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Article

On the Use of the Pseudo-Diatomic Model for Experimental Evaluation of Stabilization Energies of Weakly Bound Molecular Complexes

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Energias de estabilização para complexos moleculares fracamente ligados, relativas aos monomeros isolados, tem sido determinadas experimentalmente através do modelo pseudo-diatômico (PD) o qual faz uso de um potencial do tipo Lennard-Jones 6-12 (LJ), aqui denominado modelo PD-LJ. Este método utiliza dados espectroscópicos para avaliar a profundidade do poço de potencial para sistemas fracamente ligados. Neste trabalho é mostrada uma comparação sistemática entre valores experimentais de energias de estabilização disponíveis na literatura e calculados à nível *ab initio* para uma série de complexos binários, objetivando avaliar a eficácia do modelo PD-LJ.

Stabilization energies of weakly bound molecular complexes, relative to the isolated monomers constituents, have been evaluated experimentally using the pseudo-diatomic (PD) model employing a Lennard-Jones 6-12 potential (LJ), here denominated the PD-LJ model. This method uses spectroscopic data to estimate the potential depth of weakly bound species. In this work we report a systematic comparison between high level *ab initio* stabilization energy values and the respective experimental data available for a series of binary complexes, aiming to assess the efficaciousness of the PD-LJ model.

Keywords: *stabilization energy, weakly bound complexes,* ab initio, *pseudo-diatomic model*

Introduction

The subject of weakly bound molecular complexes has attracted the attention of many experimentalists and theoreticians and, consequently, this research field has grown considerably over the past years. Experimental studies on such molecular systems, mainly dimeric and trimeric species, have been conducted in the gas phase with structural and energy data being obtained through the aid of infrared (IR) and microwave spectroscopies. The sample is usually produced in a supersonic expansion of the mixture of the monomers where the formation of small molecular associations, mainly binary and ternary complexes, are detected. The experiments are conducted at low temperature and pressure conditions. Experimental investigations on a number of gas phase dimers have been accomplished using pulsed-nozzle Fourier-transform microwave spectroscopy. In many cases the geometry of the complex is unambiguosly determined by the experimentalists. The experimental determination of molecular properties for weakly bound complexes through spectroscopic techniques has been well documented. For a more recent review see Ref. 1 and references there cited. The reviews reported in Refs. 2-5 are also recommended.

On the other side theoretical studies of weakly bound species have been increasingly reported in the literature. Reviews on the theoretical approaches and progresses achieved in this field are given in Refs. 6-10. For a more recent review of the present status of theoretical studies of molecular associations see Ref. 1. One-electron properties like electric field gradient, have been found to be very satisfactorily predicted by *ab initio* calculations, compared to experimental reported values, as it was found for the series of B...HCl dimers, where B is a neutral monomeric species[11]. Also the vibrational spectra of weakly bound species[12,13], and the mechanical and electrical anharmonicities contributions to the vibrational frequencies and intensities of the normal modes[14,15], have been successfully addressed by *ab initio* studies. This has given a substantial contribution to the assignment of experimental gas phase spectra.

Regarding the molecular geometry the agreement between theory and experiment has been remarkable. As an example both linear and cyclic isomers of the $(HCN)_3$ trimer were detected experimentally[16,17] and theoretically predicted to exist[18,19]. Good agreement between theoretical and experimental predictions, regarding isomerism in weakly bound species has been found. An example is the CO_2...HCN complex[20,21], where both linear and T-shaped structure were theoretically predicted to coexist and the *ab initio* calculations[22] antecipated the experimental detection of the linear structure. Calculations on the parent complex $CO_2...C_2H_2$ were also realized and the agreement between theoretical[23] and experimental[24,25] results was very good. Theoretical studies, carried out at the *ab initio* level of theory including electron correlation effects, have been of great help in situations where the experiment alone is unable to provide precise information on both geometry and stabilization energy of the complex. A good example is the $(Cl_2)_2$ homodimer, where the *ab initio* calculations[26] were crucial for the correct assignement of the global minimum energy structure on the potential energy surface (PES). In other situations the existency of dimeric species has been predicted for species ($(PCCP)_2$) where experimental data are still unavailable[27]. More recently the *ab initio* studies [28] have also proved to be able to provide an unambiguous interpretation of gas phase experimental results for tetrameric species, like the $(CO_2)_3$...HCN tetramer[29].

Another phenomenon that has been successfully treated by theoretical approaches is the tunneling effect. The mechanism of tunneling in the $C_2H_4...SO_2$ [30] and $(C_2H_2)_2$ [31] dimers has been studied recently at the *ab initio* level of theory, and the theoretical treatment provided a substantial help for the interpretation of the experimental data for the ethylene-sulfur dioxide[32] and acetylene dimer[33-40]. There are some other interesting situations where a weakly bound complex play a key role for undertanding phenomena like for example mechanisms of organic reactions, and where the *ab initio* calculations, including electron correlation, were of fundamental importance. The $H_2O...CCl_2$ complex, where a carbene species is involved, is a good example of the non formation of a ylide type structure, confirmed by the theoretical study[41] and wrongly proposed experimentally.

In the previous paragraphs the agreement between theory and experiment regarding the determination of molecular properties for weakly bound species has been discussed. However the experimental determination of stabilization energies still deserve more investigation. Improvement on the theoretical determination of vdW energies has been recently achieved by using more extended and mid-bond functions within the Moller-Plesset second order perturbation theory (MP2) treatment of weakly bound species, as it has been reported for the HF...ClF dimer[42]. However the interaction energy between two or more monomer units is not usually measured directly for comparison with high level *ab intio* results. What is most commonly done is to use a pseudo diatomic (PD) model employing a Lennard-Jones (LJ) 6-12 type potential, here denominated PD-LJ model, for the evaluation of stabilization energies. This model makes use of some assumptions and this article aims to assess the quality of the experimental energy data obtained from this model. It is believed that a comparison between high level *ab initio* calculated binding energies and experimental reported values may shed some light about the reliability of the pseudo-diatomic approximation for the evaluation of stabilization energies of gas phase molecular complexes.

Methodology

The *ab initio* calculations of stabilization energies make use of the supermolecule approach, where the interaction energy is evaluated as the difference between the *ab initio* total energy of the complex and the isolated monomer energies. By doing such type of calculation it has to take into account the basis set superposition error (BSSE) effects, which cause an undesirable overestimation of the complex stabilization energy. This has been discussed extensively in the literature. For a recent review see Ref. 43. The full counterpoise (CP) method of Boys and Bernardi[44] is widely used for BSSE corrections. In this approach the monomer energies are calculated in the presence of basis set of the other subunit, placed on ghost atoms. That is, the second monomer is not actually included in the energy calculation, only its basis set. It is well known that electron correlation effects play an important role on complex formation and this has to be taken into account in the *ab initio* studies, which is more frequently done at the MP2 level of theory.

The experimental methodology for stabilization energy determination usually relies on the PD-LJ model. In this approach it is assumed that the centrifugal distortion effects arises from the stretching of the intermolecular van der Waals (vdW) bond only and so the centrifugal distortion constant, D_J, is related to the vdW stretching force constants, k_S. It is also assumed that the radial interaction between the monomer subunits can be described by the Lennard-Jones 6-12 potential which expanded as a Taylor series about the equilibrium intermolecular distance yields an expression for the depth of the intermolecular potential well, *i.e.*,

Table 1. A comparison between a Pseudo-diatomic (PD) model, using a Lennard-Jones 6-12 potential (LJ), and *ab initio* supermolecule calculations of BSSE corrected stabilization energies (in units of cm^{-1}) for some gas phase molecular complexes.

	PD-LJ model	MP2/631G**//631G**				
Kr...HCl	180[a]	79.7[b]				
Ar...HCl	PD-LJ model	Expt.	MP4/WTdf(b-ext)	MP2/6311(3d3p)//6311(3d3p)		
	123[c]	176[d]	175[d]	86.0[b]		
Ar...ClF	PD-LJ model	Expt.	MP4/spdf(b-ext)			
	227[e]	233[d]	252[d]			
HF...ClF	PD-LJ model	MP2/6-31+G*	MP2/DZ+(2d1f,2p1d)			
	689[f]	725[g]	763[h]			
	PD-LJ model	Expt.	MP2/DZP			
HCN...HF	1430[i]	2182[j]	2273[k]			
	PD-LJ model	MP2/[5s4p1d/3s1p]	MP2/[6s5p1d/4s1p]		MP2/[6s5p2d/4s2p]	
C_2H_2...CO	299[l]	324[m]	316[m]		373[m]	
	PD-LJ model	HF/6-31G**	MP2/631G**			
CO_2...HCN (Linear)	590[n]	635[o]	587[o]			
CO_2...HCN (T-shaped)	442[p]	487[o]	477[o]			
	PD-LJ model	HF/DZP	MP2/DZP	MP2/TZ2P	Electrostatic Model	
$(C_2H_2)_2$ (T-shaped)	320[q]	273[r]	339[r]	440r		
CO_2...C_2H_2 (parallel)	409[s] (513)[t]	303[r]	392[r]	568[r]	965[+] 650[++]	
$(CO_2)_2$ (Slipped-parallel)	109[u]	211[r]	195[r]	347[r]		
	PD-LJ model	HF/ 6-31G**	HF/ 6-31+G*	HF/ DZP	MP2/6-31G**// //6-31G**	MP2/DZP// //DZP
C_2H_4...SO_2 (C_s symmetry)	490[v]	374[x] (875)[+++]	404[x]	423[x]	428[x]	479[x]
	PD-LJ model	HF/6-31G	Electrostatic Model			
C_3H_6...SO_2 (Cs symmetry)	1021[y]	1214[y]	874[++++]			
	PD-LJ model	MP2/ (DZ, plus diffuse functions)				
$(CH_3)_3N$...HCl (C_{3v} symmetry)	5792[z]	6400[w]				

[a] Evaluated using structural and spectroscopic data from Ref. 45; [b] The present work. [c] Evaluated using structural and spectroscopic data from Ref. 52. [d] See Ref. 53; [e] Evaluated using structural and spectroscopic data from Ref. 54; [f] Evaluated using structural and spectroscopic data from Ref. 55; [g] See Ref. 56; [h] See Ref. 42; [i] Evaluated using structural and spectroscopic data from Ref. 57; [j] Experimental value measured from absolute intensities of rotational transitions, Ref. 4; [k] See Ref. 58; [l] Evaluated using structural and spectroscopic data from Ref. 59; [m] See Ref. 60; [n] Evaluated using structural and spectroscopic data from Ref. 61; [o] See Ref. 22; [p] Evaluated using structural and spectroscopic data from Ref. 20; [q] Evaluated using structural and spectroscopic data from Ref. 34; [r] See Ref. 49; [s] Evaluated using structural and spectroscopic data from Ref. 62; [t] Evaluated using the stretching force constant from Ref. 63; [u] Evaluated using structural and spectroscopic data from Ref. 64; [v] Evaluated using structural and spectroscopic data from refs. 32,65; [x] See Ref. 66; [y] Evaluated using structural and spectroscopic data from Ref. 67; [z] Evaluated using structural and spectroscopic data from Ref. 68; [w] See Ref. 69; [+] Point quadrupole model, Ref. 49; [++] Distributed multipole analysis (DMA) model, Ref. 49; [+++] Electrostatic model using the DMA approach from Ref. 32; ++++ DMA model from Ref. 67.

$$\in = \frac{k_s \, . \, R_{eq}^2}{72}$$

where R_{eq} is the center of mass equilibrium intermolecular distance. It is therefore implicit that the angular dependence of the interaction energy is completely neglected. This model was applied early for the Kr...HCl dimer[45] and subsequently to the Xe...HBr dimer[46]. Millen[47] has obtained a relationship between the experimentally observed D_J values and k_s for distinct types of weakly bound dimers. For triatomic linear dimers B...H-A, the following relationship was found,

$$k_s = \frac{16\,\pi^2\,\mu_D\,B_D^3}{D_j\,(1 - \frac{B_D}{B_{HA}})}$$

where μ_D is the dimer reduced mass and B_D and B_{HA} respectively the dimer (D) and monomer (HA) rotational constants. Expressions for other types of dimers than linear are given in Ref. 47. So, once the structural parameters, rotational constants and D_J values are available from rotational spectroscopy an estimate of the experimental stabilization energies can be made for gas phase complexes.

The *ab initio* calculations carried out in the present work were done with the GAMESS package[48], as implemented on a SUN ULTRA-1 workstation, at the Laboratório de Química Computacional e Modelagem Molecular (LQC-MM), Departamento de Química, Universidade Federal de Minas Gerais (UFMG).

Results and Discussions

A comparison between the PD-LJ model and *ab initio* supermolecule calculations of stabilization energies for a series of molecular complexes is reported in Table 1. It can be seen from Table 1 that the average agreement between high level *ab initio* correlated stabilization energies for weakly bound complexes and the PD-LJ model experimental $\in$ values is very satisfactory for some dimeric species, the maximum discrepancy being *ca.* 10%. One of the serious disagreement happened for the $(CO_2)_2$ dimer (79%). The carbon dioxide dimer has been investigated at the MP2 level of theory by Bone and Handy[49] and their MP2/DZP (DZP stand for double zeta plus polarization function basis set) value for the intermolecular stretching harmonic frequency was in poor agreement with the experimental value. Since the D_{2h} stable form of the $(CO_2)_2$ dimer does not possess a permanent dipole moment microwave studies are unable to measure a D_J value. Consequently the k_s was obtained directly from the experimentally reported intermolecular stretching frequency using the well known expression for a linear diatomic system, which is no longer the case of the $(CO_2)_2$ dimer. So the very poor agreement found for the carbon dioxide dimer may be related to the imprecision in the evaluation of the stretching force constant (somehow in agreement with Bone and Handy findings[49]) rather than to the failure of the PD-LJ model. The PD-LJ energies of more strongly bound dimers exibited an accentuated deviation from *ab initio* and experimental measured values. This result shows that the PD-LJ model should be used with care. From the results quoted in Table 1 it seems that as the interaction energy value increases the model loses its efficaciousness. The distributed multipole analysis (DMA) model performed better than the point quadrupole model for the prediction of the electrostatic interaction energy, but the agreement with experiment is not so good as for the MP2 BSSE corrected supermolecule approach.

It should also be said that the PD-LJ model relies strongly on the knowledge of accurate values for the intermolecular centre of mass distance (R_{CM}) and stretching force constant (k_s). This means that the curvature of the LJ curve near the minimum is quite crucial. So it is not unexpected at all that the use of *ab initio* k_s values within the PD-LJ approach may no give so good results as the supermolecule approach, as shown for the $N_2...O_2$ heterodimer[50]. The reason is that, as pointed out by Simandiras *et al.*[51], very large basis sets including f functions are needed in order to reproduce accurately harmonic frequencies. So the calculation of very reliable force constants becomes a hard computational task. On the other hand the *ab initio* MP2 BSSE CP corrected supermolecule stabilization energies are not fundamentally based on the precise determination of the curvature (second energy derivative) of the PES. Differently from harmonic frequency calculations, reliable energy values may be obtained using a not so sophisticated level of theory. It is seen that the *ab initio* and PD-LJ treatments are based on distinct grounds but the predicted stabilization energies are comparable.

By analyzing carefully the results reported in Table 1, it can be seen that the MP2 treatment of electron correlation is insufficient for the prediction of stabilization energies for the very weakly bound dimers (Kr...HCl and Ar...HCl). In this case the dispersion contribution to the interaction energy is dominant and so a higher order of perturbation theory is required for the evaluation of the correlation energy. As it has been shown recently for the $(PCCP)_2$ dimer[27], a correct description of the attractive dispersion forces is crucial in theoretical investigation of weakly bound molecular complexes.

The results of the present study gives strong support for the use of the *ab initio* supermolecule calculations employing perturbation theory for treating electron correlation, with extended-polarized basis set plus BSSE correction by the CP approach, for predicting the molecular structure and energetics of gas phase molecular complexes. The PD-LJ model was shown to yield stabilization energies in good agreement with high level *ab initio* calculations for the following molecular complexes: Ar...ClF, HF...ClF, CO_2...HCN, C_2H_4...SO_2 and $(CH_3)_3$...HCl. This result is an indication that the anisotropy of the potential functions, absent in the LJ 6-12 potential, may not be so important for the evaluation of the stability of these gas phase weakly bound complexes. However for the other complexes listed in Table 1 the agreement between the PD-LJ results and the *ab initio* ones is very poor, revealing that the pseudodiatomic model does not produce consistent results and so may not be the most adequate for accurate predictions of stabilization energies. It can also be seen from table 1 that the PD-LJ stabilization energies seem to be consistently underestimated when compared to the high level *ab initio* values. Nevertheless the PD-LJ model can still be used to make an estimate of the binding energies of weakly bound species.

Conclusion

In the present work an assessment of the efficaciousness of the pseudo-diatomic approach (the PD-LJ model) for evaluating stabilization energies has been attempted. A comparison between experimental and *ab initio* calculated energies for a series of molecular complexes has been made. For some dimers in the series of molecular complexes studied here it has been found that, despite neglecting the angular dependence of the interaction energy, the PD-LJ model $\in$ values exhibit a very satisfactory agreement with the *ab initio* supermolecule stabilization energies, calculated including electron correlation effects through the Moller-Plesset perturbation theory treatment. However, the overall agreement for the whole series of molecular systems treated in the present work is not consistent and so the pseudodiatomic approach can not be recommended as a suitable procedure for obtaining reliable stabilization energy values for weakly bound species.

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