Some Comments on the Nucleation Phenomena

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Some considerations on the nucleation phenomena are discussed. The lower energy points on the hypersurfaces generated by one up to ten molecules are obtained by means of a recently described method for the study of molecular associations. Self consistent reaction field calculations were also performed at the CNDO/2 level in order to analyse its density matrix in terms of the Armstrong, Perkins and Stewart population analysis, for the minima previously determined.

INTRODUCTION

It is well known that the properties of a molecular system are extremely sensitive to variations in the environment[1]. Several attempts have been made during the last years to analyse the influence of the medium while keeping the size of the calculations within reasonable bounds. These attempts have mainly followed two courses of action. On one side, the continuum models which are based on generating effective Schrödinger equations, which are useful in providing information relative to changes in molecular properties, and most of the usual parameters in absence of direct interactions. On the other hand, the supermolecule approach depicts the microscopic interactions, but is not a practical solution due to the large number of geometric degrees of freedom that should be handled in order to describe approximately the environmental effects. Both of these models are not able to depict the temperature effects, as well as most of the thermodynamical properties. This indicates that the link to statistical thermodynamics is of fundamental importance[2].

Basically, the supermolecule approach to the problem of solvation consists of three steps[1,3]. In the first step, one spans in every possible way the hypersurface of interaction of the substrate with one single solvent molecule, approaching it from various directions and not only turning it around the solute but also around the local axis. This kind of search yields information on the minima of the energy hypersurface, which indicate the most stable positions for a single solvent molecule. The second step consists of introducing within the same method, more solvent molecules, so as to constitute the first solvation shell around the solute, using as a guide the information gained through the first step. This procedure is a stepwise addition of the solvent molecules. This step should imply a complete optimization of all the geometrical para-

meters as pointed out by Pullman[4], however, this is not generally carried out due to the large number of degrees of freedom, and at best a partial optimization is performed. The last step is the computation of the properties of the solute in presence of the solvent molecules[5] set about the positions previously determined.

The aim of this paper is to analyse whether the method generally used, that is to say, the addition of solvent molecules to the minimum energy configuration in order to enhance the hydratation shell, is valid. The second aim is to try to determine if the continuum reaction field model[1,3] takes into account the same facts as the supermolecule one, or whether it describes a complementary aspect of the solute — solvent interaction. The first part of this study has already been carried out and the results will be published elsewhere.[6]

<center>CALCULATION PROCEDURE</center>

The geometrical parameters were all taken from those of the isolated molecule, as estimated by the CNDO/2 technique[7]. This simple approach is adopted because of the large number of configurations taken into account in this study.

Although the CNDO/2 technique depicts a minimum when two molecules approach each other[8] (if their interaction is favourable), it fails to reproduce the binding energy, as well as the most favourable geometry for the interaction[9]. Therefore, we decided to use the SOMAR technique[10] in order to obtain these parameters (binding energy and geometry of the supermolecule). Within this methodology set up in order to study molecular associations, every new solvent molecule is approached from the supermolecule starting from twenty--six positions on the sphere of an arbitrarily fixed radius. The molecule is rotated around a fixed axis frame which moves with it towards the supersystem. In this way, several minima are determined on the hypersurface of the supermolecule for all the degrees of freedom of the subsystem, since it is also allowed to describe librational movements around its approximation axis. Once the minimum energy positions were found, the CNDO/2 calculations were done in order to obtain its density matrix, and thus carry out a population analysis on the supersystem as described by Armstrong, Perkins and Stewart (APS analysis)[11].

Apart from the vacuum calculations, self consistent reaction field studies were performed, following Tapia and Constanciel[12], using their SCRF-CNDO/2 method. Two systems were studied: the hydration of the water and formaldehyde, including up to 10 water molecules around each one. Both of them lead to similar conclusions, so we prefer to carry on the latter the discussion paragraph, since it has a pi — bonding (which the water molecule lacks) and this is interesting for analysis.

<center>DISCUSSION</center>

When a new molecule was approached to a cluster, several minima were found, some of which have their energies schematized in Figure 1. The dotted lines join the relative energies associated to a cluster containing N molecules and that of $N-1$ molecules from which it is derived, that is to say, the dotted line shows where the cluster with N molecules comes from. The higher energy
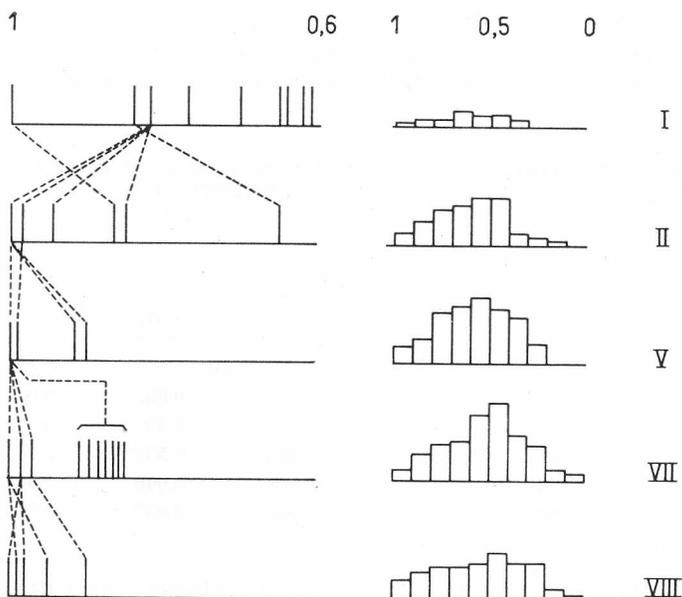
Figure 1. Schematic representation of the relative energy (E/E_{min}) of some of the obtained minima. A few of them with relative energy greater than 0.6 are represented. A histogram with the distribution of minimal configurations obtained is also shown.

clusters are not represented in order to simplify the figure; only those configurations which are representative are shown. When a new hypersurface for $N + 1$ molecules was generated, we took into consideration as starting points only those minimal configurations with N molecules which differed from that of the minimum in no more than 8 kjoule/mol. The others were disregarded. With a higher threshold it should have implied the handling of an enormously large number of configurations (over a hundred for 5 molecules).

As may be seen several crossings occur, in such a way that we cannot get the minimal energy cluster by addition of a new molecule to the minimum energy cluster of a previous step in a constructive scheme. In spite of this fact, the minimum energy clusters tend to form minimum energy configurations in the following step of such a constructive scheme. This may be noticed by means of the histogram complementary to the figure. There, the number of configurations as a function of the relative energy excess relative to the minimal energy configuration is shown. The large quantity of configurations generated are those of about a half of the lowest energy interactions, and most of the favourable ones.

In Table I, we display the results of the APS analysis for some cases which are representative of the whole. When the number of molecules in the cluster was increased the bond index diminished as a rule, and especially its pi component. This is mainly due to the strongly polarizable character of this bond. When half a shell was introduced around the solute, a slight increase in this bond index was noticed until the shell was completed. However, for none of the stable configurations was it possible to obtain its value at the

vacuum level. Thus, fluctuations around a molecule may lead to an extremely high decrement in its pi bond order. The CH bond remains almost unaffected by the presence of another solvent molecule, even in its neighbourhood.

TABLE I

APS Analysis for the Association of Formaldehyde with up to Five Water Molecules. The Values are Averages over all the Configurations from 0.9 to 1. in Relative Energy

Number of water molecules	Bond index				Anisotropy	
	CO	(CO)	CH_1	CH_2	C	O
0	2.058	0.971	0.952		0.018	0.647
1	2.034	0.970	0.953	0.952	0.018	0.648
2	2.028	0.973	0.953	0.952	0.019	0.644
3	2.028	0.967	0.953	0.952	0.020	0.639
4	2.016	0.958	0.956	0.946	0.023	0.619
5	2.028	0.967	0.953	0.952	0.016	0.639

On the other side, the anisotropy, which enhances its value in a direct interaction, decreases for any other configuration. The carbon atom increases its anisotropy since the polarization of the CO bond leaves it with a high charge defect, especially in the direction perpendicular to the molecular plane. The enlargement of the anisotropy for the direct interaction is justified bearing in mind that the bond is directionally polarized along the hydrogen bonding direction. For a larger number of molecules, the anisotropy shows a more uniform electron density distribution around the oxygen atom.

Most of the molecular properties seem to try to recover their value at the vacuum level when a shell is completed, at least for the most stable configurations.

In the reaction field study, the numerical values are exaggerated due to the fact that the function of the dielectric constant, premultying the Fock matrix elements, is not suited for a semi-empirical technique with inclusion of the zero differential overlap approximation, as was pointed out by Miertus[13]. In spite of this, the qualitative trend may be analysed since the functional dependence of the dielectric constant is criticized, but not the way the reaction field is studied or the Fock matrix elements constructed. This behaviour may be summarized as follows: The pi bond is preferentially polarized to the sigma one and the anisotropy values for the oxygen atom tend to decrease as the dielectric constant increases. The inclusion of water molecules increases the value of the anisotropy on the oxygen. This shows the directional polarization of the bond, which is not taken into account by the reaction field without the discrete description of the solvent molecules.

CONCLUSION

The large quantity of minima, close in energy to the absolute minimum, even those with a half of the energy, indicate the necessity of a statistical or dynamical study of the solute solvent interactions. A constructive model of this kind of interactions should be carefully employed.

Let us finally point out the importance of methods such as the one developed by Clementi or Fraga in order to obtain a more precise description of this kind of systems.

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SAŽETAK

O pojavi nukleacije molekula

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Razmatrani su neki aspekti nukleacije molekula u otopini. Ta se pojava simulira na slijedeći način: najprije se optimira međusobni položaj molekule otopljene tvari i prve molekule otapala. Zatim se sukcesivno dodaju molekule otapala sve dok se ne dobije dobar model za prvu solvatacijsku ljusku. Pri tome se u svakom koraku sustav reoptimira. Računi su izvedeni na razini jednostavne CNDO/2 metode, zbog velikog broja stupnjeva slobode. Učinak nukleacije na pojedine molekule analiziran je s pomoću populacijske analize koju su predložili Armstrong, Perkins i Stewart.