. Geometry of the 6 SS of anthracene in the {001} plane of the argon matrix. Arrows highlight the atoms that were strongly displaced from their perfect fcc lattice location.

Hence, with the 200 runs of the RSM, the probability to overlook a site that contributes 5% or more to the site distribution is lower than 3.5×10^{-5}, and it is lower than 0.051 for the 58 runs of SDM. If we assume that we have found every site with $P_0 = 0.01$, then we have found all sites with $P_i = 2.2\%$ in RSM and those with $P_i = 7.7\%$ in SDM. It is therefore reasonable to assume that within each model's distribution function, we have sampled the major contributing sites, but further runs with SDM may reveal additional minor sites.

The number of runs of RSM is large enough for statistical analysis, while the 58 runs of SDM are probably not enough for such an analysis. Nevertheless, on the basis of the argument concerning the probability for overlooking important sites, we assume that even though further simulation with the SDM method may change the relative contribution of each site to the ensemble, it is unlikely that the overall trend emerging from this model will change significantly.

Both models show a strong preference to form the 6 substitutional sites; RSM gives an almost equal probability to the 6a ({001} site) and the 6b ({111} site), while SDM shows clear preference for the 6a structure. RSM gives also (relatively) more weight to the larger sites than SDM does.

Figures 2 and 3 show the geometry of the two most probable trapping sites: 6 substitutional sites (6 SS) 6a and 6b, respectively. The arrows indicate the magnitude of the displacement of the argon atoms from their ideal fcc lattice positions. It is seen that in site 6a the anthracene molecules lie parallel to the {001} plane of the argon lattice, while in site 6b, they lie in the {111} plane. Both figures show a significant displacement of the argon atoms away from their fcc positions. The largest displacements are as high as 0.6 Å for the 6a site and 0.9 Å for the 6b site. This larger distortion is reflected in the higher energy of site 6b (Table 2). Inspection of the structures of the large sites shows that most of them can be classified as "avoided" 6 SS: the additional missing atoms are often those strongly displaced in the 6 SS.

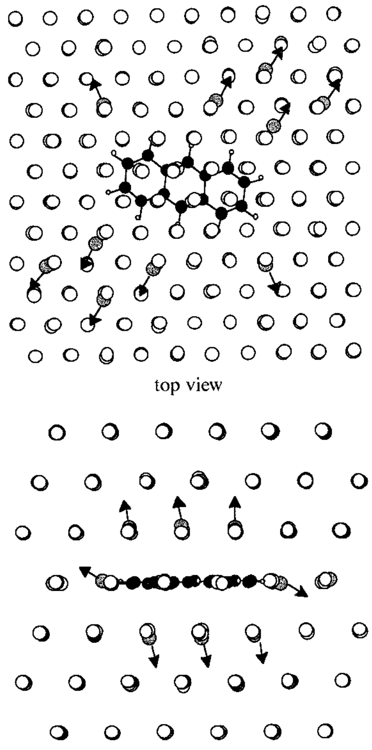

Figure 3. Geometry of the 6 SS of anthracene in the {111} plane of the argon matrix. Arrows highlight the atoms that were strongly displaced from their perfect fcc lattice location.

4. Discussion

Experimental deposition of rare-gas matrixes does not lead generally to thermodynamically stable systems. In the case of anthracene in argon, the most stable state will be a phase separation to argon and anthracene crystals. The restricted atomic and molecular motion at the deposition temperature results in the solvation of anthracene molecules in the solid argon. The deposition process is kinetically controlled, and it is therefore not surprising that more than one trapping site is frequently obtained. In contrast to molecular hosts, such as organic matrixes, rare-gas solids are more universal solvents at cryogenic temperatures since they can accommodate molecules of almost any shape either by small displacements of atoms from their fcc positions or by removing an adequate number of atoms. As demonstrated by previous simulations,[3] trapping of a guest molecule in an argon matrix only rarely causes long-range disruption of the crystalline structure. This tendency of the matrix to preserve its "natural" structure is explained qualitatively by the fact that the interaction between the argon atoms is stronger than the interaction between the argon atoms and the first row elements (H, C, N, O). For a more detailed discussion of computer simulations of matrixes and of previous work, a recent review may be consulted.[14]

Both RSM and SDM show that although the deposition of a matrix does not lead solely to the most stable trapping site, energetic considerations appear to play an important role in determining the distribution of sites. Naturally, both the removal of each solvent atom from the pure solid and the distortion of structure of the lattice reduce the stability of the system. Therefore, the most stable site is expected to be the one that accommodates the guest molecule in the smallest possible substitutional site while still does not involve too much distortion. Both models suggest that the smallest possible site for anthracene trapped in argon is a 6 SS, and both yield two alternative structures for such a site: in one (6a), the anthracene is lying in the {001} plane, and in the other (6b), the anthracene is in the {111} plane of the argon crystal. The {001} site is more stable than the {111} one and is produced with a pronounced preference in the SDM approach, while RSM finds the two 6 SS to be almost equally probable, with a slight preference to the {111} site.

In the {111} plane, the density of the atoms is highest in an fcc lattice, and there is experimental evidence[10] that this plane is the exposed one during a gas-phase deposition of argon. Therefore, provided all other factors are the same, we should have expected that the anthracene molecule will be located primarily on the {111} plane. The fact that many {001} sites are found (and even preferred in the SDM simulation) must be due to the higher stability of the {001} site. Furthermore, RSM does not impose any bias on the initial positioning of the guest molecule, and pure entropy-based considerations should have resulted in a broader distribution of planes in which the anthracene is lying. The overwhelming preference of the {001} and {111} planes over any other crystalline surfaces is another indication that energetic considerations are a major factor determining the final distribution of sites.

The impact of a freshly deposited species on the cold solid matrix inevitably causes local heating of the solid. The heating enables rearrangement of the atoms in the vicinity of the impact point, allowing the system to reach a lower energy. In SDM,[3] the system regains equilibrium a few picoseconds after the collision with the gas-phase atom. We did not consider in these simulations much longer time scales. The structure of the lattice may be affected by very slow cooperative motions of the atoms (on the time scale of seconds), but we assume that these processes do not contribute much to the distribution of trapping sites. The justification for this assumption is the experimental evidence that the number of sites is determined primarily by the deposition process itself: deposition at high temperatures (25 K for argon) leads to a small number of sites, while deposition at low temperatures results in many trapping sites. Annealing, even for elongated times, does not eliminate most sites.

The possible occurrence of local annealing is one of the major differences between the two simulation methods. In SDM, local rearrangement is happening naturally during the deposition, and relaxation processes are an integral part of the simulation. As shown in previous reports,[3] the preference of SDM for the most stable site is so pronounced that the local annealing is artificially prevented by the fast-cooling procedure and by a choice of a low deposition temperature. In RSM, however, atoms are forced initially to occupy an fcc lattice position, and relaxation is allowed only after the cavity is full to a maximum that is determined by the threshold energy value. The very high threshold value in RSM for the acceptance of insertion of atoms "compensates" for the inflexibility in positioning during the filling process. In real depositions at low temperatures, an event that raises the potential energy of the system by 100 kJ/mol will not happen. This value was chosen arbitrarily so that a broad enough distribution of sites is obtained, and it inevitably allows the formation of less stable sites. Indeed, most of the obtained static sites are later proven to be unstable and are subsequently discarded. The equal probability given in RSM to the 6a and 6b sites in contrast to the clear preference of SDM for the more stable 6a site is then understandable. Yet, the preference of SDM to the 6a site is probably amplified by the fact that the {001} plane is exposed in the deposition direction, while RSM is unbiased in that sense. The random addition of 50−100 argon atoms in most of the runs prior to the introduction of the anthracene molecule may not be effective enough to remove the tendency imposed by the initial structure of the template. Further simulations using other exposed surfaces are needed to evaluate the extent of this tendency.

From the computational point of view, the advantage of RSM over SDM is clear: RSM is much faster in giving a general picture of the possible trapping sites. For the case of anthracene, the two simulation methods used a comparable computing time (about 4 months) for the results presented in this report, while the size of the ensemble produced by RSM is 3.5 times larger than that of SDM. Thus, RSM is a much faster method for obtaining a broad picture of possible trapping sites. However, the inherently arbitrary nature of the threshold value and of the stability check obscures much of the physical insight into the process of deposition. In that respect, SDM is favored, as it enables changing "experimental" parameters and does not involve artificial filtering of results. Sampling more deposition surfaces and improving the simulation of relaxation processes within the solid should give a more realistic picture of site distribution.

For a given site, RSM and SDM produce very similar structures, despite the fact that very different production mechanisms were used. The similarity in structures proves that once a site is formed, both calculations are equally successful in obtaining a specific local minimum. Small variations of the parameters used did not change the geometry nor the relative stability of the trapping sites. Likewise, the different cutoff parameters used in the two methods did not cause a change in the stability pattern. Once a site is formed, it is stable toward conversion to other sites. Although we have not calculated the barriers for intersite conversion, such a process must involve the cooperative motion of a large number of atoms. This result conforms with the experimental observation that the spectrum of anthracene in argon shows only a small number of sites. If a matrix is prepared under extremely rapid cooling conditions, annealing may restructure some highly labile sites. Such sites were apparently not produced in the present simulations.

We have chosen to compare the energies of the sites obtained by the two methods very near to 0 K, at which the kinetic energy is minimal (zero in the classical case). At higher temperatures, one needs to consider both kinetic and potential energies, leading to relatively large fluctuations and requiring long averaging periods. In addition, at 0 K, RSM that used an NVT ensemble (fixed temperature) and SDM that used an NVE one (fixed energy), converge to the same energy.

In the absence of an adequate theory for the calculations of matrix-induced spectral shifts, any assignment of a simulated trapping site with an experimental spectral line is speculative. Still, it is appealing to compare the distribution of experimental bands with those obtained by the simulations. In the experiment,[1,11] relative intensities of the sites were calculated based on the assumption that the oscillator strength of the (0,0) transition is independent of the trapping site. On the basis of that assumption, the intensity of one of the sites, the one whose electronic transition was shifted mostly to the red, was found to be about 5 times higher than all other sites. If we accept the general concept in matrix deposition, which states that the most probable site is the most stable one, we can tentatively assign the strongest peak to the 6a site, in which anthracene is located in the {001} plane.

5. Conclusions

Both RSM and SDM offer a convenient way to determine the structure of the trapping sites of molecules in rare-gas matrixes. Both methods do not rely on any prejudicial intuition in finding the structure of the most stable or any other site. The spectrum of sites produced by the two methods is comparable despite major differences in the process of building the site and of minor differences in the potential parameters.

SDM produces a set of structures with a strong preference to the more stable sites, while in RSM relatively more high-energy sites are obtained. The advantage of SDM is in its more natural way of constructing the trapping sites, which seems better suited to simulate deposition conditions. RSM, on the other hand, performs a more thorough search in the configuration space and therefore provides a wider range of possible trapping sites. On the basis of the notion that LJ potential are reliable enough for the prediction of structural properties of rare-gas solids, we suggest a tentative assignment for the experimentally most frequent site of anthracene in argon as the 6 SS on the {001} plane.

Acknowledgment. The Farkas Center for Light Induced Processes is supported by the Minerva Gesellschaft mbH, Munich. R.F. thanks the Israeli Ministry of Sciences and Arts for the Levi Eshkol Postdoctoral Fellowship. Work in Regensburg was supported by the Deutsche Forschungsgemeinschaft (Di 299/4-2) and the Fonds der Chemischen Industrie.

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