Thermodynamics of Cation—Base Complexes L···M, Where M = H⁺, Li⁺ and L is H₂O, HF, NH₃, PH₃, SiH₂, and CO

M. REMKO

*Department of Pharmaceutical Chemistry, Faculty of Pharmacy,
Comenius University, SK-832 32 Bratislava*

Ab initio molecular orbital calculations at the G1, G2, and CBS levels of theory have been performed for complexes of water, hydrogen fluoride, ammonia, carbon monoxide, phosphane, hydrogen sulfide, and silylene in order to determine the effects of molecular structure on gas-phase basicity towards H⁺ and Li⁺ It is shown that basicities towards metal cation Li⁺ differ considerably from the corresponding gas-phase basicities towards H⁺ Calculated interaction enthalpies vary as $\Delta H_{H+} \gg \Delta H_{Li+}$. The relative basicities of the bases studied depend characteristically on the type of cation and coordination site. The G1, G2, CBS-Q, and CBS-APNO methods reproduce the known experimental gas-phase interaction energies of the complexes studied with a comparable accuracy.

The basicity and acidity of a chemical species are important thermochemical properties that attract considerable attention of both experimental [1—9] and theoretical [10—20] chemists. For the determination of the absolute gas-phase basicity (acidity) scales it is necessary to establish accurate experimental data of suitable reference standards. The addition of a proton to the base represents the simplest chemical reaction. This reaction plays an important role in many chemically and biologically relevant processes. Gaseous ammonia, water, and carbon monoxide serve as suitable proton affinity scale standards [1, 2, 4, 6, 21]. However, there is a dispute regarding the exact magnitude of the experimental gas-phase proton affinity of these compounds [6, 21, 22]. With increasing sophistication of the quantum mechanical treatment it is possible to determine the absolute basicity and acidity of simple compounds theoretically. The computed acidities and basicities are as reliable as the best experimental methods [13, 17, 20, 23, 24]. Recent developments in quantum chemistry resulted in theoretical models (Gaussian-1 (G1) and Gaussian-2 (G2)) theories introduced by *Pople* and coworkers [25, 26] and complete basis set (CBS) methods developed by *Petersson* and several collaborators [27—31] able to predict properties of neutral molecules and ions within the so-called chemical accuracy (about 10 kJ mol⁻¹). This makes these procedures extremely useful in thermochemical studies.

We now present an examination of the thermodynamics of the interaction of cations (H⁺, Li⁺) with Lewis bases, water, hydrogen fluoride, ammonia, carbon monoxide, phosphane, hydrogen sulfide, and silylene. This provides data regarding the absolute gas-phase basicities of these compounds. The results of calculations of interaction energies using different model chemistry methods are compared and discussed with the available gas-phase experimental basicities.

COMPUTATIONAL DETAILS

The geometry of complexes L···M, where M = H⁺ and Li⁺, and L denotes the Lewis bases investigated, has been completely optimized at MP2(Full)/6-31G(d) level within the G2 theory [26]. As the first step full geometry of optimization using the MP2(Full)/6-31G(d) method (G2 model chemistry) was carried out for H₂O, HF, NH₃, CO, PH₃, H₂S, and SiH₂ (Table 1). The computed geometries are in good agreement with experimental gas-phase structures and support a recent finding [32] that this method is appropriate for accurate description of geometry of species involving first- and second-row atoms.

The gas-phase basicity was defined as the enthalpy of protonation (ΔH(298 K)) for reaction (*A*).

$$B(g) + H^+(g) \rightarrow BH^+(g) \qquad (A)$$
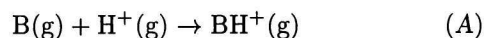
The enthalpy of protonation, ΔH(298 K), was computed using eqns (*1*) and (*2*)

$$\Delta H(298\ \mathrm{K}) = \Delta E(298\ \mathrm{K}) + \Delta(pV) \qquad (1)$$

$$\Delta E(298\ \mathrm{K}) = E(BH^+, 298\ \mathrm{K}) - [E(B, 298\ \mathrm{K}) + 3/2RT] \qquad (2)$$

where E(298 K) stands for the total energies of bases and their cations (including thermal energy correction

Table 1. MP2(Full)/6-31G(d) Optimized Geometry of Monomers Studied. The Available Experimental Gas-Phase Geometries are in the Parentheses (Ref. [34])

Species	d_{X-H} /pm	< HXH/°
H_2O	96.86 (95.75)	103.98 (104.51)
HF	93.39 (91.69)	
NH_3	101.68 (101.20)	106.34 (106.70)
CO	115.02 (112.83)	
PH_3	141.40 (142.00)	94.70 (93.345)
H_2S	133.95 (133.56)	93.33 (92.12)
SiH_2	151.83 (152.01^a)	92.57

a) For SiH.

Table 2. G2 Total Energies (in a.u.^{a}) of the Systems Studied (at 298 K)

Species	Enthalpy/a.u.	Gibbs energy/a.u.
Li^+	−7.233 480	−7.248 587
H_2O	−76.328 268	−76.349 644
HF	−100.346 702	−100.366 391
NH_3	−56.454 825	−56.477 667
CO	−113.174 192	−113.196 595
PH_3	−342.675 169	−342.700 029
H_2S	−398.926 924	−398.950 235
SiH_2	−290.163 899	−290.187 419
$H_2O\cdots H^+$	−76.588 068	−76.611 026
$\cdots Li^+$	−83.613 834	−83.640 256
$HF\cdots H^+$	−100.528 685	−100.550 294
$\cdots Li^+$	−107.616 603	−107.640 042
$NH_3\cdots H^+$	−56.777 599	−56.801 018
$\cdots Li^+$	−63.747 837	−63.774 466
$CO\cdots H^+$	−113.337 131	−113.362 805
$\cdots Li^+$	−120.426 273	−120.453 833
$OC\cdots H^+$	−113.397 687	−113.420 517
$\cdots Li^+$	−120.431 943	−120.459 009
$H_3P\cdots H^+$	−342.971 786	−342.996 147
$\cdots Li^+$	−349.945 880	−349.975 217
$H_2S\cdots H^+$	−399.194 127	−399.218 849
$\cdots Li^+$	−406.195 757	−406.224 415
$H_2Si\cdots H^+$	−290.473 683	−290.498 598
$\cdots Li^+$	−297.434 637	−297.463 442

a) 1 a.u. $\approx$ 2625.5 kJ mol^{-1}.

at $T = 298.15$ K). In eqn (1) we substituted $\Delta(pV) = -RT$ (1 mol of gas is lost in the reaction (A)).

The interaction enthalpy, $\Delta H(298$ K), for the metal ion—Lewis base complexes (eqn (B))

$$M^{n+}(g) + L(g) \rightarrow ML^{n+}(g) \qquad (B)$$

is given by the following equation

$$\Delta H(298 \text{ K}) = \{E(LM^{n+}, 298 \text{ K}) - [E(L, 298 \text{ K}) + \\ + E(M^{n+}, 298 \text{ K})]\} + \Delta(pV) \qquad (3)$$

$$M^{n+} = Li^+$$

where $E(M^{n+}, 298$ K) and $E(L, 298$ K) are the energies of the metal cation and ligand molecules, respectively, and $E(LM^{n+}, 298$ K) is the energy of the complex corrected for thermal energy at $T = 298.15$ K. For the work term in eqn (3) we substituted $\Delta(pV) = -RT$. *Ab initio* calculations were carried out with the aid of the GAUSSIAN94W package of computer codes [33].

RESULTS AND DISCUSSION

Structure and General Energetic Considerations

The G2 total energies of all calculated species are listed in Table 2. The fully optimized geometries of the complexes under study are given in Table 3. An analysis of the harmonic vibrational frequencies at the HF/6-31G(d) level of theory of the optimized species revealed that both monomers and the HF/6-31G(d) optimized complexes are minima (no imaginary frequencies). Minima were found for the pyramidal $H_2O\cdots H^+$ and $H_2S\cdots H^+$ complexes. The pyramidal structure of H_3O^+ was also proved experimentally [35]. For the rest of the complexes studied the minima correspond to the planar C_s structures. The changes of geometry of bases with complexation can be summarized as follows: *1.* Hard bases, where the donor is N, O, and F, form much shorter cation—ligand bonds than the compounds where the donor atom is Si, P or S (soft bases). *2.* The substantially shorter equilibrium distances $X\cdots M^+$ ($M^+ = H^+$ and Li^+) were computed

Table 3. MP2(Full)/6-31G(d) Optimized Geometries of the Ion—Base Systems Investigated

Par.	H_2O		HF		NH_3		CO		OC		PH_3		H_2S		H_2Si	
	H^+	Li^+	H^+	Li^+	H^+	Li^+	H^+	Li^+	H^+	Li^+	H^+	Li^+	H^+	Li^+	H^+	Li^+
d_{X-H}/pm	99.08	97.49	98.69	94.92	102.85	102.31					139.22	140.32	134.70	134.17	146.48	149.23
d_{CO}/pm							116.82	115.83	113.05	114.17						
d_{X-M}/pm	99.08	186.30	98.69	178.96	102.85	201.19	100.67	201.22	109.47	222.71	139.22	252.83	134.70	244.31	146.48	299.02
< HXH/°	111.42	105.59			109.47	105.22					109.46	99.87	96.05	95.41	120.0	100.27
< HXM/°	111.42	127.22	111.15	180.0	109.47	113.44					109.46	117.93	96.05	104.29	120.0	129.86
< COM/°							180.0	180.0	180.0	180.0						

for the protonated bases (Table 3). Protonation on water, hydrogen fluoride, ammonia, and hydrogen sulfide causes a lengthening of the corresponding X—H bond length, whereas protonation of PH_3 and SiH_2 slightly shortens the P—H and Si—H bonds (Table 3). Protonation of the carbon monoxide on carbons shortens the C—O bond length by about 2 pm, whereas protonation on oxygen causes a lengthening by the same amount. Bond angles considerably increase in going from the neutral base to the protonated species. The coordination of a lithium cation exhibits a smaller influence on the geometry of the bases studied.

Gas-Phase Interaction Energies

Table 4 contains the *ab initio* G1, G2, CBS-4, CBS-Lq, and CBS-Q, interaction enthalpies, entropies, and Gibbs energies of the systems investigated. For selected species we also present results of the very accurate and very expensive CBS-APNO method. The inclusion of electron correlation at the G1 level gives thermodynamic quantities which are close to those produced by the substantially more computer-demanding G2 procedure. The difference between these two methods is low (about 2—12 kJ mol^{-1}) for 16 complexes studied. The absolute enthalpies and Gibbs energies computed by complete basis set extrapolation CBS-4 and CBS-Lq methods are comparable with values obtained using the more expensive CBS-Q method. However, the geometry optimization at the HF/3-21G(d) level within the CBS-4 and CBS-Lq theories gives sometimes structures of intermolecular complexes which contradict to both experiments and higher level *ab initio* calculations. *E.g.* HF/3-21G(d) H_3O^+ optimal structure corresponds to the unrealistic planar C_s form. The difference between the CBS-Q and CBS-APNO model chemistries is low (about 1—5 kJ mol^{-1}), the latter values are being computed slightly higher (Table 4).

The first- and second-row hydrides studied represent the simplest Lewis bases which involve single-bonded basic centre. These hydrides can be protonated using strong acids or superacids [36]. For bases studied the proton affinities order is: $H(NH_3)$ > $H(SiH_2)$ > $H(PH_3)$ > $H(H_2S)$ > $H(H_2O)$ > $H(OC)$ > $H(HF)$ > $H(CO)$. Thus the $OC\cdots H^+$ proton affinity is higher than the $CO\cdots H^+$ one. In the case of lithium cation affinities the basicity order is: $H(NH_3)$ > $H(H_2O)$ > $H(PH_3)$ ≥ $H(SiH_2)$ > $H(HF)$ > $H(H_2S)$ ≫ $H(OC)$ > $H(CO)$. The proton is bonded substantially more strongly to the bases than the lithium cation. The absolute value of the basicity depends on both, the character of cation (Lewis acid) and type of the basic centre and no general basicity order was observed (Table 4). With the aim to establish whether or not there is any reasonably general correlation of basicities towards cations studied in Fig. 1, the interaction en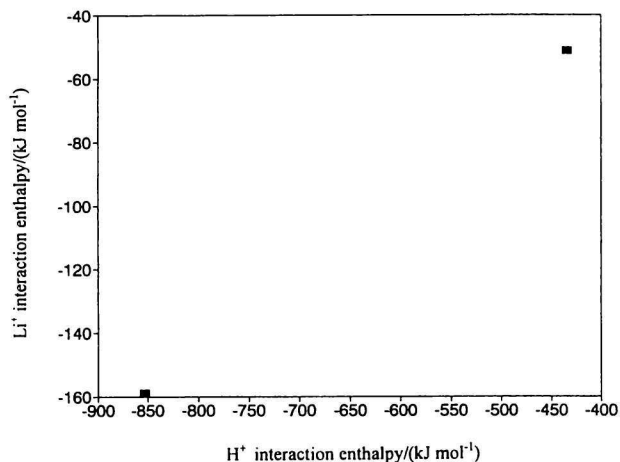thalpies of H^+ *vs.* corresponding $\Delta H(Li^+)$ are plotted. From this figure it is evident that there is indeed little general correspondence between the basicities towards H^+ and Li^+. Using the regression analysis with ΔH^o_{H+} as the independent variable the following regression equation was obtained

$$\Delta H^o_{Li+} = 5.524 + 0.158\Delta H^o_{H+}$$

$$(R^2 = 0.4865) \qquad (4)$$

A similar weak correlation of the H^+ and Li^+ affinities was also observed experimentally [5]. However, an excellent correlation was recently found [37] between the basicities of two alkali cations (Li^+ and Na^+). For the scattering of these affinities (Fig. 1), besides the effect of size of cation, the different polarization of hard and soft bases investigated is also responsible [20]. H^+ penetrates into the electron cloud of donor and forms a highly covalent bond. The adhesion of alkali cations (Li^+) to basic centres is, due to their smaller polarizing effect, much lower and results in the formation of essentially electrostatic bond.

In real molecular systems the tendency to associate and to react is described by Gibbs energies. It is therefore important to know the role of entropy in the binding processes studied. Also listed in Table 4 are the differences in S^o values of the complexes and the isolated species. The computed entropies for the protonation reaction are small (1—12 J K^{-1} mol^{-1}) and both positive and negative. Hence, the effect of entropy on this reaction is negligible and calculated enthalpies and Gibbs energies are very close and follow the same trend in the basicity of species studied. Similar small entropy effects in gas-phase proton transfer were also found experimentally [2]. A different situation was observed for binding the lithium cation. The changes in entropy were computed to be substantially larger (about 85—100 J K^{-1} mol^{-1}) and neg-

Fig. 1. Plot of $\Delta H^o(Li^+)$ values *vs.* corresponding $\Delta H^o(H^+)$ (G2 calculation).

Table 4. Calculated Numerical Values of Gas-Phase Enthalpies (ΔH/(kJ mol^{-1})), Entropies (ΔS/(J K^{-1} mol^{-1})) and Gibbs Energies (ΔG/(kJ mol^{-1})) of the Cation-Coordinated Systems

Complex	CBS-4			CBS-Lq			CBS-Q			CBS-APNO			G1			G2			Exp[a]		
	ΔH	ΔS	ΔG	ΔH	ΔS	ΔG	ΔH	ΔS	ΔG	ΔH	ΔS	ΔG	ΔH	ΔS	ΔG	ΔH	ΔS	ΔG	ΔH	ΔS	ΔG
H$_2$O···H$^+$	−684.5	−5.0	−682.9	−683.9	−5.0	−682.3	−686.6	−7.1	−684.5	−691.0	−6.5	−689.1	−689.4	−6.7	−687.4	−688.3	−6.9	−686.3	−691.2		
···Li$^+$	−136.0	−96.3	−107.3	−135.4	−101.8	−105.1	−136.4	−89.6	−109.6				−147.5	−97.0	−118.6	−134.3	−80.4	−110.4	−142.3	−94.3	−114.2
HF···H$^+$	−468.0	−4.2	−466.7	−468.4	−4.4	−467.1	−481.6	1.3	−482.0	−487.8	−2.6	−486.5	−480.5	−29.4	−471.7	−484.0	−3.9	−482.8	−484.1		
···Li$^+$	−87.1	−99.1	−57.6	−86.6	−99.4	−57.0	−94.1	−90.5	−67.1				−106.1	−108.4	−73.8	−98.1	−108.3	−65.8			
NH$_3$···H$^+$	−861.1	−16.3	−856.2	−859.6	−16.1	−854.8	−854.4	−7.1	−852.3	−855.2	−6.6	−853.1	−854.4	−15.6	−849.4	−853.6	−15.6	−849.0	−854.0		
···Li$^+$	−161.5	−110.9	−128.4	−161.4	−110.9	−128.4	−156.5	−91.2	−129.3				−164.6	−107.9	−132.4	−158.8	−108.1	−126.6	−163.6	−98.3	−134.3
CO···H$^+$	−437.0	−12.4	−433.3	−436.4	−12.5	−432.7	−433.1	7.0	−435.2	−432.2	21.8	−438.7	−428.5	8.1	−430.9	−434.0	8.0	−436.4	−426.3		
··Li$^+$	−50.1	−105.5	−18.7	−48.2	−105.3	−16.8	−52.2	−97.4	−23.2				−51.2	−95.8	−22.6	−51.3	−95.9	−22.7			
OC···H$^+$	−586.3	3.3	−587.3	−583.6	3.3	−584.6	−590.6	3.7	−591.7	−593.5	3.6	−594.6	−589.2	3.6	−590.3	−593.0	3.6	−594.1	−593.0		
···Li$^+$	−62.7	−96.3	−34.0	−63.3	−96.3	−34.6	−64.0	−92.4	−36.5				−65.1	−92.1	−37.7	−61.2	−75.2	−38.8			
PH$_3$···H$^+$	−798.0	4.6	−799.4	−790.4	4.7	−791.8	−785.4	13.8	−789.5				−784.8	−4.4	−783.5	−785.0	−4.5	−783.7	−785.7		
···Li$^+$	−105.9	−93.5	−78.0	−105.1	−93.3	−77.2	−100.2	−85.1	−74.8				−100.6	−72.8	−78.9	−101.9	−93.7	−74.0			
H$_2$S···H$^+$	−714.4	12.3	−718.1	−712.8	12.3	−716.5	−703.3	12.8	−707.1				−708.1	12.5	−711.8	−707.7	12.6	−711.4	−705.0		
···Li$^+$	−94.0	−86.2	−68.3	−94.4	−86.6	−68.6	−91.6	−85.5	−66.1				−102.1	−87.1	−76.1	−95.4	−85.7	−69.9			
SiH$_2$···H$^+$	−835.1	12.0	−838.7	−823.8	11.3	−827.2	−821.7	12.8	−825.5				−819.2	12.3	−822.9	−819.5	12.4	−823.2			
···Li$^+$	−104.4	−86.2	−78.7	−102.7	−86.3	−77.0	−99.2	−87.2	−73.2				−102.1	−85.7	−76.6	−100.4	−87.0	−74.5			

a) For experimental proton affinities see Ref. [9], experimental lithium affinities are taken from Ref. [4].

ative (destabilizing) (Table 4). The large and destabilizing entropies were determined for the $H_2O\cdots Li^+$ and $H_3N\cdots Li^+$ systems also experimentally [4]. The computed Gibbs energies ΔG° are negative and span a rather broad energy interval (from -23 kJ mol^{-1} to -820 kJ mol^{-1}) meaning that the coordination of the ions studied goes strongly towards the complex formation.

Table 4 contains also the literature data of experimental thermodynamic quantities for clustering of the H^+ and Li^+ ions to selected bases. As it is apparent from this table the CBS-Q, CBS-APNO, G1, and G2 methods reproduce thermodynamic quantities of the complexes studied within the targeted "chemical" accuracy (within 10 kJ mol^{-1}). Most of the computed proton affinities using those methods are in excellent agreement with the experimental proton affinities taken from the recent compilation done by *Hunter* and *Lias* [9] (NIST Chemistry Web Book). The differences between CBS-4 and CBS-Lq enthalpies and experimental data are slightly higher (about 5—15 kJ mol^{-1}, *cf. e.g.* H_2F^+ and PH_4^+).

A comparison of the computed enthalpies and Gibbs energies for the binding of the lithium cation to selected bases with available experimental values determined by ion cyclotron resonance spectroscopy [4] shows that the CBS-4, CBS-Lq, CBS-Q, G1, and G2 methods agree with the experimental data within the targeted range of 10 kJ mol^{-1}. To our knowledge most of the Li^+-base systems and proton affinity of silylene have not been measured until now, therefore, our high-level theoretical calculations offer a reliable order of basicities of the investigated bases towards these ions.

Natural Population Analysis

The atomic charges of the complexes studied were also evaluated by natural population analysis [38—40] using the NBO program [41]. The natural charges and atom—atom net linear NLMO/NPA bond orders are seen in Table 5. The coordination of cations considerably increases the polarization of the base molecules. The bonding of the lithium cation is connected with considerable increase of the electron density on the basic centre X (X: C, N, O, F, Si, P, and S). The electron transfer to the Li^+ is for the systems studied low (about 0.01—0.09 e). On the contrary, the protonation of bases leads to a considerable electron transfer towards the H^+ and remarkable change of the electron density at the basic centre. In the SiH_3^+ hydrogens carry net negative charge (Table 5).

The binding of bases to Li^+ results in low bond orders (0.01—0.09 e) indicating that the covalent bonding of alkali cations to these bases is very weak, *i.e.* the nature of this bonding is almost electrostatic. The bond orders of the H^+-base bonding are very high (about 0.3—0.8 e) indicating the entirely covalent

Table 5. Natural Atomic Charges (NAC) and NLMO/NPA Bond Orders (NPA) from the MP2/6-31G(d) NBO Analysis

	NAC		NPA
	X	M^{n+}	$X\cdots M^{n+}$
H_2O	−0.96		
$\cdots H^+$	−0.86	0.62	0.379
$\cdots Li^+$	−1.10	0.99	0.011
HF	−0.56		
$\cdots H^+$	−0.44	0.72	0.279
$\cdots Li^+$	−0.65	0.99	0.012
NH_3	−1.15		
$\cdots H^+$	−0.97	0.49	0.508
$\cdots Li^+$	−1.29	0.98	0.020
CO	−0.63		
$\cdots H^+$	−0.78	0.71	0.274
$\cdots Li^+$	−0.82	0.99	0.007
OC	0.63		
$\cdots H^+$	0.95	0.33	0.667
$\cdots Li^+$	0.49	0.98	0.021
PH_3	0.08		
$\cdots H^+$	0.69	0.08	0.920
$\cdots Li^+$	−0.08	0.95	0.045
H_2S	−0.27		
$\cdots H^+$	0.31	0.23	0.766
$\cdots Li^+$	−0.43	0.99	0.003
H_2Si	0.66		
$\cdots H^+$	1.49	−0.16	0.828
$\cdots Li^+$	0.55	0.91	0.092

character of this bonding. $X\cdots H^+$ bonds containing soft basic centres (Si, P, and S) possess higher covalent character. For systems with high bond orders the charge transfer from base to the cation is also very large (0.3—1.16 e).

CONCLUSION

The interaction energies of water, hydrogen fluoride, ammonia, carbon monoxide, phosphane, hydrogen sulfide, and silylene with cations H^+ and Li^+ were computed at the G1, G2, CBS-4, CBS-Lq, CBS-Q, and CBS-APNO levels of theory. The proton affinities are substantially higher than the lithium affinities. The variation in basicity of the parents is significantly changed for the different cations ("acids") and no general order between adducts is observed. The H^+ basicities *vs.* Li^+ basicities show a nonlinear behaviour. The changes in basicities are related to the variation of coordinating atom and the nature of interacting acid (cation). The covalent bond is almost entirely responsible for the formation of protonated complexes. The binding of the Li^+ cation to bases studied comes mainly from electrostatic interactions. G1, G2, CBS-Q, and CBS-APNO theoretical procedures reproduce thermodynamic quantities of the cation—Lewis base complexes within the "chemical" accuracy (10 kJ mol^{-1}).

REFERENCES

1. Yamdagni, R. and Kebarle, P., *J. Am. Chem. Soc. 98*, 1320 (1976).
2. Wolf, J. F., Staley, R. H., Koppel, I., Taagepera, M., McIver, R. T., Jr., Beauchamp, J. L., and Taft, R. W. *J. Am. Chem. Soc. 99*, 5417 (1977).
3. Džidić, I. and Kebarle, P *J. Phys. Chem. 74*, 1466 (1970).
4. Woodin, R. L. and Beauchamp, J. L., *J. Am. Chem. Soc. 100*, 501 (1978).
5. Taft, R. W., Anvia, F. Gal, J.-F., Walsh, S., Capon, M., Holmes, M. C., Hosn, K., Oloumi, G., Vasanwala, R., and Yazdani, S., *Pure Appl. Chem. 62*, 17 (1990).
6. Szulejko, J. E. and McMahon, T. B., *J. Am. Chem. Soc. 115*, 7839 (1993).
7. Klassen, J. S., Anderson, S. G., Blades, A., and Kebarle, P., *J. Phys. Chem. 100*, 14218 (1996).
8. Lias, S. G., Bartmess, J. E., Liebman, J. F., Homles, J. L., Levin, R. D., and Mallard, W. G., *J. Phys. Chem. Ref. Data 17*, 1 (1988) (Suppl. 1).
9. Hunter, E. P. and Lias, S. G., *J. Phys. Chem. Ref. Data* (1998) (http://webbook.nist.gov/chemistry/).
10. Del Bene, J. E., Frisch, M. J., Raghavachari, K., and Pople, J. A., *J. Phys. Chem. 86*, 1529 (1982).
11. Latajka, Z. and Scheiner, S., *J. Chem. Phys. 87*, 1194 (1987).
12. Jensen, F., *J. Am. Chem. Soc. 114*, 9533 (1992).
13. Smith, B. J. and Radom, L., *Chem. Phys. Lett. 231*, 345 (1994).
14. Roux, B. and Karplus, M., *J. Comput. Chem. 16*, 690 (1995).
15. Glukovtsev, M. N., Pross, A., and Radom, L., *J. Phys. Chem. 100*, 3498 (1996).
16. Remko, M., Liedl, K. R., and Rode, B. M., *J. Chem. Soc., Perkin Trans. 2 1996*, 1743.
17. Remko, M., Liedl, K. R., and Rode, B. M., *Chem. Phys. Lett. 263*, 379 (1996).
18. Remko, M., *Chem. Phys. Lett. 270*, 369 (1997).
19. Remko, M., *Mol. Phys. 91*, 929 (1997).
20. Remko, M., Liedl, K. R., and Rode, B. M., *J. Phys. Chem. 102*, 771 (1998).
21. Collyer, S. M. and McMahon, T. B., *J. Phys. Chem. 87*, 909 (1983).
22. Jenkins, H. D. and Morris, D. F. C., *J. Chem. Soc., Faraday Trans. 2 80*, 1167 (1984).
23. Smith, B. J. and Radom, L., *J. Am. Chem. Soc. 115*, 4885 (1993).
24. Smith, B. J. and Radom, L., *Chem. Phys. Lett. 245*, 123 (1995).
25. Pople, J. A., Head-Gordon, M., Fox, D. J., Raghavachari, K., and Curtiss, L. A., *J. Chem. Phys. 90*, 5622 (1989).
26. Curtiss, L. A., Raghavachari, K., Trucks, G. W., and Pople, J. A., *J. Chem. Phys. 94*, 7221 (1991).
27. Nyden, N. R. and Petersson, G. A., *J. Chem. Phys. 75*, 1843 (1981).
28. Petersson, G. A. and Al-Laham, M. A., *J. Chem. Phys. 94*, 6081 (1991).
29. Montgomery, J. A., Ochterski, J. W., and Petersson, G. A., *J. Chem. Phys. 101*, 5900 (1994).
30. Petersson, G. A., Tensfeldt, T., and Montgomery, J. A., *J. Chem. Phys. 94*, 6091 (1991).
31. Ochterski, J. W., Petersson, G. A., and Montgomery, J. A., *J. Chem. Phys. 104*, 2598 (1996).
32. Ma, B., Lii, J. H., Schaefer III, H. F., and Allinger, N. L., *J. Phys. Chem. 100*, 8763 (1996).
33. *Gaussian 94* (Revision E.3), 1995, Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. A., Keith, T. A., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Ayala, C. Y., Chen, W., Wong, M. W. Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Barker, J., Stewart, J. P., Head-Gordon, M., Gonzales, C., and Pople, J. A., Gaussian, Inc., Pittsburgh PA.
34. *CRC Handbook of Chemistry and Physics.* 77th Edition. (Lide, D. R., Editor.) CRC Press, Boca Raton, 1996.
35. Symons, M. C. R., *J. Am. Chem. Soc. 102*, 3982 (1980).
36. Shriver, D. F., Atkins, P. W., and Langford, C. H., *Inorganic Chemistry.* Second Edition, pp. 403—406. Oxford University Press, Oxford, 1996.
37. Remko, M. and Šarišský, M., *Chem. Phys. Lett. 282*, 227 (1998).
38. Reed, A. E., Weinstock, R. B., and Weinhold, F. A., *J. Chem. Phys. 83*, 735 (1985).
39. Reed, A. E. and Weinhold, F. A., *J. Chem. Phys. 83*, 1786 (1985).
40. Reed, A. E. and Schleyer, P. v. R., *J. Am. Chem. Soc. 112*, 1434 (1990).
41. *The NBO program*, Version 3.1. Glendening, E. D., Reed, A. E., Carpenter, J. E., and Weinhold, F. A.