How to Choose a One-Electron Basis Set to Reliably Describe a Dipole-Bound Anion

PIOTR SKURSKI,[1,2] MACIEJ GUTOWSKI,[2,3] JACK SIMONS[1]

[1] *Henry Eyring Center for Theoretical Chemistry, Department of Chemistry, University of Utah, Salt Lake City, Utah 84112*

[2] *Department of Chemistry, University of Gdańsk, 80-952 Gdańsk, Poland*

[3] *Materials Resources, Pacific Northwest National Laboratory, Richland, Washington 99352*

Received 20 March 2000; accepted 3 April 2000

ABSTRACT: The problem of choosing appropriate atomic orbital basis sets for ab initio calculations on dipole-bound anions has been examined. Such basis sets are usually constructed as combination of a standard valence-type basis, designed to describe the neutral molecular core, and an extra diffuse set designed to describe the charge distribution of the extra electron. As part of the present work, it has been found that the most commonly used valence-type basis sets (e.g., 6-31++G** or 6-311+G**), when so augmented, are subject to unpredictable under- or overestimating electron binding energies for dipole-bound anions. Whereas, when the aug-cc-pVDZ, aug-cc-pVTZ [or other medium-size polarized (MSP) basis sets] are so augmented, more reliable binding energies are obtained especially when the electron binding energy is calculated at the CCSD(T) level of theory. The issue of designing and centering the extra diffuse basis functions for the excess electron has also been studied, and our findings are discussed here. Int J Quantum Chem 80: 1024–1038, 2000

Key words: basis sets; anions; dipole-bond

Correspondence to: J. Simons; e-mail: simons@chem.utah.edu.

Contract grant sponsor: National Science Foundation.
Contract grant number: CHE9618904.
Contract grant sponsor: Polish State Committee for Scientific Research.
Contract grant numbers: 3 T09A 049 15; 0337/T09/98/15.
Contract grant sponsor: U.S. Department of Energy.
Contract grant number: DE-AC06-76RLO 1830.

International Journal of Quantum Chemistry, Vol. 80, 1024–1038 (2000)

Introduction

It is well known that certain bound anionic states formed by polar molecules can be classified as "dipole-bound" when binding of the excess electron is due primarily to the electrostatic dipole potential of the underlying neutral system [1]. Indeed, it has been shown that such a potential with a dipole moment greater than 1.625 D (debye) possesses an infinite number of bound anionic states with the Born–Oppenheimer (BO) approximation [2–4]. Jordan and Luken demonstrated that the loosely bound electron (lbe) in a dipole-bound state occupies a diffuse orbital localized mainly on the positive side of the molecular dipole [5]. The role of non-BO coupling has been studied by Garrett, who concluded that such couplings are negligible for dipole-bound states with electron binding energies (*D*) much larger than their molecular rotational constants [6].

The simplest theoretical approach to estimate the vertical electron detachment energy *D* of a dipole-bound anion is based on Koopmans' theorem (KT) [7]. The KT binding energy (D^{KT}) is the negative of the energy of the relevant unfilled orbital obtained from a Hartree–Fock self-consistent field (SCF) calculation on the neutral molecule. In static approximation, one neglects both electron correlation and orbital relaxation effects. The latter effects have been found to be quite small for a variety of dipole-bound anionic states [8–14]. On the other hand, we have found that electron correlation leads to a sizable stabilization of many dipole-bound anions [8, 10–14]. Probably the most spectacular case in which correlation is important involves the HNC^- anion for which electron correlation contributes 92% of the electron binding energy [14]. The electron correlation contribution to *D* also exceeds 75% for the weakly bound water–ammonia anion [10], the asymmetric tautomer of diphosphine ($\mathrm{HPPH_3}$) [13], and the *trans* minimum of $(\mathrm{H_2O})_2^-$ [14].

Based on the experience mentioned above, we concluded that the electron correlation contribution to *D* encompasses both (i) a stabilizing dynamic correlation between the lbe and the electrons of the neutral molecule and (ii) an improved description of the charge distribution (and hence the dipole moment) of the neutral. Furthermore, we found that effects beyond the second-order Møller–Plesset (MP2) level can contribute substantially to the stability of dipole-bound anionic states and solvated electrons [8, 10–14].

The diffuse character of the orbital describing a loosely bound electron necessitates the use of extra diffuse basis functions having very low orbital exponents. In addition, the basis set chosen to describe the neutral molecular host should be flexible enough to (i) accurately describe the static charge distribution of the neutral and (ii) allow for the polarization and dispersion stabilization of the anion upon electron attachment. To better establish a systematic procedure for constructing such bases, we decided to undertake a detailed study of the role of the valence and extra diffuse one-electron basis sets employed in these types of calculations.

We first discuss the effect of valence-basis choice on the electron binding energies calculated for $\mathrm{CH_3CN^-}$ and $(\mathrm{H_2O\cdots NH_3})^-$, for which experimental electron binding energies are available [15–17]. $\mathrm{CH_3CN^-}$ is a well-known organic dipole-bound anion, and $(\mathrm{H_2O\cdots NH_3})^-$ is a hydrogen-bonded anionic complex (see Fig. 1), both of which gain a significant contribution to their electronic stability from electron correlation effects. We report the electron binding energies in these species calculated for various valence-type basis sets describing the neutral molecular core with an extra diffuse basis set that is large and flexible enough to render its effect on the calculated binding energies small.

Next, to consider the role of the additional diffuse basis designed to describe the excess electron, we studied two structures of $(\mathrm{H_2O})_3^-$: the open C_1 structure with a large dipole moment and thus a large

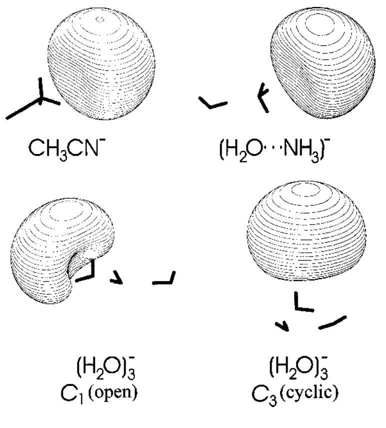

FIGURE 1. Singly occupied molecular orbitals for $\mathrm{CH_3CN^-}$ (0.04500), $(\mathrm{H_2O\cdots NH_3})^-$ (0.00330), C_1 open structure of $(\mathrm{H_2O})_3^-$ (0.01200), and C_3 cyclic structure of $(\mathrm{H_2O})_3^-$ (0.00185). The corresponding contour spacing is given in parentheses.

detachment energy [18], and a cyclic C_3 structure, with a smaller dipole moment, smaller detachment energy, but more favorable hydrogen bonding (see Fig. 1, where the "up-up-up" structure of the O—H bonds not involved in hydrogen bonds appear oriented to the same side of the cyclic structure). In these calculations, a high-quality valence basis was used so that the computed binding energies could be essentially saturated as far as the valence basis is concerned. This series of results allow us to isolate and evaluate the effect of the extra diffuse basis functions.

Methods

The calculated values of D were obtained using a supermolecular approach (i.e., by subtracting the energies of the anion from those of the neutral). This approach requires the use of size-extensive methods for which we have employed Møller–Plesset (MP) perturbation theory up to the fourth order and the coupled-cluster (CC) method with single, double, and noniterative triple excitations [CCSD(T)] [19]. In addition, D was analyzed within the perturbation framework designed for dipole-bound anions and solvated electrons [11].

In the perturbation scheme [11], we consider a neutral molecule (N) and the lbe as weakly interacting species, and we follow the analogy with the theory of intermolecular interactions [20, 21] to analyze D in terms of physically meaningful components. The total electronic Hamiltonian of the anion is partitioned into H^0, which corresponds to the Hartree–Fock level of theory for N and the KT level of theory for the lbe, and two perturbations, W^N and V^{lbe}:

$$H = H^0 + \lambda W^N + \eta V^{\mathrm{lbe}}, \tag{1}$$

where the formal expansion parameters λ and η are introduced to define the perturbation theory orders and have physical values equal to unity. The zeroth-order Hamiltonian

$$H^0 = F^N + F^{\mathrm{lbe}} \tag{2}$$

is the sum of Fock operators for all electrons in the anion, and every Fock operator is determined by the occupied orbitals of N. The fluctuation operator for the neutral molecule, W^N, results from Møller–Plesset partitioning of the electronic Hamiltonian of N, and the fluctuation-interaction operator V^{lbe} has the form:

$$V^{\mathrm{lbe}} = \sum_{i\in N} \frac{1}{r_{\mathrm{lbe},i}} - \big(J_n(\mathrm{lbe}) - K_N(\mathrm{lbe})\big), \tag{3}$$

where $r_{\mathrm{lbe},i}$ is the distance between the ith electron of N and the lbe, and J_N and K_N are, respectively, the Coulomb and exchange operators for N.

On applying double-perturbation theory [20] to the Hamiltonian (1), one obtains the perturbation expansion for the anion energy

$$E = \sum_{k=0}^{\infty}\sum_{l=0}^{\infty} \varepsilon^{(kl)}, \tag{4}$$

where $\varepsilon^{(kl)}$ is of the kth order in W^N and lth order in V^{lbe}. The sum of the three lowest-order terms reproduces the SCF energy of N and D^{KT}:

$$\varepsilon^{(00)} + \varepsilon^{(10)} + \varepsilon^{(01)} = E_N^{\mathrm{SCF}} - D^{\mathrm{KT}}. \tag{5}$$

D^{KT} takes into account the Coulomb and exchange interaction between the lbe and the SCF charge distribution of N. This is a static approximation that neglects both orbital relaxation and electron correlation effects.

The non-KT contributions to D are given by other $\varepsilon^{(kl)}$ terms with $l \geq 1$. The term $\varepsilon^{(02)}$ separates into the induction and dispersion contributions [20, 21]:

$$\varepsilon^{(02)} = \varepsilon^{(02)}_{\mathrm{ind}} + \varepsilon^{(02)}_{\mathrm{disp}}. \tag{6}$$

The term $\varepsilon^{(02)}_{\mathrm{ind}}$ describes polarization of N by the lbe and, as an orbital relaxation effect, is reproduced when D is obtained from the difference in the SCF energies of the neutral and anionic species

$$\Delta D^{\mathrm{SCF}}_{\mathrm{ind}} = D^{\mathrm{SCF}} - D^{\mathrm{KT}} \approx -\varepsilon^{(02)}_{\mathrm{ind}}, \tag{7}$$

where

$$D^{\mathrm{SCF}} = E_N^{\mathrm{SCF}} - E_A^{\mathrm{SCF}} \tag{8}$$

and E_A^{SCF} stands for the SCF energy of the anion. In fact, the term $\Delta D^{\mathrm{SCF}}_{\mathrm{ind}}$ includes not only the static polarization of N by the lbe but also the secondary effect of back-polarization. The term $\Delta D^{\mathrm{SCF}}_{\mathrm{ind}}$ is expected to grow with increasing polarizability of N and with decreasing average separation between the lbe and N.

The term $\varepsilon^{(02)}_{\mathrm{disp}}$ describes a dynamical correlation between the lbe and the electrons of N. This stabilizing effect, brought about by quantum mechanical charge fluctuations, may be very important for weakly bound anions in view of a significant polarizability of the lbe. The term $\varepsilon^{(02)}_{\mathrm{disp}}$ is approximated here by $\Delta D^{\mathrm{MP2}}_{\mathrm{disp}}$, which takes into account proper permutational symmetry for all electrons in the anion:

$$\varepsilon_{\mathrm{disp}}^{(02)} \approx \sum_{a\in N}\sum_{r<s} \frac{|\langle \phi_a \phi_{\mathrm{lbe}} || \phi_r \phi_s \rangle|^2}{e_a + e_{\mathrm{lbe}} - e_r - e_s} = -\Delta D_{\mathrm{disp}}^{\mathrm{MP2}}, \quad (9)$$

where ϕ_a and ϕ_{lbe} are spin orbitals occupied in the zeroth-order wave function, ϕ_r and ϕ_s are unoccupied orbitals, and e's are the corresponding orbital energies.

Higher order corrections to D cannot be neglected. First, there are higher order corrections in V^{lbe} given by the $\varepsilon^{(0l)}$ ($l > 2$) terms. Second, there are corrections $\varepsilon^{(kl)}$ for $k, l \neq 0$, which contribute to D not only through V^{lbe} but also through W^N. It is well established that electron correlation affects the static charge distribution of N and leads to a discrepancy between the SCF and correlated dipole moments of polar molecules. Therefore, the static Coulomb interaction between the lbe and the SCF charge density of N, which is contained in D^{KT}, has to be rectified and the first correction of this type is contained in the MP2 electron binding energy [21].

The MP2 contribution to D defined as

$$\Delta D^{\mathrm{MP2}} = D^{\mathrm{MP2}} - D^{\mathrm{SCF}} \quad (10)$$

is naturally split into the dispersion and nondispersion terms

$$\Delta D^{\mathrm{MP2}} = \Delta D_{\mathrm{disp}}^{\mathrm{MP2}} + \Delta D_{\mathrm{nondisp}}^{\mathrm{MP2}} \quad (11)$$

with the latter dominated by $\varepsilon^{(21)}$ [21]. The higher order MP contributions to D are defined as

$$\Delta D^{\mathrm{MP}n} = D^{\mathrm{MP}n} - D^{\mathrm{MP}(n-1)}, \qquad n = 3, 4. \quad (12)$$

Finally, the contributions beyond the fourth order are estimated by subtracting MP4 results from those obtained at the coupled-cluster level:

$$\Delta D^{\mathrm{CCSD(T)}} = D^{\mathrm{CCSD(T)}} - D^{\mathrm{MP4}}. \quad (13)$$

All calculations were performed with the GAUSSIAN 98 program [22] on an IBM RS/6000 3CT workstation, Pentium III computer, and an SGI Origin2000 numerical server. The three-dimensional plots of molecular structures presented in Figure 1 were generated with the MOLDEN program [23].

Results

WHICH VALENCE-TYPE BASIS SETS ARE BEST?

In order to study the dependence of D on the atomic orbital basis set used to describe the neutral molecule, we designed an algorithm to supplement any of these valence-type basis sets with a set of diffuse functions that is large and flexible enough to render it essentially complete. These extra diffuse functions were centered on the methyl C atom (CH_3CN) or the N atom in ($H_2O\cdots NH_3$). For any valence-type basis set used in this study [22], the values of the lowest s, p, and d exponents $\alpha_{\min}$ in the extra diffuse set are always the same and equal to 2.1574×10^{-5} and 0.9000×10^{-5} a.u. for CH_3CN^- and $(H_2O\cdots NH_3)^-$, respectively. These values of $\alpha_{\min}$ have earlier been shown to be sufficiently small for describing the lbe [10, 12]. For each symmetry, additional even-tempered [24] diffuse functions were added to span the gap between the smallest exponents specified above and the smallest orbital exponent of the corresponding l value in the valence-type basis set at hand. The geometric progression ratio q used to generate this even-tempered series of functions spanning this range was taken from past experience as 3.2 [25]. The number of additional diffuse functions thus depends on the nature of the valence-type basis set and is larger the larger the smallest orbital exponent in the valence set is. This even-tempered construction is continued until the exponents of extra diffuse functions approach the exponents of the valence set. The last added exponent was chosen to bisect, in the log scale, the distance d between the smallest exponent of the valence set and the next to last exponent of the extra diffuse set, with the constraint $\log(q) < d < 2\log(q)$. The resulting extra diffuse sets used in our calculations are thus expected to be consistently suitable to describe the lbe. Let us now examine the dependence of D on the choice of the valence-type basis set.

The minimum energy structures of CH_3CN^- and $(H_2O\cdots NH_3)^-$ were determined at the second-order Møller–Plesset (MP2) level with the aug-cc-pVDZ basis set supplemented with extra diffuse s and p functions to describe the excess electron [10, 12], and all results reported in Tables I–VI were obtained for these geometries. In Tables I and II we report the low- and high-order (in perturbation theory) components of D for CH_3CN^-, respectively, for a variety of valence bases. Analogous results for $(H_2O\cdots NH_3)^-$ are reported in Tables III and IV. The SCF dipole moment, μ^{SCF}, the MP2 correction to the dipole moment, $\Delta\mu^{\mathrm{MP2}}$, and the MP2 polarizabilities, α^{MP2}, of the neutral CH_3CN and $H_2O\cdots NH_3$ are presented in Tables V and VI, respectively for the same 10 valence-type basis sets shown in Tables I and III, all of which are common in quantum chemical applications. In all these calculations,

TABLE I
Dependence of the low-order components of *D* in CH_3CN^- on the quality of the initial basis set designed to describe the neutral molecular host.[a]

Basis set	D^{KT}	ΔD^{SCF}_{ind}	ΔD^{MP2}_{disp}	$\Delta D^{MP2}_{nondisp}$	D^{MP2}
(1) 6-31G*[b]	45	3	45	−36	57
(2) 6-31G**[b]	47	3	48	−43	55
(3) 6-31+G*[c]	53	4	52	−36	73
(4) 6-31+G**[c]	55	4	55	−44	70
(5) 6-31++G**[c]	55	4	55	−44	70
(6) 6-311+G**[d]	54	4	55	−46	67
(7) cc-pVDZ[e]	42	3	43	−40	48
(8) aug-cc-pVDZ[f]	52	4	57	−38	75
(9) MSP[g]	52	4	56	−37	75
(10) aug-cc-pVTZ[h]	52	3	58	−36	77

[a] Energies in cm^{-1}. See text for description of basis sets.
[b] 8(*sp*)9*d* diffuse set.
[c] 6(*sp*)9*d* diffuse set.
[d] 6(*sp*)8*d* diffuse set.
[e] 7*s*7*p*8*d* diffuse set.
[f] 6*s*6*p*7*d* diffuse set.
[g] 6*s*6*p*6*d* diffuse set.
[h] 6*s*6*p*7*d* diffuse set.

every valence-type basis set was supplemented with an extra set of diffuse functions as described above.

The main observation from this study is that the augmented correlation-consistent basis sets of double- and triple-zeta quality [26] as well as the medium-size polarized (MSP) basis set of Sadlej [27] deliver values of *D* that differ among each other by less than 3 cm^{-1} for any level of theory up to CCSD(T), whereas bases constructed from other va-

TABLE II
Dependence of the high-order components of *D* in CH_3CN^- on the quality of the initial basis set designed to describe the neutral molecular host.[a]

Basis set	D^{MP2}	ΔD^{MP3}	ΔD^{MP4}	$\Delta D^{CCSD(T)}$	$D^{CCSD(T)}$
6-31G*[b]	57	7	4	9	76
6-31G**[b]	55	6	4	5	70
6-31+G*[c]	73	6	5	14	97
6-31+G**[c]	70	6	6	10	91
6-31++G**[c]	70	5	6	11	92
6-311+G**[d]	67	5	6	11	89
cc-pVDZ[e]	48	5	4	4	60
aug-cc-pVDZ[f]	75	4	8	21	107
MSP[g]	75	4	8	22	108

[a] Energies in cm^{-1}. See text for description of basis sets.
[b] 8(*sp*)9*d* diffuse set.
[c] 6(*sp*)9*d* diffuse set.
[d] 6(*sp*)8*d* diffuse set.
[e] 7*s*7*p*8*d* diffuse set.
[f] 6*s*6*p*7*d* diffuse set.
[g] 6*s*6*p*6*d* diffuse set.

TABLE III
Dependence of the low-order components of D in $(H_2O\cdots NH_3)^-$ on the quality of the initial basis set designed to describe the neutral molecular host.[a]

Basis set	D^{KT}	ΔD_{ind}^{SCF}	ΔD_{disp}^{MP2}	$\Delta D_{nondisp}^{MP2}$	D^{MP2}
(1) 6-31G*[b]	25	1	24	−7	43
(2) 6-31G**[b]	25	1	25	−11	40
(3) 6-31+G*[c]	34	1	33	−2	66
(4) 6-31+G**[c]	34	1	35	−7	63
(5) 6-31++G**[c]	34	1	36	−7	64
(6) 6-311+G**[c]	33	1	35	−8	61
(7) cc-pVDZ[d]	19	1	21	−10	31
(8) aug-cc-pVDZ[e]	25	1	30	−8	48
(9) MSP[f]	24	1	29	−7	47
(10) aug-cc-pVTZ[g]	24	1	30	−8	47

[a] Energies in cm^{-1}. See text for description of basis sets.
[b] 8(*sp*)9*d* diffuse set.
[c] 7(*sp*)9*d* diffuse set.
[d] 8*s*8*p*9*d* diffuse set.
[e] 7*s*7*p*8*d* diffuse set.
[f] 7*s*7*p*7*d* diffuse set.
[g] 7*s*7*p*6*d* diffuse set.

lence basis sets produce wider variation. Because the extra diffuse basis sets used in all these calculations are large and flexible, we suggest that these variations result from the valence bases. Therefore, we recommend use of the aug-cc-pVDZ or MSP valence basis sets (or aug-cc-pVTZ if resources permit) augmented with additional diffuse bases as detailed earlier in routine electronic structure studies of dipole-bound anions.

Correlation Between KT Level Binding Energy and the SCF Dipole Moment of the Neutral

In the KT approximation, the electron binding energy results from the electrostatic interaction of

TABLE IV
Dependence of the high-order components of D in $(H_2O\cdots NH_3)^-$ on the quality of the initial basis set designed to describe the neutral molecular host.[a]

Basis set	D^{MP2}	ΔD^{MP3}	ΔD^{MP4}	$\Delta D^{CCSD(T)}$	$D^{CCSD(T)}$
6-31G*[b]	43	1	3	30	77
6-31G**[b]	40	1	3	29	73
6-31+G*[c]	66	−1	6	50	122
6-31+G**[c]	63	−1	7	49	118
6-31++G**[c]	64	−1	7	52	122
6-311+G**[c]	61	−1	7	51	117
cc-pVDZ[d]	31	1	3	25	59
aug-cc-pVDZ[e]	48	0	7	56	111
MSP[f]	47	0	6	59	112

[a] Energies in cm^{-1}. See text for description of basis sets.
[b] 8(*sp*)9*d* diffuse set.
[c] 7(*sp*)9*d* diffuse set.
[d] 8*s*8*p*9*d* diffuse set.
[e] 7*s*7*p*8*d* diffuse set.
[f] 7*s*7*p*7*d* diffuse set.

TABLE V

Dependence of the dipole moments μ and polarizabilities α (in CH_3CN) on the quality of the initial basis set designed to describe the neutral molecular host.[a]

Basis set	μ^{SCF}	$\Delta\mu^{MP2}$	$\alpha^{MP2}_{(\perp)}$	$\alpha^{MP2}_{(\parallel)}$
6-31G*[b]	4.241	−0.431	21.19	37.07
6-31G**[b]	4.264	−0.502	21.27	37.08
6-31+G*[c]	4.356	−0.381	21.63	39.35
6-31+G**[c]	4.380	−0.454	21.69	39.35
6-31++G**[c]	4.377	−0.456	21.92	39.38
6-311+G**[d]	4.366	−0.480	21.93	39.20
cc-pVDZ[e]	4.197	−0.510	21.22	36.31
aug-cc-pVDZ[f]	4.341	−0.406	24.29	39.88
MSP[g]	4.333	−0.403	24.60	40.02
aug-cc-pVTZ[h]	4.336	−0.387	24.57	39.87

[a] Dipole moments in D, polarizabilities in a.u. See text for description of basis sets.
[b] 8(*sp*)9*d* diffuse set.
[c] 6(*sp*)9*d* diffuse set.
[d] 6(*sp*)8*d* diffuse set.
[e] 7*s*7*p*8*d* diffuse set.
[f] 6*s*6*p*7*d* diffuse set.
[g] 6*s*6*p*6*d* diffuse set.
[h] 6*s*6*p*7*d* diffuse set.

the excess electron with the SCF charge distribution of the neutral molecule. The distribution is primarily characterized by the dipole moment, μ^{SCF}, but interactions with higher permanent multipoles as well as occupied orbital exclusion effects are also important. There is a striking correlation between μ^{SCF} and D^{KT}, as displayed in Figure 2 for CH_3CN^- and $(H_2O\cdots NH_3)^-$. Moreover, the values of D^{KT} are

TABLE VI

Dependence of the dipole moments μ and polarizabilities α (in $H_2O\cdots NH_3^-$) on the quality of the initial basis set designed to describe the neutral molecular host.[a]

Basis set	μ^{SCF}	$\Delta\mu^{MP2}$	$\alpha^{MP2}_{1(\perp)}$	$\alpha^{MP2}_{2(\parallel)}$	$\alpha^{MP2}_{3(\perp)}$
6-31G*[b]	3.814	−0.126	18.68	25.30	17.43
6-31G**[b]	3.800	−0.198	18.98	25.54	17.66
6-31+G*[c]	3.985	−0.020	19.09	25.96	19.17
6-31+G**[c]	3.982	−0.095	19.35	26.19	19.39
6-31++G**[c]	3.980	−0.097	19.56	26.35	19.49
6-311+G**[c]	3.949	−0.116	19.73	26.50	19.82
cc-pVDZ[d]	3.673	−0.215	19.17	25.78	17.88
aug-cc-pVDZ[e]	3.789	−0.132	21.97	28.56	21.72
MSP[f]	3.772	−0.127	22.57	28.72	22.28
aug-cc-pVTZ[g]	3.774	−0.132	22.35	28.44	22.02

[a] Energies in cm^{-1}. See text for description of basis sets.
[b] 8(*sp*)9*d* diffuse set.
[c] 7(*sp*)9*d* diffuse set.
[d] 8*s*8*p*9*d* diffuse set.
[e] 7*s*7*p*8*d* diffuse set.
[f] 7*s*7*p*7*d* diffuse set.
[g] 7*s*7*p*6*d* diffuse set.

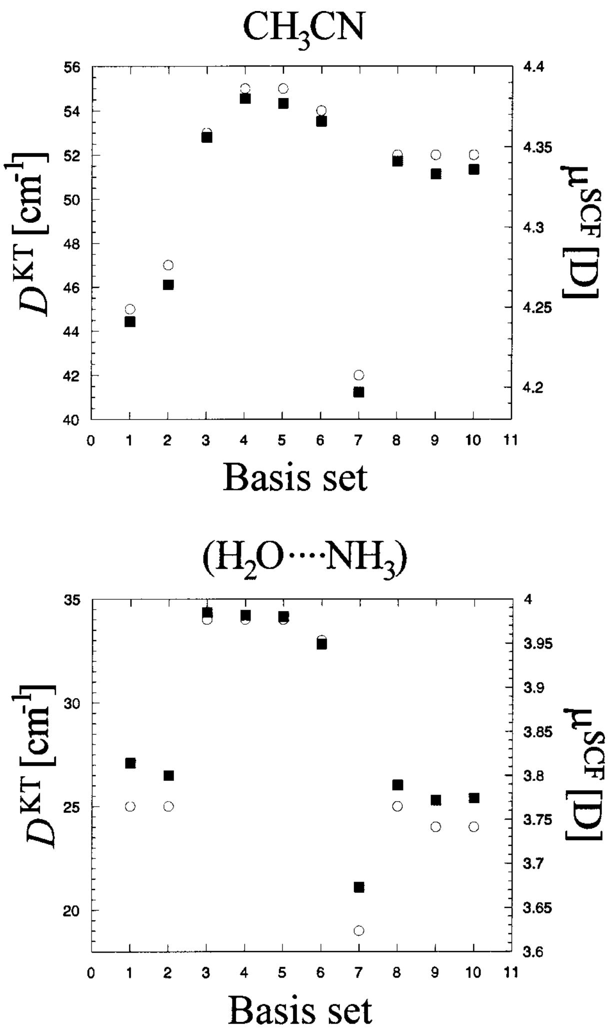

FIGURE 2. Electron binding energies calculated at the KT level (D^{KT}) with various basis sets for CH_3CN^- (top) and $(H_2O\cdots NH_3)^-$ (bottom). μ^{SCF} denotes the corresponding dipole moment calculated from the SCF charge density. The numbers on the horizontal axes correspond to the basis sets used (see Tables I and III for basis set numbering). The circles and the filled squares indicate the KT electron binding energies and the dipole moments, respectively.

numerically stable for the aug-cc-pVDZ, MSP, and aug-cc-pVTZ bases from which we conclude that these are practical basis-set-limiting values of D^{KT}.

The value of D^{KT} can be overestimated by up to 40 and 6% for $(H_2O\cdots NH_3)^-$ and CH_3CN^-, respectively, when common 6-31G* basis sets with standard diffuse functions (+) are employed (see Tables I and III). On the other hand, when the standard diffuse functions are omitted, as in the 6-31G*, 6-31G**, and cc-pVDZ basis sets, the D^{KT} values for CH_3CN^- are too small by 10–20% because of the underestimated SCF dipole moments (see Tables I and V and Fig. 2). For $(H_2O\cdots NH_3)$, the SCF dipole moment of the neutral complex is still slightly overestimated with the 6-31G* and 6-31G** basis sets. However, the lack of the standard diffuse functions compensates for the tendency to overestimate the electron binding energy, and the resulting values of D^{KT} are very close to the basis-set-limiting values. Unfortunately, this agreement results from a cancellation of errors.

The above observations explain why electron binding energies obtained for some dipole-bound anions at the KT level with the 6-31+G*-type basis sets are sometimes in surprisingly good agreement with experimental values. These basis sets may lead to a significant overestimation of D^{KT} that compensates lack of the stabilizing contribution from electron correlation effects.

Correlation Between Electron Binding Energies and Polarizabilities and Dipole Moments of the Neutral

The SCF binding energies include orbital relaxation and thus take into account both static polarization of the neutral molecule by the extra electron and the secondary effect of back polarization. These effects are usually of little importance for dipole-bound anions, in particular when the neutral species has a small dipole moment [14]. Indeed, the $\Delta D_{\mathrm{ind}}^{\mathrm{SCF}}$ term is only 1 cm^{-1} for $(H_2O\cdots NH_3)^-$ and 3–4 cm^{-1} for CH_3CN^-, see Tables I and III.

The contribution denoted $\Delta D_{\mathrm{disp}}^{\mathrm{MP2}}$ results from dynamical correlation between the extra electron and the electrons of the neutral molecule. This stabilizing effect, caused by quantum mechanical charge fluctuations, is as large as the electrostatic-exchange stabilization reproduced at the KT level (see Tables I and III). Even the basis set dependence is similar for the $\Delta D_{\mathrm{disp}}^{\mathrm{MP2}}$ and D^{KT} terms. For instance, an overestimation of D^{KT} in certain basis sets is paralleled by an overestimation of the $\Delta D_{\mathrm{disp}}^{\mathrm{MP2}}$ term, as is the case for $(H_2O\cdots NH_3)^-$ with the 6-31+G*, 6-31+G**, 6-31++G**, and 6-311+G** basis sets (see Table III).

The nature of the $\Delta D_{\mathrm{disp}}^{\mathrm{MP2}}$ contribution indicates that the size of this term should depend on the polarizability of the neutral system along the axis of the dipole ($\alpha_{(||)}^{\mathrm{MP2}}$) and the average separation of the lbe from the molecular framework. It was suggested in Ref. [12] that the latter correlates with D^{KT} and therefore with μ^{SCF}. Therefore, we depict in Fig-

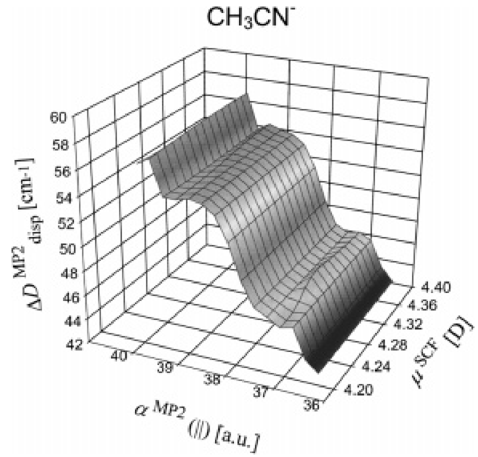

FIGURE 3. The $\Delta D^{\mathrm{MP2}}_{\mathrm{disp}}$ term calculated for the CH_3CN^- anion with various basis sets as a function of both the corresponding MP2 polarizability of the neutral system along the axis of the dipole ($\alpha^{\mathrm{MP2}}_{(||)}$), and the dipole moment of the neutral calculated from the SCF charge density (μ^{SCF}) (mesh interpolation).

ures 3 and 4 the $\Delta D^{\mathrm{MP2}}_{\mathrm{disp}}$ term as a function of both $\alpha^{\mathrm{MP2}}_{(||)}$ and μ^{SCF} for CH_3CN^- and $(H_2O\cdots NH_3)^-$, respectively. It is shown that the $\Delta D^{\mathrm{MP2}}_{\mathrm{disp}}$ contribution strongly correlates with $\alpha^{\mathrm{MP2}}_{(||)}$ but much less so with μ^{SCF}. For both systems, the values of $\Delta D^{\mathrm{MP2}}_{\mathrm{disp}}$ are numerically stable for the aug-cc-pVDZ, MSP, and aug-cc-pVTZ bases for which we assume that the basis-set-limiting values of the dispersion term have been achieved.

It is well known that the Hartree–Fock dipole moments of neutral species are frequently overestimated when compared with correlated or experimental values. This leads to overestimating the electrostatic stability of dipole-bound anions, if calculated at the KT level of theory. The correlation correction to the electrostatic stability first appears at the MP2 level and is contained in $\Delta D^{\mathrm{MP2}}_{\mathrm{nondisp}}$. The nature of the $\Delta D^{\mathrm{MP2}}_{\mathrm{nondisp}}$ contribution indicates that the size of this term should depend on $\Delta\mu^{\mathrm{MP2}}$ and the average separation of the lbe from the molecular framework, related here to μ^{SCF}. Therefore, we depict in Figures 5 and 6 the $\Delta D^{\mathrm{MP2}}_{\mathrm{nondisp}}$ term as a function of both $\Delta\mu^{\mathrm{MP2}}$ and μ^{SCF} for CH_3CN^- and $(H_2O\cdots NH_3)^-$, respectively. The trends in $\Delta D^{\mathrm{MP2}}_{\mathrm{nondisp}}$ are indeed consistent with the *changes* of the dipole moment of the neutral species brought about by the inclusion of the correlation effects. For both systems, electron correlation effects act to decrease the dipole moment; thus both $\Delta\mu^{\mathrm{MP2}}$ and $\Delta D^{\mathrm{MP2}}_{\mathrm{nondisp}}$ are negative in each basis set employed. For both systems, the values of $\Delta D^{\mathrm{MP2}}_{\mathrm{nondisp}}$ are numerically stable for the aug-cc-pVDZ, MSP, and aug-cc-pVTZ bases, and we assume that these are practical basis-set-limiting values of the $\Delta D^{\mathrm{MP2}}_{\mathrm{nondisp}}$ term.

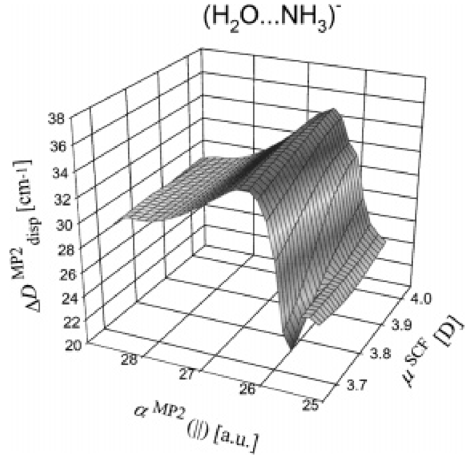

FIGURE 4. The $\Delta D^{\mathrm{MP2}}_{\mathrm{disp}}$ term calculated for the $(H_2O\cdots NH_3)^-$ anion with various basis sets as a function of both the corresponding MP2 polarizability of the neutral system along the axis of the dipole ($\alpha^{\mathrm{MP2}}_{(||)}$) and the dipole moment of the neutral calculated from the SCF charge density (μ^{SCF}) (mesh interpolation).

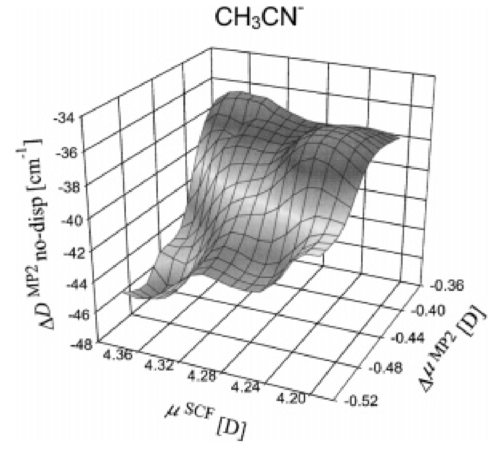

FIGURE 5. The $\Delta D^{\mathrm{MP2}}_{\mathrm{nondisp}}$ term calculated for the CH_3CN^- anion with various basis sets as a function of both the corresponding MP2 correction to the dipole moment of the neutral system ($\Delta\mu^{\mathrm{MP2}}$) and the dipole moment of the neutral calculated from the SCF charge density (μ^{SCF}) (mesh interpolation).

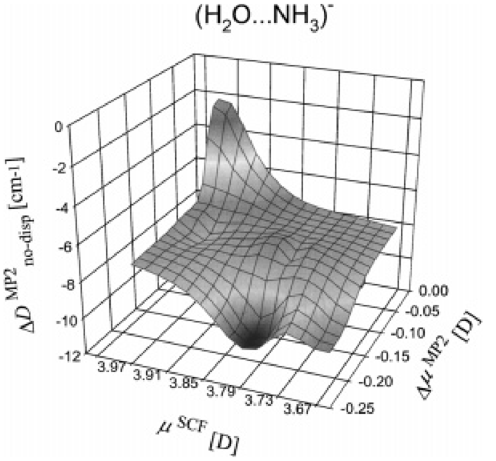

FIGURE 6. The $\Delta D^{MP2}_{nondisp}$ term calculated for the $(H_2O\cdots NH_3)^-$ anion with various basis sets as a function of both the corresponding MP2 correction to the dipole moment of the neutral system ($\Delta\mu^{MP2}$) and the dipole moment of the neutral calculated from the SCF charge density (μ^{SCF}) (mesh interpolation).

Higher-Order Components of the Electron Binding Energy

The convergence of D in the Møller–Plesset perturbative treatment of electron correlation has proven to be very slow for many dipole-bound anions [14]. The third-order contribution ΔD^{MP3} is usually small [12]. For CH_3CN^- this term is stabilizing and represents 3–9% of the total value of D, depending on the basis set used, and its value decreases with improvement of the valence-type basis set (see Table II). For $(H_2O\cdots NH_3)^-$ this term is negligible.

The fourth-order contributions ΔD^{MP4} are usually stabilizing and more important than the third-order contributions [12]. The ΔD^{MP4} represents 5–7% of the total D for CH_3CN^- and 4–6% for $(H_2O\cdots NH_3)^-$ (see Tables II and IV). For both systems, the values of ΔD^{MP4} increase with improvements of the valence-type basis set.

The correlation effects beyond fourth order, approximated in this study by $\Delta D^{CCSD(T)}$, are usually stabilizing and much more important than the third- or fourth-order contributions [12]. The $\Delta D^{CCSD(T)}$ term represents 7–20% and 39–53% of the total D for CH_3CN^- and $(H_2O\cdots NH_3)^-$, respectively. This term is seriously underestimated in poor valence-type basis sets, and the worst case found is the surprisingly small value of $\Delta D^{CCSD(T)}$ (4 cm^{-1}) obtained for the CH_3CN^- anion with the cc-pVDZ basis set (Table II). On the other hand, the results obtained with the aug-cc-pVDZ or MSP basis sets differ by less than 3 cm^{-1}.

Total Electron Binding Energy Obtained in Various Basis Sets

Having now discussed the dependence of various electron binding energy contributions on the basis sets employed, we summarize how the choice of the valence basis set affects the *total* value of D obtained at the CCSD(T) level and we compare $D^{CCSD(T)}$ results with the available experimental results: 108 [15] and 93–145 cm^{-1} [16] for CH_3CN^-, and 111 and 123–129 cm^{-1} [17] for $(H_2O\cdots NH_3)^-$.

The $D^{CCSD(T)}$ for CH_3CN^- and $(H_2O\cdots NH_3)^-$ of 107–108 and 111–112 cm^{-1}, respectively, obtained with the aug-cc-pVDZ and MSP basis sets (see Tables II and IV), to which additional diffuse functions are added as detailed earlier, are in excellent agreement with the available experimental data. Therefore, these theoretical results are not only very close to the basis-set-limiting values of the CCSD(T) method but may also be close to methodological limits. The excellent agreement with experimental results is to some extent surprising in view of the slow convergence of correlation contributions to D, (see Tables II and IV). Nevertheless, our results clearly demonstrate that the errors in electron binding energies due to basis set incompleteness may be practically suppressed when valence basis sets are of aug-cc-pV(D or T)Z or MSP quality and sufficient extra diffuse sets for the excess electron are added.

When the 6-31G* or 6-31G** basis sets are used, the values of $D^{CCSD(T)}$ are underestimated by 30–35% for both anions studied here. The addition of standard diffuse functions (+) leads to better, although still unsatisfactory, results [i.e., the values of $D^{CCSD(T)}$ obtained with the 6-31+G*, 6-31+G**, 6-31++G**, and 6-311+G** basis sets are underestimated by 11–18% for CH_3CN^-, and, surprisingly, *overestimated* by 5–10% for $(H_2O\cdots HN_3)^-$]. The underestimation for CH_3CN^- results from an overestimation of the destabilizing $\Delta D^{MP2}_{nondisp}$ term and underestimation of the stabilizing $\Delta D^{CCSD(T)}$ contribution. The latter term is also underestimated for $(H_2O\cdots NH_3)^-$, but due to the significant overestimation of the D^{KT} and ΔD^{MP2}_{disp} terms, the final values of $D^{CCSD(T)}$ for the water–ammonia anion calculated with the 6-31+G*, 6-31+G**, 6-31++G**, and 6-311+G** basis sets are too large compared to the $D^{CCSD(T)}$ results obtained with the MSP and aug-cc-pVDZ basis sets. We consider this finding important since the 6-311++G** basis set is commonly used in many quantum chemical calculations and, as we have shown above, may lead to unpredictable (under- or overestimated) results for D.

HOW TO CONSTRUCT THE ADDITIONAL DIFFUSE FUNCTIONS FOR THE EXCESS ELECTRON

With the above conclusions in mind concerning how to choose a good *valence* basis, let us now turn our attention to the design of the extra diffuse basis set. The additional basis functions, the role of which is to describe the charge distribution of the excess electron, are usually centered in the region where the excess electron is localized (i.e., on the positive side of the molecular dipole). To describe the molecular orbital occupied by the excess electron in a dipole-bound anion, it is essential that both diffuse s and p functions be contained in the supplemental set because this orbital always has qualitative hybrid sp form depicted in Figure 1. The value of the lowest exponents in the diffuse s and p set is dictated by the dipole moment of the neutral host [12]. The lower the dipole moment, the smaller the exponents needed to describe the spatial extent of the excess electron. We have found that a reliable approach to determine an adequate diffuse set is to calculate the SCF orbitals of the neutral molecule, with a diffuse basis set present, and to monitor the linear combination of atomic orbitals (LCAO) coefficients of the virtual orbital that is singly occupied by the excess electron in the anion. The LCAO coefficients of the most diffuse s and p basis functions should *not* be dominant for this molecular orbital because this suggests that even more diffuse basis functions may be needed. We have found it productive to use even-tempered diffuse functions because, for such a choice, the optimal geometric progression ratio was found to be only slightly dependent on the dipole moment of the neutral [12]. Finally, the largest exponent in the supplemental diffuse set should be smaller by at least a factor of 2 than the most diffuse exponent in the *valence* basis set used to describe the neutral polar molecule. This approach alleviates numerical linear dependencies in the final basis set [12]. The results reported below for two structures of the water trimer anion were obtained with the aug-cc-pVDZ valence basis set, whose use was shown above to yield reliable results, supplemented with additional s, p, and sometimes d and f diffuse functions, as discussed below.

Geometry Optimization and Frequency Calculations

In our previous studies, we centered the additional diffuse functions on one of the nuclei of the neutral [12]. The same approach was applied to the open chainlike C_1 structure of $(H_2O)_3^-$, for which the $5s5p$ even-tempered diffuse basis set was centered on the O atom closest to the positive end of this species' dipole (see Fig. 1). The diffuse s and p functions share exponent values, the largest exponent being 2.8125×10^{-2} a.u., and the geometric progression ratio of 5.0 is used to generate subsequent exponents by division. This basis set was used in the MP2 geometry optimization and harmonic frequency calculations for the anion. In calculations of the vertical electron detachment energy, the diffuse $5s5p$ set was further supplemented with three diffuse d and f functions that share exponent values with the first three s and p additional diffuse functions.

Not surprisingly, we did not find a local minimum for the open structure of the neutral trimer because the geometry optimization procedure, when started at the minimum-energy geometry of the open C_1 anion, converged to the cyclic up-up-down structure that is the global minimum on the potential energy structure of the neutral trimer. The SCF dipole moment of the neutral at its global minimum is only 1.1 D. Hence, it is not sufficient to bind an excess electron. On the other hand, the SCF dipole moment of the neutral at the anionic C_1 open-chainlike structure is $\sim$7.0 D.

The use of nuclei-centered basis functions can lead to numerical problems (i.e., basis set linear dependences) for the cyclic, C_3, up-up-up structure of $(H_2O)_3^-$ because diffuse functions would be centered on all three O atoms. The potential energy surface of the neutral trimer has a local minimum at this structure where the SCF dipole moment of 3.4 D is sufficient to form a weakly bound anionic state (see Fig. 1). However, more diffuse basis functions are required to describe the charge distribution of the excess electron than when the excess electron is more tightly bound in the open C_1 structure. Hence, we supplemented the $5s5p$ set described above with one additional s and one additional set of p functions, both with exponents of 9×10^{-6} a.u. If the resulting $6s6p$ diffuse set were centered on every symmetry-equivalent oxygen atom of the C_3 structure, the final basis set would have serious numerical linear dependencies. For instance, the overlap integral between the two (normalized) most diffuse *s* functions, centered on such oxygen atoms separated by 2.8 Å, would differ from 1.0 by only 1.3×10^{-4}. Therefore, multiple nucleus-centered diffuse basis sets must be avoided. Symmetry dictates that any such supplementary basis be centered on the C_3 axis, so we located a ghost atom (which we label Bq) in the center of the OOO triangle and we equipped it with the 6*s*6*p* diffuse set detailed above. This basis set was used in the MP2 geometry optimization and harmonic frequency calculations for the neutral and the anion. For the neutral, the results are compared below to those obtained with the aug-cc-pVDZ basis set (i.e., without the 6*s*6*p* functions on the Bq center). In calculations of the vertical electron detachment energy for the anion, the diffuse 6*s*6*p* set was further supplemented with four diffuse *d* and three *f* functions, which share exponent values with the four and three least diffuse *s* and *p* functions, respectively.

The geometry optimization for the C_3 structure is straightforward, but the frequency calculations require some attention because the presence of the Bq center leads to three additional modes, the frequencies of which are presented in the last two rows of Table VII. If the basis set were complete, the total energy would not depend on the position of the Bq center, and the "frequencies" of the three Bq modes would be zero. In practice, however, nonzero curvatures must be dealt with. Moreover, a nonzero mass has to be assigned to the Bq center to avoid singularities during formation of the mass-weighted Hessian.

In Table VII we present vibrational frequencies for the neutral C_3 trimer obtained with the aug-cc-pVDZ basis set (second column) followed by the vibrational shifts induced by the presence of the 6*s*6*p* functions on the Bq center. We explored the dependence of these shifts on the mass of the Bq pseudo atom (M_{Bq}), which was varied over the 10^{-5}–10^{+5} amu range, and selected results are reported in columns 3–5 of Table VII. We note that the shifts $\Delta\nu$ vibrational frequencies resulting from incom-

TABLE VII

Harmonic vibrational frequencies (in cm^{-1}) for the neutral and anionic cyclic, up-up-up, water trimer calculated at the MP2 level of theory.

	Neutral				Anion
		6*s*6*p* on Bq			6*s*6*p* on Bq
Symmetry of vibrational modes	No Bq	$\Delta\nu$ $M_{\mathrm{Bq}} = 10^{-5}$	$\Delta\nu$ $M_{\mathrm{Bq}} = 10^{-4}$	$\Delta\nu$ $M_{\mathrm{Bq}} = 10^{4}$	$\nu^A - \nu^N$ $M_{\mathrm{Bq}} = 10^{4}$
1a	3900	−0.6	−0.2	−0.5	−3.4
1e	3900	−0.6	−0.5	−0.6	−3.6
2e	3649	−1.4	−1.3	−1.4	−5.9
2a	**3596**	−2.1	**6.4**	−1.9	−7.0
3a	1664	−0.4	−0.4	−0.3	−1.2
3e	1637	−0.1	−0.2	−0.1	−0.5
4a	804	4.3	4.3	4.4	5.8
4e	528	2.2	2.2	2.2	4.0
5a	517	−0.5	−0.5	−0.2	−7.1
5e	355	1.0	1.0	1.1	−0.9
6a	215	0.4	0.4	0.4	−1.0
7a	189	3.0	3.0	3.1	−23.9
6e	183	0.4	0.4	0.5	−0.1
7e	119	6.9	6.9	7.3	9.4
8a (Bq)	—	$\nu = 11327$	$\nu =$ **3573**	$\nu = 5$	$\nu = 5$
8e (Bq)	—	$\nu = 7320$	$\nu = 2315$	$\nu = 3$	$\nu = 3$

The basis functions centered at the nuclei are of the aug-cc-pVDZ quality. The Bq center is placed on the C_3 axis and six *s* and six *p* diffuse functions are centered there. In frequency calculations, the mass of the Bq center is set to M_{Bq} (in amu). $\Delta\nu$ stands for the frequency shift for the neutral trimer induced by the presence of the diffuse 6*s*6*p* functions on the Bq center. $\nu^A - \nu^N$ stands for the difference between the frequency of the anion and the neutral. In the last two rows, vibrational frequencies of the modes associated with the Bq center are reported.

pleteness of the aug-cc-pVDZ basis set are relatively small. They are larger for the soft intermonomer modes (4a to 7e) than for the intramonomer modes (1a to 3e) and the largest shift of 7 cm^{-1} occurs for the softest mode 7e. The shifts for intramonomer modes rarely exceed 1 cm^{-1} with the exception of mode 2a for $M_{\text{Bq}} = 10^{-4}$ amu (set in boldface in Table VII). This shift of 6 cm^{-1} apparently results from the coupling between the intramonomer mode 2a and the Bq mode 8a (also boldface in Table VII). On the other hand, if the mass of the Bq center is chosen to make the frequencies of the Bq modes either significantly larger or smaller than any of the $3N - 6$ actual frequencies of $(H_2O)_3$, we observe remarkable stability of all vibrational frequencies of $(H_2O)_3$ (columns 3 and 5 of Table VII).

In the last column of Table VII we present the differences in vibrational frequencies of the neutral and the anion. The minimum energy structures of the neutral and the anion are very similar. The bond distances in the anion are slightly larger than in the neutral, but the differences do not exceed 0.001 Å, and the differences in interatomic angles do not exceed 2°. All these geometrical changes lead to an increase of the dipole moment of the neutral by only 0.1 D in comparison with the value obtained for the minimum energy structure of the neutral. The largest frequency shift of -24 cm^{-1} is observed for the 7a intermonomer mode, which describes a motion with the OH$\cdots$O hydrogen bonds nearly fixed and the other hydrogen atoms swinging in-phase. This motion, similar to breathing of a flower, is accompanied by a noticeable change of the dipole moment of the neutral. The geometrical relaxation of the system upon electron attachment is primarily along this mode. The related out-of-phase swinging mode 7e is blue-shifted by 9 cm^{-1}. The H-bond bending modes 4a and 4e are also blue-shifted by ~5 cm^{-1}, whereas the in-phase rocking-and-H-bond-bending mode 5a is red-shifted by ~7 cm^{-1}. Other intermonomer modes, in particular the H-bond stretches 6a and 6e, are red-shifted by less than 1 cm^{-1}. All intramonomer modes are red-shifted, which is consistent with an elongation of all OH bonds, but the shifts do not exceed 7 cm^{-1}.

Electron Binding Energies

The role of *d*- and *f*-symmetry basis functions in calculations of vertical electron detachment energies is documented in Table VIII for the low-order components [Eqs. (5)–(11)] and in Table IX for the MP3, MP4, and CCSD(T) [Eqs. (12) and (13)] contributions. The *d*-symmetry functions are relatively important for the weakly bound cyclic structure as they contribute 14% to the total value of *D*. Their relative importance is smaller for the more strongly bound open structure, even though the absolute contribution of 20 cm^{-1} is comparable with the typical uncertainties in photoelectron spectroscopy experiments of ±40 cm^{-1} [28]. As was noted in Ref. [12], primarily the low-order components of *D*, such as the KT term, the SCF polarization, and the MP2 contribution are affected by the presence of *d* diffuse functions, whereas the contributions beyond MP2 are relatively unchanged. The *f*-symmetry diffuse functions contribute little to electron binding energies and may be neglected even in calculations aiming at experimental accuracy of ±40 cm^{-1}.

The convergence of *D* with respect to electron correlation treatment is slow (see Table IX). The contribution ΔD^{MP3} is unimportant, but ΔD^{MP4}, which is usually dominated by the contributions from single and triple excitations, contributes more than 5% of *D* for the open structure. Finally, correla-

TABLE VIII

Dependence of the low-order components of *D* [Eqs. (5)–(11)] in $(H_2O)_3^-$ on the quality of the additional diffuse basis set designed to describe the charge distribution of the excess electron.[a]

Structure	Basis	D^{KT}	$\Delta D^{\text{SCF}}_{\text{ind}}$	$\Delta D^{\text{MP2}}_{\text{disp}}$	$\Delta D^{\text{MP2}}_{\text{nondisp}}$	D^{MP2}
Cyclic C_3	6*s*6*p*	8.3	0.2	10.4	−5.0	13.9
	6*s*6*sp*4*d*	10.8	0.2	13.0	−6.4	17.6
	6*s*6*p*4*d*3*f*	11.0	0.3	13.3	−6.5	18.1
Open C_1	5*s*5*p*	567	43	416	−113	913
	5*s*5*p*3*d*	588	46	414	−117	931
	5*s*5*p*3*d*3*f*	589	46	417	−117	935

[a] Energies in cm^{-1}. See text for description of basis sets.

TABLE IX

Dependence of the high-order components of D [Eqs. (12) and (13)] in $(H_2O)_3^-$ on the quality of the additional diffuse basis set designed to describe the charge distribution of the excess electron.[a]

Structure	Basis	D^{MP2}	ΔD^{MP3}	ΔD^{MP4}	$\Delta D^{CCSD(T)}$	$D^{CCSD(T)}$
Cyclic C_3	6*s*6*p*	13.9	0.5	2.0	26.3	42.7
	6*s*6*sp*4*d*	17.6	0.7	2.3	29.0	49.6
Open C_1	5*s*5*p*	913	−10	74	202	1178
	5*s*5*p*3*d*	931	−9	72	203	1197

[a] Energies in cm^{-1}. See text for description of basis sets.

tion beyond fourth order, approximated here by $\Delta D^{CCSD(T)}$, contributes 58 and 17% of D for the cyclic and open structures, respectively. Again, the contributions from single and triple excitations are dominant. These results indicate that a fourth-order treatment of electron correlation is, in general, not sufficient for dipole-bound anions. The results obtained within the CCSD(T) approach are usually in good agreement with experiment [14, 18]. For example, our vertical detachment energy for the open structure of 1197 cm^{-1} is in excellent agreement with the experimental result of 1145 ± 56 cm^{-1} [29].

Conclusions

The basis set saturated values of electron binding energies in dipole-bound anions can nowadays be obtained with a relatively modest computational effort. In our approach, an effective basis set is constructed as a combination of a standard valence-type basis set, designed to describe the neutral molecular core, and an extra diffuse set designed to describe the charge distribution of the extra electron.

There are two roles that the valence-type basis set must fulfill. First, it should accurately describe the static charge distribution of the neutral, and therefore the electrostatic potential experienced by the excess electron. Second, it should be flexible enough to allow for the polarization and dispersion stabilization of the anion upon electron attachment.

For two model systems, $(H_2O\cdots NH_3)^-$ and CH_3CN^-, we demonstrated that the aug-cc-pVDZ, aug-cc-pVTZ, and the MSP valence basis sets deliver electron binding energies that differ among each other by less than 3 cm^{-1} for any level of theory up to CCSD(T). Since the use of the aug-cc-pVTZ basis set leads to a relatively large number of basis functions and the MSP basis set is known to produce significant basis set superposition errors, which may affect optimization of lowest energy structures, we therefore suggest the use of the aug-cc-pVDZ basis set in routine electronic structure studies of dipole-bound anions.

The favorable behavior of the aug-cc-pVNZ type bases echoes the findings of researchers who found this kind of basis to be especially well suited for obtaining high-quality extrapolated total energies [30] and other properties [31].

The exponents of the extra diffuse basis set should be small enough to describe the diffuse charge distribution of the excess electron. Not only *s*- but also *p*- and sometimes *d*-symmetry functions are required to describe a hybrid orbital localized on the positive side of the molecular dipole. Moreover, this diffuse set should be flexible enough to describe dispersion stabilization between the excess electron and the electrons of the neutral species. For instance, for the cyclic water trimer discussed in this study, with the SCF dipole moment of the neutral of 3.4 D, the lowest exponents of extra diffuse s and p functions were as small as 9×10^{-6} a.u. We recommend constructing the extra diffuse basis as an even-tempered series of functions with a geometric progression ratio in the 3.0–5.0 range, depending on the required accuracy and the size of the dipole moment of the neutral [12]. The diffuse *s*- and *p*-symmetry functions are critical for the description of the excess electron; the d functions still contribute noticeably to the excess electron stability; but *f*-symmetry functions can probably be neglected.

The extra diffuse set may be centered on a nucleus or on a ghost atom. The latter choice is favored in the case of highly symmetric species, such as the cyclic C_3 water trimer, for which centering of the extra diffuse set on every symmetry-equivalent atom would lead to numerical linear dependencies. In frequency calculations, with extra diffuse functions centered on a ghost atom, the modes related to the motion of the ghost center must be separated and the artificial mass of the ghost center needs to be either very large (10^5 amu) or very small (10^{-5} amu) to avoid coupling between physical modes of the molecule and the modes of the ghost center.

ACKNOWLEDGMENTS

The authors thank Ms. Robyn Barrios for her help. This work was supported by the NSF Grant CHE9618904 to J.S. and the Polish State Committee for Scientific Research (KBN) Grant No. 3 T09A 049 15 (Contract No. 0337/TO9/98/15) to P.S. and M.G. The computer time provided by the Center for High Performance Computing at the University of Utah is also gratefully acknowledged. M.G. was supported by the Division of Chemical Sciences of the Office of Basic Energy Sciences of the U.S. Department of Energy. This work was performed in part under auspices of the U.S. Department of Energy, under Contract No. DE-AC06-76RLO 1830, with Battelle Memorial Institute, which operates the Pacific Northwest National Laboratory. K. D. Jordan and F. Vila are acknowledged for providing an initial geometry for the open C_1 structure of $(H_2O)_3^-$.

References

1. Castelman, Jr., A. W.; Bowen, Jr., K. H. J Phys Chem 1996, 100, 12911–12944.
2. Fermi, E.; Teller, E. Phys Rev 1947, 72, 399–408; Wightman, A. S. Phys Rev 1950, 77, 521–528.
3. Levy-Leblond, J. M. Phys Rev 1967, 153, 1–4.
4. Mittleman, M. H.; Myerscough, V. P. Phys Lett 1966, 23, 545–546.
5. Jordan, K. D.; Luken, W. J Chem Phys 1976, 64, 2760–2766.
6. Garret, W. R. J Chem Phys 1982, 77, 3666–3673.
7. Koopmans, T. Physica (Amsterdam) 1934, 1, 104–113.
8. Gutowski, M.; Skurski, P.; Boldyrev, A. I.; Simons, J.; Jordan, K. D. Phy Rev A 1996, 54, 1906–1909.
9. Gutsev, G. L.; Adamowicz, L. J Phys Chem 1995, 99, 13412–13421.
10. Skurski, P.; Gutowski, M. J Chem Phys 1998, 108, 6303–6311.
11. Gutowski, M.; Skurski, P. J Phys Chem B 1997, 101, 9143–9146.
12. Gutowski, M.; Jordan, K. D.; Skurski, P. J Phys Chem A 1998, 102, 2624–2633.
13. Skurski, P.; Gutowski, M.; Simons, J. J Chem Phys 1999, 110, 274–280.
14. Gutowski, M.; Skurski, P. Recent Res Devel Phys Chem 1999, 3, 245–260.
15. Desfrançois, C.; Abdoul-Carime, H.; Khelifa, N.; Schermann, J. P. Phys Rev Lett 1994, 73, 2436–2439.
16. Desfrançois, C. Phys Rev A 1995, 51, 3667–3675.
17. Abdoul-Carime, H.; Wakisaka, W.; Bouteiller, Y.; Desfrançois, C.; Schermann, J. P. Z Phys D 1997, 40, 55–61.
18. Smith, D. M. A.; Smets, J.; Elkadi, Y.; Adamowicz, L. J Chem Phys 1997, 107, 5788–5793.
19. Bartlett, R. J.; Stanton, J. F. In Reviews in Computational Chemistry; Lipkowitz, K. B.; Boyd, D. B., Eds.; VCH: New York, 1994; Vol. V; Taylor, P. R. In Lecture Notes in Quantum Chemistry II; Roos, B. O., Ed.; Springer: Berlin, 1994.
20. Jeziorski, B.; Moszyński, R.; Szalewicz, K. Chem Rev 1994, 94, 1887–1930.
21. Chałasiński, G.; Szczęśniak, M. M. Chem Rev 1994, 94, 1723–1765.
22. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. GAUSSIAN 98, Revision A.7; Gaussian: Pittsburgh, 1998.
23. Schaftenaar, G. MOLDEN, CAOS/CAMM Center, The Netherlands, 1991.
24. Schmidt, M. W.; Ruedenberg, K. J Chem Phys 1979, 71, 3951–3962.
25. Gutowski, M.; Simons, J. J Chem Phys 1990, 93, 3874–3880.
26. Kendall, R. A.; Dunning, Jr., T. H.; Harrison, R. J. J Chem Phys 1992, 96, 6796–6806.
27. Sadlej, A. J. Theor Chim Acta 1991, 79, 123–140.
28. Hendricks, J. H.; de Clercq, H. L.; Lyapustina, S. A.; Bowen, Jr., K. H. J Chem Phys 1997, 107, 2962–2967.
29. Hendricks, J. H.; de Clercq, H. L.; Lyapustina, S. A.; Fancher, C. A.; Lippa, T. P.; Collins, J. M.; Arnold, S. T.; Lee, G. H.; Bowen, K. H. In Proceedings of the Yamada Conference No. XLIII, May 1995; Structure and Dynamics of Clusters; Universal Academy Press: Tokyo, 1995.
30. Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. J Chem Phys 1997, 106, 9639–9646.
31. Halkier, A.; Klopper, W.; Helgaker, T.; Jørgensen, P.; Taylor, P. R. J Chem Phys 1999, 111, 9157–9167.