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On the Different Characteristics of Medium-Sized van der Waals Molecules Obtainable from *ab initio* Calculations*

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Nonempirical *ab initio* calculations with inclusion of the correlation energy are used to generate, directly or indirectly (*via* an analytical form of the potential-energy surface), various properties of medium-sized van der Waals molecules. As shown for benzene...Ar and the benzene dimer, the calculated characteristics agree with the experimental results. If the experimental values are lacking or if they are uncertain, the theoretical characteristics can be used with confidence.

I. INTRODUCTION

Experimental determination of different characteristics of van der Waals (vdW) molecules is not easy and straightforward. There are some properties, such as the intermolecular vibrational frequencies and geometry, that can be determined with high precision. Determination of the other properties, like stabilization energy, is more complicated and is usually accompanied by large experimental error. Sometimes, the range of experimental values originating from different techniques is so broad that almost all the theoretical values fit into the interval.

For a long time the theory was able to estimate only some properties of a complex, and, moreover, their accuracy was not sufficiently high. The exceptions were only very small vdW molecules with up to 4 electrons. The rapid progress of theoretical disciplines and of hardware technology in the last years made the theory really applicable. Nevertheless, in order for the theory to become interesting and helpful for experimentalists in the realm of vdW chemistry, it must determine, with high precision, a broad spectrum of properties of vdW molecules. The aim of this communication is to demonstrate the ability of the theory to treat vdW molecules up to medium size, *i.e.* for complexes having up to 100 electrons.

* Dedicated to Prof. Dr. D. Hadži on the occasion of his 70th birthday.

II. OUTLINE OF THEORETICAL PROCEDURES FOR GENERATING DIFFERENT PROPERTIES OF VDW MOLECULES

II.1. Evaluation of the Potential Energy Surface (PES) of a vdW Molecules

The evaluation of the PES of any vdW molecule should include the correlation energy. Among different techniques, the Møller-Plesset perturbation theory is especially suitable. At the fourth order, the method covers a substantial portion of the correlation energy. At this level, however, the method is limited only to rather small vdW molecules with no more than 30 electrons. For medium-sized vdW molecules, the second-order perturbation theory (MP2) can be recommended. All the points on the PES must be corrected for the basis set superposition error, which affects the SCF interaction energy, as well as the correlation interaction energy. In order, to obtain reliable values of the interaction energy, a large basis set with polarization functions should be used; moreover, these functions should be diffuse. The structure, multipole moments and stabilization energy of the vdW molecule can be obtained from the treatment mentioned. The stabilization energy is more sensitive to the quality of the theoretical treatment than other properties. To evaluate the real stabilization energy, it is necessary to estimate the errors originating in neglecting of the higher perturbation correlation contributions and in truncation of the basis set. These high-level calculations are to be performed for the structurally related smaller vdW molecules.

II.2. Fitting the PES to the Analytical Function

From the calculations described above, discrete points on the PES are obtained. Several theoretical treatments (see later) require an analytical form of the corresponding potentials energy functions, which would be sufficiently flexible and would contain a manageable number of free parameters.

The form of the analytical function is usually based on the nature of forces acting between the subsystems, and potentials in the form of eq. 1 and eq. 2 are mostly used for interaction of nonpolar and polar subsystems, respectively.

$$\phi = c_1 r^{-12} - c_2 r^{-6} \quad (1)$$

$$\phi = c_1 r^{-12} - c_2 r^{-6} + c_3 r^{-1} \quad (2)$$

c_1 , c_2 and c_3 are adjustable parameters and r is the intersystem distance. Formally, discrete terms in eqs 1 and 2 correspond to repulsion and dispersion terms and to repulsion, dispersion and electrostatic terms, resp. However, as all parameters were adjusted simultaneously, there is no sense in considering the physical meaning of discrete terms. In order to retain the physical meaning of single terms, it is necessary to adjust them separately to the components of the total interaction energy, e.g. to the H. F. interaction energy and correlation interaction energy. For evaluation of some properties, such as vibrational frequencies, another form of the analytical functions can be used (e.g. Morse-type potential). It should be mentioned that different parts of the PES are important for the evaluation of different properties. The analytical potential, used for the determination of vibrational frequencies, should mimic as accurately as possible the region around the minimum. On the other hand, potentials used in computer experiments should also accurately describe the short-range and long-range parts of the PES. Evidently, different potentials should be used for evaluation of different pro-

properties of the vdW molecule. We can conclude this part by stating that fitting the PES to an analytical function represents a very difficult and complicated problem.

II. 3. Utilization of the Analytical Potential for Evaluation of Other Properties of a vdW Molecule

The rotational-vibrational spectrum of a vdW molecule is evaluated by variational or perturbational solution of the multidimensional vibrational Schrödinger equation. The dynamical structure of a vdW molecule at temperature T and also the thermodynamic properties of a vdW molecule are generated by molecular dynamics. Finally, the structure of 1:n complexes can be determined from Monte Carlo calculations.

III. EXAMPLES

III. 1. Benzene...Ar

The PES of the title vdW molecule was generated¹ using the 6-31+G*/[7s4p2d] basis set; the energetically most favourable structure was recalculated using the 6-31++G*/[7s4p2d1f] basis set. Two types of analytical functions were fitted² to the scaled PES (the scaling factor was determined as the ratio of the stabilization energy determined using both basis sets). The exponential (spectroscopic) potential was adjusted² to only the three energetically most favourable (sandwich) structures with the prime aim to accurately fit the region around the respective minimum. The second potential in the form of eq. 1 was adjusted² to all the structures studied (three of the sandwich type and two planar) with the same weight for all points. The calculated and experimental properties are given in Table I. From the Table it is evident that the agreement between the calculated and experimental values is reasonable. Let us only add that, after including the effect of the zero-point energy, we can expect even closer agreement for the equilibrium distance. The vibrational frequencies were evaluated with two different potentials. The first, the spectroscopic one, is applicable only for the determination of vibrational frequencies (see above), while the second (in the form of eq. 1) is more general and is used at present⁶ in Monte Carlo and Molecular Dynamics calculations.

III. 2. Benzene Dimer

The PES of the benzene dimer was studied⁷ with the MIDI-1 basis set augmented by diffuse s- and p-orbitals. The energetically most favourable structure (T-shaped) was also investigated with the larger 6-31+G* basis set. The calculated and experimental properties of the dimer are summarized in Table II. The theory predicts identical stabilization for the T shaped and bent structures: the wagging motion of the proton donor in the range of $\pm 10^\circ$ is nonhindered, in the broader range of $\pm 20^\circ$ the energy increase is only marginal. It was concluded from the experiment that the dihedral angle between the two ring planes is 70–80°. Calculation yields⁷ an extremely shallow $\pm 10^\circ$ minimum around the T-shaped structure, hence predicting large amplitude motions around this structure, which is consistent with experimental spectroscopic measurements.⁸ Also, the calculated dipole moment agrees nicely with the experimental value. The predicted stabilization energy⁷ is 2.67 kcal/mol; the respective experimental value¹⁰ is 1.6 ± 0.5 kcal/mol. The calculated stabilization energy (MP2/6-31G*; Ref. 7) suffers from two sources of error: i) lack of higher polarization functions, ii) truncation of the perturbation theory at the second order. The size of the benzene dimer prevents one from studying both effects more carefully and, thus, from determining the stabilization

TABLE I

Calculated and experimental properties of the benzene...Ar complex

	Calculated	Ref.	Experiment	Ref.
Structure	C _{6v}	1	C _{6v}	3
R(Å)	3.53 ^a	1	3.58	3
μ(D)	0.091	1	0.115±0.04	4
ΔE(cm ⁻¹)	429	1	—	
ν _i (cm ⁻¹)	38.8 ^b , 29.0 ^b 36.5 ^c , 25.4 ^c	2 2	39.7, 30.9	5

^a Effect of zero-point energy not included; this would shift the calculated distance to larger values.

^b Spectroscopic potential used.

^c Potential in the form of eq. 1 used.

TABLE II

Calculated and experimental properties of the benzene dimer

	Calculated	Ref.	Experiment	Ref.
Structure	T-shape	7	distorted T-shape (α = 70–80°)	8
R(Å)	5.0 ^a	7	—	
μ(D)	0.51	7	0.44±0.04	9
-ΔE(kcal/mol)	2.673	7	1.6±0.5	10

^a Distance between molecular centers.

energy more accurately. These effects were investigated¹¹ for the structurally similar complex – the acetylene dimer. It was found that the MP2/6-31+G* stabilization energy is underestimated in comparison with the real value by as much as 30%. Taking this factor into account, the real stabilization energy of the benzene dimer was estimated to be 3.5 kcal/mol. Correcting the estimated stabilization energy of the benzene dimer for the zero-point energy yielded a stabilization enthalpy value of 3.2 kcal/mol.¹¹ The respective experimental value¹⁰ (1.6±0.5 kcal/mol) is, therefore, far too low.

IV. CONCLUSIONS

Various properties of a medium-sized vdW molecule can be determined theoretically with reasonable accuracy. If the experimental values are lacking or if they are uncertain, the theoretical values could be used with confidence. The respective theoretical calculations can be performed at a high level, *i.e.* with an extended basis set and with inclusion of a substantial portion of the correlation energy.

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SAŽETAK

O različitim karakteristikama van der Waalsovih molekula srednje veličine dobivenim iz proračuna *ab initio*

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Neempirijskim proračunima *ab initio* uz uključenje korelacijske energije, direktno ili indirektno (putem analitičkih oblika plohe potencijalne energije) dobivaju se različita svojstva van der Waalsovih molekula srednje veličine. Kako je pokazano na primjerima molekula benzen...argon i dimera benzena, proračunane karakteristike slažu se s eksperimentalnim rezultatima. Ako eksperimentalne vrijednosti nedostaju ili su nepouzdana, teorijske karakteristike mogu se koristiti s pouzdanjem.