Utah State University
DigitalCommons@USU

Chemistry and Biochemistry Faculty Publications | Chemistry and Biochemistry, Department of

1-1-1989

Analysis of the potential energy surface of Ar–NH3

G. Chalasinski

S. M. Cybulski

M. M. Szczesniak

Steve Scheiner
Utah State University

Recommended Citation

Analysis of the potential energy surface of Ar--NH[sub 3] G. Chalasinski, S. M. Cybulski, M. M. Szczesniak, and S. Scheiner, J. Chem. Phys. 91, 7809 (1989), DOI:10.1063/1.457249

This Article is brought to you for free and open access by the Chemistry and Biochemistry, Department of at DigitalCommons@USU. It has been accepted for inclusion in Chemistry and Biochemistry Faculty Publications by an authorized administrator of DigitalCommons@USU. For more information, please contact becky.thoms@usu.edu.

Analysis of the potential energy surface of Ar–NH_3

G. Chałasiński,[a] S. M. Cybulski, M. M. Szczęśniak, and S. Scheiner
Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901

(Received 30 May 1989; accepted 8 September 1989)

The combination of supermolecular Møller–Plesset treatment with the perturbation theory of intermolecular forces is applied in the analysis of the potential energy surface of Ar–NH_3. Anisotropy of the self-consistent field (SCF) potential is determined by the first-order exchange repulsion. Second-order dispersion energy, the dominating attractive contribution, is anisotropic in the reciprocal sense to the first-order exchange, i.e., minima in one nearly coincide with maxima in the other. The estimated second-order correlation correction to the exchange effect is nearly as large as a half ΔE^{SCF} in the minimum and has a "smoothing" effect on the anisotropy of $\epsilon_{\mathrm{disp}}^{(20)}$. The model which combines ΔE^{SCF} with dispersion energy (SCF + D) is not accurate enough to quantitatively describe both radial and angular dependence of interaction energy. Comparison is also made between Ar–NH_3 and Ar–PH_3, as well as with the Ar dimer.

I. INTRODUCTION

van der Waals complexes display unusual structural and dynamic properties resulting from the shapes of their potential energy surfaces.[1] The weak interactions in these complexes lead to surfaces that are very flat and contain multiple minima. At present, there is no simple rationalization for the structures of such complexes. For example, Shea and Campbell[2] explain the position of the Ar atom with respect to F_2CO, as well as in a number of other complexes, on the basis of preference of the rare gas atom for the more electropositive atoms. However, the experimentally known structure of the Ar–NH_3 complex cannot be predicted by this rule. As found by Klemperer and co-workers,[3] the Ar–N line is nearly perpendicular to the C_3 axis of the ammonia molecule. Recent calculations by Latajka and Scheiner confirmed the same type of structure for the Ar–PH_3 complex.[4] These authors found that despite the fact that the bonding is largely due to correlation, the minimum energy structure is determined by the anisotropy of the self-consistent field (SCF) interaction energy. No further details as to the origin of this anisotropy were given.

The potential energy surface represents the superposition of a number of various interaction energy terms such as electrostatic, exchange, induction, dispersion, and their respective intrasystem correlation corrections. These terms each have different distance and angular dependencies. In order to explain and qualitatively predict the structures of van der Waals complexes, anisotropies of each of these terms should be examined separately. With some of them, such as those occurring within the Hartree–Fock interaction energy, the properties are quite well understood (although rigorous calculations of these terms are surprisingly scarce). However, the complexes in question are mainly bound by correlation effects whose properties are not as yet very thoroughly characterized.[5] Our goal is to rationalize the experimentally known structure of the Ar–NH_3 complex on the basis of analysis of each interaction energy term separately and in this way devise a set of rules which could help in predicting structures of other complexes.

The Ar–NH_3 complex is very attractive for such a study. First of all, the detailed molecular beam study by Klemperer *et al.*[3] provides not only the structural features, but also some estimate of the dissociation energy. The system is small enough so that a high accuracy treatment can be applied. Finally, due to the fact that one of the subsystems is spherically symmetric, the multipole part of the electrostatic energy vanishes at the HF level, as well as at correlated levels, which simplifies certain aspects of the analysis.

In this paper we propose an approach to the study of intermolecular interactions which combines the supermolecular Møller–Plesset Perturbation Theory with the Perturbation Theory of Intermolecular Forces. The goal of this paper is to demonstrate that such combination may serve as a very powerful tool in studies of molecular complexes at quantitative levels of theory.

II. METHOD AND DEFINITIONS

Most *ab initio* calculations of interaction energies with the inclusion of correlation effects are performed using the supermolecular method based on the Møller–Plesset perturbation theory (MPPT).[6,7] Such a treatment is well justified in that it properly includes intermolecular exchange effects. However, the interpretative power of this method is quite limited since it does not allow for separate analysis of individual interaction energy terms. On the other hand, the partitioning of the interaction energy into meaningful and physically interpretable terms is achieved naturally through perturbation theory of intermolecular forces which treats the intermolecular interaction as a perturbation. One example of such a theory is the intermolecular Møller–Plesset perturbation theory (IMPPT),[8] which was designed by Jeziorski, Szalewicz, and collaborators in its most complete, symmetry-adapted form.[9,10] Unfortunately, the latter approach has some disadvantages too, mainly with reference to the treatment of intermolecular exchange effects.

The recently established connection between MPPT

[a] Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

 © 1989 American Institute of Physics

Downloaded 09 Jun 2011 to 129.123.124.169. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

and IMPPT helps to alleviate weaknesses of both methods.[11] In particular, the simultaneous application of both methods allows one to take advantage of the interpretability of IMPPT interaction energy terms within the framework of MPPT. Meanwhile, the questionable treatment of exchange terms can be avoided, the information concerning these effects extracted from MPPT which properly deals with the intersystem symmetry. By exploring such a combined treatment in application to a model system, we hope to provide a further justification for its usefulness in studies of weak intermolecular interactions.

The correlation energy was derived using the MPPT treatment[6] through the full fourth order of perturbation theory employing the frozen core approximation (i.e., the first five orbitals of Ar were frozen). The latter has proven reliable in calculations of the interaction energy of the Ar dimer.[12] The MPPT interaction energy corrections are derived as a difference between the values for the total energy of the dimer and the sum of the subsystem energies, derived in the basis set of the dimer in every order of perturbation theory

$$\Delta E^{\mathrm{SCF}} = E_{AB}^{\mathrm{SCF}} - E_A^{\mathrm{SCF}} - E_B^{\mathrm{SCF}}, \qquad \Delta E^{(n)} = E_{AB}^{(n)} - E_A^{(n)} - E_B^{(n)}, \quad n = 2,3,4. \tag{1}$$

The sum of corrections through the nth 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 IMPPT are denoted $\epsilon^{(ij)}$, where i and j refer to the order with respect to the intermolecular interaction operator and the intramolecular correlation operator, respectively.

A. Partitioning of ΔE^{SCF}

ΔE^{SCF} may be decomposed as

$$\Delta E^{\mathrm{SCF}} = \Delta E^{\mathrm{HL}} + \Delta E_{\mathrm{def}}^{\mathrm{SCF}}. \tag{2}$$

The Heitler–London interaction energy is defined as

$$\Delta E^{\mathrm{HL}} = E_{AB}^{\mathrm{HL}} - E_A^{\mathrm{SCF}} - E_B^{\mathrm{SCF}}, \tag{3}$$

$$E_{AB}^{\mathrm{HL}} = \langle \mathscr{A}\Phi_A^{\mathrm{SCF}}\Phi_B^{\mathrm{SCF}} | \mathscr{H} | \mathscr{A}\Phi_A^{\mathrm{SCF}}\Phi_B^{\mathrm{SCF}}\rangle / \langle \mathscr{A}\Phi_A^{\mathrm{SCF}}\Phi_B^{\mathrm{SCF}} | \Phi_A^{\mathrm{SCF}}\Phi_B^{\mathrm{SCF}}\rangle,$$

where $\mathscr{A}$ denotes antisymmetrizer, Φ^{SCF} denotes the SCF wave function for isolated A or B monomers, and $\mathscr{H}$ refers to the total Hamiltonian. ΔE^{HL} may be separated into electrostatic and exchange contributions[13]

$$\epsilon_{\mathrm{elst}}^{(10)} = \langle \Phi_A^{\mathrm{SCF}}\Phi_B^{\mathrm{SCF}} | V | \Phi_A^{\mathrm{SCF}}\Phi_B^{\mathrm{SCF}}\rangle, \tag{4}$$

where V denotes the interaction operator and

$$\epsilon_{\mathrm{exch}}^{(10)} \equiv \Delta E^{\mathrm{HL}} - \epsilon_{\mathrm{elst}}^{(10)}. \tag{5}$$

$\epsilon_{\mathrm{exch}}^{(10)}$ so defined differs slightly from the definition of Ref. 13 by the presence of so-called "zeroth-order exchange" terms Δ_F and Δ_W. As shown by Gutowski *et al.*,[14] Δ_F vanishes for exact Φ_A^{SCF}, Φ_B^{SCF} functions or when they are derived within the dimer centered basis set (DCBS). Δ_W is of the order of the fourth power of the intersystem overlap integral; it is thus small. Both Δ_F and Δ_W are of exchange type, therefore it seems legitimate to incorporate them into $\epsilon_{\mathrm{exch}}^{(10)}$.[14,15]

The SCF interaction energy ΔE^{SCF} differs from the Heitler–London energy by the presence of terms which are due to deformations of the subsystems' wave functions. The SCF deformation term is defined by Eq. (2):

$$\Delta E_{\mathrm{def}}^{\mathrm{SCF}} = \Delta E^{\mathrm{SCF}} - \Delta E^{\mathrm{HL}}. \tag{6}$$

For large intersystem distances, $\Delta E_{\mathrm{def}}^{\mathrm{SCF}}$ may be interpreted as the induction energy.[16] However, since induction evaluated with neglect of exchange effects may lead to collapsing of the electrons of one fragment into the occupied orbitals of the other fragment,[17] we avoid any further partitioning of $\Delta E_{\mathrm{def}}^{\mathrm{SCF}}$.

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

$\Delta E^{(2)}$ may be decomposed as follows[7,11]:

$$\Delta E^{(2)} = \epsilon_{\mathrm{disp}}^{(20)} + \epsilon_{\mathrm{elst}}^{(12)} + \text{induction correlation} + \text{exchange terms}, \tag{7}$$

where $\epsilon_{\mathrm{disp}}^{(20)}$ denotes the second-order UCHF dispersion energy as defined in Ref. 18, and $\epsilon_{\mathrm{elst}}^{(12)}$ represents the second-order intrasystem correlation correction to the electrostatic effect. The definition of this term was proposed by Jeziorski and collaborators[10(a)] and recently augmented by the "response" or "orbital relaxation" terms.[10(b),10(c)]

The "exchange terms" in Eq. (7) encompass the exchange counterparts of dispersion, electrostatic, and induction correlation, which are extremely difficult to calculate directly.[7,8] Equation (7) provides a recipe for an indirect estimate of those effects. If induction correlation could be assumed small which is certainly the case in Ar–NH_3, the second-order exchange effect may be approximately evaluated as

$$\Delta E_{\mathrm{exch}}^{(2)} \cong \Delta E^{(2)} - \epsilon_{\mathrm{disp}}^{(20)} - \epsilon_{\mathrm{elst}}^{(12)}. \tag{8}$$

If additionally the $\epsilon_{\mathrm{elst}}^{(12)}$ term is small, especially in atom–molecule interactions where it has no multipole component, an even simpler approximation for the second-order exchange effect may be used

$$\Delta E_{\mathrm{exch}}^{(2)\sim} \cong \Delta E^{(2)} - \epsilon_{\mathrm{disp}}^{(20)}. \tag{9}$$

C. Calculations of interaction energies

Calculations of all the supermolecular and perturbational interaction terms are performed using dimer centered basis sets (DCBS). With supermolecular interaction energies, this prescription amounts to applying the counterpoise procedure of Boys and Bernardi.[19] There is strong evidence that this is the only consistent means of evaluation of interaction energy at the SCF[20,21] as well as at correlated levels.[15,22,23] With perturbation terms the description of subsystem wave functions in dimer basis sets has important implications. First, as mentioned earlier, the DCBS treatment leads to vanishing of the unphysical Δ_F term within the Heitler–London energy ΔE^{HL} [Eq. (3)].[14,15] Second, it also improves the description of $\epsilon_{\mathrm{exch}}^{(10)}$,[14] $\epsilon_{\mathrm{ind}}^{(20)}$, and $\epsilon_{\mathrm{disp}}^{(20)}$.[18] It may, however, deteriorate $\epsilon_{\mathrm{elst}}^{(10)}$. Third, using DCBS consistently is absolutely necessary if individual components of interaction energy are extracted by means of subtraction as in Eqs. (6), (8), and (9). Failure to comply with this condition led Collins and Gallup to obtain unphysical repulsive deformation energies.[21,24]

Downloaded 09 Jun 2011 to 129.123.124.169. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

1. Basis sets

The [7*s*,4*p*,2*d*] and [7*s*,4*p*,2*d*,1*f*] basis sets for Ar originate from the study of $(Ar)_2$ by Chałasiński *et al.*[12] The exponents of *d* functions are 0.84, 0.174, and for the *f* function 0.23 (unfortunately, there is a misprint of the second *d* and the *f* exponents in Ref. 12). Their values are chosen to maximize the intersystem correlation effects. The energetic characteristics of both basis sets are provided in Ref. 12. The values of dipole polarizability are presented here in Table I.

For NH_3, we used the "medium-polarized" basis sets proposed by Sadlej[25]: N [5*s*,3*p*,2*d*], H [3*s*,2*p*]. These basis sets have proven very reliable in calculations of intermolecular forces.[26] The polarization functions in medium-polarized basis sets are chosen as the electric field derivatives of the atomic energy optimized *sp* (N) and *s* (H) sets; they are contractions of four primitives.[25] Selected points were calculated with the basis set further augmented by an *f* function with exponent 0.228.[27] Electric properties of NH_3 in both basis sets are shown in Table I. The internal geometry of NH_3 was assumed to be undistorted by the interaction: the experimental geometry with $r(NH) = 1.012\,42$ Å and $\theta(HNH) = 106.67°$ was the same as in Ref. 27. The supermolecular calculations were carried out using the Gaussian 86 program.[31]

III. RESULTS

A. Anisotropy of interaction energy

The geometrical parameters of the Ar–NH_3 complex are shown in Fig. 1. The angle Θ and the R(N–Ar) distance are defined in the same manner as in Ref. 4. For clarity of presentation, positive values of Θ correspond to position of the Ar between two H atoms as pictured in Fig. 1. The Ar lies in a plane encompassing the C_3 axis and a N–H bond on NH_3 when $\Theta < 0$. The scan of the potential energy surface varies Θ between $-180°$ and $180°$ with an increment of 20°; R ranges from 3.0 to 4.0 Å in 0.25 Å steps. Around the minimum energy orientation with $\Theta = 80.0°$, additional calculations were done for $R = 4.5$ and 5.0 Å.

Calculated energetics are presented in Table II and Figs. 2 and 3 for $R = 3.75$ Å. Figure 2 shows clearly that the anisotropy of the SCF potential is determined principally by the first-order exchange repulsion term which is the most orientation dependent. The curve representing the first-order electrostatic interaction looks very much like a mirror image of the exchange curve, albeit substantially flatter. This is due to the fact that both terms are overlap dependent. When the latter two terms are summed together, the Heitler–London curve in Fig. 2 hence retains the general shape of the exchange term. Combination with the relatively flat SCF deformation energy leaves the entire SCF interaction little changed from the ΔE^{HL} curve.

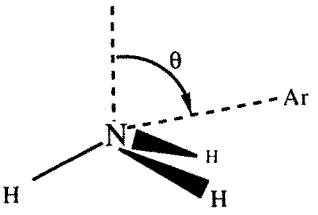

FIG. 1. Definition of the coordinate system for Ar–NH_3. R refers to the N–Ar distance and Θ to the angle between the N–Ar vector and the z axis (shown as a broken line) which is collinear with the C_3 axis of NH_3.

The behaviors of the various post-SCF terms are illustrated in Fig. 3. It is important to note first that the anisotropy of the dispersion energy, the major contributor to $\Delta E^{(2)}$, is reciprocal to that of the exchange energy $\epsilon_{exch}^{(10)}$ (cf. Fig. 2), i.e., the minima in one nearly coincide with the maxima in the other. However, this behavior is not fully reflected in $\Delta E^{(2)}$. The $\Delta E_{exch}^{(2)\sim}$ term which represents the difference between $\Delta E^{(2)}$ and dispersion terms [Eq. (9)] has the same general shape as the first-order exchange contribution. It has thus a "smoothing" effect on the anisotropy of $\epsilon_{disp}^{(20)}$, making its extrema less pronounced and shifting it higher in energy when proceeding from $\epsilon_{disp}^{(20)}$ to $\Delta E^{(2)}$.

$\Delta E_{exch}^{(2)}$, also shown in Fig. 3, is obtained from its parent term $\Delta E_{exch}^{(2)\sim}$ by subtracting the $\epsilon_{elst}^{(12)}$ term [Eq. (8)]. $\Delta E_{exch}^{(2)}$ has its maxima slightly reinforced in comparison to $\Delta E_{exch}^{(2)\sim}$, but both minima and maxima occur in the same positions. Except for the region of strong repulsion (from $-60°$ to $-160°$) $\Delta E_{exch}^{(2)}$ amounts to nearly 1/2 to 2/3 of ΔE^{SCF}. From the close similarity of $\Delta E_{exch}^{(2)\sim}$ and $\Delta E_{exch}^{(2)}$ curves, we may conclude that in the absence of multipole

TABLE I. Finite-field calculations of electric properties of Ar and NH_3. All values are in atomic units.

	Ar		NH_3					
	α[a]		μ[b]		$\alpha_{\parallel}$[c]		$\alpha_{\perp}$[d]	
Basis	*spd*	*spdf*	*spd*	*spdf*	*spd*	*spdf*	*spd*	*spdf*
SCF	9.57	9.57	0.6368	0.6364	13.29	13.30	12.77	12.77
(2)	0.20	0.41	−0.036	−0.036	2.44	2.51	1.02	1.06
(3)	0.01	0.00	0.004	0.004	−0.80	−0.81	−0.34	−0.38
(4)	0.06	0.09	−0.014	−0.014	0.74	0.75	0.33	0.34
MP4[e]	9.85	10.07	0.590	0.590	15.67	15.75	13.78	13.80

[a] Best MBPT: 11.33 (Ref. 28); experiment: 11.06 (Ref. 29).
[b] Other MBPT: 0.5898 (Ref. 27); experiment: 0.5789 (Ref. 30).
[c] Other MBPT: 15.66 (Ref. 27).
[d] Other MBPT: 13.73 (Ref. 27); experiment: $\alpha = 14.56$, $\Delta\alpha = 1.94$, quoted after Ref. 27.
[e] MP4 = SCF + (2) + (3) + (4).

Downloaded 09 Jun 2011 to 129.123.124.169. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

TABLE II. Θ dependence of interaction energy terms for the Ar–NH_3 complex at $R = 3.75$ Å (for definitions see text). All values in μH.

Θ	ΔE^{SCF}	$\Delta E^{(2)}$	$\epsilon_{elst}^{(10)}$	$\epsilon_{exch}^{(10)}$	$\epsilon_{disp}^{(20)}$	$\epsilon_{elst}^{(12)}$	$\epsilon_{elst,r}^{(12)}$	SCF + D[a]
−180	705.7	−647.9	−405.1	1164.4	−991.8	−137.1	−208.9	−286.1
−160	756.7	−689.5	−418.6	1247.7	−1028.8	−131.6	−198.3	−272.2
−140	914.1	−816.8	−462.6	1527.3	−1145.1	−116.4	−168.3	−231.0
−120	1020.3	−953.9	−463.5	1730.4	−1238.5	−87.0	−115.7	−218.2
−100	861.0	−952.4	−360.2	1447.6	−1157.0	−50.8	−60.8	−296.0
−80	566.1	−814.1	−245.3	942.1	−958.2	−41.1	−50.2	−392.1
−60	389.3	−673.0	−218.0	703.4	−813.1	−55.8	−75.2	−423.8
−40	351.9	−598.1	−255.2	733.0	−763.5	−74.1	−103.1	−411.6
−20	368.8	−573.1	−299.8	835.1	−761.3	−86.8	−120.9	−392.5
0	380.9	−569.0	−318.5	883.2	−765.4	−91.6	−127.2	−384.5
20	364.8	−571.5	−298.6	830.0	−759.0	−86.6	−120.6	−394.2
40	317.0	−583.5	−245.2	686.6	−743.0	−72.9	−101.6	−426.0
60	261.0	−614.2	−177.7	518.1	−733.0	−53.2	−72.6	−472.0
80	252.5	−667.2	−132.9	437.8	−757.0	−33.2	−42.8	−504.5
100	345.5	−727.1	−155.3	551.9	−832.2	−29.5	−37.8	−486.7
120	522.0	−755.5	−249.4	835.3	−931.9	−55.5	−78.1	−409.9
140	673.5	−729.7	−352.6	1095.4	−998.5	−98.0	−144.7	−325.1
160	718.5	−676.6	−400.9	1180.7	−1005.7	−128.4	−194.1	−287.2
180	705.7	−647.9	−405.1	1164.4	−991.8	−137.1	−208.9	−286.1

[a] $\Delta E^{SCF} + \epsilon_{disp}^{(20)}$.

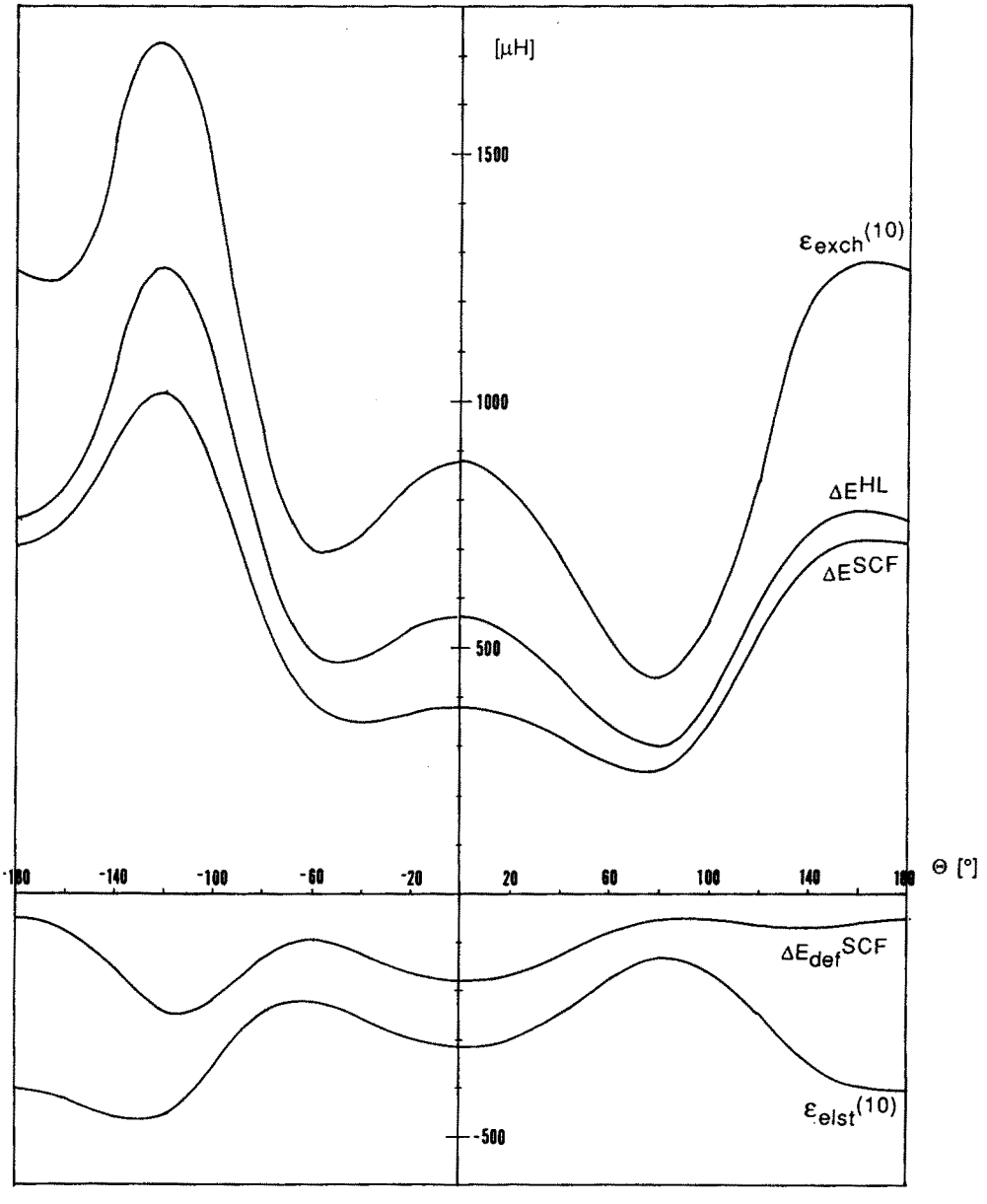

FIG. 2. Θ dependence of Ar–NH_3 interaction energy terms which belong to ΔE^{SCF} (for definitions, see the text). R is kept at 3.75 Å.

Downloaded 09 Jun 2011 to 129.123.124.169. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

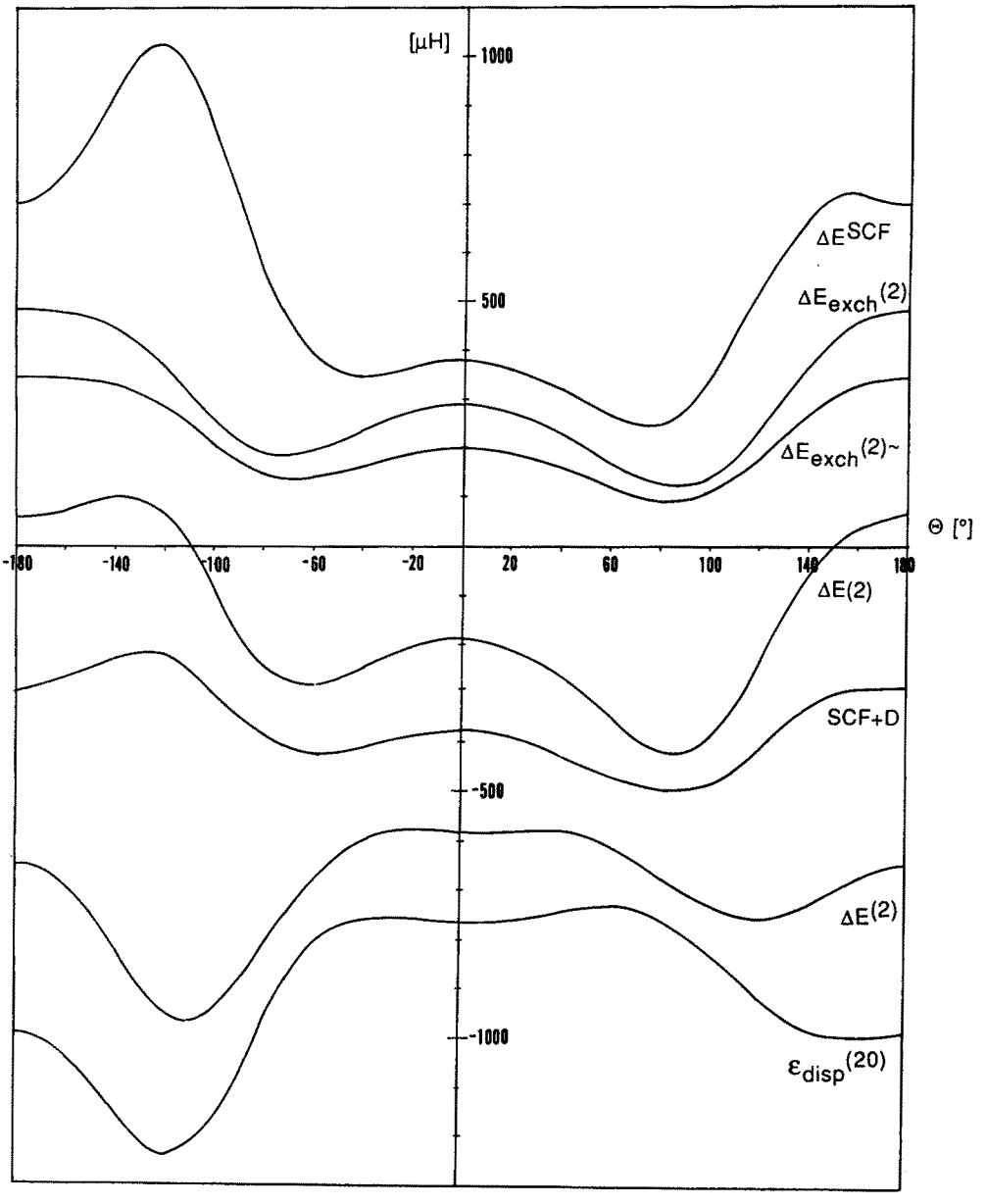

FIG. 3. Θ dependence of Ar–NH_3 interaction energy terms involving correlation (for definitions, see the text). R is kept at 3.75 Å.

electrostatics, as is the case of Ar–NH_3, $\Delta E_{\rm exch}^{(2)\sim}$ seems to be a reasonable approximation to the second-order exchange effect.

Calculated values of $\epsilon_{\rm elst}^{(12)}$ are presented in Table II. $\epsilon_{\rm elst}^{(12)}$ is not very large, roughly of the same order of magnitude as the SCF deformation energy. Just as the uncorrelated electrostatic term $\epsilon_{\rm elst}^{(10)}$ (see Table II), it shows preference for regions of better overlap of Ar and NH_3 charge distributions. For example, there is a shallow minimum around $\Theta = 0°$ (the N lone-pair region) as well as the more pronounced one observed for $\Theta = 180°$, i.e., where Ar overlaps with the three N–H charge distributions simultaneously.

When this study had already been completed it was shown[10(b,c)] that $\epsilon_{\rm elst}^{(12)}$, which enters Eq. 7, should allow for additional "response" terms with respect to the original definition of Jeziorski *et al.*[10(a)] The values of $\epsilon_{\rm elst}^{(12)}$ with response terms, $\epsilon_{\rm elst,r}^{(12)}$, are also given in Table II. The contribution from these terms is not negligible but the above discussed properties of the electrostatic correlation term remain unaffected.

Comparison of the energetics for positive and negative values of Θ (negative Θ corresponds to Ar "eclipsing" an N–H bond) reveals that there are two competing factors which ultimately determine the structure of this complex. Dispersion prefers the structure with $\Theta = -120.0°$, i.e., when the Ar charge distribution best overlaps with that around a N–H bond. On the other hand, such a structure is strongly disfavored by $\epsilon_{\rm exch}^{(10)}$, thus also by $\Delta E^{\rm SCF}$. The latter prefers a geometry with Θ around $+80.0°$, i.e., when Ar approaches between two N–H bonds and the overlap between the Ar and N–H (or N lone pair) charge distributions is minimal. This SCF-minimized structure coincides almost exactly with the global minimum as indicated by $\Delta E(2)$, the sum of $\Delta E^{\rm SCF}$ and $\Delta E^{(2)}$. In other words, the anisotropy of the dispersion is not strong enough to counter the much greater angular dependence of the exchange forces.

Downloaded 09 Jun 2011 to 129.123.124.169. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

The interaction energy of van der Waals systems is often approximated as a sum of two contributions: ΔE^{SCF} and $\epsilon_{disp}^{(20)}$, i.e., by the so-called SCF + D treatment.[32] One may conclude from a comparison with the $\Delta E(2)$ curve in Fig. 3 that the SCF + D treatment yields a surface which is too flat and $\Delta E_{exch}^{(2)}$ is clearly necessary to properly describe its anisotropy.

Further insights concerning the SCF + D approximation can be gleaned by considering the R dependence of the interaction energy (see Table III and Fig. 4). The dispersion energy increases in absolute value substantially more rapidly than does $\Delta E^{(2)}$ as R decreases. As a result, comparison between the $\Delta E(2)$ and SCF + D curves indicates that the latter is too deep and its minimum occurs at too short a distance. Thus the SCF + D potential has some clear deficiencies in predicting the equilibrium geometry of a weak complex such as this.

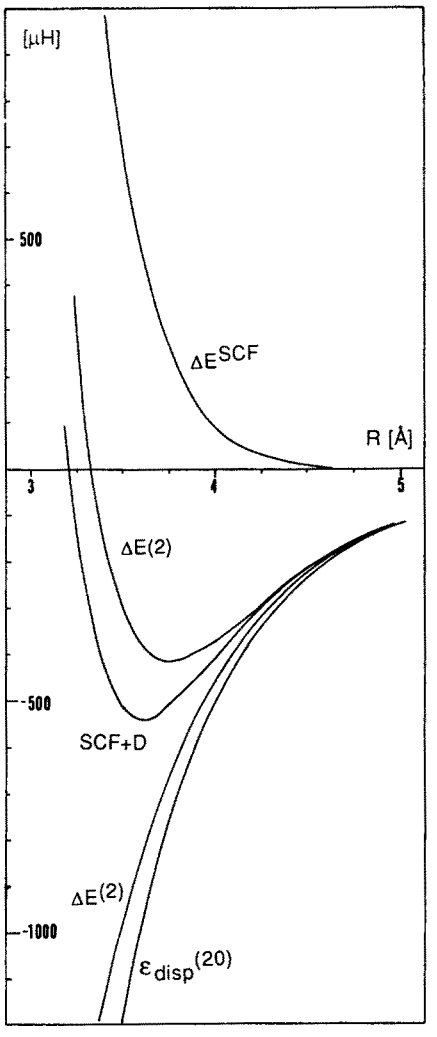

FIG. 4. R dependence of interaction energy terms (for definition, see the text). Θ is kept at 80°.

B. Comparison with Ar_2

The energy minimum for the Ar–NH_3 complex was located at $R = 3.75$ Å, $\Theta = 80.0°$. For this minimum energy orientation, interaction energies were derived up to the MP4 level. Also computed were MP2 energetics in a basis set augmented by f functions on both Ar and N. The results are displayed in Table IV. This table also contains the previously published data for the Ar dimer[12] (as well as some newly generated results) which are included here for comparison.

Qualitatively and quantitatively very similar energetics patterns are observed for Ar–NH_3 and $(Ar)_2$. First of all, ΔE^{SCF} provides in both cases the dominant repulsive contribution. The most important attractive contribution arises from the $\Delta E^{(2)}$ term. The third-order contribution $\Delta E^{(3)}$ is much smaller in magnitude than $\Delta E^{(2)}$ and in both cases is repulsive. $\Delta E^{(4)}$ is slightly smaller still and is attractive in both cases. The contributions of single, double, and quadruple excitations are all repulsive in the fourth order of MPPT; the most important contribution which determines the sign and magnitude of the $\Delta E^{(4)}$ correction hence comes from triple excitations. Finally, in both complexes the inclusion of f functions has very little influence upon the SCF interaction, but leads to a 100 μhartree increase in the magnitude of $\Delta E^{(2)}$. This greater attraction is no doubt due to improvement in the $\epsilon_{disp}^{(20)}$ term.

There are of course some significant differences between the two systems. Due to the polarity of NH_3 and its associated, more efficient perturbation of the charge cloud of Ar, the deformation term ΔE_{def}^{SCF} is more pronounced in Ar–NH_3.

TABLE III. R dependence of interaction energy terms for the Ar–NH_3 complex at $\Theta = 80.0°$ (for definitions, see the text). All values in μhartree.

R,Å	ΔE^{SCF}	$\Delta E^{(2)}$	$\epsilon_{disp}^{(20)}$	$\epsilon_{elst}^{(12)}$	$\epsilon_{elst,r}^{(12)}$	SCF + D	$\Delta E(2)^b$
3.25	1735.2	−1442.8	−1906.8	−143.5	−186.3	−171.6	292.4
3.50	672.8	−977.9	−1185.0	−68.4	−88.9	−512.2	−305.1
3.75	252.5	−667.2	−757.0	−33.2	−42.8	−504.5	−414.6
4.00	90.0	−459.0	−496.8	−16.6	−21.1	−406.8	−369.1
4.50	6.8	−225.2	−230.8	−4.9	−5.8	−224.0	−218.4
5.00	−2.4	−117.2	−117.4	−1.9	−2.0	−119.8	−119.6

[a] $\Delta E^{SCF} + \epsilon_{disp}^{(20)}$.
[b] $\Delta E(2) = \Delta E^{SCF} + \Delta E^{(2)}$.

Downloaded 09 Jun 2011 to 129.123.124.169. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

TABLE IV. Interaction energy contributions to Ar–NH_3 and Ar_2 in the minimum (for definitions, see the text). All values are in μhartree.

	Ar–NH_3(R = 3.75 Å, Θ = 80°)				Ar_2(R = 3.97 Å)	
	spd		*spdf*			
Basis		$BSSE_{uncor}$		$BSSE_{uncor}$	*spd*	*spdf*
ΔE^{SCF}	+252.5	−39.8	+248.4	−72.1	196.9	196.6
$\Delta E^{(2)}$	−667.2	−1344.2	−770.8	−1659.4	−448.0	−557.2
$\Delta E^{(3)}$	+73.5	+63.2			+85.4	+86.0
DQ	+36.5	+56.3			+12.6	+18.2
SDQ	+13.4	+36.5			+3.4	+3.1
$\Delta E^{(4)}$	−68.4	−88.9			−39.4	−63.7
$\Delta E(n)$	−409.6[a]	−1409.7[a]	−522.4[b]	−1731.5[b]	−205.1	−338.3
$\epsilon_{exch}^{(10)}$	437.8	432.1			291.1	
$\epsilon_{elst}^{(10)}$	−132.9	−137.0			−83.1	
ΔE_{def}^{SCF}	−52.4				−11.1	
$\epsilon_{ind}^{(20)}$	−126.4				−84.6	
$\epsilon_{elst}^{(12)}$	−33.2				−17.4	
$\epsilon_{disp}^{(20)}$	−757.0				−499.9	
$\Delta E_{exch}^{(2)}$	+123.0				69.3	

[a] Values when $n = 4$.
[b] Values when $n = 2$.

The greater polarizability of NH_3 vs Ar increases the dispersion attraction in the latter complex, making the $\Delta E^{(2)}$ term more negative.

The nature of ΔE_{def}^{SCF} warrants a more detailed analysis. As pointed out earlier, the major component of deformation is expected to arise from the second-order induction effect $\epsilon_{ind}^{(20)}$. Comparison of the latter term with ΔE_{def}^{SCF} in both systems indicates that the $\epsilon_{ind}^{(20)}$ term is more than twice the magnitude of ΔE_{def}^{SCF}, indicating that exchange effects play a major role at the equilibrium distance. Indeed, as shown by Gutowski and Piela, the induction effect is very strongly coupled with exchange.[17] On the other hand, when recomputed at the SCF minimum which occurs at the longer distance of $R = 5.0$ Å ($\Theta = 80.0°$), ΔE_{def}^{SCF} is almost precisely equal to $\epsilon_{ind}^{(20)}$ (-4.2 vs -4.5 μhartree) as exchange becomes progressively less important. In fact, according to Sadlej, ΔE_{def}^{SCF} asymptotically approaches the CHF induction ϵ_{ind}^{CHF} when R goes to infinity.[16]

The second-order exchange effect is here approximated by $\Delta E_{exch}^{(2)}$ as defined in Eq. (8). In the equilibrium configuration, this term amounts to $+123.0$ μhartree which equals 28% of the first-order exchange effect $\epsilon_{exch}^{(10)}$, -16% of $\epsilon_{disp}^{(20)}$, and -30% of the total $\Delta E(4)$. In the Ar dimer, the percentage comparison of $\Delta E_{exch}^{(2)}$ is very similar: 23% of $\epsilon_{exch}^{(10)}$, -14% of $\epsilon_{disp}^{(20)}$, and -28.0% of $\Delta E(4)$. (For the sake of comparison, in He_2 $\Delta E_{exch}^{(2)}$ amounts to -8% of $\epsilon_{disp}^{(20)}$ and -12% of the total interaction energy.[11]) Thus, the second-order exchange effect is very important in determining the depth of the potential minimum. As pointed out earlier in this paper, the neglect of this term may lead to an incorrect position of the minimum as well.

It is now possible to estimate the bond energy for the Ar–NH_3 complex. For the Ar_2 complex, calculations with the [7*s*,4*p*,2*d*,1*f*] basis set at the MP2 and MP4 levels resulted in bond energies of 360.6 and 338.3 μhartree,[12] respectively, amounting to 80% and 75% of the exact depth of the potential minimum. Taking into account the very similar convergence pattern for MPPT in Ar_2 and Ar–NH_3 (see above), it is concluded that the accuracy in the two should be comparable. Consequently, one may assume that our *spdf* MP2 value of 522.4 μhartree = 115 cm^{-1} represents a lower bound to the bond energy of this complex. It is interesting that our lower bound lies slightly above the experimental estimate of 102.3 cm^{-1} arrived at by Klemperer and coworkers.[3]

Although all the calculations reported here were performed in dimer centered basis sets and are thus free from basis set superposition effects, it may, however, be instructive to analyze the error that would arise if the monomer centered basis were used. The values shown in Table IV in the $BSSE_{uncor}$ column represent results derived within the MCBS treatment. As may be noted by comparison with the preceding column, the BSSE is quite large, comparable to ΔE^{SCF} and $\Delta E^{(2)}$ themselves. These errors induce a spurious minimum in the repulsive part of the SCF interaction energy curve and artificially deepen $\Delta E^{(2)}$ by a factor of 2. BSSE is less pronounced in the third and fourth orders, conforming to prior observation.[12] As noticed a number of times before, upon enlargement of the basis set (by *f* functions), the BSSE increases simultaneously with an improvement of the interaction energy.[22,23] Thus, the magnitude of BSSE is not necessarily any indication of the quality of the interaction energy, contrary to some allusions in the literature.[34,35]

The MCBS treatment can also be applied to the perturbation terms $\epsilon_{elst}^{(10)}$ and $\epsilon_{exch}^{(10)}$ and indeed such values are shown in the $BSSE_{uncor}$ column of Table IV. It should be mentioned that the MCBS $\epsilon_{elst}^{(10)}$ and $\epsilon_{exch}^{(10)}$ terms correspond to the electrostatic and exchange effects in the Morokuma

Downloaded 09 Jun 2011 to 129.123.124.169. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

partitioning scheme.[36] There is strong evidence that the proper description of the exchange phenomenon requires the use of dimer basis sets.[7,14,15] Nevertheless, the difference between DCBS and MCBS treatments of the exchange term is very small, 1.3%. However, the DCBS treatment of electrostatics does introduce certain unphysical effects. For example, the charge distribution of the Ar atom evaluated in the Ar–NH_3 basis is no longer spherically symmetric, leading to the appearance of a spurious multipole contribution to electrostatics. Such effects, dubbed secondary BSSE by Sadlej and Karlstrom, are also implicitly present in the supermolecular interaction energies.[37] It is thus important to compare the values of $\epsilon_{\rm elst}^{(10)}$ evaluated in both dimer and monomer basis sets. The data in Table IV indicate that the DCBS and MCBS treatments of $\epsilon_{\rm elst}^{(10)}$ differ by only 3%, with the difference probably attributable to the spurious multipole electrostatics. This is in agreement with previous results for He_2 and $HeLi^+$ systems,[20] where no serious distortions in $\epsilon_{\rm elst}^{(10)}$ due to DCBS were found in extended basis sets. Overall, the Heitler–London energy is underestimated by the MCBS treatment by about 10 μhartree or 3%.

C. Comparison with Ar–PH_3

Supermolecular MP2 calculations were recently performed for the Ar–PH_3 complex by Latajka and Scheiner.[4] Their basis set for the Ar atom was composed of the well-tempered *sp* set augmented by two *d* functions: exponents 0.836 35 and 0.332 53. To analyze the quality of their results, this basis set was tested here in Ar_2. These tests produced an SCF interaction energy nearly identical to that derived with our basis set. While the SCF BSSE computed with Latajka and Scheiner's basis set was considerably smaller, $\Delta E^{(2)}$ was seriously underestimated (about 13% with respect to our value, or 18% when their *sp* set was augmented by our *d* functions). These observations suggest that the Latajka–Scheiner *sp* set was very good (thus the repulsive part of the potential was very reliable), but the *d* exponents were not optimal for description of dispersion energy, the dominant attractive contribution. This contention is supported by the fact that Latajka and Scheiner's SCF dipole polarizability for Ar was equal to 8.16 a.u. (in their better basis set II), while our value is 9.57 a.u. One may thus conclude that the bond energy of Ar–PH_3 was underestimated in the study of Latajka and Scheiner, but due to the correct description of $\Delta E^{\rm SCF}$, the main direction sensitive contribution, their equilibrium orientation is probably accurate.

Both complexes have nearly identical geometrical configurations with the Θ angle equal to 75° in Ar–PH_3 and 80° in Ar–NH_3. The former appears weaker when comparing the values of $\Delta E(2)$ in the minimum (-331 μhartree for Ar–PH_3 vs -415 μhartree for Ar–NH_3 here). One possible factor in this difference is the much stronger SCF repulsion in the Ar–PH_3 system (776 vs 253 μhartree in the NH_3 complex). On the other hand, the dispersion attraction is expected to be much stronger in the complex with PH_3 due to its polarizability which is twice as large as that of NH_3 (SCF mean polarizabilities are $\alpha_{PH_3} = 26.7$ a.u. vs $\alpha_{NH_3} = 12.9$ a.u.). Consequently, $\Delta E^{(2)}$, which is dominated by the dispersion interaction, amounts to about -1100 μhartree in Ar–PH_3, while our value for Ar–NH_3 is -667.2 μhartree. Due to the abovementioned serious deficiency of the Ar basis set used in calculations of the Ar–PH_3 complex, the value of $\Delta E^{(2)}$ is underestimated. One may expect a roughly 13%–18% increase in this quantity upon a better choice of *d* exponents on Ar (based upon the comparison of computed dipole polarizabilities and Ar_2 data). Even a 13% increase would be sufficient to make Ar–PH_3 stronger than Ar–NH_3.

ACKNOWLEDGMENTS

This work was supported by the National Institutes of Health (GM36912) and by the Polish Academy of Sciences (CPBP01.12). Allocations of Cray time by the National Center for Supercomputer Applications at the University of Illinois and the San Diego Supercomputer Center are acknowledged. We are thankful to Dr. M. Gutowski for reading and commenting on the manuscript.

[1] P. Hobza and R. Zahradník, *Intermolecular Complexes. The role of van der Waals Systems in Physical Chemistry and in the Biodisciplines* (Academia, Prague, 1988); *Structure and Dynamics of Weakly Bound Molecular Complexes*, edited by H. Weber (Reidel, Dordrecht, 1987); P. Hobza and R. Zahradnik, Topic Curr. Chem. **93**, 53 (1980).
[2] J. A. Shea and E. J. Campbell, J. Chem. Phys. **79**, 4724 (1983).
[3] D. D. Nelson, G. T. Fraser, K. I. Peterson, K. Zhao, W. Klemperer, F. J. Lovas, and R. D. Suenram, J. Chem. Phys. **85**, 5512 (1986); G. T. Fraser, D. D. Nelson, A. Charo, and W. Klemperer, *ibid.* **82**, 2535 (1985).
[4] Z. Latajka and S. Scheiner, J. Mol. Struct. Theochem. **198**, 205 (1989).
[5] M. M. Szczęśniak, G. Chałasiński, Chem. Phys. Lett. **161**, 5321 (1989).
[6] R. J. Bartlett and D. H. Silver, Int. J. Quantum Chem. Symp. **9**, 183 (1975); J. S. Binkley and J. A. Pople, *ibid.* **9**, 227 (1975); J. A. Pople, J. S. Binkley, and R. Seeger, Int. J. Quantum Chem. Symp. **10**, 1 (1976).
[7] G. Chałasiński and M. Gutowski, Chem. Rev. **88**, 943 (1988); P. Hobza and R. Zahradnik, *ibid.* **88**, 871 (1988).
[8] B. Jeziorski and W. Kołos, in *Molecular Interactions*, edited by H. Ratajczak and W. J. Orville-Thomas (Wiley, Chichester, 1982), Vol. 3.
[9] K. Szalewicz and B. Jeziorski, Mol. Phys. **38**, 191 (1979); S. Rybak, K. Szalewicz, B. Jeziorski, and M. Jaszuński, J. Chem. Phys. **86**, 5652 (1987).
[10] (a) B. Jeziorski, R. Moszyński, S. Rybak, and K. Szalewicz, in *Many-Body Methods in Quantum Chemistry*, edited by U. Kaldor (Springer, New York, 1989), p. 65; (b) R. Moszyński, S. Rybak, S. M. Cybulski, K. Szalewicz, and G. Chalasiński, Chem. Phys. Lett. (submitted); (c) S. M. Cybulski, G. Chałasiński, and R. Moszyński, J. Chem. Phys. (in press).
[11] G. Chałasiński and M. M. Szczęśniak, Mol. Phys. **63**, 205 (1988).
[12] G. Chałasiński, D. J. Funk, J. Simons, and W. H. Breckenridge, J. Chem. Phys. **87**, 3569 (1987).
[13] B. Jeziorski, M. Bulski, and L. Piela, Int. J. Quantum Chem. **10**, 281 (1976).
[14] M. Gutowski, G. Chałasiński, and J. van Duijneveldt-van de Rijdt, Int. J. Quantum Chem. **26**, 971 (1984); W. A. Sokalski, S. Roszak, P. C. Hariharan, and J. J. Kaufman, *ibid.* **23**, 847 (1983); G. Alagona, C. Ghio, R. Cammi, and J. Tomasi, in *Molecules in Physics, Chemistry, and Biology*, edited by J. Maruani (Kluwer Academic, Dordrecht, 1988) vol. 2, p. 507; J. H. van Lenthe, J. G. C. M. van Duijneveldt-van de Rijdt, and F. B. van Duijneveldt, Adv. Chem. Phys. **69**, 521 (1987).
[15] G. Chałasiński and M. Gutowski, Mol. Phys. **54**, 1173 (1985).
[16] A. J. Sadlej, Mol. Phys. **39**, 1249 (1980).
[17] M. Gutowski, and L. Piela, Mol. Phys. **64**, 337 (1988).
[18] B. Jeziorski and M. van Hemert, Mol. Phys. **31**, 713 (1976).
[19] S. F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).
[20] M. Gutowski, F. B. van Duijneveldt, G. Chałasiński, and L. Piela, Mol. Phys. **61**, 233 (1987).

Downloaded 09 Jun 2011 to 129.123.124.169. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

[21]M. Gutowski, F. B. van Duijneveldt, G. Chałasiński, and L. Piela, Chem. Phys. Letts. **129**, 325 (1986).
[22]M. Gutowski, J. H. van Lenthe, J. Verbeek, F. B. van Duijneveldt, and G. Chałasiński, Chem. Phys. Lett. **124**, 370 (1986).
[23]M. M. Szczęśniak and S. Scheiner, J. Chem. Phys. **84**, 6328 (1986).
[24]J. R. Collins and G. A. Gallup, Chem. Phys. Lett. **123**, 56 (1986).
[25]A. J. Sadlej, Coll. Czech. Chem. Commun. **53**, 1995 (1988).
[26]M. M. Szczęśniak, S. M. Cybulski, R. Brenstein, and S. Scheiner, J. Phys. Chem. (in press); G. Chałasiński, S. M. Cybulski, M. M. Szczęśniak, and S. Scheiner J. Chem. Phys. (in press).
[27]A. J. Sadlej, Mol. Phys. **57**, 509 (1986).
[28]I. Cernusak, G. H. F. Diercksen, and A. J. Sadlej, Chem. Phys. Lett. **128**, 18 (1986).
[29]H. B. Levine and G. Birnbaum, J. Chem. Phys. **55**, 2914 (1971).
[30]M. D. Marshall and J. S. Muenter, J. Mol. Spectrosc. **85**, 322 (1981).
[31]Gaussian 86, 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, Carnegie–Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984.
[32]C. Douketis, J. M. Hutson, B. J. Orr, and G. Scoles, Mol. Phys. **52**, 763 (1984); A. Palma, S. Green, D. J. DeFrees, and A. D. McLean, J. Chem. Phys. **89**, 1401 (1988).
[33]K. Szalewicz, S. J. Cole, W. Kołos, and R. J. Bartlett, J. Chem. Phys. **89**, 3662 (1988).
[34]G. H. F. Diercksen and A. J. Sadlej, Mol. Phys. **59**, 889 (1986); G. H. F. Diercksen, V. Kellö, and A. J. Sadlej, Chem. Phys. **96**, 59 (1985).
[35]Z. Latajka and S. Scheiner, J. Comput. Chem. **8**, 663 (1987).
[36]K. Morokuma and K. Kitaura, in *Molecular Interactions*, edited by H. Ratajczak and W. J. Orville-Thomas (Wiley, Chichester, 1982), Vol. 1 and references therein.
[37]G. Karlström and A. J. Sadlej, Theor. Chim. Acta **61**, 1 (1982).

Downloaded 09 Jun 2011 to 129.123.124.169. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions