

## A bi-dipole-bound dianion

Piotr Skurski<sup>a,b</sup>, Maciej Gutowski<sup>c</sup>, Jack Simons<sup>a,\*</sup>

<sup>a</sup> Henry Eyring Center for Theoretical Chemistry, Department of Chemistry, University of Utah, Salt Lake City, UT 84112, USA

<sup>b</sup> Department of Chemistry, University of Gdańsk, 80-952 Gdańsk, Poland

<sup>c</sup> Materials Resources, Pacific Northwest National Laboratory, Richland, WA 99352 USA

Received 28 January 2000

### Abstract

The possibility of binding one and two excess electrons by a molecule with two polar ends, each of which is capable of binding one electron, is studied using electronic structure methods. In the case of the singly charged anion, we find, as expected, a pair of nearly degenerate  ${}^2\Sigma_g^+$  and  ${}^2\Sigma_u^+$  states. For the dianion, stable open-shell triplet and singlet electronic states are reported, both of which have one electron on each polar terminus. Numerical results are presented for the mono- and di-anions of  $(\text{LiCN})_2 \cdots \text{HCCH} \cdots (\text{NCLi})_2$ , and our estimation of the vertical electronic stability of  $((\text{LiCN})_2 \cdots \text{HCCH} \cdots (\text{NCLi})_2)^{2-}$  is 0.84 eV. © 2000 Elsevier Science B.V. All rights reserved.

### 1. Introduction

It is well known that valence-saturated polar molecules can bind an excess electron by their dipole potential [1]. Recently, the possibility of binding *two* extra electrons to the positive terminus of a highly polar molecular system was also studied and critical conditions for such binding were formulated within the fixed-finite-dipole model [2]. Subsequently, a real molecule that fulfills the two-electron critical binding requirements was found and characterized [3]. Our efforts to study the existence and properties of such unusual mono- and di-anionic species also involved mixed valence/dipole-bound molecular dianions possessing one valence-bound excess electron and one that is bound by the dipole potential of the molecule [4]. Very recently, we also reported a nu-

merical study of electron binding to linear molecules having *two* polar ends and a vanishing total dipole moment, and we termed the resulting anionic states as bi-dipole-bound states (bdbbs) [5].

For an electron that is bound due primarily to its static Coulomb interaction with the charge distribution of the neutral molecule, the one-particle Schrödinger Eq. (1)

$$\left( -\frac{1}{2}\Delta + V_{\text{elst}}^{\text{exact}} + V_{\text{ooe-exch}}^{\text{exact}} \right) \phi = \varepsilon \phi \quad (1)$$

possesses a bound solution [6]. Here,  $V_{\text{elst}}^{\text{exact}}$  represents the classical electrostatic potential from the exact charge distribution  $\rho^{\text{exact}}$  of the neutral molecule

$$V_{\text{elst}}^{\text{exact}} \phi(1) = \int \frac{\rho^{\text{exact}}(2)}{r_{1,2}} d\tau_2 \phi(1) \quad (2)$$

and the occupied-orbital exclusion effects (ooe) and the exchange interaction between the excess electron

\* Corresponding author. Fax: +1-801-581-4353; e-mail: simons@chemistry.utah.edu

and the other electrons are included in the  $V_{\text{ooe-exch}}^{\text{exact}}$  potential. Since, in practical calculations,  $V_{\text{elst}}^{\text{exact}}$  and  $V_{\text{ooe-exch}}^{\text{exact}}$  are not known, we often approximate Eq. (1) at the Hartree–Fock self-consistent field (SCF) level, with  $\rho^{\text{exact}}$  replaced by the SCF density for the neutral ( $\rho^{\text{HF}}$ ) and  $V_{\text{ooe-exch}}^{\text{exact}}$  replaced by the SCF exchange operators  $K$  [7]. In this manner Eq. (1) becomes equivalent to the Koopmans' theorem (KT) description of the excess electron binding, with  $\varepsilon$  being equal to the energy of the virtual orbital  $\phi$  obtained in the SCF calculation for the neutral molecule [7].

The  $V_{\text{elst}}$  operator for a neutral molecule of  $D_{\infty h}$  symmetry with two polar ends separated by a distance  $2L$  may be approximated (especially at distances exterior to the charge density of the neutral system) by a sum of two dipole potentials having opposite orientations. With  $V_{\text{ooe-exch}}$  neglected and  $V_{\text{elst}}$  so approximated, Eq. (1) reduces to

$$\left( -\frac{1}{2} \nabla^2 + V_1(+\mu, +L) + V_2(-\mu, -L) \right) \phi^{\text{bdbbs}} = \varepsilon^{\text{bdbbs}} \phi^{\text{bdbbs}} \quad (3)$$

where  $V_1$  and  $V_2$  describe the electron–dipole interactions. The solutions of Eq. (3) for large  $L$ s are expected, by symmetry, to be of the form

$$\phi_{\pm}^{\text{bdbbs}} \approx \frac{1}{\sqrt{2}} (\chi_1 \pm \chi_2) \quad (4)$$

$$\varepsilon_{\pm}^{\text{bdbbs}} \approx e \pm H_{12} \quad (5)$$

where  $\chi$  and  $e$  are the eigenfunctions and energies of the one-particle Schrödinger equation for the dipole-bound anion

$$\left( -\frac{1}{2} \nabla^2 - \frac{\mu \cos \theta}{r^2} \right) \chi = e \chi \quad (6)$$

with  $\chi_1$  centered at  $L$  and  $\chi_2$  at  $-L$ . The  $+$  and  $-$  solutions in Eq. (4) describe  $\sigma_g$  and  $\sigma_u$  orbitals, respectively. The term  $H_{12}$

$$H_{12} = \left\langle \chi_1 \left| -\frac{1}{2} \nabla^2 + V_1(+\mu, +L) + V_2(-\mu, -L) \right| \chi_2 \right\rangle \quad (7)$$

which relates to the through-bond coupling of the two dipole-bound orbitals, approaches zero as  $L \rightarrow \infty$ , but produces a non-vanishing  $\varepsilon_+^{\text{bdbbs}} - \varepsilon_-^{\text{bdbbs}}$  energy splitting for finite  $L$ s. Knowledge of these couplings, even for small van der Waals complexes such as we

have examined, is important because of the role such interactions play in many biological electron and excitation transfer processes. On the basis of ab initio calculations, we recently reported the strength of these couplings for the monoanions of  $(\text{HCN})_n \cdots \text{HC} \equiv \text{CH} \cdots (\text{NCH})_n$  (where  $n = 2-4$ ) [5]; in the present contribution we extend this study to a system in which the electrons are more tightly bound.

Our ab initio study on linear  $(\text{HCN})_n \cdots \text{HC} \equiv \text{CH} \cdots (\text{NCH})_n$  ( $n = 1-4$ ) showed that such molecules support two electronically stable anionic states of  ${}^2\Sigma_g^+$  and  ${}^2\Sigma_u^+$  symmetry, for  $n > 1$  [5]. These states are nearly degenerate (the coupling  $H_{12}$  is less than  $5 \text{ cm}^{-1}$ ) even for the shortest ( $n = 2$ ) stable monoanion. Therefore, we concluded that the through-bond coupling of the two dipole-bound orbitals is very small in the  $(\text{HCN})_n \cdots \text{HCCH} \cdots (\text{NCH})_n$  species. The electron binding energy ( $E$ ) for the corresponding monoanions depends both on the polarity of the  $(\text{HCN})_n$  group and the spacing between the groups, which relates to the dipole–dipole repulsion. In particular, our vertical electron attachment energies calculated at the MP2 level for the  $u$  states were 197, 637, and  $982 \text{ cm}^{-1}$ , for  $n = 2, 3$  and  $4$ , respectively [5].

In the present contribution, we study the possibility of binding *two* excess electrons to a system possessing two more strongly polar ends. Our preliminary search undertaken for  $(\text{HCN})_n \cdots \text{HCCH} \cdots (\text{NCH})_n$  suggested that stronger dipoles are required to bind *two* electrons for chemically achievable system lengths ( $n$ ) [5]. Therefore, we decided to replace  $(\text{HCN})_n$  with  $(\text{LiCN})_n$  because: (i) it is known that LiCN and  $(\text{LiCN})_2$  are very polar and possess large dipole moments (9.4 and 21.2 D, respectively [4]); and (ii) we have experience studying electron binding to these species [4,8]. Hence, we focused our studies on  $(\text{LiCN})_n \cdots \text{HCCH} \cdots (\text{NCLi})_n$  ( $n = 1, 2$ ), and we investigated the stabilities of the corresponding dianions.

## 2. Computational methods

The equilibrium geometries of the neutral and anionic species for  $n = 1$  and  $2$  were optimized and their harmonic vibrational frequencies were calculated at the second-order Møller–Plesset (MP2) per-

turbation theory level. In all calculations, the values of  $\langle S^2 \rangle$  never exceeded 2.0003 for triplets, and 0.7502 for doublet states, respectively, so we are confident that spin-contamination effects are not serious. The electronic stabilities of the anions in their ground states were calculated using a supermolecular approach (i.e., by subtracting the energies of the anion from those of the neutral). Since the largest system studied contains 14 heavy atoms (which involves almost 400 contracted basis functions), we had to limit the level of our calculations to the MP4 level. In order to study open-shell singlet states of the dianions, we employed the complete active space SCF (CASSCF) method [9–12] with the active space limited to two orbitals ( $\sigma_g, \sigma_u$ ), and we then computed the second-order electron correlation correction (i.e., the CAS-PT2 energy) [13].

All calculations were performed with the GAUSSIAN 98 program [14], on 500 MHz dual processor Intel Pentium III computers and on an SGI Origin2000 numerical server. The three-dimensional plots of molecular orbitals were generated with the MOLDEEN program [15].

The choice of the atomic orbital basis sets used to describe the neutral molecule and the excess bound electrons is very important for reproducing the correct value of the electron binding energy. The basis sets must be flexible enough to describe the static charge distribution of the neutral molecular host, and to allow for polarization and dispersion stabilization of the anions upon electron attachment. For these purposes, we used the aug-cc-pVDZ [16] basis set supplemented with additional diffuse functions. The addition of extra diffuse functions having very low exponents was necessary especially in order to describe properly the dianion's pair of excess electrons. In particular, we supplemented the aug-cc-pVDZ basis set with extra even-tempered [17] three-term s and three-term p sets of diffuse functions centered on all Li atoms. The extra diffuse s and p functions do not share exponent values and the geometric progression ratio was equal to 3.2 [18], and we started to build up the exponents from the lowest s and p exponents included in the aug-cc-pVDZ basis set designed for lithium. As a consequence, we achieved lowest exponents of  $2.6367188 \times 10^{-5}$  and  $1.7669678 \times 10^{-5}$  a.u. for s and p symmetry, respectively. In order to check if our calculated binding

energies can be improved by using an even better basis set, we replaced the aug-cc-pVDZ basis with an aug-cc-pVTZ [16] basis and we calculated the vertical stabilities of the dianion at the SCF level (the triple-zeta basis set involves almost 750 basis functions). We found that the electron binding energy of the dianion increases only by 0.03 eV so we are confident that the aug-cc-pVDZ basis that we originally use to describe the neutral core is good enough to reproduce correct binding energies.

### 3. Results

#### 3.1. Electrostatic estimations

A first-order electrostatic argument suggests that a dianion, with its two centers of excess charge spatially separated by a distance  $r$ , may be electronically stable if the Coulomb repulsion  $e^2/r$  between the two extra electrons is smaller than the electron binding energy for the monoanion. For the  $\text{LiCN} \cdots \text{HCCH} \cdots \text{NCLi}$  species the equilibrium distance  $r$  between the terminal Li atoms is 14.285 Å and hence the  $e^2/r$  repulsion is 1.01 eV whereas the KT electron binding energy for the  $(\text{LiCN} \cdots \text{HCCH} \cdots \text{NCLi})^-$  is only 0.58 eV and even for the  $\text{LiCN}^-$  anion the  $E^{\text{KT}}$  is only 0.66 eV. We therefore conclude that the  $(\text{LiCN} \cdots \text{HCCH} \cdots \text{NCLi})^{2-}$  doubly charged system is unlikely to be electronically stable.

In order to reduce the  $e^2/r$  repulsion and also increase the electron binding energy of the terminal polar group we switched to  $(\text{LiCN})_2 \cdots \text{HCCH} \cdots (\text{NCLi})_2$ , for which the  $e^2/r$  repulsion is 0.59 eV (the equilibrium distance between terminal Li atoms in the neutral molecule  $r = 24.614$  Å) whereas the electron binding energy for  $((\text{LiCN})_2 \cdots \text{HCCH} \cdots (\text{NCLi})_2)^-$  calculated at the Koopmans' level is 1.217 eV. We conclude that the resulting  $((\text{LiCN})_2 \cdots \text{HCCH} \cdots (\text{NCLi})_2)^{2-}$  dianion should be electronically stable and its KT binding energy should be ca. 0.6 eV.

#### 3.2. MP2 equilibrium geometries of neutral $(\text{LiCN})_2 \cdots \text{HCCH} \cdots (\text{NCLi})_2$ and its mono- and di-anion

The  $D_{\infty h}$  symmetry minima on the MP2 potential energy surface of the neutral, mono- and dianionic

Table 1

MP2 equilibrium geometries for the neutral ( $^1\Sigma_g^+$ ), monoanion ( $^2\Sigma_g^+ / ^2\Sigma_u^+$ ) and dianion ( $^3\Sigma_u^+$ ) of  $(\text{LiCN})_2 \cdots \text{HC} \equiv \text{CH} \cdots (\text{NCLi})_2$  at their  $D_{\infty h}$  minima<sup>a</sup> (distances in Å)

Parameter	$^1\Sigma_g^+$	$^2\Sigma_u^+$	$^3\Sigma_u^+$
	neutral	monoanion	dianion
$r(\text{CC})$	1.236	1.236	1.237
$r(\text{CH})$	1.084	1.085	1.085
$l_1$	2.252	2.263	2.316
$k_1$	1.197	1.198	1.198
$m_1$	1.991	2.006	2.026
$l_2$	1.986	1.966	1.953
$k_2$	1.190	1.192	1.194
$m_2$	1.988	2.036	2.106

<sup>a</sup>For the definition of the parameters, see Fig. 1.

molecules are characterized in Table 1 and the geometric parameters are defined in Fig. 1.

Our calculations indicate that an attachment of the first and second electrons leads to only marginal changes in the neutral acetylene spacer (the differences in bond lengths are as small as 0.001 Å, see Table 1). This is also the case for the intramonomer C≡N bonds (parameters  $k_1$  and  $k_2$ ) for which the changes are less than 0.002 Å. However, the Li–C bond lengths are increased by attachment of the first and second electron. In particular, the value of  $m_2$  increases by 0.12 Å from the neutral to the dianion.

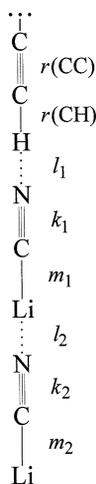


Fig. 1. Schematic structure of  $(\text{LiCN})_2 \cdots \text{HC} \equiv \text{CH} \cdots (\text{NCLi})_2$  and the definition of the geometrical parameters used in this work (only half of the molecule is shown since the system possesses  $D_{\infty h}$  symmetry).

There are also some distortions of the intermolecular bonds between LiCN monomers as  $l_1$  increases by 0.06 and  $l_2$  decreases by 0.03 Å upon attachment of two electrons. Taking all the geometrical changes that occur during the attachment of excess electrons into account, we find that the dianion is longer than the neutral system by 0.38 Å. This is likely related to reducing the Coulomb  $e^2/r$  repulsion between two extra negative charges that are localized at the ends of the molecule.

### 3.3. Electron binding energies for mono- and dianion of $(\text{LiCN})_2 \cdots \text{HC} \equiv \text{CH} \cdots (\text{NCLi})_2$

There are two electronically bound  $^2\Sigma_g^+$  and  $^2\Sigma_u^+$  anionic states of  $(\text{LiCN})_2 \cdots \text{HC} \equiv \text{CH} \cdots (\text{NCLi})_2$ . In Table 2 we report electron binding energies for the  $u$  state only as the energy difference between these two anionic states is 4  $\text{cm}^{-1}$  which is similar to the 5  $\text{cm}^{-1}$  found for  $((\text{HCN})_2 \cdots \text{HC} \equiv \text{CH} \cdots (\text{HCN})_2)^-$  [5]. The electron binding energy is dominated by the Koopmans' contribution which takes into account the electrostatic and exchange interactions of the excess electron with the SCF charge distribution of the neutral molecule. The values of this term are 1.217, 1.255, and 1.308 eV for the equilibrium geometries of the neutral, monoanion, and dianion, respectively. The effect of orbital relaxation, which is given by the difference between  $E^{\text{SCF}}$  and  $E^{\text{KT}}$  and which describes polarization of the

Table 2

Vertical electron binding energies  $E$  (in eV) for the monoanion of  $(\text{LiCN})_2 \cdots \text{HC} \equiv \text{CH} \cdots (\text{NCLi})_2$  at the equilibrium  $D_{\infty h}$  geometries of the neutral, anionic and dianionic systems<sup>a</sup>

	$D_{\infty h}$ geometry of the neutral	$D_{\infty h}$ geometry of the monoanion	$D_{\infty h}$ geometry of the dianion
$E^{\text{KT}}$	1.217	1.255	1.308
$E^{\text{SCF}}$	1.259	1.297	1.350
$E^{\text{MP2}}$	1.266	1.301	1.350
$E^{\text{MP3}}$	1.293	1.329	1.379
$E^{\text{MP4}}$	1.303	1.337	1.386

<sup>a</sup>All results obtained with the aug-cc-pVDZ basis set augmented with the 3s3p diffuse set centered at all Li atoms.

neutral molecule by the excess electron, is very small and amounts to 0.042 eV for the geometry of the monoanion. The MP2 electron binding energy includes electron correlation effects that are found to be relatively unimportant in the case of the monoanion, as indicated by the small MP2 contributions to the total binding energy (0.001–0.007 eV). Higher order corrections calculated at the MP3 and MP4 levels are also small and lead to our final estimation of the first ( ${}^2\Sigma_u^+$ ) electron binding energy 1.337 and 1.303 eV, at the anion and neutral geometries, respectively.

The electrostatic estimation from Section 3.1 is validated in Table 3, where the vertical electron binding energies for the dianion of  $(\text{LiCN})_2 \cdots \text{HCCH} \cdots (\text{NCLi})_2$  are presented. The ground  ${}^3\Sigma_u^+$  electronic state of  $((\text{LiCN})_2 \cdots \text{HCCH} \cdots (\text{NCLi})_2)^{2-}$  is dominated by the  $\sigma_g^1\sigma_u^1$  configuration, with the  $\sigma_g$  and  $\sigma_u$  molecular orbitals localized primarily outside the molecular framework (see Fig. 2 where the singly occupied  $\sigma_g$  and  $\sigma_u$  orbitals of the  ${}^3\Sigma_u^+$  state are depicted). The  ${}^1\Sigma_g^+$  state of  $((\text{LiCN})_2 \cdots \text{HCCH} \cdots (\text{NCLi})_2)^{2-}$  is dominated by the  $\sigma_g^2$  and  $\sigma_u^2$  configurations. The CAS-PT2 electron binding energy for the singlet state is higher by only 0.06 meV than the MP2 electron binding energy of the triplet state. Therefore, in Table 3, the electron binding energies are reported for the  ${}^3\Sigma_u^+$  state only.

The vertical electron binding energy for the dianion at its equilibrium geometry calculated at the SCF level is 0.921 eV. The inclusion of electron correla-

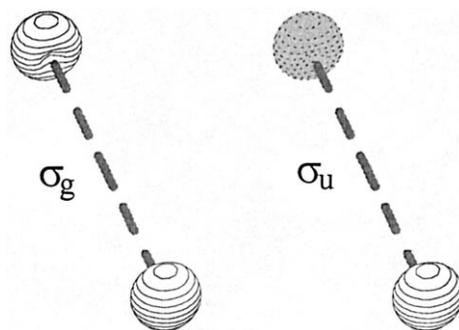


Fig. 2. Singly occupied  $\sigma_g$  and  $\sigma_u$  molecular orbitals in the ground  ${}^3\Sigma_u^+$  state of the dianion of  $(\text{LiCN})_2 \cdots \text{HCCH} \cdots (\text{NCLi})_2$ .

tion effects at the MP2 level decreases the dianion's stability to 0.824 eV (see Table 3). The contributions from third and fourth order MP corrections are relatively unimportant and our MP4 estimation of the (second) vertical detachment energy is 0.843 eV. The dianion remains electronically stable at the equilibrium geometry of its monoanionic daughter (by 0.789 eV) and neutral granddaughter (by 0.753 eV).

#### 4. Summary

Linear molecules with two polar ends may form dianions with one electron localized on each polar terminus. A simple electrostatic model can be used to estimate the electronic stability of the dianion on the basis of the effective separation between the two excess charges and the electronic stability of the monoanion.

We presented numerical results for the mono- and di-anion of  $(\text{LiCN})_2 \cdots \text{HCCH} \cdots (\text{NCLi})_2$ . The equilibrium geometries and electron binding energies were determined at the MP2 and MP4 level of theory, respectively, and extended one-electron basis sets were used to describe diffuse charge distributions of excess electrons.

The nearly degenerate  ${}^2\Sigma_g^+$  and  ${}^2\Sigma_u^+$  states of the monoanion are bound by 1.3 eV with respect to the neutral molecule. The nearly degenerate  ${}^1\Sigma_g^+$  and  ${}^3\Sigma_u^+$  states of the dianion are bound by 0.8 eV with respect to the monoanion. It is our desire to nurture interest in these novel anions within the theoretical and experimental communities.

Table 3

Vertical electron binding energies  $E$  (in eV) for the ground  ${}^3\Sigma_u^+$  electronic state of the  $((\text{LiCN})_2 \cdots \text{HC} \equiv \text{CH} \cdots (\text{NCLi})_2)^{2-}$  dianion at the equilibrium  $D_{\infty h}$  geometries of the neutral, anionic and dianionic systems<sup>a</sup>

	$D_{\infty h}$ geometry of the neutral	$D_{\infty h}$ geometry of the monoanion	$D_{\infty h}$ geometry of the dianion
$E^{\text{SCF}}$	0.823	0.863	0.921
$E^{\text{MP2}}$	0.732	0.769	0.824
$E^{\text{MP3}}$	0.778	0.815	0.870
$E^{\text{MP4}}$	0.753	0.789	0.843

<sup>a</sup>All results obtained with the aug-cc-pVDZ basis set augmented with the 3s3p diffuse set centered at all Li atoms.

## Acknowledgements

This work was supported by the NSF Grant CHE9618904 to J.S. and the Polish State Committee for Scientific Research (KBN) Grant DS/8000-4-0026-0. 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 US Department of Energy. This work was performed in part under auspices of the US Department of Energy, under Contract No. DE-AC06-76RLO 1830, with Battelle Memorial Institute, which operates the Pacific Northwest National Laboratory.

## References

- [1] J. Simons, K.D. Jordan, *Chem. Rev.* 87 (1987) 535.
- [2] P. Skurski, M. Gutowski, J. Simons, *Int. J. Quantum Chem.* 76 (2000) 197.
- [3] P. Skurski, J. Simons, *J. Chem. Phys.* 112 (2000) 6563–6570.
- [4] P. Skurski, M. Gutowski, J. Simons, *J. Chem. Phys.* 111 (1999) 9469.
- [5] M. Gutowski, P. Skurski, J. Simons, *Int. J. Mass Spectrom.*, in press (2000).
- [6] M. Gutowski, P. Skurski, *Chem. Phys. Lett.* 303 (1999) 625.
- [7] A. Szabo, N.S. Ostlund, *Modern Quantum Chemistry*, Dover Publications, Mineola, New York, 1996.
- [8] P. Skurski, J. Simons, *J. Phys. Chem. A* 104 (2000) 712.
- [9] D. Hegarty, M.A. Robb, *Mol. Phys.* 38 (1979) 1795.
- [10] R.H.E. Eade, M.A. Robb, *Chem. Phys. Lett.* 83 (1981) 362.
- [11] H.B. Schlegel, M.A. Robb, *Chem. Phys. Lett.* 93 (1982) 43.
- [12] N. Yamamoto, T. Vreven, M.A. Robb, M.J. Frisch, H.B. Schlegel, *Chem. Phys. Lett.* 250 (1996) 373.
- [13] J.J. McDouall, K. Peasley, M.A. Robb, *Chem. Phys. Lett.* 148 (1988) 183.
- [14] M.J. Frisch et al., *GAUSSIAN 98*, Revision A.7, Gaussian, Pittsburgh, PA, 1998.
- [15] G. Schaftenaar, *MOLDEN*, CAOS/CAMM Center, The Netherlands, 1991.
- [16] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, *J. Chem. Phys.* 96 (1992) 6796.
- [17] M.W. Schmidt, K. Ruedenberg, *J. Chem. Phys.* 71 (1979) 3961.
- [18] M. Gutowski, J. Simons, *J. Chem. Phys.* 93 (1990) 3874.