

Intermolecular interactions of sulfur trioxide and sulfuric acid dimers studied by the DFT method

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Density functional theory with 6-311++G** basis sets has been applied to the investigation of intermolecular interactions of sulfur trioxide and sulfuric acid dimers. Counterpoise procedure was used for the basis set superposition error (BSSE) correction. The corrected binding energy for (HSO₄)₂ is -71.37 kJ/mol at the B3LYP/6-311++G** level, and -37.79 and -39.04 kJ/mol for two H₂SO₄/SO₃ binary complexes (denoted as dimers **B** and **C**) respectively. Dimers **B** and **C** can be spontaneously produced when gaseous sulfur trioxide mixes with sulfuric acid, which is in agreement with the experimental fact that sulfur trioxide is prone to dissolve in sulfuric acid. The O...S interacting is stronger than the O...H interacting in the heterodimer of H₂SO₄/SO₃. Electron density at bond critical points and natural bond orbital analysis were performed to probe the origin of the intermolecular interactions.

Keywords: density functional theory, sulfuric acid and sulfur trioxide dimers, intermolecular interaction, binding energy.

Intermolecular forces play a key role in determining the structures as well as the properties of supermolecules. Study of van der Waals forces continues to interest both physicists and chemists.¹⁻⁷ Although the chemistry of individual molecules is generally dominated by covalent or ionic bonding, van der Waals forces govern the molecule-molecule interactions that are responsible for the stability of intermolecular complexes. Consequently, studies of atomic and molecular clusters can be expected to clarify some chemical behaviour, such as molecular recognition, physical adsorption, and aggregation. For example, sulfuric acid in high concentration can easily adsorb sulfur trioxide to form oleum. To elucidate the formation and the structure of non-covalent H₂SO₄/SO₃ binary complexes, we performed DFT calculations on an adequate model.

Calculating model and methods

To study the intermolecular interaction of such a complex, either first principles or semiempirical methods can be employed. Computational practices show that first principle methods are superior to the latter for supermolecular systems formed through weak interaction instead of chemical bonding. So we used DFT method for the study of the title systems. Computational practice showed that the method is efficient for supermolecular systems with strong hydrogen bonds. In this paper we wish to report the structures, the binding energies in the process of the dimerisation.

For this type of study, usually a substantial size of basis set is required for an accurate description of the structures and energies of clusters. Hence we employed the triple-zeta-quality 6-311++G** basis sets,⁸⁻⁹ which has been proved valid for intermolecular interaction studies.¹⁰

The monomers, sulfuric acid and sulfur trioxide, and their most stable dimers obtained from Chem3D software were fully optimised by using the Berny method at the DFT levels with 6-311++G** basis sets. In this study, sulfur trioxide was treated as an ideal gas without any intermolecular interaction between the molecules, while sulfuric acid and its SO₃-adsorbed solution were modeled as dimers of (H₂SO₄)₂ and H₂SO₄/SO₃ respectively. When sulfuric acid and sulfur trioxide form a heterodimer, the decomposition of the sulfuric acid dimer is actually involved. Therefore, the homodimer of sulfuric acid was also studied.

The basis sets commonly used to calculate the energies in the above equation are far from saturated and, hence in any

complex, each subsystem will tend to lower its energy by using the basis functions of the other subsystem. The energies obtained at the equilibrium geometry of the complex for each subsystem are lower than those calculated at the same geometry with the basis functions of the respective subsystem alone. This energy difference is the so-called BSSE that can be checked by the Boys and Bernardi's counterpoise procedure (CP).¹¹⁻¹³

All quantum chemical calculations were performed with the GAUSSIAN 98 suite of programs.¹⁴ The evaluation of electron density is derived from the AIM2000 program. The atoms in molecules (AIM) theory of Bader¹⁵ defines a discrete rather than a fuzzy boundary on which space partitioning can be based. It is relatively basis-set independent compared with other methods such as Mulliken population analysis and its variations.

Results and discussion

Optimised geometries

Of all possible stable dimers, only the most stable structures of homogeneous dimer and heterodimers are shown in Figure 1. Table 1 lists some optimised geometrical parameters.

Dimers **B** possesses C_s symmetry. It was found that these cyclic dimers are more stable than the chained one (a dimer with single hydrogen bond), that is, it is favourable to form multi-hydrogen bonds instead of a single H-bond. For example, when optimised from the initial chained structure of dimer **C** (let angle O₄-H₆...O₉ of **C** to be 180°), the structure automatically collapses to the cyclic one as shown in Fig. 1. A noticeable geometrical feature for **B** is its planarity of two hydroxyl groups in the sulfuric acid moiety, where the dihedral angle of H₆O₄O₅H₇ became ca. zero. The necessary energy of 8.6 kJ/mol required to deform the torsion angle is compensated for by the formation of two strong hydrogen bonds in dimer **B**. Similarly, two hydroxyl groups in a submolecule of **A** are also coplanar. The intermolecular distances in **A** are shorter than those in **B** and **C**, at the same time, there exists three H...O contacts in **A**. Judged from the distance and the number of intermolecular contacts, the strength of interaction in **A** is larger than that in **B** and **C**. Compared with the corresponding bond in SO₃ and H₂SO₄ monomers, all the bonds associated with the intermolecular contacts increase by 0.8–2.2 pm, while all the bonds outside the intermolecular interacting ring decrease somewhat. For example, the lengths of S₁-O₂, O₄-H₆, O₅-H₇, S₈-O₉, S₈-O₁₀ and O₁₁-H₁₃ increase, while those of O₁-H₄,

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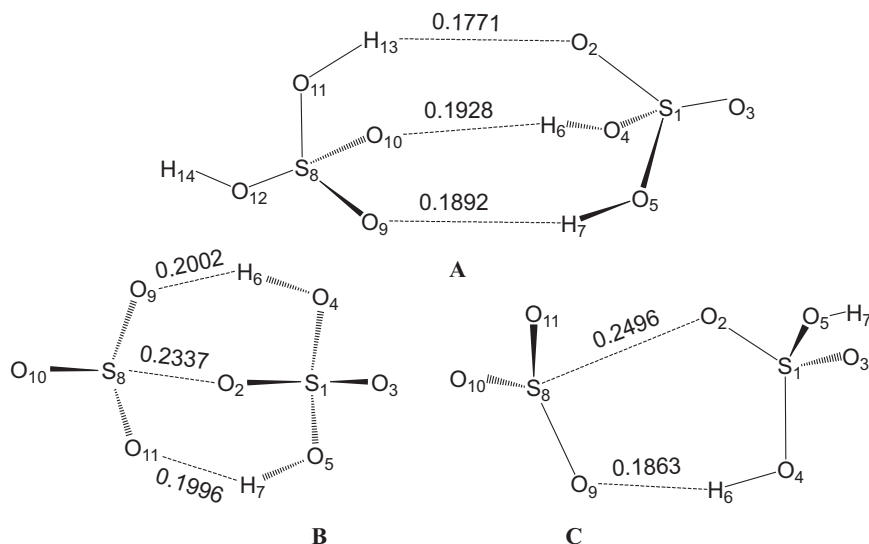


Fig. 1 Optimised structures of the stable dimers (data on dashed lines are intermolecular distances in nm).

Table 1 Optimised parameters at the B3LYP/6-311++G** level (bond length in nm, bond angle and dihedral angle in degrees)

	A		B		C
R ₁₋₂	0.1467 (0.1448)	R ₁₋₂	0.1479 (0.1448)	R ₁₋₂	0.1457 (0.1448)
R ₁₋₃	0.1429 (0.1436)	R ₁₋₃	0.1426 (0.1436)	R ₁₋₃	0.1435 (0.1436)
R ₁₋₄	0.1605 (0.1637)	R ₁₋₄	0.1602 (0.1637)	R ₁₋₄	0.1601 (0.1637)
R ₁₋₅	0.1604 (0.1610)	R ₁₋₅	0.1602 (0.1610)	R ₁₋₅	0.1618 (0.1610)
R ₄₋₆	0.0982 (0.0970)	R ₅₋₇	0.0980 (0.0970)	R ₈₋₉	0.1460 (0.1447)
R ₅₋₇	0.0983 (0.0970)	R ₈₋₉	0.1455 (0.1447)	R ₈₋₁₀	0.1440 (0.1447)
R ₈₋₉	0.1460 (0.1448)	R ₈₋₁₀	0.1436 (0.1447)	R ₈₋₁₁	0.1441 (0.1447)
R ₈₋₁₀	0.1449 (0.1436)	R ₈₋₁₁	0.1455 (0.1447)	R ₄₋₆	0.0983 (0.0970)
R ₈₋₁₁	0.1593 (0.1610)	θ ₂₋₁₋₃	121.0 (122.3)	R ₅₋₇	0.0971 (0.0970)
R ₈₋₁₂	0.1594 (0.1637)	θ ₂₋₁₋₄	107.5 (107.7)	θ ₂₋₁₋₃	122.2 (122.3)
R ₁₁₋₁₃	0.0992 (0.0970)	θ ₂₋₁₋₅	107.5 (110.6)	θ ₂₋₁₋₄	109.1 (107.7)
R ₁₂₋₁₄	0.0971 (0.0970)	θ ₃₋₁₋₄	107.8 (110.2)	θ ₂₋₁₋₅	104.1 (110.6)
θ ₂₋₁₋₃	121.3 (122.3)	θ ₃₋₁₋₅	107.9 (106.2)	θ ₃₋₁₋₄	107.0 (110.2)
θ ₂₋₁₋₄	107.9 (107.7)	θ ₄₋₁₋₅	103.8 (96.9)	θ ₃₋₁₋₅	109.9 (106.2)
θ ₄₋₁₋₅	103.8 (96.9)	θ ₁₋₄₋₆	110.9 (108.8)	θ ₄₋₁₋₅	102.9 (96.9)
θ ₁₋₄₋₆	111.3 (108.8)	θ ₉₋₈₋₁₀	120.7 (120.0)	θ ₁₋₄₋₆	110.0 (108.8)
θ ₄₋₆₋₁₀	163.7	θ ₉₋₈₋₁₁	117.5 (120.0)	θ ₁₋₅₋₇	110.1 (110.3)
θ ₅₋₇₋₉	163.8	φ ₁₀₋₈₋₁₁	120.7 (120.0)	θ ₄₋₆₋₉	156.6
θ ₉₋₈₋₁₀	118.3 (122.3)	φ ₂₋₁₋₄₋₆	-27.1 (40.2)	θ ₉₋₈₋₁₀	119.0 (120.0)
φ ₄₋₆₋₁₀₋₈	1.2	φ ₂₋₁₋₅₋₇	26.2 (39.9)	θ ₁₀₋₈₋₁₁	121.5 (120.0)
φ ₅₋₇₋₉₋₈	2.1	φ ₁₋₂₋₈₋₁₀	-179.9	φ ₄₋₆₋₉₋₈	-3.8

O₁-H₅, S₁-O₃, S₈-O₁₁ and S₈-O₁₂ decrease to facilitate the combination of submolecules. The discrepancies of the bond angles between dimers and the corresponding monomers are less than 6.9°. However, changes of the absolute values of the dihedrals are as large as 67°, indicating that the internal rotation of the hydroxyl group around S-O bond occurs in the dimerisation.

Binding energies

Table 2 summarises the binding energies. The discrepancies of the uncorrected binding energies from the BSSE corrected energies are 5.61–6.75 kJ/mol for the dimers, indicating that the BSSE cannot be neglected, while corrections for the zero-point vibrational energies hardly influence the binding energies. The binding energy of dimer **A** is much larger than those of **B** and **C**. Although there exists only one H...O interaction in **C**, its binding energy is comparable with that of **B**, indicating the strength of the individual H...O bond of **C** is much stronger than those in the latter. The corrected binding energies for **A**, **B** and **C** are -71.37, -37.79 and -39.04 kJ/mol at the B3LYP/6-311++G** level, respectively. It is interesting to note that the changes the energies in the process of 2SO₃ + **A** → 2(H₂SO₄/SO₃) are all negative. It can be then deduced

that dimers **B** and **C** would be favourably produced when SO₃ is being mixed with dimer **A**. The binding energies of dimers **B** and **C** are large enough to compensate for the energy needed for the dissociation of dimer **A**, which is in agreement with the experimental fact that the gaseous sulfur trioxide easily dissolves into the sulfuric acid solution.

NBO charges and charge transfer

Table 3 lists the atomic charges obtained by the natural bond orbital (NBO) analysis. Oxygen atoms that contact with neighbor H or S atoms carry more negative charge than those in the monomer, while hydrogen atoms that contact with neighbor O atoms carry more positive charge than those in the monomer, which facilitates the formation of O...H or O...S in the dimers. For dimers, the net result of charge transfer is that a submolecule of dimer **A** acquires 0.0108 e, whereas the sulfuric acid moiety of dimers **B** and **C** lost 0.0636 and 0.0226 e respectively. The dipole moments are 5.57, 2.71 and 3.08 Debye for **A**, **B** and **C** respectively.

Table 2 Binding energies of the dimers (kJ/mol)^a

Binding energies	A	B	C
$\Delta E(\text{DFT})$	-77.66	-47.26(-16.86) ^b	-46.32(-14.98)
$\Delta E(\text{DFT})_{\text{C}}$	-71.77	-40.51(-9.25)	-40.71(-9.65)
$\Delta E(\text{DFT})_{\text{C,ZPEC}}$	-71.37	-37.79(-4.20)	-39.04(-6.70)

^a ΔE_{C} is the 50% BSSE corrected binding energy and $\Delta E_{\text{C,ZPEC}}$ the BSSE and ZPE corrected energy. Binding energy for dimer **A** refers to the process of $2\text{H}_2\text{SO}_4 = (\text{H}_2\text{SO}_4)_2$, and binding energies for dimers **B** and **C** refer to $\text{SO}_3 + \text{H}_2\text{SO}_4 = \text{SO}_3 \cdots \text{H}_2\text{SO}_4$. ^bData in parenthesis are the changes of energies in the process of $2\text{SO}_3 + (\text{H}_2\text{SO}_4)_2 \rightarrow 2(\text{SO}_3 \cdots \text{H}_2\text{SO}_4)$, i.e., $2 \times \Delta E_{\text{C or B}} - \Delta E_{\text{A}}$.

Table 3 Atomic NBO charges (a.u.) at the B3LYP/6-311++G** level^a

A		B		C	
Atom	Charges	Atom	Charges	Atom	Charges
S ₁	2.4667 (2.4167)	S ₁	2.4596 (2.4167)	S ₁	2.4533 (2.4167)
O ₂	-0.9721 (-0.8743)	O ₂	-0.9354 (-0.8743)	O ₂	-0.9216 (-0.8743)
O ₃	-0.8325 (-0.8407)	O ₃	-0.8109 (-0.8407)	O ₃	-0.8391 (-0.8407)
O ₄	-0.8574 (-0.8607)	O ₄	-0.8476 (-0.8607)	O ₄	-0.8566 (-0.8607)
O ₅	-0.8585 (-0.8430)	O ₅	-0.8478 (-0.8430)	O ₅	-0.8461 (-0.8430)
H ₆	0.5215 (0.5000)	H ₆	0.5228 (0.5000)	H ₆	0.5272 (0.5000)
H ₇	0.5215 (0.5020)	H ₇	0.5229 (0.5020)	H ₇	0.5055 (0.5020)
S ₈	2.4569 (2.4167)	S ₈	2.3581 (2.2856)	S ₈	2.3491 (2.2856)
O ₉	-0.9189 (-0.8743)	O ₉	-0.8398 (-0.7607)	O ₉	-0.8618 (-0.7607)
O ₁₀	-0.8945 (-0.8407)	O ₁₀	-0.7419 (-0.7639)	O ₁₀	-0.7545 (-0.7639)
O ₁₁	-0.8556 (-0.8607)	O ₁₁	-0.8400 (-0.7610)	O ₁₁	-0.7554 (-0.7610)
O ₁₂	-0.8285 (-0.8430)				
H ₁₃	0.5396 (0.5000)				
H ₁₄	0.5117 (0.5020)				

^aData in parenthesis are those of monomer.

Electron density at bond critical points

Based on the B3LYP/6-311++G** optimised structure, the electron densities at bond critical points and the ratio of $\rho_{\text{O}\cdots\text{H}(\text{S})}$ to $\rho_{\text{O-H}}$ are calculated and listed in Table 4. The discrepancies of the electron densities from the AIM theory at different levels are very small. This indicates that the values of ρ are insensitive to both the basis set and the electron correlation. The ratios of electron density on intermolecular O...H or O...S to that on the neighbor O-H are in the range of 0.06–0.13, which reveals that there exist strong intermolecular interactions in the dimers. The ratios of $\rho_{\text{O}\cdots\text{H}(\text{S})}/\rho_{\text{O-H}}$ also indicated that the strength of O...S is stronger than that of O...H.

Natural bond orbital analysis

Table 5 summarises the second-order perturbative estimates of ‘donor-acceptor’ (bond-antibond) interactions in the NBO basis for all the dimers. This is carried out by examining all possible interactions between ‘filled’ (donor) Lewis-type NBOs and ‘empty’ (acceptor) non-Lewis NBOs, and estimating their stabilisation energy by second order perturbation theory.^{15–17} The stabilisation energies $E(2)$ are proportional to the NBO interacting intensities. When the donor and the acceptor belong to different submolecules in a cluster, we call it intermolecular NBO interaction. It is the intermolecular NBO interaction that reveals the origin of intermolecular interactions. As can be seen from the intermolecular NBO interaction in Table 5, the main NBO interactions in dimers are that the lone pair on oxygen of one submolecule acts as donor and that the O-H or O-S antibond of another submolecule as acceptor. Two lone pairs of each oxygen interact with O-H or O-S antibonds in the dimers, and the total stabilisation energies of the largest two NBO interactions are over 50 kJ/mol, forming an intermolecular interaction. Judged from the stabilisation energies, the O...S interaction is stronger than the O...H interaction, which is consistent with the result from the electron density at bond critical points as mentioned above.

Table 4 Electron density at bond critical points from different levels

Dimer	Bond	$\rho/\text{a.u.}^{-3}$	$\rho_{\text{O}\cdots\text{H}(\text{S})}/\rho_{\text{O-H}}$
A	O ₂ ...H ₁₃	0.2349	0.11
	O ₉ ...H ₇	0.1800	0.08
	O ₁₀ ...H ₆	0.1650	0.08
	O ₁₁ -H ₁₃	2.1940	1.00
B	O ₂ ...S ₈	0.3067	0.13
	O ₉ ...H ₆	0.1436	0.06
	O ₁₁ ...H ₇	0.1452	0.06
	O ₄ -H ₆	2.2951	1.00
C	O ₂ ...S ₈	0.2064	0.09
	O ₉ ...H ₆	0.1891	0.08
	O ₄ -H ₆	2.2660	1.00

Table 5 Intermolecular natural bond orbital interacting and the corresponding the stabilisation energy $E(2)$ associated with delocalisation for the dimers^a

Dimers	Donor NBO (i)	Acceptor NBO (j)	$E(2)/\text{kJ/mol}$
A	LP(1) O ₂	BD* O ₁₁ -H ₁₃	38.5
	LP(3) O ₂	BD* O ₁₁ -H ₁₃	21.8
	BD* S ₁ -O ₂	BD* O ₁₁ -H ₁₃	20.0
	LP(1) O ₉	BD* O ₅ -H ₇	15.5
	LP(3) O ₉	BD* O ₅ -H ₇	26.1
	LP(1) O ₁₀	BD* O ₄ -H ₆	13.2
	LP(3) O ₁₀	BD* O ₄ -H ₆	21.8
	LP(1) O ₂	BD*(2) S ₈ -O ₁₀	13.4
	LP(3) O ₂	BD O ₉ -O ₁₁	7.0
B	LP(3) O ₂	BD* S ₈ -O ₉	9.2
	LP(3) O ₂	BD*(2) S ₈ -O ₁₀	70.5
	LP(3) O ₂	BD* S ₈ -O ₁₁	9.2
	BD* S ₁ -O ₂	BD* S ₈ -O ₁₀	5.1
	LP(1) O ₉	BD* O ₄ -H ₆	7.8
	LP(2) O ₉	BD* O ₄ -H ₆	5.8
	LP(1) O ₁₁	BD* O ₅ -H ₇	8.0
	LP(2) O ₁₁	BD* O ₅ -H ₇	5.9
	C	LP(1) O ₂	BD*(2) S ₈ -O ₁₀
LP(3) O ₂		BD*(2) S ₈ -O ₁₀	36.4
LP(1) O ₉		BD* O ₄ -H ₆	19.4
LP(3) O ₉	BD* O ₄ -H ₆	24.8	

^aLP means lone pair, BD* represents antibond and BD(2) denotes ≠ bond. Threshold for $E(2)$ is 5 kJ/mol.

Conclusions

The *ab initio* calculations on the title dimers demonstrate that there exist cyclic structures in all the dimers with binding energies of much larger than double of the experimental dissociation energy (*ca* 15×2 kJ/mol) of the water dimer.²⁰⁻²¹ The binding energy of dimers **B** and **C** are high enough to compensate for the energy needed for the dissociation of dimer **A**. The process of $A + 2SO_3 \rightarrow 2B$ (or $2C$) is energetically favourable.

The authors gratefully thank the National Natural Science Foundation of China (Grant 20173028) and the start-up foundation for a new faculty provided by NJUST of P. R. China.

Received 15 September 2006; accepted 13 November 2006
Paper 06/4199

References

- 1 P. Hobza and R. Zahradnik, *Chem. Rev.*, 1988, **88**, 871.
- 2 P. Hobza, H.L. Selzle and E.W. Schlag, *Chem. Rev.*, 1994, **94**, 1767.
- 3 J. Sauer, P. Uglietto, E. Garrone and V.R. Saunders, *Chem. Rev.*, 1994, **94**, 2095.
- 4 P. Hobza and J. Sponer, *Chem. Rev.*, 1999, **99**, 3247.
- 5 P.E.S. Wormer and Ad van der Avoird, *Chem. Rev.*, 2000, **100**, 4109.
- 6 G. Chalasinski and M.M. Szczesniak, *Chem. Rev.*, 2000, **100**, 4227.
- 7 O. Engkvist, P.O. Astrand and G. Karlstrom, *Chem. Rev.*, 2000, **100**, 4087.
- 8 W.J. Hehre, R. Ditchfield and J.A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.
- 9 P.C. Hariharan and J.A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
- 10 B. Paizs and S. Suhai, *J. Comput. Chem.*, 1998, **19**, 575.
- 11 H.M. Xiao and X.H. Ju, *Intermolecular interactions in energetic systems*. Beijing: Science Press, 2004.
- 12 S.F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553.
- 13 A. Johansson, P. Kollman and S. Rothenberg, *Theor. Chem. Acta*, 1973, **29**, 167.
- 14 G. Chalasinski and M.M. Szczesniak, *Mol. Phys.* 1988, **63**, 205.
- 15 M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, 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, 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, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle and J.A. Pople, Gaussian 98 (Revision A.7), Gaussian, Inc., Pittsburgh PA, 1998.
- 16 R.F. Bader, *Atoms in Molecules: a Quantum Theory*. Oxford: Clarendon Press, 1990.
- 17 A.E. Reed, R.B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735.
- 18 A.E. Reed and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 1736.
- 19 A.E. Reed, L.A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.
- 20 L.A. Curtiss, D.J. Frurip and M. Blander, *J. Chem. Phys.*, 1979, **71**, 2703.
- 21 J.R. Reimers, R.O. Watts and M.L. Klein, *Chem. Phys.*, 1982, **64**, 95.