Hyperfine coupling constants of Mg-centered radicals and radical ions

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The energies, geometric parameters, spin densities, and HFC constants of the Mg-centered radicals $^{\bullet}$MgH, $^{\bullet}$MgOH, $^{\bullet}$MgMe, and monovalent magnesium aqua complexes $Mg(H_2O)_n^+$ (n = 0—3) were calculated using the density functional theory. As n increases, the HFC constants decrease for Mg atoms and increase for O atoms. The theoretical HFC constants in the Mg-centered radicals are in good agreement with experimental data.

Key words: magnesium aqua complexes, radical cations, Mg-centered radicals, hyperfine coupling constants, quantum chemical calculations, density functional theory.

Enzymes responsible for biochemistry of a living cell are molecular machines that execute biochemical reactions and the synthesis of biomolecules. The mechanical energy of such a machine is stored in the nonequilibrium conformation of the enzyme macromolecule and then transformed to the energy of the chemical bonds. The key role in chemistry of living systems is played by phosphorylating enzymes producing molecular energy carriers (*e.g.*, adenosine triphosphate (ATP) and other nucleotide triphosphates) that keep organisms in the living state.

The chemical mechanism of phosphorylation has always been enigmatic because it was unclear how the mechanical energy of a macromolecular machine distributed over a great variety of conformations is transformed into the energy of the P—O chemical bond in the ATP molecule and how the mechanical motion of the macromolecule induces the chemical reaction (phosphorylation).

Magnesium-containing radicals and complexes were calculated by various methods.[1—8] However, no studies concerned with not only their geometric parameters and energy characteristics, but also magnetic characteristics (unpaired electron spin density and the constants of hyperfine electron-nuclear interaction) have been reported so far.

The aim of this work was to establish a relation between the charge (and, therefore, electron affinity) and degree of hydration (number of water molecules in the hydration shell) of the Mg^{2+} ion and to calculate the HFC constants $a(^{25}Mg)$ for the $Mg^{\bullet+}$ radical cation at different numbers of water molecules in the hydration shell.

Calculation Procedure

Calculations with full geometry optimization for all structures, that is, $^{\bullet}$MgOH, $^{\bullet}$MgH, $^{\bullet}$MgMe, and $Mg(H_2O)_n^{m+}$ aqua complexes (m = 1, 2; n = 1—6) were carried out by the density functional theory (DFT)[9] with different basis sets using the GAUSSIAN-98 program.[10] The HFC constants were calculated using various combinations of functionals (B3LYP, B1LYP, B3PW91, B3P86, BHandH, BHandHLYP, and SVWN5)[9] and basis sets. The results of vibrational frequency calculations of $Mg(H_2O)_n^{m+}$ aqua complexes characterize the optimized structures as the energy minima or saddle points on the corresponding potential energy surfaces. The energies of the $Mg(H_2O)_n^{m+}$ aqua complexes formation in the reaction $Mg^{m+} + n\,H_2O \rightarrow Mg(H_2O)_n^{m+}$ were calculated with inclusion of zero-point energy (ZPE) differences between the aqua complexes and water molecules. Earlier,[1,2] it was shown that taking into account the basis set superposition error (BSSE) in the calculations of the formation energies (E) of Mg^{2+} complexes has little effect on the accuracy of the results obtained. Therefore, no BSSE correction was applied to the E calculations carried out in this work.

Results and Discussion

HFC constants of Mg-centered radicals. The HFC constants of Mg^+ aqua complexes are unknown and, therefore, it is impossible to compare the theoretically predicted values with the corresponding experimental data. To choose the most accurate and reliable methods of calculation of HFC constants, we carried out quantum chemical calculations of the Mg-centered radicals $^{\bullet}$MgH, $^{\bullet}$MgOH, and $^{\bullet}$MgMe for which the experimental HFC constants $a(^{25}Mg)$, $a(^{1}H)$, and $a(^{13}C)$ are known. The

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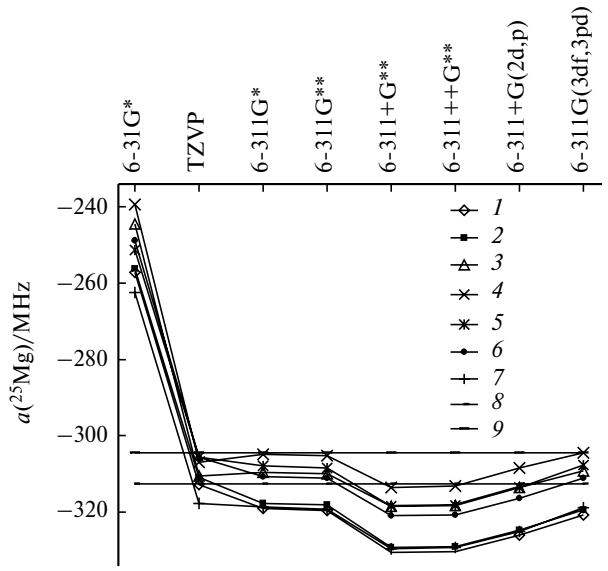

Fig. 1. HFC constants $a(^{25}Mg)$ of $^{\bullet}$MgOH radical obtained from the B3LYP (*1*), B1LYP (*2*), B3P86 (*3*), B3PW91 (*4*), BHandH (*5*), BHandHLYP (*6*), and SVWN5 (*7*) calculations and corresponding experimental values[11] in Ar (*8*) and Ne (*9*) matrices.

HFC constants in the $^{\bullet}$MgOH radical calculated using various functionals and basis sets are shown in Fig. 1. Only five basis sets, namely, TZVP, 6-311G*, 6-311G**, 6-311+G(2d,p), and 6-311G(3df,3pd) provide good agreement with the experiment irrespective of the functional used (Table 1). The calculated HFC constants $a(^{25}Mg)$ for the $^{\bullet}$MgH radical lie between 187 and 193 MHz (this work, see also Ref. 6), whereas the experimental value is 220 MHz.[11,12] The HFC constants $a(^{1}H)$ also show good agreement between theory and experiment. Theory predicts that the $a(^{1}H)$ values lie in the range 283—329 MHz (this work, see also Ref. 6) *vs.* 296 MHz (experimental data[11,12]). The same computational methods give the HFC constants $a(^{25}Mg)$ for the $^{\bullet}$MgOH radical to be in the range 305—313 MHz (this work, see also Ref. 7), which is in good agreement with the experimental $a(^{25}Mg)$ values of 312.7 MHz (in argon matrix[11]) and 304.4 MHz (in neon matrix[11]).

Table 1. HFC constants of Mg-centered radicals

Radical	Nucleus	HFC constant/MHz	
		Experiment	Calculations*
$^{\bullet}$MgH	^{25}Mg	220[12]	−(191—192)
	^{1}H	296[11]	−(283—332)
$^{\bullet}$MgOH	^{25}Mg	304.7—312.7,[11] 304.7[8]	−(304.4—312.8)
	^{1}H	11.7[11]	17—25
$^{\bullet}$MgMe	^{25}Mg	188.3[8]	−(156.2—167.2)
	^{13}C	145.3[8]	−(141.3—152)
	^{1}H	7.0[8]	−(5.1—6.9)

* For the functionals and basis sets used, see caption to Fig. 1.

The HFC constants $a(^{25}Mg)$ in the $^{\bullet}$MgMe radical calculated analogously lie between 160 and 170 MHz and agree with those calculated[8] in other approximations as well as with the experimental HFC constant (188.3 MHz).[8] The calculated HFC constants $a(^{13}C)$ are 130—150 MHz (*cf.* experimental value[8] of 145.3 MHz) and the $a(^{1}H)$ constants are in the range 5—7 MHz (*cf.* experimental value of 7 MHz).[8]

Thus, the basis sets mentioned above combined with various DFT functionals allow the HFC constants of the Mg-centered radicals with different atomic environment of magnesium to be calculated with reasonable accuracy. In addition, from Table 2 containing the theoretical and experimental[13,14] bond lengths and bond angles in the $^{\bullet}$MgMe radical it follows that these methods reliably determine the geometric parameters of the radicals. This also holds for the other two radicals. For instance, the calculated Mg—H bond lengths in the $^{\bullet}$MgH radical are 1.728 Å (*cf.* experimental value[15] of 1.729 Å). The calculated Mg—O and O—H bond lengths in the $^{\bullet}$MgOH radical are equal to 1.76 and 0.95 Å, respectively (*cf.* experimental values of 1.761 Å (Ref. 16) and 1.767 Å (Ref. 16) for the Mg—O bond length). In all cases theory and experiment are in reasonable agreement.

After the examination we used the methods chosen to calculate unknown HFC constants for the $Mg(H_2O)_n^{\bullet+}$ radical cations as they provide good agreement between the experimental and theoretical HFC constants of radicals with different atomic environment of the magnesium central atom.

Structure and properties of magnesium aqua complexes. *Geometry*. The geometric parameters of the aqua com-

Table 2. Geometric parameters of $^{\bullet}$MgMe radical

Method	*d*/Å		Angle H—C—Mg/deg	Reference
	Mg—C	C—H		
Experiment	2.11	—	—	13[a]
	2.102	1.105	110.7	14[b]
Calculations	2.140	1.097	110.5	This work[c]
	2.138	1.093	110.1	8[d]
	2.126	1.094	111.6	8[e]

[a] Microwave spectroscopy data.
[b] Laser induced fluorescence spectroscopy data.
[c] Calculated in the B3LYP/6-31G*, B3LYP/6-311+G**, and B3LYP/6-311++G** approximations.
[d] Calculated in the UB3LYP approximation with the cc-pVDZ (Mg) and DZP (C, H) basis sets.
[e] Calculated in the B3PW91 approximation with the cc-pVDZ (Mg) and DZP (C, H) basis sets.

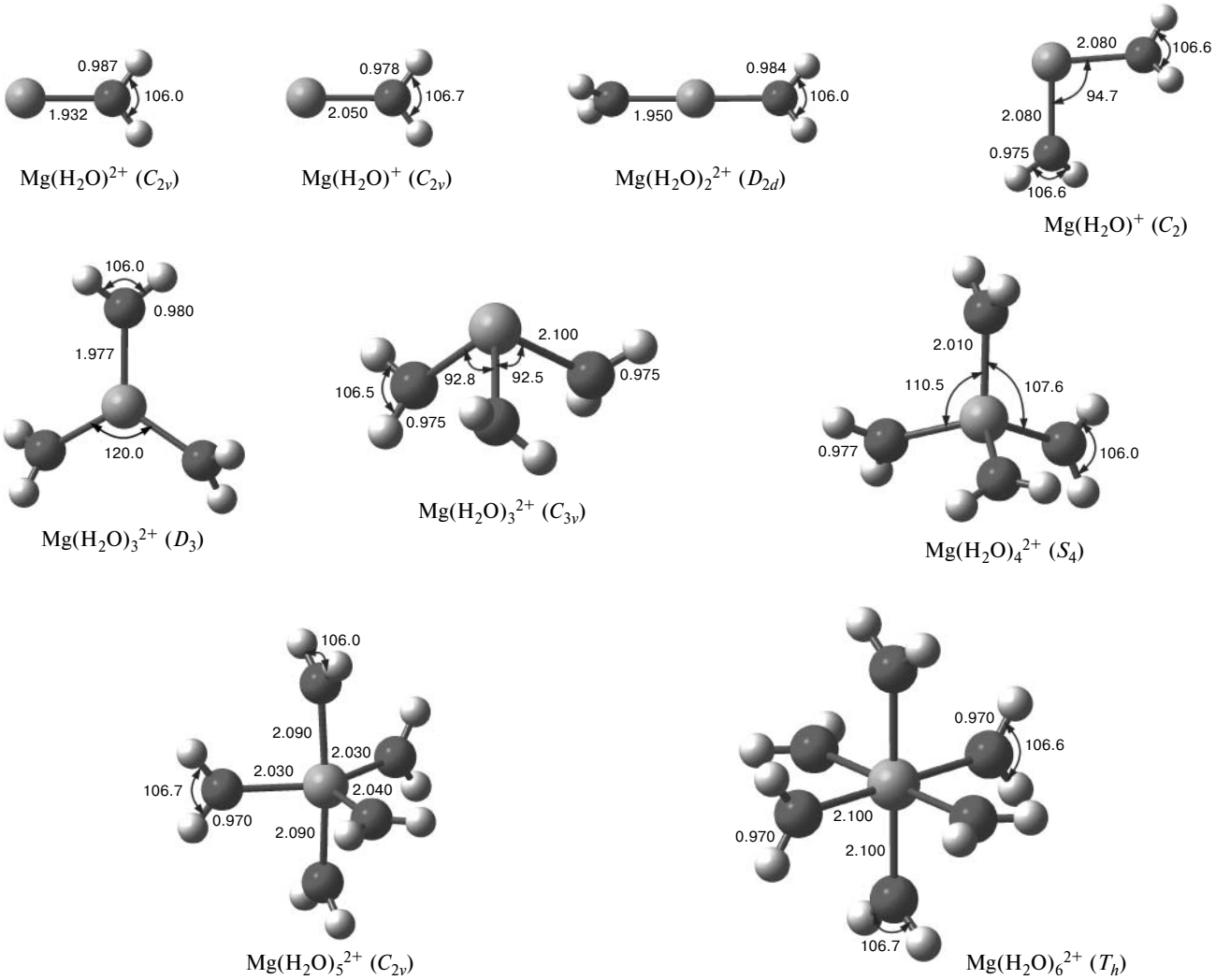

Fig. 2. Geometric parameters of some $Mg(H_2O)_n^{2+}$ and $Mg(H_2O)_n^{+}$ aqua complexes obtained from B3LYP/6-31G* calculations. Shown are the symmetry groups of the complexes, bond lengths (in Å), and bond angles (in degrees).

plexes are shown in Fig. 2 and listed in Table 3. The $Mg(H_2O)^{2+}$ and $Mg(H_2O)^{+}$ ions have planar structures with C_{2v} symmetry. The $Mg(H_2O)_n^{m+}$ aqua complexes have different geometries depending on the charge. Namely, a linear structure with D_{2d} symmetry is the most stable for Mg^{2+} while an angular structure with C_2 symmetry is the most stable for Mg^{+} at $n = 2$. Among the complexes with three water molecules, the energy minimum corresponds to a planar triangular structure with D_{3h} symmetry for $Mg(H_2O)_3^{2+}$ and to a trigonal-pyramidal structure with C_{3v} symmetry for $Mg(H_2O)_3^{+}$. In the complex $Mg(H_2O)_4^{2+}$ the Mg atom is in tetrahedral environment and the structure with the square-planar geometry (C_{4h} symmetry) corresponds to the transition state ($N_{imag} > 1$). The most stable structure of the $Mg(H_2O)_5^{2+}$ aqua complex has C_{2v} symmetry; in the complex $Mg(H_2O)_6^{2+}$ the Mg ion is in octahedral environment (T_h symmetry). The $Mg(H_2O)_n^{+}$ complexes with $n = 4$—6 are characterized by imaginary lowest vibrational frequencies, correspond to saddle points, and are unstable. Be-

Table 3. Mg—O Bond lengths and energies E of formation of aqua complexes obtained from B3LYP/6-31G* with inclusion of zero-point vibration energy (ZPE)

n	d_{Mg-O}/Å		$-(E + ZPE)$/kcal mol^{-1}	
	$Mg(H_2O)_n^{+}$	$Mg(H_2O)_n^{2+}$	$Mg(H_2O)_n^{+}$	$Mg(H_2O)_n^{2+}$
1	2.05	1.93	38.1	88.9
2	2.08	1.95	68.8	167.5
3	2.10	1.98	94.7	231.0
4	—	2.01	—	282.3
5	—	2.03[a], 2.09[b]	—	316.4
6	—	2.1	—	347.3

[a] Equatorial bonds (see Fig. 2).
[b] Axial bonds (see Fig. 2).

cause of this only the Mg^+ complexes with $n = 1$—3 will be discussed in the text below.

Table 3 shows that an increase in n causes elongation of the Mg—O coordination bonds in both the $Mg(H_2O)_n^+$ and $Mg(H_2O)_n^{2+}$ complexes; the calculated Mg—O distance in the $Mg(H_2O)_6^{2+}$ complex is in good agreement with the experimental values 2.05—2.10 Å (see Ref. 2 and references cited therein). The coordination bonds Mg—O in the $Mg(H_2O)_n^{2+}$ complexes are much shorter than in the $Mg(H_2O)_n^+$ ones; this reliably indicates that the Coulomb interaction between the charged central ion and the coordinated water dipoles contributes largely to the Mg—O bond energies in the aqua complexes.

Energy. The water binding energies E listed in Table 3 were calculated as the energy differences between the complexes and corresponding noninteracting reactants

$$E = E[Mg(H_2O)_n^{m+}] - E[Mg^{m+}] - nE[H_2O],$$

where $m = 1$ (2) for the singly (doubly) charged ions, respectively. All the E energies are negative, *i.e.*, the energies of the complexes are lower than the total energies of the initial reactants, and complexation is exothermic process. The binding energies of the water ligands in the Mg^{2+} complexes are almost twice as high as in the Mg^+ complexes; this ratio of energies correlates with the ratio of the Mg—O bond lengths in the same complexes and also unambiguously indicates the determining contribution of the Coulomb interaction to energy characteristics of the complexes. The energies E (see Table 3) determine the total binding energy of n ligands. The average binding energy per ligand in the Mg^+ (Mg^{2+}) complexes is 38.1 (88.9), 34.4 (83.8), and 31.6 (77.0) kcal mol^{-1} for $n = 1$, 2, and 3, respectively. This means that each succeeding ligand is bound in the complexes less strongly than the preceding ligand.

The electron affinity energies of the $Mg(H_2O)_n^{2+}$ complexes were calculated as the differences between the total energies of the $Mg(H_2O)_n^{2+}$ and $Mg(H_2O)_n^+$ complexes, the latter having much lower energies. Thus, attachment of an electron to the $Mg(H_2O)_n^{2+}$ systems is accompanied by the formation of more stable $Mg(H_2O)_n^+$ structures (electron affinity energy is positive). As n increases, the electron affinity energy decreases from the maximum value of 15.5 eV for "anhydrous" Mg^{2+} ion ($n = 0$) to 13.2, 11.1, and 9.5 eV for $n = 1$, 2, and 3, respectively.

Charges. The charge on the central ion in the $Mg(H_2O)_n^{2+}$ aqua complexes monotonically decreases from 1.7 ($n = 1$) to 1.0 ($n = 6$) as n increases. The charge on the magnesium cation in the $Mg(H_2O)_n^+$ aqua complexes also decreases from 0.8 ($n = 1$) to 0.5 ($n = 3$). This is consistent with the published results.[3,4] Clearly, the positive charge on the central ion is compensated by the negative charge of the ligands.

Spin densities and HFC constants of $Mg(H_2O)_n^+$ aqua complexes. *Spin densities*. The spin density (ρ) on the Mg atom and the total spin density on the O atoms in the $Mg(H_2O)_n^+$ complexes are plotted *vs.* number of ligands in Fig. 3. The appearance of nonzero ρ(O) values at $n = 1$—3 indicates that the bonds between the central atom and the ligands are not purely electrostatic, having some covalent component. It is the covalent component that is responsible for the fact that the π-electron of the Mg^+ ion induces (i) spin polarization of the coordination bond and (ii) negative spin density on oxygen atoms and additional (compensating) positive spin density on the Mg^+ cation, As a result the total (positive) spin density on the Mg^+ cation is greater than unity, but the total spin of the complex equal to unity remains unchanged (spin density on H atoms is negligible, being at most 10^{-3}). As n increases, the additional contributions ρ(Mg) and ρ(O)

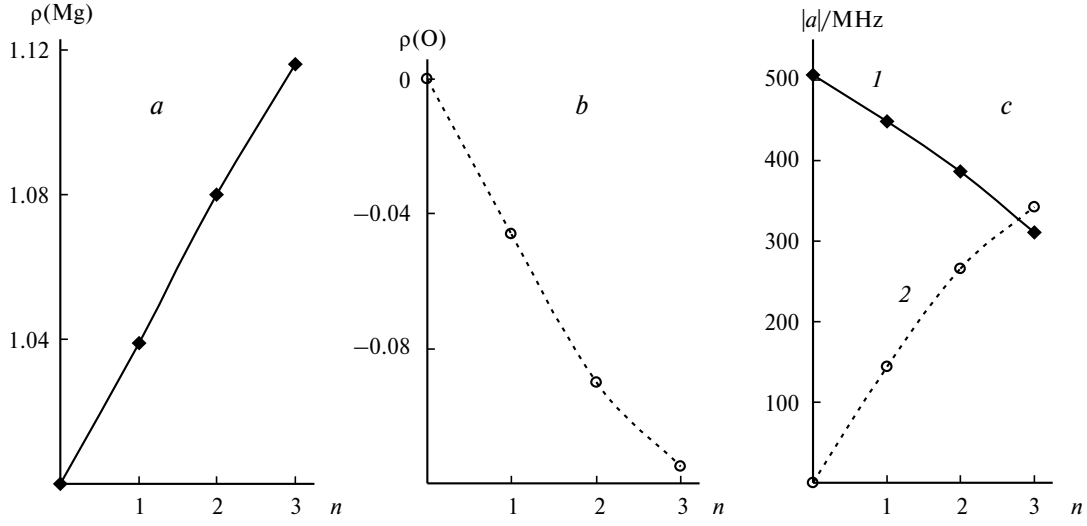

Fig. 3. Spin densities (ρ) on Mg (*a*) and O (*b*) atoms and HFC constants $|a(^{25}Mg)|$ (*1*) and $|a(^{17}O)|$ (*2*) (*c*) of $Mg(H_2O)_n^+$ aqua complexes obtained from B3LYP/TZVP//B3LYP/6-31G* calculations plotted *vs.* number of ligands n.

increase almost additively (see Fig. 3), namely, the spin polarization of the ligands causes an equal increase in the positive density on the Mg atom and in the negative density on oxygen atoms.

HFC constants. The HFC constants $a(^{25}Mg)$ and $a(^{17}O)$ are plotted *vs*. *n* in Fig. 3, *c*. The $a(^{17}O)$ constants are negative and increase in absolute value ($|a(^{17}O)|$) as *n* increases similarly to the spin density ρ(O).

The HFC constants $a(^{25}Mg)$ are also negative. They decrease in absolute value with an increase in the number of ligands, which is quite unexpected because the spin density increases in the same order. The reason is as follows. Hyperfine coupling arises from the spin density on the inner Mg s-AO, which is created due to spin polarization of the coordination bonds and spin polarization of inner s-electrons by the π-electron of the Mg^+ ion. These contributions can partially compensate each other. As a result, the spin density on the inner s-shell becomes positive and decreases with an increase in *n*; the HFC constant $a(^{25}Mg)$ is negative (^{25}Mg nucleus has a negative magnetic moment) and decreases as *n* increases, as shown in Fig. 3, *c*.

Thus, the energy characteristics, geometric and magnetic parameters of $^{25}Mg(H_2O)_n^+$ aqua complexes depend on the number of ligands in the hydration shell of the magnesium cation.

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References

1. E. D. Glendening and D. Feller, *J. Phys. Chem.*, 1996, **100**, 4790.
2. G. D. Markham, J. Glusker, and C. W. Bock, *J. Phys. Chem. B*, 2002, **106**, 5118.
3. M. Pavlov, P. E. M. Siegbahn, and M. Sandström, *J. Phys. Chem. A*, 1998, **102**, 219.
4. C. W. Bock, A. Kaufman, and J. P. Glusker, *Inorg. Chem.*, 1994, **33**, 419.
5. R. C. Dunbar and S. Petrie, *J. Phys. Chem. A*, 2005, **109**, 1411.
6. P. J. Bruna and F. Grein, *Phys. Chem. Chem. Phys.*, 2003, **5**, 3140.
7. L. Hermosilla, P. Calle, J. M. García de la Vega, and C. Sieiro, *J. Phys. Chem. A*, 2005, **109**, 1114.
8. A. McKinley and E. Karakyriakos, *J. Phys. Chem. A*, 2000, **104**, 8872.
9. J. B. Foresman and E. Frish, *Exploring Chemistry with Electronic Structure Methods*, 2nd Ed., Gaussian Inc., Pittsburgh, 1996, 302 pp.
10. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *GAUSSIAN-98*, Gaussian Inc., Pittsburgh (PA), 1998.
11. J. Broom and W. Weltner, *J. Chem. Phys.*, 1973, **58**, 5322.
12. L. Knight and W. Welter, *J. Chem. Phys.*, 1971, **54**, 3875.
13. M. A. Anderson and L. M. Ziurys, *Astrophys. J.*, 1995, **452**, L157.
14. R. Rubino, J. M. Williamson, and T. A. Miller, *J. Chem. Phys.*, 1995, **103**, 5964.
15. K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. **4**, *Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979.
16. P. R. Bunker, M. Kolbuszewski, P. Jensen, M. Brumm, M. A. Anderson, W. L. Barclay, Jr., L. M. Ziurys, Y. Ni, and D. O. Harris, *Chem. Phys. Lett.*, 1995, **239**, 217.
17. A. J. Apponi, M. A. Anderson, and L. M. Ziurys, *J. Chem. Phys.*, 1999, **111**, 10919.

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