

ISSN 0011-1643
UDC 541
CCA-2038

Original Scientific Paper

Structure and Energy of Ar-Molecule Complexes from *ab initio* Calculations*

G. Chałasiński and M. M. Szczyński,

*Department of Chemistry, University of Warsaw, ul. Pasteura 1,
02-093 Warsaw, Poland*

and

*Department of Chemistry and Biochemistry, Southern Illinois University
Carbondale, Illinois 62901, USA*

Received July 17, 1991

Structure and energy of Ar-molecule complexes is analyzed in terms of the anisotropy of separate contributions to the interaction energy: exchange, dispersion, and induction (SCF-deformation). Individual terms are obtained from an *ab initio* approach, a combination of the super-molecular Moller-Plesset perturbation theory with the perturbation theory of intermolecular forces. An analysis, performed for several prototype Ar-molecule dimers, elucidates the principal factors which determine the shape of the potential energy surface and the equilibrium geometry of the rare-gas-molecule van der Waals complexes.

1. INTRODUCTION

The van der Waals complexes of molecular species bound to rare gas (Rg) atoms are of fundamental importance to our understanding of weak chemical interactions. These complexes are of special interest since the rare gas atom may be regarded as a structureless probe of the molecule's charge distribution. Description of this shape may be given in terms of the anisotropy of the Rg-molecules interaction energy surface. Molecular spectroscopy serves as an extremely sensitive tool to observe the anisotropy of the potential energy surface. At present, several experimental groups perform impressive high-resolution infrared spectroscopy of such complexes (*cf.* recent reviews by Saykally¹ and Nesbitt²). Yet, the experimental determination of the anisotropy of the potential energy surface is far from a trivial task. Inversion procedures for spectroscopic and scattering experiments require arbitrary assumptions of the form and parametrization of the potential function. One must *a priori* postulate the physical nature and details of the potential energy surface. If the experimental data are sparse or not very

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

sensitive to the surface shape, they may be fitted with several potential forms which have even qualitatively different topologies. For instance, there are two minima on the Ar-HCl potential energy surface but for some time the empirical fit was so constrained that only the Ar...H-Cl one was reproduced.³ Yet, the fit was remarkably good and only *ab initio* calculations revealed unambiguously the existence of the secondary minimum, for Ar...Cl-H^{4,5} (*cf.* also discussion by Hutson⁶). Another impressive example was recently provided by Nesbitt.⁷ Nesbitt showed that the spectra of two model triatomic systems, a »pinwheel« and a »hinge«, might be remarkably well fitted to a standard semirigid, asymmetric-top Hamiltonian.

In such circumstances, *ab initio* calculations are the unique source of direct information on the details of potential energy surfaces. In this context, the *ab initio* approach which combines the perturbation theory of intermolecular forces^{8,9} with the supermolecular Møller-Plesset perturbation theory (MPPT) treatment, has been recently advocated.^{10,11,12} Such approach proved to be reliable and efficient in the case of several Ar-molecule complexes: Ar-NH₃,¹² Ar-H₂O,¹³ Ar-HCl¹⁴ and Ar-CH₄.¹⁵ This paper reviews the above results. We also attempt to determine the factors that are essential for the shape of potential energy surface and for the equilibrium geometry of the Ar-molecule complexes.

2. METHOD AND DEFINITIONS

The Supermolecular MPPT (S-MPPT) interaction energy corrections are derived as the difference between the values for the total energy of the dimer and the sum of the subsystem energies, in every order of perturbation theory

$$\Delta E^{\text{SCF}} = E_{\text{AB}}^{\text{SCF}} - (E_{\text{A}}^{\text{SCF}} + E_{\text{B}}^{\text{SCF}}) \quad (1)$$

$$\Delta E^{(n)} = E_{\text{AB}}^{(n)} - (E_{\text{A}}^{(n)} + E_{\text{B}}^{(n)}), \quad n = 2, 3, 4 \dots \quad (2)$$

The sum of corrections through the *n*-th order will be denoted $\Delta E^{(n)}$; thus, *e.g.* $\Delta E^{(3)}$ will symbolize the sum of ΔE^{SCF} , $\Delta E^{(2)}$, and $\Delta E^{(3)}$. The interaction energy corrections of the Intermolecular Møller-Plesset Perturbation Theory (I-MPPT) are denoted $\epsilon^{(ij)}$, where *i* and *j* refer to the order of the intermolecular interaction operator and intramolecular correlation operator, respectively.^{8,9}

2.1. Partitioning of ΔE^{SCF}

ΔE^{SCF} may be decomposed as follows (*cf.* Ref [11])

$$\Delta E^{\text{SCF}} = \Delta E^{\text{HL}} + \Delta E_{\text{def}}^{\text{SCF}} \quad (3)$$

$$\Delta E^{\text{HL}} = \epsilon_{\text{es}}^{(10)} + \epsilon_{\text{exch}}^{\text{HL}} \quad (4)$$

where ΔE^{HL} and $\Delta E_{\text{def}}^{\text{SCF}}$ are the Heitler-London energy and the SCF-deformation contribution, respectively. ΔE^{HL} is further decomposed into electrostatic, $\epsilon_{\text{es}}^{(10)}$ and exchange $\epsilon_{\text{exch}}^{\text{HL}}$ components which describe the electrostatic and exchange repulsion energies, respectively, obtained with the unperturbed SCF monomer wavefunctions. The deformation effect, $\Delta E_{\text{def}}^{\text{SCF}}$, is due to mutual polarization restrained by the Pauli

Principle.¹⁶ One may also consider the second-order I-MPPT approximations to $\Delta E_{\text{def}}^{\text{SCF}}$: the *uncoupled Hartree-Fock* (UCHF), $\epsilon_{\text{ind}}^{(20)}$, and the *coupled Hartree-Fock* (CHF), $\epsilon_{\text{ind}}^{\text{CHF}}$, induction energies. In general both provide reliable approximation to $\Delta E_{\text{def}}^{\text{SCF}}$ only for distances larger than the SCF minimum distance. Moreover, $\Delta E_{\text{def}}^{\text{SCF}}$ converges exactly to $\epsilon_{\text{ind}}^{\text{CHF}}$ at large R .

2.2. Partitioning of $\Delta E^{(2)}$

$\Delta E^{(2)}$ may be decomposed as follows (cf. Ref. [11])

$$\begin{aligned} \Delta E^{(2)} &= \epsilon_{\text{es,r}}^{(12)} + \epsilon_{\text{disp}}^{(20)} \\ &+ 2^{\text{nd}} - \text{order} - \text{deformation} - \text{correlation} \\ &+ 2^{\text{nd}} - \text{order} - \text{exchange} - \text{correlation} \end{aligned} \quad (5)$$

where $\epsilon_{\text{es,r}}^{(12)}$ denotes the second-order electrostatic correlation energy (caused by the intramonomer correlation effect) in the response effects formalism,¹⁷ and $\epsilon_{\text{disp}}^{(20)}$ is the so called *uncoupled Hartree-Fock dispersion energy*. The second-order deformation-correlation describes the intramonomer correlation correction to the SCF-deformation contribution. It may be interpreted as the induction-correlation energy which allows for exchange effects. Asymptotically, this effect is represented by the intramonomer correlation correction to the induction contribution within the *response effects* formalism, $\epsilon_{\text{ind,r}}^{(22)}$.²⁰ The second-order exchange-correlation term is also difficult to decompose rigorously. It encompasses the exchange-correlation effects related to the electrostatic-correlation energy and dispersion energy. This total exchange effect can be approximated as follows, provided that the deformation-correlation contribution is negligible:¹²

$$\Delta E_{\text{exch}}^{(2)} = \Delta E^{(2)} - \epsilon_{\text{disp}}^{(20)} - \epsilon_{\text{es,r}}^{(12)} \quad (6)$$

2.3. Counterpoise Correction and Dimer Centred Basis Set

Calculations of all the supermolecular and perturbational interaction energy terms are performed using the basis set of the whole dimer, the *dimer centred basis set* (DCBS). Similarly, if one deals with a many component cluster, one should use the basis set of the whole cluster. With supermolecular interaction energies, this prescription amounts to applying the counterpoise procedure of Boys and Bernardi.²¹ There is strong evidence that this is the only consistent means of evaluation of interaction energy at the SCF level^{22,18,19,23} as well as correlated levels.^{24,28,19,23} With perturbation terms, the description of subsystem wave functions in DCBS has important implications. First, some unphysical contributions to ΔE^{HLL} (sometimes referred to as 'zeroth-order exchange' terms) disappear.^{25,26} Second, it generally improves the description of the exchange,²⁵ induction and dispersion terms.²⁷ Third, using DCBS consistently is absolutely necessary if individual components of interaction energy are extracted by means of subtraction (e.g. ΔE^{SCF} or $\Delta E_{\text{exch}}^{(2)}$).

3. APPLICATION TO AR-MOLECULE COMPLEXES

3.1. Basis Set Selection

All calculations reviewed in this paper were carried out using the Gaussian 86 program²⁸ and the intermolecular package linked to Gaussian 86.²⁹

3.1.1. Ar

We used the basis set proposed by Chalasiński *et al.*:³⁰ (14s10p2d) contracted to [7s4p2d]. This basis set is hereafter referred to as the *spd* basis. Additional calculations were carried out with this basis set augmented with a f-symmetry orbital of the exponent 0.18³⁰. This basis set is referred to as the *spdf* basis.

3.1.2. CH₄, NH₃, H₂O, HCl

We used the medium-size polarized basis set proposed by Sadlej:³¹

- spd* basis: (10s6p4d/5s4p) contracted to [5s3p2d/3s3p] for CH₄, NH₃, H₂O.
- spdf* basis: *spd* augmented with one f-symmetry orbital at C, N, and O. A medium-size polarized basis set was also prepared for HCl:³²
- spd* basis: (14s10p4d/5s4p) contracted to [7s5p2d/3s2p].
- spdf* basis: *spd* augmented with one f-symmetry orbital at Cl.

According to our findings, the exchange and SCF-deformation (induction) terms are already accurately approximated with the *spd* basis (they may cause error of the interaction energy of a few %). The most basis set dependent are the electrostatic and dispersion terms. Since the electrostatic effect for Ar complexes is small, the basis set effects on the total interaction energy may be practically identified with the basis set dependence of the dispersion term. For the *spdf* basis, the dispersion term is expected to be too small, by 10%–15% with respect to its exact value. This causes underestimation of the total interaction energy of 15%–20%. The *spd* basis gives worse results and may underestimate the interaction energy by as much as 25%–30%. Yet, according to our findings the anisotropy is qualitatively correct.

3.2. Convergence of Supermolecular MPPT

The convergence of the perturbation series for intermolecular energies eqs. (1)–(2) through the 4th order is shown in Tables I and II. The geometry is always close to

TABLE I

Contributions to the interaction energy for the Ar-molecule complexes, in the equilibrium geometries with the *spd* basis. Energies in microhartrees.

complex:	Ar ₂	ArCH ₄	ArNH ₃	ArH ₂ O		ArHCl	
Ref.	[30]	[15]	[12]	T-conf [13]	H-bond [13]	H-bond [14]	Ar-ClH [14]
ΔE^{SCF}	196.9	199.0	252.5	156.8	111.7	272.2	292.3
$\Delta E^{(2)}$	-450.0	-597.9	-667.2	-528.8	-474.7	-826.6	-763.9
$\Delta E^{(3)}$	87.6	60.5	73.5	58.4	43.0	159.0	177.3
$\Delta E_{\text{DQ}}^{(4)}$	11.8	32.3	36.5	27.7	31.5	41.9	20.3
$\Delta E_{\text{SPQ}}^{(4)}$	1.4	17.7	13.4	-0.2	2.4	14.1	0.7
$\Delta E^{(4)}$	-42.4	-45.9	68.4	-72.0	67.1	-88.5	-81.8
$\Delta E(4)$	-207.8	-384.3	-409.6	-385.5	-387.1	-484.0	-376.1
$\epsilon_{\text{exch}}^{\text{HL}}$	291.1	298.9	437.8	323.1	341.1	733.5	472.7
$\epsilon_{\text{elst}}^{(10)}$	-83.1	-86.0	-132.9	-80.6	-72.8	-163.2	-139.5
$\Delta E_{\text{def}}^{\text{SCF}}$	-11.1	-13.9	-52.4	-85.7	-156.5	-298.1	-41.0
$\epsilon_{\text{ind}}^{(20)}$	-84.6	-64.1	-126.4	-114.8	-176.3	-343.1	-146.3
$\epsilon_{\text{disp}}^{(20)}$	-499.9	-663.9	-757.0	-582.6	-542.5	-926.6	-847.4
$\Delta E_{\text{exch}}^{(2)}$	72.0	90.9	123.0	71.6	76.9	105.1	111.5
$\epsilon_{\text{disp}}^{(21)}$	88.3	62.0	78.7	56.7	41.5	139.9	180.4

TABLE II

Contributions to the interaction energy for the Ar-atom and -ion complexes, in the equilibrium geometries. Energies in microhartrees.

complex	Ar ₂	ArMg	ArCl ⁻	ArNa ⁺	NO-Ar
basis	spdf	spdf	spdf	spdf	spdf
Rcf.	[30]	[33]	[34]	[34]	[35]
ΔE^{SCF}	196.9	304.7	-405.4	-4675.3	148.1
$\Delta E^{(2)}$	-557.2	-558.1	-1517.9	-688.1	-603.0
$\Delta E^{(3)}$	85.7	23.7	190.5	11.6	56.7
$\Delta E_{\text{DQ}}^{(4)}$	18.2	47.0	63.3	19.4	32.1
$\Delta E_{\text{SDQ}}^{(4)}$	3.1	48.1	0.3	-0.2	-1.6
$\Delta E^{(4)}$	-63.7	-24.0	-193.3	-72.0	-90.6
$\Delta E^{(4)}$	-338.6	-253.7	-1926.0	-385.5	-488.8
$\epsilon_{\text{exch}}^{\text{HL}}$	291.4	-	3419.4	1758.8	-
$\epsilon_{\text{elst}}^{(10)}$	-82.9	-	-1658.6	-317.4	-
$\Delta E_{\text{def}}^{\text{SCF}}$	-11.6	-	-2166.2	-6116.4	-
$\epsilon_{\text{disp}}^{(20)}$	-614.3	-	-2223.0	-578.2	-
$\Delta E_{\text{exch}}^{(2)}$	78.0	-	-	-	-
$\epsilon_{\text{disp}}^{(21)}$	85.6	-	246.2	7.3	-

that of the global minimum geometry. To appreciate better the convergence properties of van der Waals complexes with Argon, we included in Table II complexes with a closed-shell atom (Mg)³³ and ions (Na⁺,³⁴ Cl⁻,³⁴ and NO⁻³⁵).

We should start with a general observation that in the majority of cases that have been studied so far, the convergence properties of the supermolecular MPPT series eqs. (1)–(2) for the Ar-molecule complexes follow the pattern of the Ar–Ar interaction rather than the molecule-molecule interaction.

ΔE^{SCF} provides the primary repulsive effect. It is dominated by the HL exchange contribution. The only exceptions are complexes with ions, Na⁺ and Cl⁻. Then ΔE^{SCF} is large and attractive, this time dominated by induction effects, embodied by $\Delta E_{\text{def}}^{\text{SCF}}$.

$\Delta E^{(2)}$ provides the primary attractive correlation effect. It is dominated by the dispersion contribution. It is worthwhile to note that deformation correlation is less important, even for Ar-ion interactions.

Both ΔE^{SCF} and $\Delta E^{(2)}$ reveal the same general character for all Rg-molecule complexes. However, certain details may be different. For instance, $\epsilon_{\text{disp}}^{(20)}$ which dominates $\Delta E^{(2)}$, overestimates accurate intra-monomer correlated dispersion, $\epsilon_{\text{disp}}^{(2)}$, for Ar complexes but underestimates $\epsilon_{\text{disp}}^{(2)}$ for complexes with He and Ne.

$\Delta E^{(3)}$ provides secondary repulsion. It is dominated by the $\epsilon_{\text{disp}}^{(21)}$ correction. This dispersion correction appears always positive for Ar-molecule interactions but it may be negative for complexes with other Rg atoms. This is, for instance, the case for He-molecule complexes, (cf. He₂,³⁶ HeMg,³³ He–H₂O,³⁷ He–F⁻,³⁸ He–Cl⁻,³⁹ He–NO⁻,³⁵ and He–CO₂⁴⁰).

$\Delta E^{(4)}$ provides the secondary attractive effect. It is dominated by triple (T) excitations terms. The double-quadruples (DQ) terms provide repulsive contribution, in general smaller than $\Delta E^{(3)}$ (the exceptions are ArMg and ArNa⁺ which is an indication of poor convergence). The single (S) excitation terms provide some minor attraction (again, the exceptions are: ArMg and ArNa⁺). Finally, the T terms always provide large

attraction which eventually makes the total fourth order attractive. It is important to stress here that the basis set requirements of various 4th-order terms are different. The SDQ terms are relatively less demanding, satisfied with the spdf or even spd basis. However, the T terms require very extended basis sets and are not saturated in our calculations.

It has often been suggested that $\Delta E^{(3)}$ and $\Delta E^{(4)}$ cancel to a large extent. While this is not true as a general rule (an example is He and its complexes) it seems to occur for several classes of van der Waals complexes. For Ar complexes under consideration in this work we can distinguish three cases:

1. $\Delta E^{(4)}$ cancels $\Delta E^{(3)}$ and the result is repulsive (examples: Ar₂, Ar-CH₄, Ar-NH₃).
2. $\Delta E^{(4)}$ largely cancels $\Delta E^{(3)}$ and the result is attractive (examples: Ar-H₂O, ArMg, ArCl⁻).
3. $\Delta E^{(4)}$ is much larger than $\Delta E^{(3)}$. One may wonder if S-MPPT is still convergent. Even then, however, the 4th-order result may be quite good if compared with the experimental one (examples: ArNa⁺ and Ar-NO⁻).

4. STRUCTURE AND ENERGY OF Ar-MOLECULE COMPLEXES

4.1. Anisotropy of Various Interaction Energy Terms

Anisotropies of various contributions to $\Delta E^{(2)}$ interaction energy for Ar-NH₃, Ar-H₂O and Ar-HCl, at the geometry close to that of the global van der Waals minimum, are shown in Figures 1, 2 and 3, respectively. For all these systems, the following general regularities are observed:

1. The anisotropy of the SCF potential is determined principally by the HL exchange term. This term is also the most orientation dependent. The curves representing the SCF electrostatic interaction and the SCF-deformation energy (the latter not explicitly shown) look very much like the mirror image of the exchange curve, albeit substantially flatter. When these terms are summed together, the SCF interaction curve retains the shape of the exchange curve, only flatter.
2. The post-SCF terms reveal similar patterns of anisotropy. It is important to note first that the anisotropy of the dispersion energy, the major contribution to the total correlation term, $\Delta E^{(2)}$, is reciprocal to that of the HL exchange energy. This anisotropy determines the anisotropy of the total correlation part although it is »smoothened« by the second-order exchange effect (the latter not explicitly shown on Figures 1, 2 and 3). The role of electrostatic-correlation is secondary and may be neglected (unlike in the polar molecules interactions).¹⁷

Although individual interaction energy terms behave similarly, each of the systems under consideration represents a different balance of various contributions.

On the one hand, for Ar-NH₃, the anisotropy of the total interaction energy, represented by $\Delta E(2)$, reflects the anisotropy of the HL exchange term.¹² On the other hand, for Ar-HCl, the total anisotropy is largely determined by the anisotropy of induction (SCF-deformation) and dispersion term.¹⁴ Finally, for Ar-H₂O, all the terms are so isotropic and the balance so delicate that $\Delta E(2)$ reveals the anisotropy which differs from any other term. The result is a very wide minimum (trough) which spreads from the H-bond to the T-shape geometries.¹³ Unfortunately, such a complex shape of the global minimum may be quite common. Another example is the Ar-HCN dimer where the global minimum also appears to have a trough-like shape.⁴¹

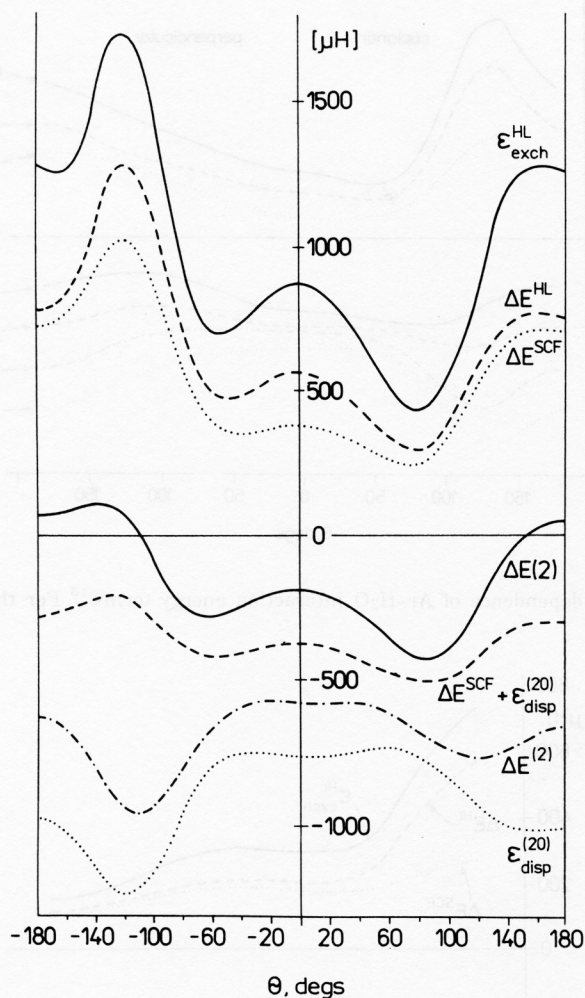


Figure 1. Angular dependence of Ar-NH₃ interaction terms.¹² For the definitions of R and θ cf. Ref. [12].

Perusal of the results in Table I leads to other interesting observations. First, the magnitude and role of the individual interaction energy components (in particular the role of the exchange repulsion anisotropy) is similar for all non-hydrogen-bonded complexes, as well as for Ar₂. Next, the pronounced difference between hydrogen-bonded structures and non-hydrogen-bonded structures consists in that for the former case the SCF-deformation, $\Delta E_{\text{def}}^{\text{SCF}}$, is relatively large and in the latter case small. In addition, classical induction approximation, $\epsilon_{\text{ind}}^{(20)}$, provides a fair approximation to $\Delta E_{\text{def}}^{\text{SCF}}$ for the hydrogen-bonded structures but fails completely for non-bonded ones.

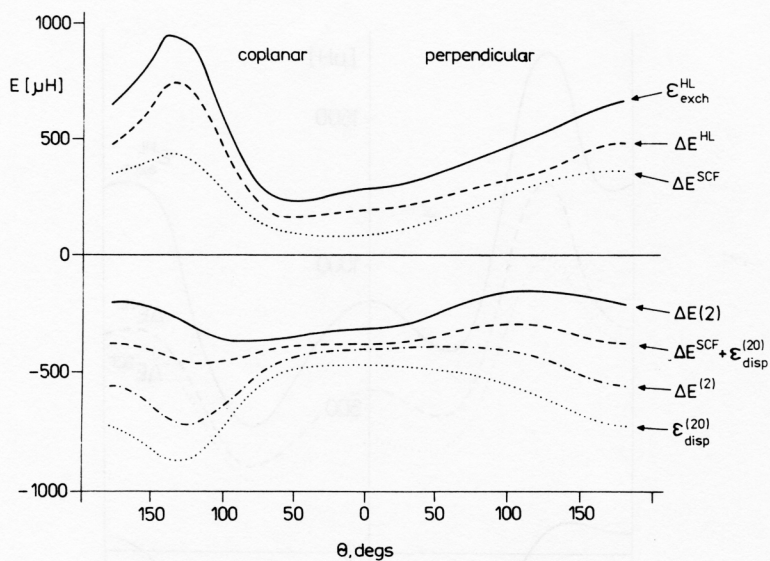


Figure 2. Angular dependence of Ar-H₂O interaction energy terms.¹³ For the definitions of R and θ cf. Ref. [13].

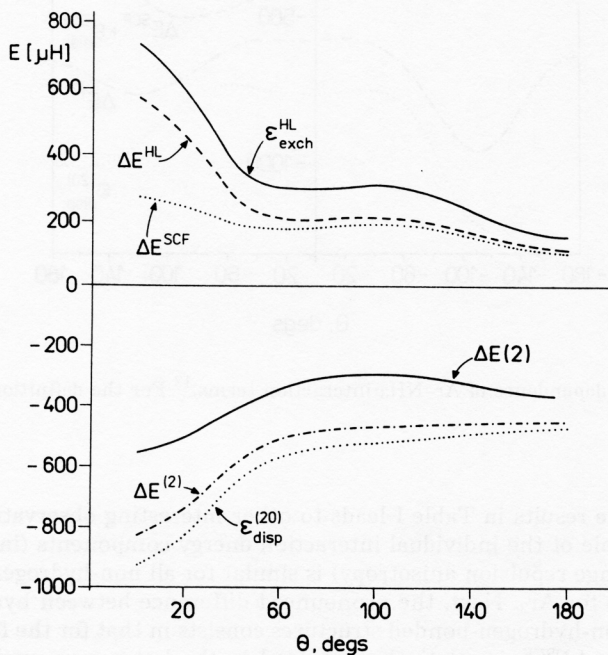


Figure 3. Angular dependence of Ar-HCl interaction energy terms.¹⁴ For the definitions of R and θ cf. Ref. [14].

4.2. Rg as a Probe of Molecular Electronic Structure

How does the anisotropy of the systems under consideration reflect the electronic structure of HCl, H₂O and NH₃?

In the NH₃ case, one notices that Ar detects both the hydrogens and the hypothetical lone pair. The absolute values of individual terms reach the primary maximum when Ar faces the H 'vertex', the secondary maximum is caused by the H-H 'edge', and the lone pair is reflected by a distinct tertiary maximum. Concluding, the shape of the potential energy surface of the Ar-NH₃ complex confirms the simplistic picture of pyramidal ammonia with one lone pair.

In the H₂O case, the situation is different. Ar similarly detects the hydrogens but does not detect any distinct lone pairs. (Interestingly, in the analysis of the water dimer interaction energy lone pairs are also barely detected except for the electrostatic component.⁴³)

Finally, in the case of Ar-HCl there is clear indication of a hydrogen atom but not much of a directional electronic structure around Cl.

4.3. General Factors Determining the Shape of Potential Energy Surface

In the absence of classic electrostatic energy (arising from the interaction of permanent multipoles) the exchange repulsion energy is the largest anisotropic component of the interaction energy. Therefore, if the Rg atom electronic charge is not significantly perturbed by the molecular field, the shape of potential energy surface and the equilibrium structure will be qualitatively determined by the exchange repulsion term. This happens when either the polarizability of the Rg atom is small (*e.g.* for He) or the partner molecule creates a weak field. The examples are the equilibrium structure of Ar-CH₄, Ar-NH₃ and He-H₂O (Figure 4). When analyzing the strength of a molecular field, it is important to note the following. On the one hand, even non-polar molecules may create fairly strong fields because of higher multipole moments, for example CO₂. On the other hand, even significantly polar molecules may create a weak field, in certain directions. Moreover, the polarization effect may be substantially restrained and weakened by the Pauli Principle, for example NH₃.

In all the above cases, one may even venture to predict the respective structures by considering a simplistic LCAO MO picture of a molecule, built of localized bonds and lone pairs, and using the following rule: »Rg atom will avoid hydrogens, lone pairs and any accumulations of electron density«. For example, this rule would correctly pre-

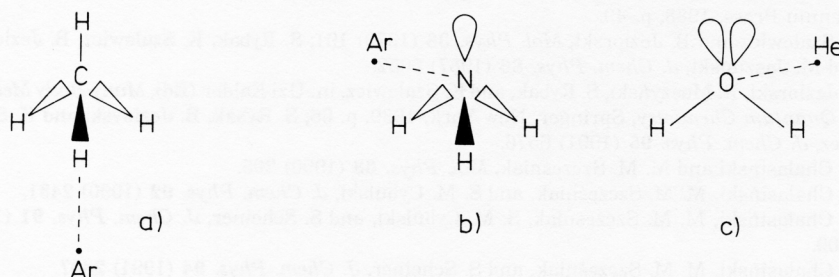
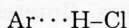


Figure 4. Equilibrium structure of some rare-gas-molecule complexes. a) Ar-CH₄, b) Ar-NH₃, c) He-H₂O.

dict the perpendicular structure of the Ar-benzene complex (D_{6h} symmetry) resulting from *ab initio* calculations.⁴⁴ Of course, it is important to remember that, due to the flatness of the potential energy surface, the structure of van der Waals complexes may not be fully characterized by location of the equilibrium on this surface. Yet, the concept of »structure« is still useful and often used.

The situation becomes more complicated when the Rg atom is reasonably polarizable and the molecule creates a strong, directional field. Then, the anisotropy of two dominant attractive terms: the induction (SCF-deformation) and dispersion, cannot be disregarded. In the extreme case, these two terms may be deciding factors. An example is the Ar-HCl discussed above. The primary minimum configuration:



is related to the maximum of the exchange repulsion term but is favored (stabilized) by induction and dispersion contributions. Of course, we will encounter a wealth of intermediate situations. For instance, a related complex, with a less polarizable Rg atom and a less polar molecule, the Ar-HBr system is known to have the primary and secondary minimum very close in energy.⁴⁵ A very unusual case is the Ar-H₂O discussed above. In general, the balance between exchange-repulsion on the one side, and the induction and dispersion on the other side, will be more difficult to predict *a priori*. It is then very important to continue studies of the Ar-molecule potential energy surfaces for other representative classes of molecules, like diatomics, oxides of the first and second row elements, hydrocarbons with conjugate bonds *etc.*

Acknowledgements. - This work was supported by the National Institutes of Health (GM36912) and Ministry of National Education, Poland, (KBN UW-CHE-BST40).

REFERENCES

1. R. J. Saykally, *Acc. Chem. Lett.* **22** (1989) 295.
2. D. J. Nesbitt, *Chem. Rev.* **88** (1988) 843.
3. J. M. Hutson and B. J. Howard, *Mol. Phys.* **43** (1981) 493.
4. J. H. van Lenthe, T. van Dam, F. B. van Duijneveldt, and L. M. J. Kroon-Batenburg, *Faraday Symp. Chem. Soc.* **19** (1984) 125.
5. T. van Dam, *Ph. D. Thesis*, Utrecht, 1984.
6. J. M. Hutson, *J. Chem. Phys.* **89** (1988) 4550.
7. D. J. Nesbitt, in: Ron Naaman, Zaev Vager (Eds), *The Structure of Small Molecules and Ions*, Plenum Press, 1988, p. 49.
8. K. Szalewicz and B. Jeziorski, *Mol. Phys.* **38** (1979) 191; S. Rybak, K. Szalewicz, B. Jeziorski, and M. Jaszuński, *J. Chem. Phys.* **86** (1987) 5652.
9. B. Jeziorski, R. Moszyński, S. Rybak, and K. Szalewicz, in: Uzi Kaldor (Ed), *Many-Body Methods in Quantum Chemistry*, Springer, New York, 1989, p. 65; S. Rybak, B. Jeziovski and K. Szalewicz, *J. Chem. Phys.* **95** (1991) 6576.
10. G. Chałasinski and M. M. Szczęśniak, *Mol. Phys.* **63** (1990) 205.
11. G. Chałasinski, M. M. Szczęśniak, and S. M. Cybulski, *J. Chem. Phys.* **92** (1990) 2481.
12. G. Chałasinski, M. M. Szczęśniak, S. M. Cybulski, and S. Scheiner, *J. Chem. Phys.* **91** (1989) 7809.
13. G. Chałasinski, M. M. Szczęśniak, and S. Scheiner, *J. Chem. Phys.* **94** (1991) 2807.
14. G. Chałasinski, M. M. Szczęśniak, and B. Kukawska-Tarnawska, *J. Chem. Phys.* **94** (1991) 6677.
15. M. M. Szczęśniak and G. Chałasinski, *J. Chem. Phys.* **96** (1992) 463.
16. M. Gutowski and L. Piela, *Mol. Phys.* **64** (1988) 337.

17. S. M. Cybulski, G. Chalaśiński, and R. Moszyński, *J. Chem. Phys.* **92** (1990) 4357; R. Moszyński, S. Rybak, S. M. Cybulski, and G. Chalaśiński, *Chem. Phys. Lett.* **166** (1990) 609.
18. G. Chalaśiński and M. Gutowski, *Chem. Rev.* **88** (1988) 943.
19. P. Hobza and R. Zahradnik, *Chem. Rev.* **88** (1988) 871.
20. S. M. Cybulski, R. Moszyński and G. Chalaśiński, to be published.
21. S. F. Boys and F. Bernardi, *Mol. Phys.* **19** (1970) 553.
22. M. Gutowski, F. B. van Duijneveldt, G. Chalaśiński, and L. Piela, *Mol. Phys.* **61** (1987) 233; *Chem. Phys. Lett.* **129** (1986) 325.
23. J. H. van Lenthe, J. G. C. M. van Duijneveldt-van de Rijdt, and F. B. van Duijneveldt, *Adv. Chem. Phys.* **69** (1987) 521.
24. M. Gutowski, J. H. van Lenthe, F. B. van Duijneveldt, and G. Chalaśiński, *Chem. Phys. Lett.* **124** (1986) 370.
25. M. Gutowski, G. Chalaśiński, and J. G. C. M. van Duijneveldt-van de Rijdt, *Int. J. Quant. Chem.* **26** (1984) 971.
26. M. Gutowski and G. Chalaśiński, *Mol. Phys.* **54** (1985) 1173.
27. B. Jeziorski and van Hemert, *Mol. Phys.* **31** (1976) 713.
28. M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. DeFrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fluder, and J. A. Pople, *Gaussian 86*, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984.
29. S. M. Cybulski, TRURL package, 1989.
30. G. Chalaśiński, D. J. Funk, J. Simons, and W. H. Breckenridge, *J. Chem. Phys.* **87** (1987) 3569.
31. A. Sadlej, *Coll. Czech. Chem. Commun.* **53** (1988) 1995.
32. G. Chalaśiński, S. M. Cybulski, M. M. Szczechśniak, and S. Scheiner, *J. Chem. Phys.* **91** (1989) 7048.
33. D. J. Funk, G. Chalaśiński, J. Simons, and W. H. Breckenridge, *J. Chem. Phys.* **91** (1989) 1114.
34. G. Chalaśiński, S. M. Cybulski, and M. M. Szczechśniak, to be published.
35. G. Chalaśiński and B. Kukawska-Tarnawska, *J. Phys. Chem.* **94** (1990) 3450.
36. J. Sauer, P. Hobza, P. Carsky, and R. Zahradnik, *Chem. Phys. Lett.* **134** (1987) 553.
37. S. Green, D. J. DeFrees, and A. D. McLean, *J. Chem. Phys.* **94** (1991) 1346.
38. G. H. F. Diercksen and A. Sadlej, *Chem. Phys.* **131** (1989) 215.
39. G. H. F. Diercksen and A. Sadlej, *Chem. Phys. Lett.* **156** (1989) 269.
40. J. Sadlej, to be published.
41. T. D. Klots, C. E. Dykstra, and H. S. Gutowski, *J. Chem. Phys.* **90** (1988) 30.
42. M. M. Szczechśniak, R. J. Brenstein, S. M. Cybulski, and S. Scheiner, *J. Phys. Chem.* **94** (1990) 1781.
43. G. Chalaśiński, M. M. Szczechśniak, P. Cieplak, and S. Scheiner, *J. Chem. Phys.* **94** (1991) 2873.
44. P. Hobza, H. L. Selzle, and E. W. Schlag, *J. Chem. Phys.* **95** (1991) 391.
45. J. M. Hutson, *J. Chem. Phys.* **91** (1989) 4455.

SAŽETAK

Struktura i energija kompleksa molekule Ar prema proračunima *ab initio*

G. Chalaśiński i M. M. Szczechśniak

Analizirana je struktura i energija kompleksa molekule Ar s pomoću anizotropije pojedinih doprinosa energiji interakcije: izmjene, raspršenja i indukcije (SCF-deformacija). Pojedinačni izrazi dobivaju se iz pristupa *ab initio*, kombinacijom supermolekulske Moller-Plessetove teorije smetnje s teorijom smetnje intermolekulskih sila. Analiza, provedena na nekoliko prototipova dimera molekula Ar, otkriva glavne čimbenike koji određuju oblik površine potencijalne energije i ravnotežnu geometriju van der Waalsovih kompleksa molekula plemenitih plinova.