Molecular Mechanics and Dynamics Calculations to Bridge Molecular Structure Information and Spectroscopic Measurements on Complexes of Aromatic Compounds

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Abstract. Molecular dynamics approaches are applied to the analysis of some properties of the anisole-water and benzene-argon complex. To this end, semiempirical pairwise additive potentials are used. The analysis of the potential energy surface allows to select the most probable conformation among the calculated ones. Then further calculations allow to estimate rotationally resolved spectra and interconversion ratios.

1   Introduction

The interpretation of high resolution spectroscopy experiments on molecular complexes is often a difficult task because of the lack of reliable hypotheses on the structure of the complexes. For several simple systems these hypotheses can be based on chemical intuition. However, as the complexity of the potential energy surface (PES) increases a more systematic approach is needed. To this end, when the system is strongly bound, *ab initio* methods can be used (especially when only a few electrons are involved). Unfortunately, when the complexity of the system under investigation increases and the forces coming into play are weak *ab initio* calculations may not be accurate enough. For example, Density Functional Theory (DFT) based approaches well account for cluster interactions when forces have a strong electrostatic character (*e.g.* systems with ions, highly dipolar molecules or H-bonding) whereas they strongly underestimate van der Waals interactions like those present in nonpolar molecular aggregates. On the other hand, other *ab initio* methods, such as the perturbative Møller-Plesset

ones[1,2]. suffer exactly of the opposite problem than DFT (electrostatic forces are underestimated).

An example of this type is the anisole-water 1:1 complex. For this system accurate estimates of the rotational constants were obtained from high resolution laser induced fluorescence measurements[3]. There we showed that anisole and water form a H-bond and that the center of mass of water falls on the plane defined by the aromatic ring of anisole. Previous accurate *ab initio* calculations based on[4] high level of theory (MP2/aug-cc-pVDZ) had indicated, instead, that in the most stable complex geometry (called AW1) anisole and water are H-bonded and the water is displaced over the aromatic ring. At the same time, a geometry similar to that obtained in our experiment was found[4] to exist and to have an energy larger than AW1. Only subsequent calculations at the B3LYP/6-311++G(d,p) level were able to show that a theoretical evaluation of the OH frequencies is not accurate enough to allow a discrimination among different configurations of the H-bonded anisole-water complexes. A similar situation of unsatisfactory *ab initio* determination of the PES applies to benzene-Ar complexes for which experimental findings are not matched by theoretical conclusions[5].

Thus, to the aim of interpreting experimental measurements like the rovibronic bands obtained from high resolution spectroscopy, it could be adopted a hierarchical two step computational procedure. In the first instance, simple empirical potential models, such as the pairwise additive ones, or a slightly more sophisticated semiempirical potential model (though still computationally cheap) like the one we use for the benzene-argon complex, is used. Eventually, a second step, relying on more accurate methods, can be used to improve the agreement with the experimental data.

In the present paper the anisole-water and the benzene-argon cases are discussed using two different semiempirical potential models.

In section 2 the adopted potential models are discussed. In section 3 calculated and measured spectra are compared. In section 4 the benzene-Ar$_3$ cluster is studied.

2   Potential Energy Surfaces

2.1   Anisole – Water

All possible energy minima of the anisole-water 1:1 complex have been determined by quenching 3700 configurations of anisole and water[3] (see Ref.[6] and references therein for details on the computational protocol). These configurations were extracted randomly from a molecular dynamics simulation performed in the canonical thermodynamical ensemble (simulation box: cube of 15 Å sidelength; temperature: 300 K). The simulation conditions were sufficient to allow the complex to break and reform several times during the run. The anisole molecule has been modeled by the AMBER force field[7], and its atomic charges
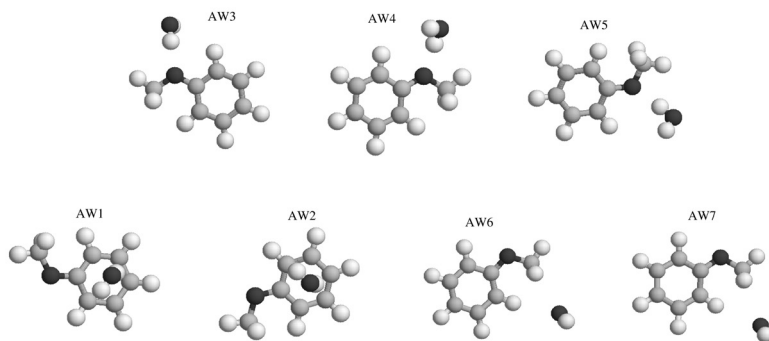
Fig. 1. Minimum energy structures of the anisole-water complex obtained by molecular mechanics calculations (structural class 1: AW1, AW2; structural class 2: AW3, AW4, AW5; structural class 3: AW6, AW7).

have been obtained by a fit of the *ab initio* (B3LYP/6-31G(d,p) level of theory) derived electrostatic potential[8]. The TIP3P model[9] has been utilized for water.

Seven minimum energy structures have been obtained (see Fig. 1) whose binding energy and rotational constants are reported in Tab. 1. The minimum energy configurations of Fig. 1 can be grouped in three structural classes (first class: AW1 and AW2; second class: AW3, AW4 and AW5; third class: AW6 and AW7). Each class is characterized by the fact of having structural configurations with similar anisole-water mutual arrangement. This geometrical similarity appears also evident from the differences in the binding energies of the complexes belonging to the same structural class (see Tab. 1) that are of the order of 0.1 kJ mol^{-1}. This could mean that the PES for the anisole-water 1:1 complex is quite flat around the class representative geometries. The structural geometries of the first and the second class seem to be physically reliable also on the basis of previous studies on complexes of water with aromatic compounds[4,10,11].

The complexes of the first class are characterized by a H-bond involving the π-system of anisole. In the complexes of the second class, anisole and water form instead a conventional nearly in plane σ H-bond, where water acts as hydrogen donor. From the calculations the complexes of the first class result more stable than those of the second one. We stress again that these data must be considered only in a semiquantitative fashion, since we are interested mainly in finding possible candidate structures for interpreting the experiments rather than the most stable of them. On the other hand, we notice incidentally that also for the p-cresol dimer, able to form both conventional and non conventional H-bonds, the binding energy of structures with conventional H-bond was found to be slightly lower than that of structures with non conventional H-bond[6].

Table 1. E_b: binding energy (in units of kJ mol^{-1}) for the anisole-water 1:1 complexes found during the energy minimization; A, B and C: rotational constants (in units of cm^{-1}).

complex	E_b	A	B	C
AW1	-17.93	0.0742	0.0369	0.0348
AW2	-17.67	0.0742	0.0366	0.0347
AW3	-15.69	0.0861	0.0329	0.0241
AW4	-15.63	0.0968	0.0300	0.0233
AW5	-15.56	0.0995	0.0294	0.0231
AW6	-9.97	0.0778	0.0299	0.0218
AW7	-9.60	0.0783	0.0297	0.0217

In the complexes of the third class the oxygen atom of water lies on the plane of the aromatic ring, while the hydrogen atoms are displaced out of the plane (C$_s$ symmetry). For this class of complexes the binding energy is the lowest. Given that, contrarily to AW3, AW4 and AW5, H-bond between anisole and water is not established in the AW6 and AW7 configurations, we can estimate the additional energy stabilization due to H-bonding to be in the range of 5-10 kJ mol^{-1}. This low value is consistent with the quite large O···H distance (1.88 Å) that agrees satisfactorily with the experimental value of 1.95Å.

2.2   Benzene – Argon

The Benzene-Ar complex is considered to be a suitable prototype of the van der Waals type interaction of aromatic molecules and rare gas atoms for both theory and experiment (see Ref.[12] and references therein). The system is sufficiently small to make it possible to use potential models more realistic than the atom-atom pair-additive ones. In previous works[13,14] we showed how this kind of potential is able to describe both the equilibrium geometries and the isomerization process of the benzene-Ar$_2$ complex. In that study the global potential (PES-H) of Pirani et al.[12] was used in the calculation. The same potential model is used in this work to calculate the minimum energy configuration. This minimum was obtained by a standard conjugate gradient searching technique. The corresponding structure has a C$_{6v}$ symmetry, with the argon atom placed above the benzene ring at 3.53Å distance. The rotational constant used to reproduce the spectra are (A=0.09554 cm^{-1}, B=C=0.04037 cm^{-1}).

   Calculations performed on PES-H, however, showed some critical features associated with the handling of atom-molecule rotations that caused large fluctuations in the total energy. Moreover, PES-H cannot be easily extended to systems in which more Ar atoms are clustered around the benzene molecule. For both these reasons, in view of extending the calculation to the simulation of more realistic clusters, a new functional form based on the atom-bond interactions (PES-AB) was derived[5] and used for the present work.
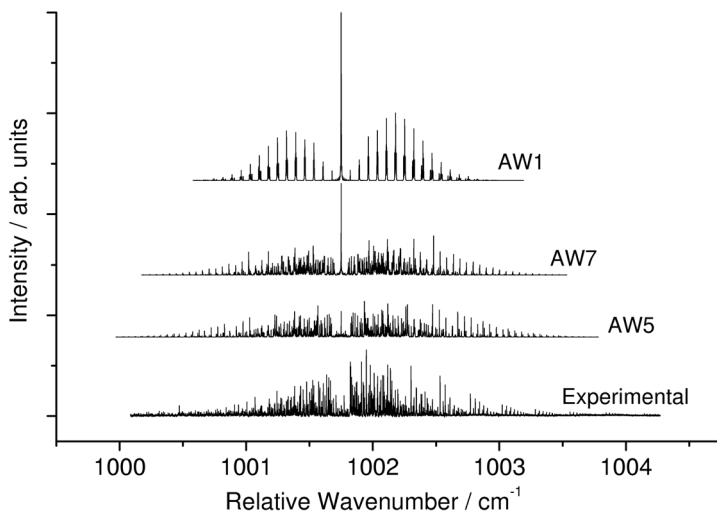
Fig. 2. Comparison between experimental and simulated spectra of the 0_0^0 band of the anisole-water complex.

3   Comparison between Calculated and Observed Spectra

3.1   Anisole – Water

The experimental spectrum of the origin band of the $S_1 \leftarrow S_0$ electronic transition of the anisole-water complex was recorded using a high resolution molecular beam spectrometer, described elsewhere in literature[15]. The complex is formed during the first stages of the supersonic expansion and lives long enough to perform the experiment thanks to the high vacuum kept in the molecular beam chamber.

The rotational structure of the spectra corresponding to the different complex geometries (see Fig. 2) was simulated using an asymmetric top, rigid rotor hamiltonian, with the rotational constants obtained from the calculation (one for each representative class). The other used information was the polarization of electronic transition and the orientation of the principal axis of inertia of the complex with respect to that of the anisole isolated molecule. No geometrical distortion of the complex in going from the S_0 to the S_1 electronic states was assumed.

From a comparison with the experimentally obtained spectrum, we were able to make a guess on the more probable structure of the complex and start the iterative procedure of fitting and simulating, that allows the complete assignment of the rotational fine structure of the spectra[3]. The almost planar AW3-5 struc-
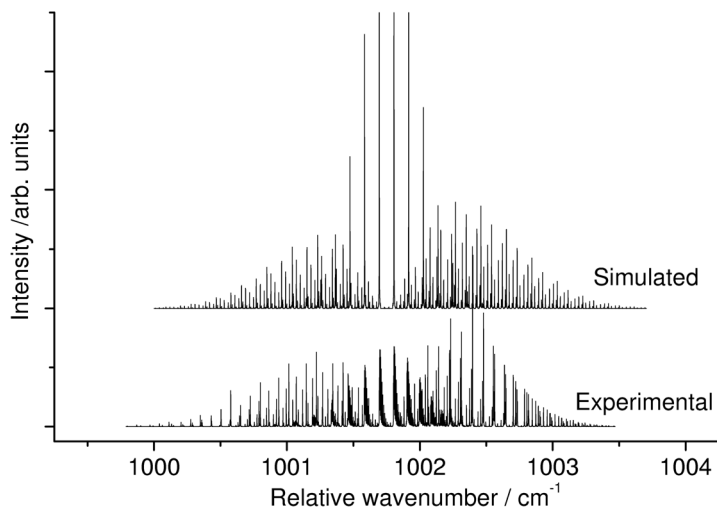
Fig. 3. Comparison between experimental and simulated spectrum of the 6_0^1 band of the benzene-argon complex.

tures are indicated as being the most probable by the simulation. The complete assignment of the rotational structure did also confirm this.

3.2   Benzene – Argon

The experimental spectra of several vibronic bands of the $S_1 \leftarrow S_0$ electronic transition for the benzene-argon complex was recorded under high resolution condition by Riedle *et al.*[16]. The structure of the benzene-argon complex was calculated according to the potential optimized as described in section 2.2. We compare the vibronic spectrum simulated according to the rotational and centrifugal distortion constants as obtained from the assignment of the rotational fine structure of the experimentally obtained spectrum[16], with the spectrum simulated using the rotational constants obtained from the calculation, using the same rotational constants both for the lower and the upper electronic state. The agreement between the two spectra, shown in Fig. 3, agree sufficiently well to take the structure as a good starting point for the iterative procedure.

4   Benzene – Ar$_3$ Simulation

As already mentioned, we extended the study to the clustering of additional Ar atoms around the benzene molecule. For this reason we started by considering the system benzene-Ar$_3$.
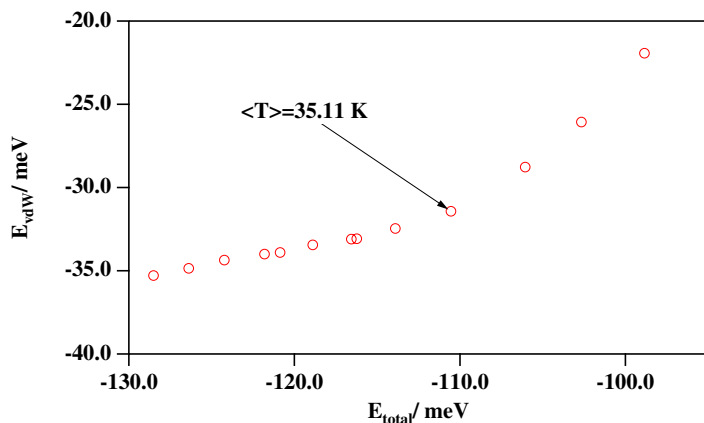
Fig. 4. Van der Waals energy due to the interaction between Ar atoms vs total energy

Simulations have been carried out using a microcanonical ensemble. As a first step a short simulation to equilibrate the temperature was carried out. A equilibration time of 75 ps with a temperature scaling of the velocities allowed to obtain the desired temperature. After obtaining the desired temperature, a long simulation of 100 ns is performed. To this end, as in our previous studies, the benzene molecule was taken as a rigid body. A time step of 0.0025 ps was proved to be sufficiently small to obtain converged values. Relative fluctuations of the total energy in the overall range are smaller than 10^{-6}.

Calculations have been performed for the interconversion between isomers having all the Ar atoms placed on the same side of the benzene plane (3—0 structures) to isomers having the Ar atoms placed in opposite sides of the plane (2—1 structures). A particular isomer was considered as formed when the time spent by the cluster in a particular configuration is equal or larger than 5 ps.

The calculations results show that isomerization processes begin to occur temperatures around 35 K. At this temperature isomeric interconversions are frequent though the probability of dissociation is rather small. When the temperature increases, the interconversion frequency and the dissociation probability increase. However, up to the highest investigated temperature (T=40 K), the cluster lifetime is always larger than 5 ns. The simulation time has been found to be large enough to ensure that the population ratio of the various isomers does not change when extending the simulation to longer times.

The beginning of the isomerization process is evidenced in Fig. 4 where the van der Waals energy (interaction energy of the Ar atoms, E_{vdW}) is plotted as a function of the total energy (E_{total}). At low values of total energy, only the most stable 3—0 isomer is found. By increasing total energy more configurations are explored leading to an increase of the van der Waals energy. Above a certain value of E_{total}, when interconversions between 3—0 and 2—1 isomers become possible, the E_{vdW} plot shows a clear change of slope.

The simulation also shows that the time spent by the benzene-Ar_3 cluster spends in the 2—1 configuration increases with E_{total}. The relative population of isomer 3—0 diminishes from a value of 92.8% at E_{total}=-106.6 meV ($<T>$=38.63 K) to a value of 61.6 % when the total energy is equal to -98.86 meV ($<T>$=42.18 K).

5   Conclusions

Molecular mechanics calculations have been used to start an iterative process to single out the most stable structures of aromatic molecular complexes and assign the rotational fine structure of the rovibronic spectra. The method has the advantage of allowing a complete exploration of the possible structures. It also estimates the relative energy of the various structures and the probability of their formation. This reflects the hybrid character of the control regime leading to the formation of the complex in supersonic expansions.

The method has been applied to two different systems. In the benzene-argon case, the molecular system is symmetrical and the interactions between the two partners in the complex are of pure dispersive nature; in the anisole-water case, the complex is scarcely symmetrical and the interaction responsible for the stabilization of the adduct is much stronger (hydrogen bond).

The quality of the calculated potential energy surfaces adopted in this work good enough to start a complete assignment of the rotationally resolved spectra and to support a rationalization of the experiments.

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