

Interaction Energies in a System of Three Organic Molecules Versus Their Structure and Mutual Induction

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Abstract—A method for the analysis of the interaction energies in a three-molecule nanocluster containing hydrocarbon molecules with double carbon–carbon bonds is presented. It is assumed that one of the molecules (pentene) has a dipole moment; the other two (aromatic molecules) have no dipole moments. The molecules in the considered three-molecule nanocluster are bounded by the long-range dispersion and induction interactions with the Coulomb repulsive forces at short intermolecular distances taken into account. Analytical expressions are obtained in terms of the presented method to calculate the dispersion and induction energies. In these expressions, the Coulomb repulsion at short distances is taken into account for each pair of molecules, which is possible owing to the specific charge properties of the double bonds in the considered molecules, which lead to the residual positive charges at the carbon atoms in these bonds. It was shown that the total interaction energy reached its minimum at smaller intermolecular distances between each pair of molecules compared with those in the corresponding isolated two-molecular nanocluster consisting of the same molecules.

Keywords: multimolecular nanoclusters, intermolecular interactions, induction processes.

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INTRODUCTION

The interest in experimental and theoretical investigations of intermolecular interactions has grown, in particular, for the interaction energy of two molecules that form a nanocluster due to the Van der Waals forces [1–6]. The interest in these investigations is explained by the fact that these clusters are the main elements in nanocrystals and amorphous nanoparticles used in modern electronics, medicine, pharmacology, and many other domains. The studies of the intermolecular interaction energy have been carried out mainly for systems of neutral molecules that have no dipole moments. Such a problem formulation meant that the molecular interaction is determined by the dispersion long-range Van der Waals forces at intermolecular distances R under the condition $R \geq R_0$. Here, R_0 is the sum of the Van der Waals radii of the molecules that participate in the interaction. The Coulomb repulsion of the interacting molecules at short distances was taken into account by multiplying the calculated energy of the dispersion interaction by a dampening function whose form was chosen according to the conditions of its minimum at $R = 0$ and its equality to 1 at $R > R_0$ [5]. In addition, it was required

that the product of the dispersion-energy function and the dampening function have a minimum at $R = R_0$.

Previously, we studied the interaction energy of three molecules that form a nanocluster [7–12]. It was assumed in these works that the molecules are neutral and one of them has a dipole moment. The calculated interaction energy of each pair of molecules was assumed to be dispersion with the Coulomb repulsion taken into account by introducing a dampening function. In these works, the calculations of the induction energy of molecules were performed. With this purpose, we have developed a method for determining the induced dipole moments that takes the process of the mutual induction of molecules into account. In terms of this method, the analytical expressions were obtained to calculate the induced dipole moments and induction energies for each molecule. To take the influence of the Coulomb field of each molecule on the field of its dipole moment into account, a method for determining the dampening function was developed, which is similar to the method for obtaining this function with consideration of the repulsive force when calculating the dispersion energy.

In this work, we propose a new method for analyzing the interaction energy in a nanocluster consisting

of three and more hydrocarbon molecules with double carbon-carbon bonds on the assumption that all molecules are neutral and none of them has a dipole moment. The main peculiarity of this method is that we do not construct a dampening function for consideration of the repulsive forces between molecules at small intermolecular distances. Instead, we propose to consider the role of positive charges at carbon atoms in the groups (C=C) with double bonds [4, 6, 7]. These charges are associated with the structural properties of such double bonds.

It should be noted that in a molecular cluster, provided that one of the molecules has a dipole moment while the others are neutral, the intermolecular interaction energy depends on the number of molecules. In a molecular cluster of three or more molecules, the energies of dispersion and Coulomb interactions are determined by all possible two-molecular interactions (the interaction of molecular pairs), the induction energies of each molecule in this nanocluster, unlike a two-molecular cluster, are essentially multi-particle, since each molecule is induced by the electrostatic fields of the surrounding molecules that form the nanocluster.

1. PROBLEM FORMULATION. DETERMINING THE INTERACTION ENERGY IN A SYSTEM OF THREE HYDROCARBON MOLECULES WITH DOUBLE BONDS OF THE (–CH=CH–) TYPE

Let us consider a system of three hydrocarbon molecules M_1 , M_2 , and M_3 . It is assumed that M_1 is a pentene molecule C_5H_{10} belonging to the ethylene hydrocarbon molecules. The structural formula of this molecule is $(CH_3-CH_2-CH=CH-CH_3)$ with a carbon-carbon double bond (–CH=CH–) situated on a plane. A pentene molecule has the dipole moment $\mu = 0.6$ D. Molecules M_2 and M_3 are the aromatic pyrene molecules $C_{16}H_{10}$.

A pentene molecule contains an ethylene group (–CH=CH–) situated on a plane. One of the double bonds is the σ -bond formed by two electrons: one electron from each carbon atom. The σ bond in the (C=C) group of this molecule lies on the ethylene group plane, whereas the π -bond consisting of two π -electrons is situated on the plane perpendicular to that of the ethylene group. Such a difference in the spatial position of π - and σ -electrons makes it possible to consider them independently when calculating the positive charges of carbon atoms that form the double bond. The physical properties of π -electrons in the ethylene group with double bonds in a pentene molecule, as is shown in [3, 13], may be considered on the basis of the quantum mechanics model of two-dimensional potential box with the base equal to the length of the ethylene bond L_1 and infinitely high sides. Let us consider the (C₁=C₂) group. Since the two π -elec-

trons that form the π -bond in this group are identical, it is sufficient to consider the properties of one π -electron belonging to atom C₁; in this case, the base of the box coincides with the x axis and the C₁ carbon atom is situated at the point $x = 0$, while the C₂ atom is situated at the point $x = L_1$. In this potential box, the nonperturbed π -electrons have the zero-point potential energy. The wave function $\Psi(x)$ of the π -electron free motion along the box bottom is defined by the Schrödinger equation for the zero potential and has a form

$$\Psi(x) = (2/L_1)^{1/2} \sin(\pi nx/L_1), \quad (1)$$

where $n = 1, 2, 3, \dots$ is the quantum number, x is the variable along the box bottom, measured in parts of L_1 . The probability density $\rho_1(x_1, x_2)$ of finding a π -electron on L_1 between the points x_1 and x_2 is defined by the equation

$$\rho_1(x_1, x_2) = (2/L_1) \int_{x_1}^{x_2} \sin(2\pi x/L_1) dx \quad (2)$$

$$= [(x_2 - x_1)L_1] - (2\pi)^{-1} [\sin(2\pi x_2/L_1) - \sin(2\pi x_1/L_1)].$$

As is shown in [3, 4], the value of the function $\rho_1(x_1, x_2)$ can be considered as the value of a negative charge generated by the π -electron and lumped in some region between the points x_1 and x_2 . The charge value is measured in parts of electron [4].

The analysis of the function $\rho_1(x_1, x_2)$ has shown that the π -electron may be situated in the center of the π -bond on the interval between the points $x_1 = 0.2L_1$ and $x_2 = 0.8L_1$; $\rho_1(x_1, x_2) = 0.97L_1$, which corresponds to the negative charge qe generated by the π -electron in this region. Therefore, at the C₁ carbon nucleus in the considered double bond of pentene (C₁=C₂), instead of the positive charge $Qe^+ = 1e^+$, appeared after the extraction of one electron to the π -bond formation, it is the Qe^+ charge with a value of $0.03e^+$ that remains. At the C₂ carbon nucleus in the double pentene bond, it is also the charge $Qe^+ = 0.03e^+$ that remains due to the identity of π -electrons.

The condensed aromatic pyrene molecules M_1 and M_2 contain a closed sequence of conjugated bonds (–CH=CH–CH–). Each carbon nucleus provides two electrons to form the σ -bonds with neighboring carbon nuclei and one electron to form a π -electron [3], whose physical properties can be considered on the basis of the quantum mechanics model of a potential box with the bottom length equal to the sum of the bonds situated on the left and on the right from the nucleus producing the π -electron. Carrying out the reasoning similar to that above-presented for the properties of the pentene π -electrons, we can show that the pyrene π -electron is situated in the vicinity of the box bottom, i.e., in the vicinity of the carbon

nucleus. Its charge is $qe = 0.97e$, the residual charge of the carbon nucleus $Qe^+ = 0.03e^+$.

2. ENERGIES OF DISPERSION AND INDUCTION INTERACTIONS IN A THREE-MOLECULAR NANOCUSTER CONTAINING UNSATURATED HYDROCARBONS

Let us consider a three-molecule cluster that consists of neutral hydrocarbon molecules, one of which, a pentene molecule (M_1), C_5H_6 , has a dipole moment. Two others, aromatic pyrene molecules (M_2 and M_3), $C_{16}H_{10}$, do not have dipole moments. In this geometry, the centers of masses of all three molecules are situated along one axis and the constant dipole moment D_1 of molecule M_1 is directed along this axis. Let us designate the distance between molecules M_1 and M_2 and that between M_2 and M_3 as R and R_d , respectively. The planes of the aromatic molecules are parallel; the axis on which the centers of mass of molecules are situated is perpendicular to the plane of the aromatic molecules. The interaction energy of molecules $E(1,2,3)$ in such a nanocluster has the form [14, 15]:

$$E(1,2,3) = \sum_{\substack{ij=1,2,3 \\ i \neq j}} [E_{\text{dis}}(M_i, M_j) + E^c(M_i, M_j)] + \sum_{ij=1,2,3} E_{\text{ind}}^c(M_i), \quad (3)$$

where $E_{\text{dis}}(M_i, M_j)$ is the dispersion energy of the long-range interaction between molecules M_i and M_j , $E_c(M_i, M_j)$ is the energy of the Coulomb repulsion of molecules M_i and M_j at short distances. The next three terms in (3) are the induction energies of each molecule, which are the result of action of the fields of induced dipole moments and residual charges of neighboring molecules. The dispersion interaction energy $E_{\text{dis}}(M_i, M_j)$ has the form [5]

$$E_{\text{dis}}(M_i, M_j) = C_6(M_i, M_j)/R_{ij}^6, \quad (4)$$

where R_{ij} is the distance between the centers of mass of molecules M_i and M_j ; $C_6(M_i, M_j) = (3/2)\alpha_i\alpha_j J_i J_j / (J_i + J_j)$.

The function $C_6(M_i, M_j)$ depends on the average polarization coefficients of molecules α_i and α_j . The polarization parameters show the degree of the shift of the center of mass of the electron cloud volume of molecules caused by the electrostatic field. The values of polarization parameters depend on the number of atoms in the molecule, determining the degree of induction of dipole molecules. The role of induction interaction grows as the number of molecules in the nanocluster and that of atoms in these molecules grow. As follows from [5], J_i and J_j can be chosen in the form $J_i = 10.4(N_i/\alpha_i) J_i J_j / (J_i + J_j)$, where N_i is the number of valence electrons in molecule (i). The Coulomb

energy contribution to the dispersion energy (2) has the form

$$E_{\text{dis}}^c(M_i, M_j) = A_{ij} \exp(-a_{ij} R_{ij}). \quad (5)$$

The parameters A_{ij} and a_{ij} can be found from the minimum condition of the dispersion energy function $[E_{\text{dis}}(M_i, M_j) + E^c(M_i, M_j)]$ in the system of two molecules (M_i, M_j) at $R_{ij} = R_{0,ij}$. Mathematically, this condition is expressed by the equality of the sum of the first derivatives of $E_{\text{dis}}(M_i, M_j)$ and $E^c(M_i, M_j)$ to zero at $R_{ij} = R_{0,ij}$. This implies the following equation for A_{ij} :

$$A_{ij}(R_{ij}) = [6(C_6/R_{0,ij}^7)/a_{ij}] \exp(a_{ij} R_{0,ij}). \quad (6)$$

Correspondingly, the contribution of the Coulomb repulsion energy in formula (3) for the dispersion energy of interaction between two molecules has the form

$$E^c(M_i, M_j) = [6(C_6/R_{0,ij}^7)/a_{ij}] \exp(-a_{ij}(R - R_{0,ij})). \quad (7)$$

The value of the parameter a_{ij} can be found from the condition of the equality of the energy of Coulomb interaction between two molecules M_i and M_j obtained on the basis of the Born–Mayer equation (7) at $R_{ij} = R_{0,ij}$ to that obtained from the electrostatics equation of the form $E_{\text{dis}}^c(R_{0,ij}) = Q_i e Q_j e / R_{0,ij}$, where $Q_i e$ and $Q_j e$ are the sums of residual charges of carbon atoms in double bonds in molecules M_i and M_j . Thus, we obtain

$$a_{ij} = [6(C_6/R_{0,ij}^7)/Q_i e Q_j e / R_{0,ij}]. \quad (8)$$

As was shown in [10], the functions of the induction energy of each molecule M_1, M_2 , and M_3 in the considered three-molecule nanocluster have the form [11, 12]:

$$\begin{aligned} E_{\text{ind}}(M_1) &= \alpha_1 [P_2(R) + P_3(R + R_d)]^2, \\ E_{\text{ind}}(M_2) &= \alpha_2 [P_1(R) + P_3(R_d)]^2, \\ E_{\text{ind}}(M_3) &= \alpha_3 [P_2(R) + P_1(R + R_d)]^2. \end{aligned} \quad (9)$$

Here, the function P_j is the electrostatics field intensity at the center of mass of molecule (i), $i = 1, 2, 3$ at the distance R_{ij} from the center of mass of molecule (j). These functions have the form:

$$P_j(R_{ij}) = -2D_j/R_{ij}^3 + P_j^c(R_{ij}), \quad (10)$$

where D_j is the sum of the induced and permanent (if exists) dipole moments of molecules in the three-molecule nanocluster [9, 10]. The second term in (10) is defined by the equation

$$P_j^c(R_{ij}) = -B_{ij} \exp(-b_{ij} R_{ij}). \quad (11)$$

The parameters B_{ij} and b_{ij} in the Born–Mayer function (11) determine the intensity of the field cre-

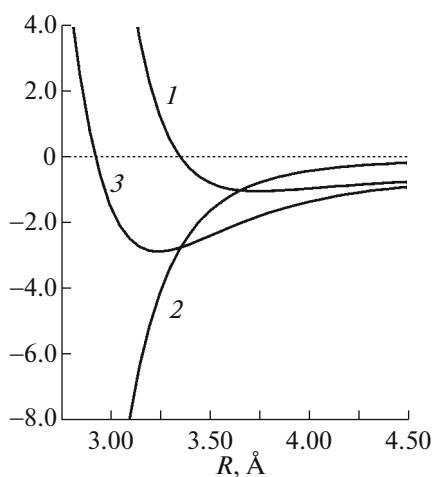


Fig. 1. The calculated energies of the molecular interactions (eV) in a three-molecule cluster consisting of one pentene molecule and two pyrene molecules, depending on the intermolecular distances R (Å). Curve 1 is the sum of the dispersion and Coulomb energies; curve 2 is the induction energy; curve 3 is the total energy of all possible interactions.

ated by the residual charges $Q_j e^+$ of carbon atoms in double bonds of molecule M_j at the distance R_{ij} from the center of mass of molecule M_i and can be determined by the method proposed in [13]: $B_{ij} = (2Q_i e)^2 / a_0^2 + Q_i e / R_{ij}^2 + Q_i e b_i / R_{ij}$; $b_i = 2Q_i / a_0$, where a_0 is the Bohr radius. In the vicinity of the positive charge $Q_i e^+$, an electron cloud with the distributed charge density $\rho_i = (Q_i^3 e / \pi) \exp(2Q_i / a_0) R_{ij}$ occurs. Using this function, we can obtain the values of the electrostatic potential from the charge $Q_i e$ at the distance R_{ij} from the Poisson equation and the field produced by this charge. In the suggested method, the dampening function for the dispersion energy [16, 17] can be obtained from formulae (4), (7) in the form $F = 1 - E^c(M_i, M_j) / E_{\text{dis}}(M_i, M_j)$.

3. THE MAIN RESULTS

Let us present the results of calculations for the values of the energy of intermolecular interactions $E(1,2,3)$ in a three-molecule nanocluster consisting of one neutral pentene molecule M_1 with a constant dipole moment $\mu = 0.6$ D and two neutral pyrene molecules M_2 and M_3 with no dipole moments, equation (3). The sum of the dispersion energies is calculated according to formula (4) with the use of the Born–Mayer equation and the London formula. The values of the parameters were taken as follows: $\alpha_1 = 12 \times 10^{-24}$ cm³, $\alpha_2 = \alpha_3 = 24 \times 10^{-24}$ cm³; $j_1 = 10$ eV, $j_2 = j_3 = 8.7$ eV [5, 12]. The values of charges Q^+ for calculating the Coulomb energies in hydrocarbon molecules with double carbon–carbon bonds (C=C) were

taken from quantum theory of chemical reactions [6]. The calculated sum of dispersion energies, including the Coulomb sum of dispersion energies depending on the intermolecular distances R within the interval 2.75–4.5 Å, is presented in Fig. 1, curve 1. The induction energies were calculated according to formula (9); the values of the induced dipole moments, $D_{\text{ind}}(M_1)$, $D_{\text{ind}}(M_2)$, and $D_{\text{ind}}(M_3)$, depending on R , were taken from [10, 11]. The values of charges Q_1 , Q_2 , and Q_3 are considered in Section 2 of this paper. The total values of induction energies are presented in Fig. 1, curve 2. The dependence of the total energy of intermolecular interaction in the considered three-molecule nanocluster on the intermolecular distance is presented in Fig. 1, curve 3. The numerical analysis has shown that in the considered three-molecule nanocluster of a given configuration, the minimum of the total energy is reached at a distance between the pyrene M_2 and pentene M_1 of 3.24 Å.

CONCLUSIONS

In this work, we proposed a method for analyzing the energy of interaction between three neutral hydrocarbon molecules that form a nanocluster due to the long-range two-particle Van der Waals forces with consideration of the Coulomb repulsion interaction at short distances. The energy of interaction between two molecules in the considered nanocluster at large distances is the dispersion energy, which is calculated in the second order of the perturbation theory. To consider the coulomb interaction, we apply the method of a dampening function, whose form is determined phenomenologically. In our method, we propose to add the energy of the Coulomb interaction of the considered molecules to the energy of the dispersion interaction; this is calculated on the basis of particular charge properties of carbon atoms in double bonds (C=C). One of these bonds is formed by π -electrons. These properties consist in the occurrence of residual charges with values of hundredths of the electron charge at the carbon atoms in the above-mentioned bonds. This made it possible to calculate the Coulomb energy, which together with the dispersion energy constitutes the intermolecular interaction energy. The proposed method allows us to calculate the Coulomb field intensities for each molecule of the investigated nanocluster. Thus, we can determine the intensity of the electrostatic field of each molecule, which is the sum of the intensities of the field of the induced dipole moment and the above-mentioned Coulomb field. On the basis of the obtained analytical expressions, it is possible to calculate the induction energies for each molecule. The total energy of intermolecular interaction in the considered nanocluster is the sum of the unitedly obtained dispersion and Coulomb energies for each pair of molecules and the sum of the induction energy of all molecules. As is was shown in our previous works, in the considered clusters, the

induced dipole moments play an important role in induction processes, making a significant contribution to the induction energy of molecules comparable to the dispersion energy. It was shown that the total potential energy in the three-molecule nanocluster reduces the intermolecular distances compared with the similar distances in two-molecular systems.

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