# LETTERS

## LaO$^+$: A Diatomic Cation with a Sizable Proton Affinity upon Generation of the LaOH$^{2+}$ Dication

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Charge stripping of the monocationic counterparts allows for the generation of the dicationic species LaO$^{2+}$ and LaOH$^{2+}$ by mass spectrometric means. Energy-resolved measurements establish vertical ionization energies of IE$_v$(LaO$^+$) = 16.0 ± 0.3 eV and IE$_v$(LaOH$^+$) = 10.8 ± 0.3 eV. These figures are in reasonable agreement with IE$_v$(LaO$^+$) = 15.62 eV and IE$_v$(LaOH$^+$) = 10.61 eV predicted by ab initio calculations using the CCSD(T) approach. Further, the calculated properties can be used to convert the experimental IE$_v$ values to adiabatic values, i.e., IE$_a$(LaO$^+$) = 15.2 ± 0.4 eV and IE$_a$(LaOH$^+$) = 10.8 ± 0.4 eV. Evaluation of the dication energetics in terms of Born−Haber cycles reveals that the diatomic LaO$^+$ monocation has a proton affinity (PA) similar to that of methane. Accordingly, reactions of LaO$^+$ with strong Brønstedt acids AH$^+$ could provide a route for the generation of gaseous dications in cation/cation reactions. However, for the exothermic model reaction LaO$^+$ + NeH$^+$ → LaOH$^{2+}$ + Ne, CCSD(T) calculations predict a sizable barrier of about 38 kcal mol$^{-1}$ eV$^{-1}$ due to Coulomb repulsion of the monocationic reactants.

Protonation is the most common method for cationization of neutral molecules in the condensed as well as in the gas phase. Multiple protonations, however, are hindered by Coulomb barriers due to the repulsion of the cationic reactants. Moreover, multiple protonation of most small molecules is endothermic for the very same reason, i.e., the doubly protonated molecules MH$_2$$^{2+}$ are less stable than the corresponding MH$^+$ + H$^+$ asymptotes. Thus, cations are usually not considered to exhibit significant proton affinities (PAs) in the gas phase. Solvation dramatically stabilizes multiply charged species, and even such small dications as CH$_6$$^{2+}$ and H$_4$O$^{2+}$ are accessible in superacidic solutions.[1] Likewise, the situation very much changes for larger molecules (e.g., multiply protonated peptides), as with increasing distance of the charge centers Coulomb repulsion can be regarded as a minor perturbation.[2]

During our studies of multiply charged ions we asked ourselves whether there are also small monocations M$^+$ which exhibit significant proton affinities. If so, this would lead to the fascinating possibility of studing the occurrence of cation/cation reactions at near-thermal energies.[3] An obvious prerequisite for a large PA(M$^+$) is a particular stability of the MH$^{2+}$ dication. Inspired by earlier work of McCullough-Catalano and Lebrilla on dicationic metal compounds,[4] we have chosen to examine the couple LaO$^+$/LaOH$^{2+}$ in more detail. Lanthanum appears attractive because the first, second, and third ionization energies are relatively low, IE(La) = 5.58 eV, IE(La$^+$) = 11.06 eV, and IE(La$^{2+}$) = 19.18 eV,[5] thereby providing a basis for low-energy dications. The oxo ligand was chosen because LaO$^+$ monocation is a particularly stable, singlet ground-state species which is easy to generate experimentally and to describe theoretically. Protonation of LaO$^+$ at the O atom would not disturb the singlet situation and thus affords the singlet LaOH$^{2+}$

**TABLE 1: Geometric[a] and Electronic Structures As Well As Calculated Total Energies (in Hartree) of LaOH$_m^{n+}$ species at the MP2 and CCSD(T) Levels of Theory Using Valence Triple-$\zeta$ Basis Sets**

| | state | MP2 | MP2 geometry | ZPE[b] | CCSD(T)[c] |
|---|---|---|---|---|---|
| LaO$^+$ | $^1\Sigma^+$ | $-106.382350$ | $r_{LaO} = 1.861$ Å | 0.001877 | $-106.396308$ |
| LaO$^{2+}$ | $^2\Pi$ | $-105.811064$ | $r_{LaO} = 2.065$ Å | 0.001516 | $-105.846870$ |
| LaO$^{2+}$ | Vertical[d] | $-105.787594$ | $r_{LaO} = 1.861$ Å | | $-105.822216$ |
| LaOH$^+$ | $^2\Sigma^+$ | $-106.953489$ | $r_{LaO} = 2.049$ Å | 0.012529 | $-106.979836$ |
| | | | $r_{OH} = 0.965$ Å | | |
| LaOH$^+$ | $^2\Delta$ | $-106.948998$ | $r_{LaO} = 2.018$ Å | 0.012312 | $-106.977379$ |
| | | | $r_{OH} = 0.965$ Å | | |
| LaOH$^{2+}$ | $^1\Sigma^+$ | $-106.565189$ | $r_{LaO} = 1.971$ Å | 0.012670 | $-106.590915$ |
| | | | $r_{OH} = 0.978$ Å | | |
| LaOH$^{2+}$ | vertical[d] | $-106.563824$ | $r_{LaO} = 2.049$ Å | | $-106.589862$ |
| | | | $r_{OH} = 0.965$ Å | | |
| [Ne·LaOH$^{2+}$][e] | $^1A'$ | $-235.366742$ | f | 0.012932 | $-235.398646$ |
| TS[e] | ($^1\Sigma^+$) | $-235.204556$ | g | 0.009640 | $-235.227470$ |
| NeH$^+$ | $^1\Sigma^+$ | $-128.883713$ | $r_{NeH} = 0.992$ Å | 0.006712 | $-128.891135$ |
| NeH | vertical[d] | $-129.155754$ | $r_{NeH} = 0.992$ Å | | $-129.163849$ |
| Ne | $^1S$ | $-128.796184$ | | | $-128.802454$ |
| Ne$^+$ | $^2P$ | $-128.005709$ | | | $-128.019720$ |
| La$^+$ | $^3F$ | $-31.113830$ | | | $-31.137148$ |
| La$^{2+}$ | $^2D$ | $-30.717714$ | | | $-30.739724$ |
| La$^{3+}$ | $^1S$ | $-30.034876$ | | | $-30.053880$ |
| O | $^3P$ | $-74.954902$ | | | $-74.973962$ |
| O$^+$ | $^4S$ | $-74.468010$ | | | $-74.484671$ |
| OH | $^2\Pi$ | $-75.618907$ | $r_{OH} = 0.967$ Å | 0.008704 | $-75.637711$ |
| OH$^+$ | $^3\Sigma^-$ | $-75.147949$ | $r_{OH} = 1.024$ Å | 0.007318 | $-75.169216$ |
| H | $^2S$ | $-0.499810$ | | 0.000000 | $-0.499810$ |

[a] Geometry optimization was performed only at the MP2 level. [b] Zero-point energies (in Hartree) obtained by frequency calculations at the MP2 level. [c] Single-point calculations using the MP2 optimized geometries. [d] Single-point calculations of the indicated species at the geometry of the corresponding monocation ground state. [e] See text for definition. [f] $r_{LaO} = 1.974$ Å, $r_{LaNe} = 3.001$ Å, $r_{OH} = 0.978$ Å, $\alpha_{OLaNe} = 156°$. [g] $r_{LaO} = 1.884$ Å, $r_{OH} = 3.558$ Å, $r_{NeH} = 0.993$ Å, $\alpha_{LaOH} = 180°$.

dication. Likewise, ionization of the doublet LaOH$^+$ mono- to the LaOH$^{2+}$ dication should not be much more demanding than for the atom because the unpaired electron is centered on lanthanum. These qualitative arguments suggest LaO$^+$ as an attractive candidate for a monocation having a sizable PA.

To elucidate the situation, LaO$^+$ and LaOH$^+$ monocations were examined by charge stripping-mass (CS) spectrometry.[6,7] In these experiments, mass-selected monocations having 8 keV kinetic energies are collided with a neutral target gas (i.e., O$_2$) to afford mono- and dicationic fragments. The CS spectra of the mass-selected ions of interest are straightforward and give no indications for the presence of any impurities. Thus, CS of LaO$^+$ yields the La$^+$ monocation as the base peak (100%) along with sizable dication signals for LaO$^{2+}$ (40%) and La$^{2+}$ (10%). Likewise, CS of LaOH$^+$ yields LaO$^+$ (100%) and La$^+$ (20%) monocations along with dication signals for LaOH$^{2+}$ (5%) and La$^{2+}$ (4%); LaO$^{2+}$ is barely formed. The reasonable dication signals obtained in both cases allow the determination of the ionization energies of the monocations by means of energy-resolved CS experiments. In keV collisions, the interaction time of the projectile with the target is in the femtosecond regime, so that experiments are assumed to sample vertical ionization energies.[3] Experimentally, several independent measurements using two different methods for ion generation (electron ionization of La(acac)$_3$ and fast atom bombardment of LaCl$_3$ solution) consistently lead to IE$_v$(LaO$^+$) = 16.0 ± 0.3 eV and IE$_v$(LaOH$^+$) = 10.8 ± 0.3 eV, respectively (see experimental details).

In the theoretical study, the species LaOH$_m^{n+}$ ($m$ = 0, 1; $n$ = 1, 2) were examined at the MP2 and CCSD(T) levels of theory using valence triple-$\zeta$ basis sets (Table 1). A comprehensive survey of the relative stabilities and derived properties is given in Table 2. While certainly not of ultimate accuracy, the computational predictions are clearly suitable to semiquantitatively describe the energetics of the LaOH$_m^{n+}$ ions. For

example, IE(La$^+$) = 10.81 eV and IE(La$^{2+}$) = 18.66 eV obtained with CCSD(T) agree reasonably well with the experimental figures mentioned above; note that the slight underestimation of the IE values is fully expected at this level of theory. Similarly, the computed IE$_v$(LaO$^+$) = 15.62 eV and IE$_v$(LaOH$^+$) = 10.61 eV are close to—though a bit below again—the values derived from the CS experiments.

The large difference of the IE values of both cations can simply be explained by reference to the corresponding ground states. LaO$^+$ has a $^1\Sigma^+$ ground state with a strong La–O interaction formally corresponding to a triple bond; this reasoning also accounts for the rather large binding energy of $D_0$-(La$^+$–O) = 178 kcal/mol with CCSD(T). Ionization of LaO$^+$ ($^1\Sigma^+$) to the dication must remove one of the bonding electrons and is thus fairly energy demanding. Consequently, the binding energy shrinks to $D_0$(La$^{2+}$–O) = 82.6 kcal/mol in the LaO$^{2+}$ ($^2\Pi$) dication. Removal of a binding electron is further associated with a considerable change in bond lengths, i.e., from $r_{La–O}$ = 1.861 Å in the mono- to $r_{La–O}$ = 2.065 Å in the dication. As a result, IE$_v$(LaO$^+$) is 0.67 eV larger than IE$_a$(LaO$^+$) = 14.95 eV. Applying this difference $\Delta IE_{v/a}$ to the experimental value leads to a final estimate of IE$_a$(LaO$^+$) = 15.2 ± 0.4 eV; conservatively, an additional error of ±0.1 eV is assigned to $\Delta IE_{v/a}$. In contrast, ionization of the doublet LaOH$^+$ monocation to the LaOH$^{2+}$ ($^1\Sigma^+$) dication removes a nonbonding electron from a 5d-type orbital; the ground-state assignment for LaOH$^+$ is ambiguous because the splitting of the $^2\Delta$ and $^2\Sigma^+$ states is rather small. As a consequence of the increased charge on lanthanum, $r_{La–O}$ even decreases slightly from 2.018 Å in LaOH$^+$ ($^2\Delta$) to 1.971 Å in LaOH$^{2+}$ ($^1\Sigma^+$). However, the change in geometry is small and IE$_{v/a}$ (0.03 eV) is almost negligible resulting in a final estimate of IE$_a$(LaOH$^+$) = 10.8 ± 0.4 eV.

Using complementary thermochemical data, Born–Haber cycles allow us to construct stability diagrams for the dicationic species LaOH$_m^{2+}$ ($m$ = 0, 1). Thus, both dications are

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**TABLE 2: Calculated Energetic Properties (at 0 K in kcal/mol)[a] of the [La,O,H,Ne][n+] System at the MP2 and CCSD(T) Levels of Theory Relative to the LaOH[2+] + Ne Asymptote**

| species[b] | $E_{rel}$(MP2) | $E_{rel}$(CCSD(T)) | derived properties (CCSD(T) |
|---|---|---|---|
| LaO[+] + Ne[+] + H | 290.4 | 292.9 | IE(Ne) = 21.30 eV |
| La^{+} + O[+] + Ne + H | 295.5 | 286.5 | IE(O) = 13.31 eV |
| La^{2+} + O + Ne + H | 238.5 | 228.9 | $D_0$(La^{2+}−O) = 82.6 kcal/mol |
| La^{+} + OH[+] + Ne | 187.0 | 175.2 | IE(OH) = 12.71 eV |
| LaO[2+] + Ne + H | 152.6 | 146.3 | $IE_a$(LaO[+]) = 14.94 eV |
| La^{2+} + OH + Ne | 140.9 | 131.5 | $D_0$(La^{2+}−OH) = 131.5 kcal/mol |
| LaO[+] + Ne + H^{+} | 108.0 | 115.3 | PA(LaO[+]) = 115 kcal/mol |
| TS | 96.5 | 102.2 | $E_a$ = 38.3 kcal/mol |
| LaO[+] + NeH[+] | 57.2 | 63.9 | PA(Ne) = 51.4 kcal/mol |
| LaOH[2+] + Ne | 0.0 | 0.0 | $IE_a$(LaOH[+]) = 10.59 eV |
| [Ne·LaOH[2+]] | −3.2 | −3.1 | |
| La^{+} + O + Ne + H | −10.1 | −20.5 | $D_0$(La^{+}−O) = 177.8 kcal/mol |
| La^{+} + OH + Ne | −107.6 | −117.9 | $D_0$(La^{+}−OH) = 126.2 kcal/mol |
| LaO[+] + H + Ne | −205.7 | −198.3 | $D_0$(LaO[+]−H) = 45.8 kcal/mol |
| LaOH[+] + Ne | −243.8 | −244.1 | |

[a] Zero-point energies obtained by frequency calculations at the MP2 level. [b] Single-point calculations using the MP2 optimized geometries. [c] Single-point calculations of the indicated species at the geometry of the corresponding monocation ground state.
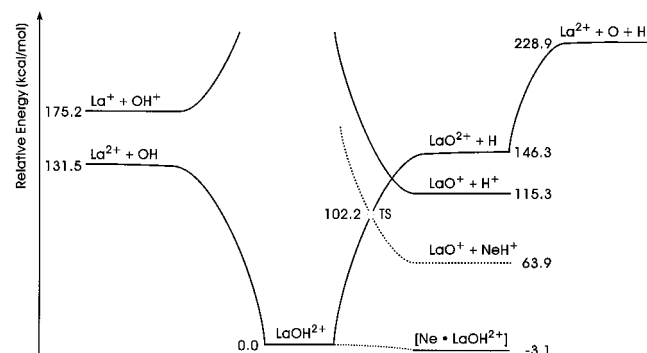


**Figure 1.** Relative stabilities of LaO[2+] and LaOH[2+] according to the CCSD(T) calculations with respect to various dissociation asymptotes; the dashed lines refer to the respective species involved in the putative cation/cation reaction 1 described in the text.

thermochemically stable with respect to all possible dissociation asymptotes (Figure 1). Most interesting is the fact that dissociation of LaOH[2+] into the monocationic fragments LaO[+] + H^{+} is also quite endothermic. Thus, CCSD(T) predicts that the LaO[+] cation has a proton affinity of 115 kcal mol^{−1}. Such a value is comparable to the PAs of several neutral molecules typically used as reagent gases in chemical ionization experiments,[8] e.g., between PA(H₂) = 102 kcal mol^{−1} and PA(CH₄) = 131 kcal mol^{−1}.[9,10]

$$LaO^+ + NeH^+ \rightarrow LaOH^{2+} + Ne \qquad (1)$$

In view of the significant PA of LaO[+], we examined the protonation of LaO[+] by NeH[+] as a prototype Brønstedt acid (PA(Ne) = 48.4 kcal mol^{−1})[9,10] according to reaction 1. The results are included as dashed lines in Figure 1. The associated transition structure (TS) shows a linear arrangement of the four atoms, i.e., La−O−H−Ne, thereby maximizing the distance between the charge centers. Both MP2 and CCSD(T) levels of theory predict sizable barriers of almost 40 kcal/mol for the putative cation/cation reaction 1. While the height of the TS clearly excludes occurrence of reaction 1 at thermal energies, the barrier might be overcome at elevated kinetic energies.[11] After passage of the barrier, LaOH[2+] is formed in a continuously exothermic manner. In view of the significant reaction exothermicity, the weak van der Waals type complex [Ne·LaOH[2+]] is not expected to have any significant lifetime when formed via reaction 1.

We ask ourselves, however, what is the origin of the barrier of reaction 1 and whether there might exist means to further

enhance the propensity for cation/cation reactions. The reason for the barrier is simply that the associated TS is located rather early, that is at an O−H distance of 3.6 Å. Consequently, neither the geometric or electronic structures of the LaO[+] and NeH[+] subunits are notably perturbed in the TS compared to the isolated molecules. In other words, there is not much binding in the TS. In fact, the magnitude of the barrier can by and large be attributed to the mere Coulomb repulsion of two cations at such a distance. For the same line of reasoning, it appears unlikely that quantum mechanical tunneling could facilitate proton transfer as the imaginary mode of i61 cm^{−1} is rather low and the associated reduced mass of 11 amu correlates with a coupled motion of all atoms rather than movement of hydrogen atom alone. Hence, the barrier is thick and thereby disfavoring tunneling phenomena. To analyze whether the barrier of cation protonation could even be lowered, let us consider the attractive asymptote. In the present case, this corresponds to LaO[2+] + NeH, or better LaO[2+] + Ne + H because neutral NeH is unbound. This view of reaction 1 implies that the seemingly simple proton transfer involves a sequence of electron transfer followed by translocation of a neutral hydrogen atom. As discussed above, formation of LaO[2+] has a considerable energy demand, however. Choice of other central atoms and/or further stabilization of the dicationic species by dipolar ligands[12] may therefore lower the barrier of similar cation/cation reactions, and we will continue our efforts in these respects.

In summary, the examination of the LaOH$_m$[n+] cations reveals that the LaOH[2+] dication is particularly stable. The rather low ionization energy $IE_a$(LaOH[+]) = 10.8 ± 0.4 eV in conjunction with the huge oxophilicity of early transition metals suggest LaOH[2+] as a candidate for dication formation via chemiionization processes in flames[13] or in the upper layers of the earth's atmosphere due to metal ablation from meteorites or abandoned space crafts.[14] Further, a Born−Haber cycle implies a proton affinity of about 115 kcal/mol for the LaO[+] monocation. While protonation of LaO[+] by NeH[+] as a model reaction is associated with an appreciable kinetic barrier due to Coulomb repulsion of the monocationic reactants, the calculated energetics of reaction 1 propose that cation/cation reactions on a molecular level may occur at hyperthermal energies. In this respect, it appears timely to think about experimental techniques to study such processes.

**Experimental and Theoretical Details**

The experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE config-

uration (B stands for magnetic and E for electric sectors) which has been described elsewhere.[15] $LaO^+$ and $LaOH^+$ monocations were generated by electron ionization (EI) of lanthanum acetylacetonate $La(acac)_3$ as well as fast atom bombardment (FAB, Xe, 10 keV) of a slurry of $LaCl_3$ in water. In the charge-stripping experiments, the monocations having a kinetic energy of 8 keV were mass selected by means of B(1), collided with oxygen (80% transmission), and the resulting fragments were scanned using E(1). For the overview CS spectra, slits were fully opened, while energy resolutions $E/\Delta E$ of ca. 5000 were used in the energy-resolved experiments. In the CS process, ionization of mono- to dications is brought about by the kinetic energy of the incident beam leading to a shift of the dication signals on the kinetic energy scale. This kinetic energy deficit is determined from the onsets of the mono- and dication signals and is usually referred to as $Q_{min}$ value which roughly corresponds to the vertical ionization energy of the monocation $IE_v(M^+)$.[6,7] The values given below refer to the average of more than 10 separate experiments, and the errors given comprise the standard deviation of the measured energy balances as well as systematic errors of the associated calibration schemes. Note, that these measurements are sensitive to accidental changes in the ionization conditions (discharges in particular) because they require the constancy of the absolute ion kinetic energies. Therefore, we recommend that any set of data in which serious changes of the ion's kinetic energies occur (either for the ions of interest or the references) is excluded from further consideration. For the required calibration of the energy scale, we used charge-stripping of the molecular ion of toluene $C_7H_8^+ \rightarrow C_7H_8^{2+}$ with $Q_{min}(C_7H_8^+) = 15.7$ eV[7] in the EI experiments and the transitions $Mg^+ \rightarrow Mg^{2+}$ with $IE(Mg^+) = 15.03$ eV and $Ca^+ 6 Ca^{2+}$ with $IE(Ca^+) = 11.89$ eV[5] in FAB. Further, $Q_{min} = 11.2 \pm 0.3$ eV determined for the process $La^+ \rightarrow La^{2+}$ agrees pretty well with $IE(La^+) = 11.06$ eV,[5] and the latter value was therefore used as a supporting reference.

The ab initio calculations employed the MP2 and CCSD(T) methods implemented in the Gaussian98 program together with polarized triple-$\zeta$ basis sets.[16] Specifically, the cc-pVTZ basis[17] was used for H, O, and Ne, and the Stuttgart relativistic ECP[18] on La, together with a (7s6p5d2f)/[6s5p4d2f] valence basis set to describe the valence and outermost core (5s5p) electrons. This last basis was obtained by partially uncontracting the (7s6p5d)/[5s4p3d] basis associated with the ECP,[18] and adding two uncontracted *f* functions (energy-optimized exponents $\alpha = 0.85, 0.35$). The 1s orbitals on O and Ne were kept frozen during the correlation treatment. All structures were fully optimized at the MP2 level, and characterized by frequency calculations. The final energetics were derived from single point calculations at the CCSD(T) level using the MP2 optimized structures. Corrections for zero point energies (ZPEs) are also adopted from the MP2 level; note that ZPEs were not included in the evaluation of $\Delta IE_{v/a}$.

### References and Notes

(1) (a) Olah, G. A. *Angew. Chem.* **1993**, *105*, 805; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767. (b) Olah, G. A. *Angew. Chem.* **1995**, *107*, 1519; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1393.

(2) Vekéy, K. *Mass Spectrom. Rev.* **1995**, *14*, 195.

(3) Schröder, D.; Schwarz, H. *J. Phys. Chem. A* **1999**, *103*, 7385.

(4) McCullough-Catalano, S.; Lebrilla, C. B. *J. Am. Chem. Soc.* **1993**, *115*, 1441.

(5) Taken from the NIST atomic spectra database, see: http://physics.nist.gov/cgi-bin/AtData/main_asd.

(6) Ast, T. *Adv. Mass Spectrom. A* **1980**, *8*, 555.

(7) Lammertsma, K.; Schleyer, P. v. R.; Schwarz, H. *Angew. Chem.* **1989**, *101*, 1313; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1321.

(8) Harrison, A. G. *Chemical Ionization Mass Spectrometry*; CRC Press: Boca Raton, FL, 1983.

(9) Here, we use kcal mol$^{-1}$ as the more common unit. Note that the data compiled in ref 10 are converted to 0 K for the sake of comparison.

(10) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.

(11) See also: Beyer, M.; Williams, E. R.; Bondybey, V. E. *J. Am. Chem. Soc.* **1999**, *121*, 1565.

(12) Schröder, D.; Bärsch, S.; Schwarz, H. *J. Phys. Chem. A* **2000**, *104*, 5101.

(13) (a) Goodings, J. M.; Hassanli, C. S.; Patterson, P. M.; Chow, C. *Int. J. Mass Spectrom. Ion Processes* **1994**, *132*, 83. (b) Patterson, P.; Goodings, J. M. *Int. J. Mass Spectrom. Ion Processes* **1995**, *148*, 55. (c) Chen, Q. F.; Goodings, J. M. *Int. J. Mass Spectrom.* **1998**, *181*, 181.

(14) Plane, J. M. C.; Helmer, M. *Faraday Discuss.* **1995**, *100*, 411.

(15) Schalley, C. A.; Schröder, D.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1996**, *153*, 173.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; 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, Inc.: Pittsburgh, PA, 1998.

(17) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(18) Dolg, M.; Stoll, H.; Savin, A.; Preuss, H. *Theor. Chim. Acta* **1989**, *75*, 173.