J. Phys. Chem. A **2005,** *109,* 1603−1607

Comparison of Quantum Mechanical and Experimental Gas-Phase Basicities of Amines and Alcohols

Eirik F. da Silva*

Department of Chemical Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

Received: October 19, 2004; In Final Form: November 25, 2004

A comparison was made between the experimental and B3LYP relative gas-phase basicities and proton affinities of a series of 9 amine, 3 alcohol, and 3 alkanolamine molecules. While agreement is good for most of the species studied, it is poor for the alkanolamines and 1,2-ethanediol. A series of calculations were undertaken at the B3LYP and MP2 levels using various basis sets to see if the uncertainties in the calculations can account for the discrepencies. The results suggest that this is unlikely and that the theoretical values are likely to be reasonably accurate. Calculations are also presented for the dimer formation energies of alkanolamine molecules, diamine molecules, and 1,2-ethanediol. These calculations suggest that all of these species can form proton-bound dimers. The alkanolamines and 1,2-ethanediol also appear to have relatively high formation energies for neutral dimers.

Introduction

Gas-phase basicities and proton affinities have been the subject of substantial experimental[1] and theoretical[2−4] work. These properties offer a useful benchmark for quantum mechanical calculations, and high-level calculations have been successful in reproducing experimental data. Calculations have also been used to interpret the experimental data.[5] In addition to the inherent interest in gas-phase basicities, they are also important when studying properties in solution. If gas-phase basicity, solution-phase basicity, and the free energy of solvation of the neutral solute are known, then the free energies of solvation of the ionic form can be derived. This quantity is otherwise difficult to estimate.[6] Accurate quantum mechanical calculation of the gas-phase basicity is also required for predicting basicities in solution.

Amines are organic bases of importance in many contexts. Our interest lies in the application of amines for the removal of CO_2 from exhaust gases. Alkanolamines are of particular interest in this context.[7] In a previous study,[8] poor agreement was found between the experimental and calculated gas-phase basicities for some alkanolamine molecules; the present work is intended to further study the accuracy of the calculated and experimental values.

Methods

Calculations for the gas-phase basicity have been carried out at the B3LYP and MP2 levels. The propensity to form intramolecular hydrogen bonds[8] is an important feature of the alkanolamines. The accurate calculation of the energies of species containing hydrogen bonds is not trivial; one of the difficulties is the basis-set superpositon error (BSSE). While the counterpoise correction can be applied for bonding between different molecules, it cannot easily be applied to intramolecular bonds.[9,10] The effect of BSSE is, however, expected to decrease with the increasing size of the basis set and with the inclusion of diffuse basis functions.[10] In this work, relatively large basis sets will be used to limit the effect of BSSE and the results from different basis sets will be compared.

Experimental data are at 298 K and zero-point energies, and therefore, thermal corrections should be added to the calculated values. They are calculated at the HF/6-31G(d) level.

Calculations are also carried out to determine the likelihood of the alkanolamines forming dimers in the gas phase. They are carried out at the HF/6-311++G(d,p) level. They are intended to give a quantitative picture of dimer formation. The omission of electron correlation in the HF calculations means that the energies calculated with this method are less accurate than the gas-basicity calculations. For the ethanolamine, a dimer calculation was also carried out at the MP2/6-311++G(2d,2p)//HF/6-311++G(2d,2p) level.

All calculations were carried out in Gaussian 98.[11]

Results and Discussion

Figure 1 shows the conformers that were identified as the most stable at the B3LYP/6-311++G(d,p) level for the alkanolamines, diamines, 1,2-ethanediol, and their protonated forms. For the neutral forms of the three alkanolamines, the conformers are characterized by hydrogen bonding between the alcohol and amine functionalities. The H(O)−N bond seems to be the most energetically favored. For the protonated forms, only H(N)−O hydrogen bonds are found. The conformers of the diamines and 1,2-ethanediol are also characterized by intramolecular hydrogen bonds. The lengths of these bonds are given in Table 1.

The selected conformers are drawn from a conformer search at the HF/3-21G(d) level.[8] Some of the most stable conformers identified at that level have also been studied at the B3LYP/6-311++G(d,p) level, and it seems likely that these are, in fact, the most stable conformers at this level of theory. It should, however, be noted that a full study of the conformers at the B3LYP/6-311++G(d,p) level has not been undertaken. Diethanolamine has a large number of potential conformers, and therefore, for the neutral form of this molecule, there is less confidence

---

* E-mail: silva@chemeng.ntnu.no.

10.1021/jp0452251 CCC: $30.25

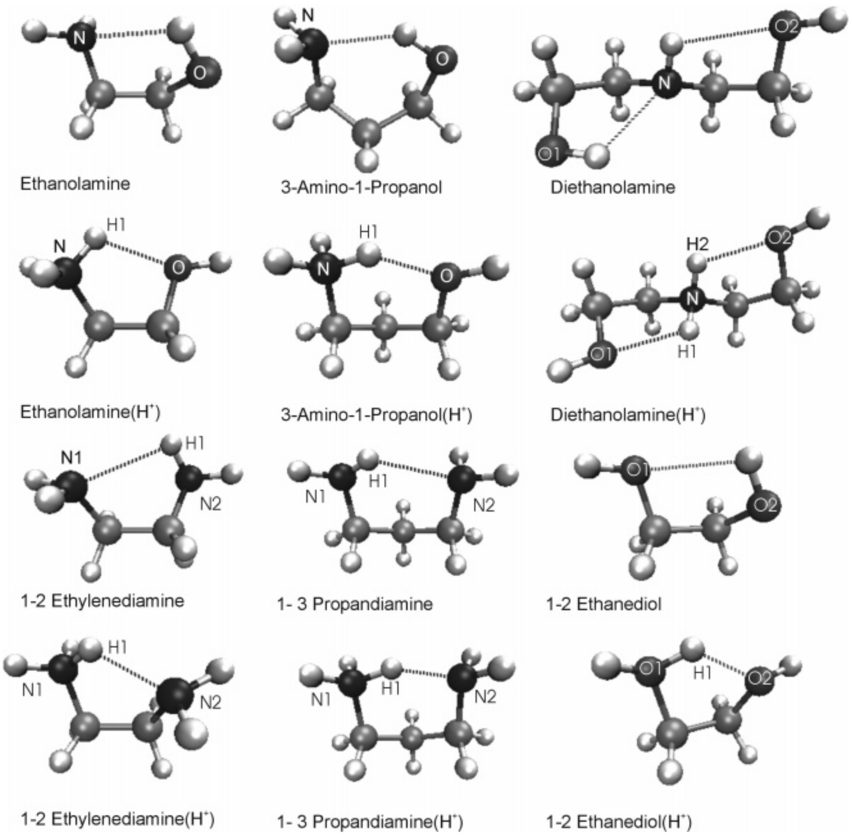

Figure 1. Stable conformers of alkanolamines, diamines, and 1,2-ethanediol. Dashed lines indicate hydrogen bonds.

TABLE 1: Hydrogen Bond Lengths

molecule	bond	length (Å)[a]
ethanolamine	H(O)−N	2.273
ethanolamine(H$^+$)	H1(N)−O	2.034
diethanolamine	H(O1)−N	2.296
	H(N)−O2	2.433
diethanolamine(H$^+$)	H1(N)−O1	2.084
	H2(N)−O2	2.084
3-amino-1-propanol	N−H(O)	2.033
3-amino-1-propanol(H$^+$)	H1(N)−O	1.760
1,2-ethylenediamine	H1(N2)−N1	2.508
1,2-ethylenediamine(H$^+$)	H1(N1)−N2	1.906
1,3-propanediamine	H1(N1)−N2	2.305
1,3-propanediamine(H$^+$)	H1(N1)−N2	1.684
1,2-ethanediol	H(O2)−O1	2.303
1,2-ethanediol(H$^+$)	H1(O1)−O2	1.642

[a] B3LYP/6-311++G(d,p) geometry.

TABLE 2: Relative Gas-Phase Basicities and Proton Affinities[a]

	gas basicity		proton affinity	
molecule	theoretical[b]	experimental[c]	theoretical[b]	experimental[c]
ammonia	0.0	0.0	0.0	0.0
ethanolamine	16.2	18.6[d]	16.2	18.3[d]
diethanolamine	28.2	24.1[e]	28.4	23.8[e]
3-amino-1-propanol	23.4	23.5[d]	23.6	26.0[d]
1,2-ethylenediamine	22.8	22.3[d]	23.2	23.4[d]
1,3-propanediamine	29.9	28.9[d]	30.6	31.9[d]
methylamine	10.2	10.9	11.0	10.9
ethylamine	14.3	14.1	14.4	14.0
dimethylamine	17.9	18.5	18.0	18.1
trimethylamine	22.2	23.7	22.3	22.8
piperidine	24.2	24.4	24.3	24.0
piperazine	23.3	22.9	23.5	21.5
morpholine	17.0	17.3	17.2	16.9
pyrrolidine	23.6	23.0	23.7	22.6
methanol	−23.1	−22.6[f]	−23.2	−23.7[f]
ethanol	−17.0	−17.4	−17.3	−18.5
1,2-ethanediol	−13.1	−10.9[g]	−12.6	−9.0[g]

[a] Results in kcal/mol. [b] B3LYP/6-311++G(d,p) energy with thermal correction and zero-point energy calculated at the HF/6-31G(d) level. [c] Data from Hunter and Lias,[1] also available at webook.nist.gov.[15] Original papers indicated for alkanolamines, diamines, and 1,2-ethanediol. [d] Data from Meot-Ner et al.[16] [e] Data from Sunner et al.[17] [f] Value is theoretical. [g] Data from Chen and Stone.[18]

in the determination of the most stable conformer. The conformers for neutral ethanolamine are consistent with those found, both theoretically and experimentally, by other authors (Tubergen et al.[13] and Vorobyov et al.[12] and the references therein). The conformer identified for 3-amino-1-propanol is in agreement with theoretical work by Kelterer and Ramak.[14]

In Table 2 the relative basicity of these amines together with other amine and alcohol molecules calculated at the B3LYP/6-311++G(d,p) level is shown. Data are given relative to ammonia. For piperazine, calculations were done on the chair conformer. The conformers of ethanol are shown in the Supporting Information, and the other molecules have only one conformer form.

The data in Table 2 show good agreement for most of the molecules. For the alkanolamines, there is, however, a significant disagreement between the experimental data and the calculated results. The experimental and theoretical gas-phase basicities differ by 2.4 kcal/mol for ethanolamine and by 4.1 kcal/mol for diethanolamine. The relative basicity for these two alkanolamines differs by 6.5 kcal/mol. A similar trend can be seen for the proton affinities of these molecules. For 3-amino-1-propanol, the final alkanolamine in this study, there is also a considerable difference between the experimental and theoretical proton affinities. However, the gas-phase basicities, in this case, are in better agreement. For 1,2-ethanediol, significant differences can also be seen between the experimental and theoretical values.

As the largest deviations occur for molecules displaying intramoleculer hydrogen bonds, this would suggest that there might be errors in the calculation of strengths of these bonds.

To explore the method and basis-set dependency of the results, the basicities of the alkanolamines, 1,2-ethanediol, and ammonia were calculated with different basis sets and using both the MP2 and B3LYP level of theory. The results are shown in Table 3.

From the values in Table 3, one can see that there is some variation in the results with variation in the level of theory and size of the basis set. However, the B3LYP/6-311++G(d,p) results are in fairly good agreement with MP2 calculations with larger basis sets. More importantly, the relative basicity of the alkanolamines and 1,2-ethanediol remains almost unchanged. Therefore, it seems unlikely that there is any level of quantum mechanical calculation that will be in agreement with the experimental data. The MP2/Aug-cc-pVTZ//B3LYP/6-311++G(d,p) calculations use the largest basis set, and these results are probably the most accurate.

Gas-Phase Dimer Formation. Quantum mechanical calculations were performed to investigate the likelihood of the alkanolamines, diamines, and 1,2-ethanediol forming dimers. Calculations are carried out both for proton-bound dimers and neutral dimers.

The initial geometries were based on conformers that would give the largest number of hydrogen bonds, in particular the H(O)−N-type bonds that appear to be the most energetically favored for alkanolamines. The determination of conformers was not based on any rigorous exploration of the potential dimers of these molecules; for diethanolamine, in particular, there are a large number of potential dimers. The ethanolamine dimer is the same as that reported to be the most stable in calculations by Vorobyov et al.[12] The 1,2-ethanediol dimer geometry is from work by Bako et al.[19]

Calculations are carried out at the HF/6-311++G(d,p) level, and only the binding energy of the dimer is calculated. This is the energy difference between the dimers and the monomers calculated at the same level. The dimers are shown in Figure 2 and Figure 3, and the hydrogen bond lengths are given in Table 4. The dimer formation energy is given in Table 5.

The geometries and the data in Table 5 suggest that all of these molecules form stable proton-bound dimers. They, apparently, can act as bidentate ligands to a protonated molecule. Proton-bound dimers have also been observed experimentally for diethanolamine[17] and 1,2-ethanediol.[18] In the experimental work on 1,2-ethanediol,[18] it was also proposed that one molecule acts as a bidentate ligand. In the same paper, it was observed that 1,2-ethanediol had a stronger propensity to form proton-bound dimers than diols with longer carbon chains. A similar trend can be seen in Table 5; the results suggest that 1,3-propanediamine forms a weaker proton-bound dimer than 1,2-ethanediamine. Apparently, 3-amino-1-propanol also forms a less stable proton-bound dimer than ethanolamine. It appears that molecules with longer carbon chains can form less strained intramolecular hydrogen bonds, and therefore, the additional stability gained by bonding to a second molecule is less.

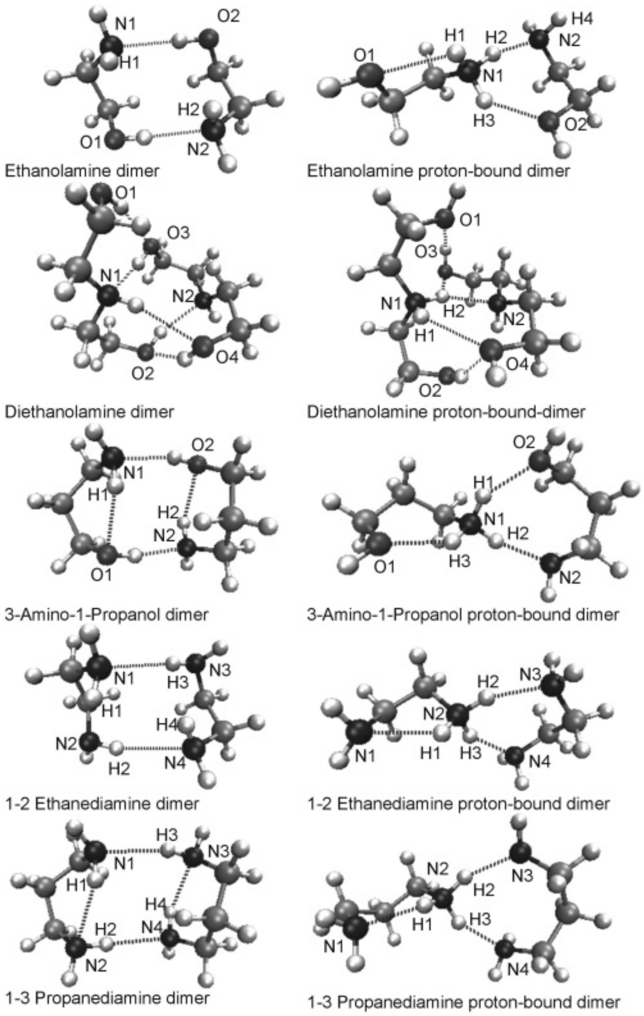
Ethanolamine dimer
Ethanolamine proton-bound dimer
Diethanolamine dimer
Diethanolamine proton-bound-dimer
3-Amino-1-Propanol dimer
3-Amino-1-Propanol proton-bound dimer
1-2 Ethanediamine dimer
1-2 Ethanediamine proton-bound dimer
1-3 Propanediamine dimer
1-3 Propanediamine proton-bound dimer

Figure 2. Dimers optimized at the HF/6-311++G(d,p) level. Dashed lines indicate hydrogen bonds.

At the MP2/6-311++G(2d,2p)//HF/6-311++G(2d,2p) level, the dimer binding energy of ethanolamine is calculated to be −11.00 kcal/mol. As a comparison, the dimer formation energy of water has been calculated to be −5.18 kcal/mol using a

TABLE 3: Gas-Phase Basicities and Proton Affinities Relative to Ammonia[a]

	ethanolamine		diethanolamine		3-amino-1-propanol		1,2-ethanediol	
B3LYP/6-311++G(d,p)//[b] B3LYP/6-311++G(d,p)	16.2	16.2	28.2	28.4	23.4	23.6	−13.1	−12.6
B3LYP/6-311++G(3df,2p)// B3LYP/6-311++G(3df,2p)	16.8	16.8	28.7	28.9	23.8	24.0	−12.3	−11.8
MP2/6-311++G(d,p)// B3LYP/6-311++G(d,p)	14.8	14.8	26.7	26.9	21.9	22.0	−14.6	−14.1
MP2/6-311++G(2d,2p)// B3LYP/6-311++G(d,p)	15.9	15.9	27.7	27.9	22.9	23.0	−13.9	−13.4
MP2/Aug-cc-pVTZ// B3LYP/6-311++G(d,p)	16.1	16.1	28.0	28.2	23.0	23.2	−12.9	−12.5
experimental	18.6	18.3	24.1	23.8	23.5	26.0	−10.9	−9.0

[a] Results in kcal/mol. [b] Same data as in Table 1.

TABLE 4: Dimer Hydrogen Bond Lengths

dimer	bond	length (Å)	dimer(H^+)[a]	bond	length (Å)
ethanolamine	N1−H(O2)	2.119	ethanolamine	O1−H1(N1)	2.249
	H(O1)−N2	2.118		H2(N1)−N2	1.913
	H1(N1)−O1	2.628		H3(N1)−O2	2.092
	H2(N2)−O2	2.627	diethanolamine	H1(N1)−O4	2.321
diethanolamine	H(N1)−O4	2.361		H2(N1)−N2	2.112
	N1−H(O3)	2.017		H2(N1)−O3	2.319
	H(O1)−O3	2.094		O1−H(O3)	2.505
	H(O2)−N2	2.100		H(O2)−O4	2.109
	H(O4)−O2	2.065	3-amino-1-propanol	O1−H3(N1)	1.989
3-amino-1-propanol	N1−H(O2)	2.080		H1(N1)−N2	1.965
	H(O1)−N2	2.069		H2(N1)−O2	1.993
	H1(N1)−O1	2.252	1,2-ethanediamine	N1−H1(N2)	2.285
	H2(N2)−O2	2.295		H2(N2)−N3	1.999
1,2-ethanediamine	N1−H3(N3)	2.560		H3(N2)−N4	2.041
	H1(N1)−N2	2.625	1,3-propanediamine	N1−H1(N2)	2.069
	H2(N2)−N4	2.544		H2(N2)−N3	1.967
	H4(N4)−N3	2.776		H3(N2)−N4	2.003
1,3-propanediamine	N1−H3(N3)	2.405	1,2-ethanediamine	O1−H1(O2)	2.286
	H1(N1)−N2	2.399		H1(O2)−O3	1.789
	H2(N2)−N4	2.447		H2(O3)−O4	1.632
	H4(N4)−N3	2.336			
1,2-ethanediamine	H(O1)−O4	2.051			
	O1−H(O3)	2.155			
	H(O1)−O2	2.699			
	O2−H(O4)	2.160			
	H(O3)−O4	2.748			

[a] Proton-bound dimer.

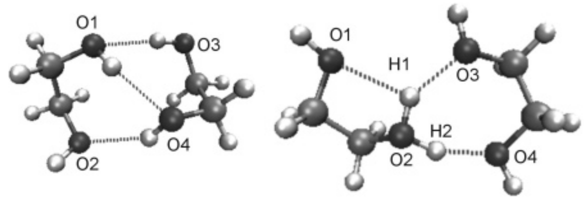

Figure 3. 1,2-Ethanediol dimers optimized at the HF/6-311++G(d,p) level. Dashed lines indicate hydrogen bonds.

TABLE 5: Dimer Binding Energies[a]

	neutral dimer	proton-bound dimer
ethanolamine	−5.9	−25.2
diethanolamine	−5.3	−14.8
3-amino-1-propanol	−4.7	−23.2
1,2-ethanediamine	−2.3	−26.2
1,3-propanediamine	−2.9	−23.2
1,2-ethanediol	−5.4	−32.2

[a] Results in kcal/mol.

similar level of theory.[20] This would suggest that the alkanolamines and 1,2-ethanediol have relatively stable dimers. The diamines appear to form weaker dimers.

Experimental Values

The experimental basicity and proton affinity data for ethanolamine, 3-amino-1-propanol, 1,2-ethanediamine, and 1,3-propanediamine are from pulsed high-pressure mass spectrometry work by Meot-Ner et al.[16] The diethanolamine data are from fast atom bombardment mass spectroscopy work by Sunner et al.,[17] and the 1,2-ethanediol data are from pulsed electron beam high-pressure mass spectrometry experiments.[18] It was noted in the work on 1,2-ethanediol that the presence of proton-bound dimers created problems in determining the proton affinity and basicity of this molecule. The present work suggests that all of the alkanolamines have a comparable propensity to form dimers. While the basicity of these molecules was determined with different experiments, it seems that dimer effects may have affected the experimental results for all of these molecules. The relatively low volatility of these alkanolamines may also make the experimental determination of their gas-phase basicities more difficult. Therefore, it appears that there is considerable uncertainty regarding the experimental data for alkanolamines and 1,2-ethanediol.

Conclusion

Gas-phase basicities from quantum mechanical calculations are generally shown, in this article and work of other authors, to be in good agreement with experimental data. However, poor agreement was observed for a series of alkanolamines and 1,2-ethanediol. Calculations using the MP2 and B3LYP methods with different basis sets revealed some method and basis-set dependency in the results, but these uncertainties cannot account for the differences between the calculated results and the experimental data. Therefore, the current MP2/Aug-cc-pVTZ results are probably the most reliable estimate of the basicity of these molecules.

Calculations on dimer forms suggest that the alkanolamines, diamines, and 1,2-ethanediol form stable proton-bound dimers. Less stable neutral dimers can also be formed. Dimer effects and low volatility suggest high uncertainty in the experimental basicities for the alkanolamines and 1,2-ethanediol.

Acknowledgment. This work has received support from The Research Council of Norway (Program for Supercomputing) through a grant of computing time.

Supporting Information Available: Underlying values for data in Table 2 and Table 3, geometric parameters and Cartesian coordinates of the alkanolamines, and illustrations of other conformers of diethanolamine. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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

(2) Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 4885.

(3) East, A. L. L.; Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 9014.

(4) Pokon, E. K.; Liptak, M. D.; Feldgus, S.; Shields, G. C. *J. Phys. Chem. A* **2001**, *105*, 10483.

(5) Pople, J. A.; Curtiss, L. A. *J. Phys. Chem.* **1987**, *91*, 155.

(6) Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109.

(7) Versteeg, G. F.; van Dijck, L. A. J.; van Swaaij, W. P. M. *Chem. Eng. Commun.* **1996**, *144*, 113.

(8) da Silva, E. F.; Svendsen, H. F. *Ind. Eng. Chem. Res.* **2003**, *42*, 4414.

(9) Reiling, S.; Brickmann, J.; Schlenkrich, M.; Bopp, P. A. *J. Comput. Chem.* **1996**, *17*, 133.

(10) Lii, J. H.; Ma, B.; Allinger, N. L. *J. Comput. Chem.* **1999**, *20*, 1593.

(11) 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.; 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.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(12) Vorobyov, I.; Yappert, M. C.; DuPre, D. B. *J. Phys. Chem. A* **2002**, *106*, 668.

(13) Tubergen, M. J.; Torok, C. R.; Lavrich, R. J. *J. Chem. Phys.* **2003**, *119*, 8397.

(14) Kelterer, A. M.; Ramak, M. *THEOCHEM* **1991**, *232*, 189.

(15) *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, http://webbook.nist.gov, March 2003.

(16) Meot-Ner(Mautner), M.; Hunter, E. P.; Hamlet, P.; Field, F. H. *Proceedings of the 28th Annual Conference on Mass Spectrometry and Allied Topics*, May 25−30, 1980, 233.

(17) Sunner, J. A.; Kulatunga, R.; Kebarle, P. *Anal. Chem.* **1986**, *58*, 1312.

(18) Chen, Q. F.; Stone, J. A. *J. Phys. Chem.* **1995**, *99*, 1442.

(19) Bako, I.; Grosz, T.; Palinkas, G.; Bellissent-Funel, M. C. *J. Chem. Phys.* **2003**, *118*, 3215.

(20) Frisch, M. J.; Del Bene, J. E.; Binkley, J. S.; Schaefer, H. F., III. *J. Chem. Phys.* **1986**, *84*, 2279.