A Density Functional Study of the Equilibrium Structure, Vibrational Spectrum, and Heat of Formation of Br_2O_3

Sujata Guha and Joseph S. Francisco*

Department of Chemistry and Department of Earth and Atmospheric Sciences, Purdue University, West Lafayette, Indiana 47907-1393

Received: April 20, 1998; In Final Form: June 12, 1998

The geometry, vibrational spectrum, and energetics of $BrOBrO_2$ have been examined using the B3LYP and B3PW91 ab initio density functional methods. The estimated heat of formation of $BrOBrO_2$ is 57.4 ± 4 kcal mol^{-1} at 0 K. We find that, within the $XOBrO_2$ series (X = H, Cl, Br), $BrOBrO_2$ is the least stable.

I. Introduction

Halogen oxides have been known, for a long time, to play important roles in the destruction of stratospheric ozone.[1,2] The discovery of dramatically elevated concentrations of ClO and OClO in the polar stratosphere has focused increased attention on the oxides of chlorine.[3,4] The OClO radicals, which are known to result from the coupling of ClO and BrO radicals, have been reported by field measurements.[5,6] From this coupling, it has been suggested that higher chlorine oxides may be formed, which are believed to play critical roles in the catalytic destruction of ozone[7] and which have been postulated to serve as temporary reservoirs of chlorine during the early springtime.[8]

A higher chlorine oxide that has governed considerable attention is Cl_2O_3. It results from the reaction between ClO and OClO and is found to be very stable at low temperatures, due to the equilibrium constant for the ClO + OClO reaction being extremely temperature-dependent.[9,10] Renard et al.[11] have reported the observation of OBrO in the stratosphere. The authors suggested that OBrO could be the principal bromine species at night in the stratosphere at mid-latitudes. A reaction between BrO and OBrO radicals in the stratosphere, analogous to the reaction between ClO and OClO, is quite possible in the regions where bromine concentrations are significant. Such a reaction could potentially produce Br_2O_3.

Our knowledge of bromine oxides is limited.[12] Ozonization of bromine in $CFCl_3$ yielded a lemon-yellow precipitate which dissolved partially in CH_2Cl_2, forming an orange solution, and left an insoluble colorless solid.[13] From the solution, orange needles crystallized at −90 °C, which decomposed above −40 °C and detonated if warmed rapidly to approximately 0 °C. The crystal structure investigation gave $Br-O-BrO_2$ (bromine bromate) as the molecular composition.[13]

Bromine bromate is formally the anhydride of hypobromous acid and bromic acid. Experiments reported the Br atom in bromine bromate to be in a pyramidal environment with two short Br=O bonds and an angled Br−O−Br unit.[14] The Raman spectrum of $Br-O-BrO_2$ shows it to be a new compound, which seems to be more strongly oxidized, since the colorless-residue/Br_2O_3 ratio increased with increasing ozonization time. Kuschel and Seppelt postulated that bromine bromate might have been formed by a bimolecular reaction of Br_2 and O_3 in the ozonization process.[14]

In this paper we examine the stability of Br_2O_3. There have been no computational studies on Br_2O_3 in the literature. Our present report examines the structure, vibrational spectrum, and energetics of Br_2O_3.

TABLE 1: Equilibrium Geometry for Br_2O_3.

species	coordinates[a]	6-311+G(3df) B3LYP	6-311+G(3df) B3PW91
$BrOBrO_2$	Br′O′	1.827	1.814
	O′Br	1.931	1.910
	BrO	1.612	1.602
	OBr	1.610	1.600
	Br′O′Br	115.3	114.3
	O′BrO	104.2	103.8
	OBrO	96.2	96.4
	Br′O′BrO	49.9	49.2
	O′BrOO	165.3	164.5

[a] Bond distances are in angstroms and bond angles are in degrees.

II. Computational Methods

Ab initio molecular orbital calculations are performed using the GAUSSIAN 94 program.[15] The equilibrium geometry of Br_2O_3 is fully optimized to better than 0.001 Å for bond distances and 0.1° for bond angles. The B3LYP (Becke's nonlocal three-parameter exchange with Lee−Yang−Parr correlation functional)[16] and B3PW91[17] density functional methods are used with the 6-311+G(3df) basis set. The harmonic vibrational frequencies and intensities are calculated at both the B3LYP and B3PW91 levels of theory in conjugation with the 6-311+G(3df) basis set, using the geometry calculated at these levels of theory. The heat of formation of Br_2O_3 is determined using isodesmic reaction schemes at the B3LYP and B3PW91 levels of theory.

III. Results and Discussion

A. Equilibrium Structure of Br_2O_3. The optimized structural parameters for $BrOBrO_2$, calculated at the B3LYP and the B3PW91 levels of theory using the 6-311+G(3df) basis set, are presented in Table 1 and illustrated in Figure 1.

The structure of $BrOBrO_2$ is very similar to that of $ClOClO_2$, often referred to as the Hehre structure. The geometrical parameters of $BrOBrO_2$ can be compared to the corresponding parameters of $HOBrO_2$ and $ClOBrO_2$. The Br′−O′ bond length in $BrOBrO_2$ is predicted to be 1.827 Å at the B3LYP/6-311+G(3df) level of theory, while it is 1.814 Å at the B3PW91/6-311+G(3df) level of theory. The central O′−Br bond length in $BrOBrO_2$ is 1.931 Å at the B3LYP level of theory and quite

S1089-5639(98)01918-5 CCC: $15.00

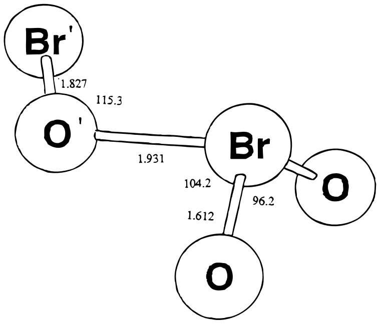

Figure 1. Equilibrium structure of Br_2O_3. The values are at the B3LYP/6-311+G(3df) level of theory. See Table 1 for a complete list of geometrical parameters.

closely agrees with the central O−Br lengths in $HOBrO_2$ (1.844 Å)[18] and $ClOBrO_2$ (1.984 Å).[19] The terminal BrO bond lengths of the three $XOBrO_2$ (X = H, Cl, Br) species also agree well with each other, being 1.619 Å in $HOBrO_2$,[18] 1.613 Å in $ClOBrO_2$,[19] and 1.612 Å in $BrOBrO_2$. The central O′−Br bond in $BrOBrO_2$ (1.931 Å) is much larger than the bonds formed between bromine and the terminal oxygen atoms in $BrOBrO_2$. This is because the lone pairs of electrons on the terminal oxygen atoms enter into partial resonance with their immediate bonding electron neighbors, thus rendering a partial double-bond character to the bonds formed between bromine and the terminal oxygen atoms.

The Br′O′Br angle in $BrOBrO_2$ is 115.3° at the B3LYP level of theory and is much larger than the HOBr angle in $HOBrO_2$ (104.5°)[18] and the ClOBr angle in $ClOBrO_2$ (112.9°),[19] because of the greater amount of repulsion between the lone pairs of electrons on the large bromine atoms, compared to the smaller electron pair repulsion between the bromine and hydrogen atoms (in $HOBrO_2$) and between bromine and chlorine atoms (in $ClOBrO_2$). At the B3PW91 level of theory, the Br′O′Br angle is 114.3°. The OBrO angle in $BrOBrO_2$ is 96.2° and is within range of the OBrO angles in $HOBrO_2$ (101.7°)[18] and $ClOBrO_2$ (111.6°).[19] The O′BrO angle in $BrOBrO_2$ (104.2°) is in good agreement with the corresponding O′BrO angles in $HOBrO_2$ (104.2°)[18] and $ClOBrO_2$ (103.8°).[19] The Br′O′BrO and O′BrOO dihedral angles show some reduction in values going from the B3LYP to the B3PW91 basis set. From Table 1 it is observed that, at both the B3LYP and the B3PW91 levels of theory, the values of the bond lengths and bond angles of $BrOBrO_2$ agree well with each other.

A comparison of our calculated values of the bond lengths and bond angles of $BrOBrO_2$ with those calculated by Seppelt in the solid state[13] show certain similarities as well as differences. The Br′−O′ bond length estimated by Seppelt is 1.849 Å, and is within the vicinity of our calculated Br′−O′ bond length of 1.827 Å. Seppelt found that the O′−Br bond length in the solid phase (1.849 Å) is the same as the Br′−O′ length,[13] while our calculation of the O′−Br length yielded a different result (1.931 Å). Our calculated BrO length of 1.612 Å agreed with Seppelt's. In the solid state of $BrOBrO_2$, the Br′O′Br angle was found to be 111.2°, while our gas-phase calculations yielded a Br′O′Br angle of 115.3°. Seppelt's estimated value of the O′BrO angle (103.2°) is quite close to our estimated value of 104.2°. However, the values for the OBrO angle in the solid and gaseous phases are quite different from each other, being 106.4° in the solid phase and 96.2° in the gaseous phase. One reason for these differences may lie in the fact that, in the solid phase, Br_2O_3 exists as a dimer. The bonding in the dimer could account for some of the differences between our calculated Br_2O_3 structure and that observed in the solid phase.

TABLE 2: Vibrational Frequencies for $BrOBrO_2$ Using the 6-311+G(3df) Basis Set

		B3LYP		B3PW91	
mode no.	mode description	freq (cm^{-1})	int (km mol^{-1})	freq (cm^{-1})	int (km mol^{-1})
1	BrO asym. stretch	966	106	996	109
2	BrO sym. stretch	911	64	940	61
3	Br′O′ stretch	649	11	670	15
4	BrO′ stretch	458	74	476	81
5	OBrO scissor	371	21	380	21
6	OBrO rock	285	10	294	10
7	O′BrO bend	214	1	221	1
8	Br′O′Br bend	117	1	121	1
9	Br′O′BrO torsion	46	3	51	3

B. Harmonic Vibrational Frequencies of Br_2O_3. The calculated vibrational frequencies and intensities for $BrOBrO_2$ are provided in Table 2. All vibrational frequencies noted in the table are calculated at the B3LYP and B3PW91 levels of theory using the 6-311+G(3df) basis set. The values of the frequencies and intensities at both levels of theory agree very well with each other.

In the prediction of the vibrational frequencies of $BrOBrO_2$ the most intense band is predicted to be the BrO asymmetric stretch at 966 cm^{-1}, while the least intense bands are O′BrO bend, Br′O′Br bend, and the Br′O′BrO torsion at 214, 117, and 46 cm^{-1}, respectively. The frequencies of $BrOBrO_2$ can be compared to those of $HOBrO_2$ and $ClOBrO_2$. The Br′−O′ stretch (649 cm^{-1}) in $BrOBrO_2$ is smaller than the Cl−O stretch (739 cm^{-1}) in $ClOBrO_2$,[19] which is consistent with the Br−O bond length being larger than the Cl−O bond length.[19] The central Br−O stretches in $BrOBrO_2$ and $ClOBrO_2$ are quite similar, being 458 cm^{-1} in the former and 411 cm^{-1} in the latter,[19] at the B3LYP level of theory. The BrO asymmetric and symmetric stretches in $HOBrO_2$, $ClOBrO_2$, and $BrOBrO_2$ are also comparably similar. At the B3LYP level of theory, the OBrO modes in $HOBrO_2$ (382 cm^{-1}),[18] $ClOBrO_2$ (364 cm^{-1}),[19] and $BrOBrO_2$ (371 cm^{-1}) are quite similar. The torsional frequencies in $BrOBrO_2$ and $ClOBrO_2$ are very close to each other in value.

A comparison of the experimental Raman spectrum of solid $BrOBrO_2$, reported by Kuschel and Seppelt[14] with the results obtained according to our density functional calculations, shows similarities. In the solid state the Raman spectrum of $BrOBrO_2$ shows prominent absorption bands at 449, 588, and 849 cm^{-1}. Our gas-phase calculations suggest prominent absorbances at 458, 911, and 966 cm^{-1} corresponding to the Br−O′ stretch, the BrO symmetric stretch, and the BrO asymmetric stretch, respectively, while the weakest absorption take place at 117 cm^{-1} (Br′O′Br bend) and 214 cm^{-1} (O′BrO bend). The 449 and 849 cm^{-1} absorption frequency bands in solid $BrOBrO_2$ reasonably agree with the 458 and 911 cm^{-1} absorption bands of $BrOBrO_2$ in the gaseous phase. There is no prominent absorption for gaseous $BrOBrO_2$ around 588 cm^{-1} as is present in the solid phase. The 588 cm^{-1} band in the Raman spectrum of the solid-phase $BrOBrO_2$ could be due to the existence of Br_2O_3 as a dimer.

C. Heat of Formation of Br_2O_3. The total energies for the species involved in the $BrOBrO_2$ reaction schemes are presented in Table 3, while the heat of formation estimates for $BrOBrO_2$, at the B3LYP and B3PW91 levels of theory, are provided in Table 4. Isodesmic reaction schemes are used to calculate the heat of formation for $BrOBrO_2$. Isodesmic reactions, which have been used to obtain the heats of formation for many molecules, are those in which the reactants and products contain the same types of bonds (i.e., the number of

TABLE 3: Total Energies[a] for Br_2O_3 and Species in the Isodesmic Reaction

species	B3LYP	B3PW91
$BrOBrO_2$	−5373.781 74	−5373.658 67
$ClOBrO_2$	−3259.849 02	−3259.688 88
$HOBrO_2$	−2800.287 68	−2800.183 60
HOBr	−2649.956 29	−2649.907 84
HOCl	−536.022 04	−535.936 67
H_2O	−76.464 51	−76.434 16

[a] In units of hartrees.

TABLE 4: Heat of Formation[a] Estimates for Br_2O_3

	B3LYP		B3PW91	
isodesmic schemes	$\Delta H^\circ_{r,0}$	$\Delta H^\circ_{f,0}$ ($BrOBrO_2$)	$\Delta H^\circ_{r,0}$	$\Delta H^\circ_{f,0}$ ($BrOBrO_2$)
$HOBrO_2 + HOBr \rightarrow H_2O + BrOBrO_2$	−2.2	56.4	−1.7	56.9
$ClOBrO_2 + HOBr \rightarrow HOCl + BrOBrO_2$	2.7	58.2	2.6	58.1

[a] In units of kcal mol^{-1}.

bonds broken and formed is conserved). Such a scheme of reactions requires that the heats of formation of all the molecules involved in the reactions be known to high accuracy, with the exception of the heat of formation of the particular isomer. Due to this property, errors in the energy that might occur due to defects in the basis set and electron correlation cancel to a large extent. For $BrOBrO_2$, the following two isodesmic reaction schemes have been employed

$$HOBrO_2 + HOBr \rightarrow H_2O + BrOBrO_2 \tag{1}$$

$$ClOBrO_2 + HOBr \rightarrow HOCl + BrOBrO_2 \tag{2}$$

The results from the isodesmic reaction 2 are, probably, a much better determination, because the chlorine and bromine bonding are more similar in these compounds than they are in $HOBrO_2$ (e.g., the bonding in the $-OBrO_2$ part of $ClOBrO_2$ and $BrOBrO_2$ is much more similar compared to that in $HOBrO_2$ and $BrOBrO_2$).

In the calculation of the heat of formation from the isodesmic schemes, literature values for the heats of formation for HOH (−57.1 ± 0.1 kcal mol^{-1}),[20] HOCl (−17.1 ± 0.5 kcal mol^{-1}), HOBr (−10.93 ± 1 kcal mol^{-1}),[21] $HOBrO_2$ (12.4 ± 3 kcal mol^{-1}),[18] and $ClOBrO_2$ (49.3 ± 3 kcal mol^{-1})[19] are used. Using these results, we are also able to calculate the heats of reaction for the two isodesmic schemes at the B3LYP and B3PW91 levels of theory.

In Table 4, the calculated density functional values for the heat of formation of $BrOBrO_2$ are in close agreement. The mean of the four density functional values gives $\Delta H^\circ_{f,0}$ ($BrOBrO_2$) = 57.4 kcal mol^{-1} as the heat of formation for $BrOBrO_2$. Comparing the density functional and coupled-cluster results for $HOBrO_2$[18] and $ClOBrO_2$,[19] we find that the differences between the results are within 4 kcal mol^{-1}. This leads to the probable uncertainty in our estimate of the heat of formation for BrOBr(O)O, using the density functional theory, as being ±4 kcal mol^{-1}. Thus, the heat of formation for BrOBr(O)O is 57.4 ± 4 kcal mol^{-1}.

To independently check the reasonableness of our estimate for the heat of formation for $BrOBrO_2$, let us assume the bonding on the −Br(O)O unit to be similar for ClOBr(O)O and BrOBr(O)O. An examination of the bonding in these two molecules suggests that this is a valid assumption. The BrO bond length in the −Br(O)O unit is 1.613 Å for ClOBr(O)O[19] and 1.612 Å for BrOBr(O)O. It is, thus, reasonable to assume that the bond dissociation energy (BDE) for breaking the Br−O bond in the −Br(O)O unit could be the same.

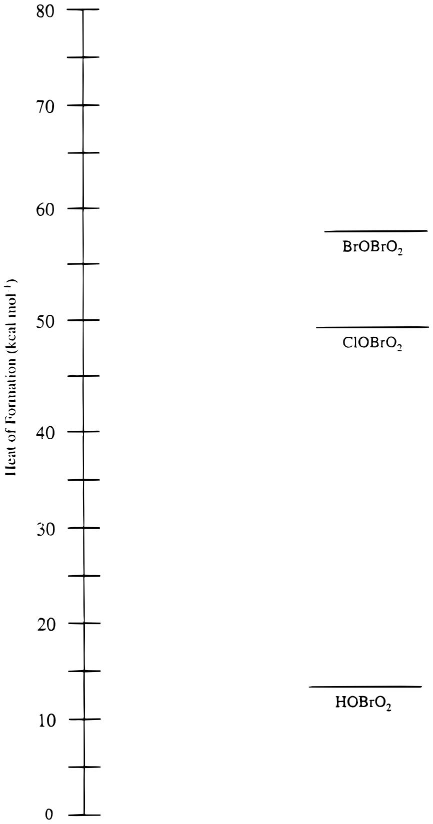

Figure 2. Relative energies of $XOBrO_2$ isomers (where X = H, Cl, Br).

$$ClOBr(O)O \rightarrow ClOBrO + O$$

$$BrOBr(O)O \rightarrow BrOBrO + O$$

Such an assumption leads to the equation

$$\Delta H_f[BrOBr(O)O] - \Delta H_f[ClOBr(O)O] = \Delta H_f(BrOBrO) - \Delta H_f(ClOBrO)$$

Guha and Francisco[22] have estimated the heats of formation for ClOBrO and BrOBrO to be 48.3 ± 3 and 54.8 ± 3 kcal mol^{-1}, respectively. Francisco and Clark[19] have estimated the heat of formation for ClOBr(O)O to be 49.3 ± 3 kcal mol^{-1}. These heats of formation were estimated at the CCSD(T)/6-311+G(3df)//B3LYP/6-311+G(3df) level of theory. Combining these numbers in the above expression, we obtain 55.8 ± 3 kcal mol^{-1} as the heat of formation value for BrOBr(O)O. This result is in reasonable agreement with our density functional estimate of 57.4 ± 4 kcal mol^{-1}.

D. Comparison of the Relative Stability of $XOBrO_2$ Species (Where X = H, Cl, Br). Figure 2 shows a comparison of the relative energetic stability of the $XOBrO_2$ species (X = H, Cl, Br) and clearly indicates that the most stable isomeric form is $HOBrO_2$[18] with a heat of formation of 12.6 kcal mol^{-1}. The next in stability is the $ClOBrO_2$ isomer[19] (49.3 kcal mol^{-1}), and the least stable is the $BrOBrO_2$ isomer with a 57.4 kcal mol^{-1} heat of formation. It is very important to consider the form of bonding within each isomeric form and the types of linkages in which each isomer is involved to gain a proper insight into the relative stability and instability among the isomers. In general, when a hydrogen atom in an isomeric form is replaced by higher halogens (chlorine and bromine), the stability of the isomer decreases because the higher p and d orbitals of the halogens influence the bonding within the species. The hydrogen atom uses its 1s orbital for bonding, which has relatively lower energy than the higher 2p and 3d orbitals of chlorine and bromine, respectively. The small hydrogen atom can overlap very effectively with the oxygen atom, thus making it hard to break the strong H−O bond easily. However, the chorine and bromine atoms are much larger in size, and the bond formed between them and the oxygen atoms are weaker. Thus, the Cl−O bond strength is much lesser than the H−O bond strength. The Br−O bond is the weakest due to the large size of the bromine atom and the participation of the 3d orbitals of bromine in bonding, and the Br−O bond can be easily broken, in comparison. Thus, the $BrOBrO_2$ species has the highest energy (57.4 kcal mol^{-1}) and lies above the $HOBrO_2$[18] and $ClOBrO_2$[19] species on the relative energy scale.

IV. Summary

The equilibrium structure, vibrational spectrum, energetics, and heat of formation of the Br_2O_3 species have been investigated with the B3LYP and B3PW91 density functional methods. The heat of formation of $BrOBrO_2$ is calculated to be 57.4 ± 4 kcal mol^{-1}. A comparison of the relative stablity of $BrOBrO_2$ with that of $HOBrO_2$[18] and $ClOBrO_2$[19] shows that $BrOBrO_2$ is quite unstable, relative to $HOBrO_2$ and $ClOBrO_2$.

References and Notes

(1) Waters, J. W.; Froidevaux, L.; Read, W. G.; Manney, G. L.; Elson, L. S.; Flowers, D. A.; Jarnot, R. F.; Harwood, R. S. *Nature* **1993**, *362*, 597.

(2) Wofsy, S. C.; Molina, M. J.; Salawitch, R. J.; Fox, L. E.; McElroy, M. B. *J. Geophys. Res. A* **1988**, *93*, 2442.

(3) de Zafra, R. L.; Jaramillo, M.; Parrish, A.; Solomon, P.; Conner, B.; Barrett, J. *Nature* **1987**, *328*, 408.

(4) Brune, W. H.; Anderson, J. G.; Chan, K. R. *J. Geophys. Res.* **1989**, *94*, 16649.

(5) Solomon, S.; Sander, R. W.; Jakoubek, R. O.; Arpag, K.; Stephens, S. L.; Keys, J. G.; Garcia, R. R. *J. Geophys. Res.* **1994**, *99*, 3509.

(6) Brandtjen, R.; Klupfel, T.; Perner, D.; Knudsen, B. M. *Geophys. Res. Lett.* **1994**, *21*, 1363.

(7) Molina, L. T.; Molina, M. J. *J. Phys. Chem.* **1987**, *91*, 433.

(8) Sander, S. P.; Friedl, R. R.; Yung, Y. L. *Science* **1989**, *249*, 1095.

(9) Hayman, G. D.; Cox, R. A. *Chem. Phys. Lett.* **1989**, *155*, 1.

(10) Burkholder, J. B.; Mauldin, R. L. III; Yokelson, R. J.; Solomon, S.; Ravishankara, A. R. *J. Phys. Chem.* **1997**, *97*, 9597.

(11) Renard, J. B.; Pirre, M.; Robert, C.; Huguenin, D. *C. R. Acad. Sci.* **1997**, *325*, 921.

(12) Chase, M. W. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1069.

(13) Seppelt, K. *Acc. Chem. Res.* **1997**, *30*, 111.

(14) Kuschel, R.; Seppelt, K. *Angew. Chem.* **1993**, *32*, 1632.

(15) GAUSSIAN 94, Revision D.2: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. P. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, 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.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkeley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

(16) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *41*, 785.

(17) Perdes, J. P.; Wong, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(18) Guha, S.; Francisco, J. S. *J. Phys. Chem. A* **1998**, *102*, 2072.

(19) Francisco, J. S.; Clark, J. *J. Phys. Chem. A* **1998**, *102*, 2209.

(20) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, E. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data, Suppl.* **1985**, *1*.

(21) Francisco, J. S.; Sander, S. P.; Lee, T. J.; Rendell, A. P. *J. Phys. Chem.* **1994**, *98*, 5644.

(22) Guha, S.; Francisco, J. S. *J. Phys. Chem. A* **1997**, *101*, 5347.