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A quantum chemistry study on reaction mechanisms of SO₂ with O₃ and H₂O₂[*]

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Abstract: Reaction mechanisms of SO_2 with O_3 and H_2O_2 were investigated using quantum chemistry ab initio methods. Structures of all reactants, products, and transition states were optimized at the B3LYP/6-311G+(3df,2p) level, and energy calculations were made at the G2M level. SO_2 reactions with O_3 and H_2O_2 occurred by O-abstraction and OH-abstraction by SO_2, respectively, at length forming SO_3+O_2 ($^3\Sigma_g^-$) and H_2SO_4. For SO_2+O_3 reactions the barrier height was predicted to be 9.68 kcal/mol with a rate constant of 3.61×10^{-23} cm³/(molecule·s) at 300 K, which is below the experimental upper limit. The rate constant predicted for this reaction accords well with the one provided by National Institute for Standards and Technology (NIST) in 250~500 K. For $SO_2+H_2O_2$ reactions the barrier height was predicted to be 62.39 kcal/mol with a rate constant of 2.48×10^{-61} cm³/(molecule·s) at 300 K.

Key words: Sulfur dioxide, Ozone, Hydrogen peroxide, Reaction mechanism, Rate constant, Quantum chemistry
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INTRODUCTION

A large amount of sulfur dioxide is released to atmosphere by fossil fuel combustion. It turns to be a critical environment problem for SO_2 can be converted to sulfuric acid and sulfate in atmosphere. The oxidation of sulfur dioxide takes place in both gas and solution phases (Urone and Schroeder, 1969; Eggleton and Cox, 1978; Möller, 1980). O_3 and H_2O_2, two interesting species in atmosphere chemistry, are oxidizing substances that may react with SO_2 contributing to its conversion by the following reactions:

$$SO_2+O_3\rightarrow SO_3+O_2\ (^3\Sigma_g^-),\qquad (R1)$$

$$SO_2+H_2O_2\rightarrow H_2SO_4.\qquad (R2)$$
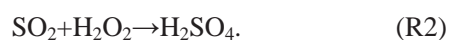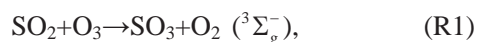
Considerable interest has been paid to studying

the above two reactions on account of their relevance in atmospheric chemistry. Although a number of potentially contributing mechanisms about the SO_2 conversion have been identified (Möller, 1980), reaction mechanisms about title reactions are unknown and kinetics data are hardly available. Besides, ozone injection has recently been studied to remove NO_x, SO_2 and Hg simultaneously in flue gas (Mok and Lee, 2006; Wang *et al.*, 2007). Mechanisms of reactions involved in this multi-pollutant control process should be clarified and rate constants are needed. Reactions of O_3 with NO and Hg have been studied theoretically (Julio and Ignacio, 2002; Zheng *et al.*, 2005), but few experimental or theoretical studies were conducted for both R1 and R2. Davis *et al.*(1974) appears to be the only experimental research about R1, once employing mass spectrometer and UV spectroscopy and obtaining an upper limit of the rate constant 2×10^{-22} cm³/(molecule·s) at 300 K. An Arrhenius expression $k=3.0\times10^{-12}\exp(-Ea/RT)$ ($Ea/R>$ 7000) has been recommended by Jet Propulsion

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Laboratory (JPL, California Institute of Technology) (Sander *et al.*, 2006). So far, seemingly no experimental or theoretical studies have been witnessed on R2 in its gas phase.

The quantum chemistry ab initio method, useful to explore chemistry reaction mechanisms, has been used to study reactions involving SO_2 by excellent researchers (Friedlander *et al.*, 1983; Berthe-Gaujac *et al.*, 1995; Bishenden and Donaldson, 1998; Groves and Lewars, 2000; Albrecht *et al.*, 2001; Tachikawa *et al.*, 2001; Choo *et al.*, 2002). Considering that the reaction mechanism is unclear and there are few kinetics data about the title reactions, a quantum chemistry study was carried out to clarify mechanisms of the two reactions and to provide a predicted reaction rate constant for further studies.

COMPUTATIONAL DETAILS

The hybrid density functional (DFT) B3LYP method, i.e., Becke (1992a; 1992b; 1993)'s three-parameter nonlocal exchange functional with the correlation functional of Lee *et al.*(1988), has been used to optimize geometric parameters of reactants, products, and transition states of title reactions with the 6-311+G(3df,2p) basis set. All stationary points have been identified for local minima or transition states by vibrational frequency calculations at this theory level. With this method, stationary points can be classified as minima if no imaginary frequencies are shown or as transition states if only one imaginary frequency is obtained. These calculations also provided zero-point energies (ZPE), thermal corrections at 298 K. Intrinsic reaction coordinate calculations (IRC) (Gonzalez and Schlegel, 1989) have been performed to confirm transition states connecting designated reactants and products.

G2M(RCC2) and G2M(CC2) (Mebel *et al.*, 1995) calculations have been carried out to obtain more reliable high-level single point energy of stationary points on geometries optimized at the B3LYP/6-311+G(3df,2p) level. G2M(RCC2) and G2M(CC2) are both methods of a number of modified Gaussian-2 (G2M) calculational schemes; the G2M(RCC2) is for closed shell species, and the G2M(CC2) for open ones. Geometries and frequencies calculated at B3LYP/6-311G(3df,2p) are used in

the G2M method in our study, but ZPE calculated at this level is not scaled. The energy in G2M(RCC2) is therefore calculated as

$$E[G2M(RCC2)]=E_{bas}+\Delta E(+)+\Delta E(2df)+\Delta E(RCC)+\Delta+\Delta(HLC,RCC2)+ZPE,$$

where $E_{bas}=E[MP4/6-311G(d,p)]$ stands for energy calculated on the MP4/6-311G(d,p) level, and the correction for diffuse functions is

$$\Delta E(+)=E[MP4/6-311+G(d,p)]-E_{bas}.$$

The correction for higher polarization on nonhydrogen atoms is

$$\Delta E(2df)=E[MP4/6-311G(2df,p)]-E_{bas}.$$

The coupled cluster correction is

$$\Delta E(RCC)=E[RCCSD(T)/6-311G(d,p)]-E_{bas},$$
$$\Delta=E[MP2/6-311G+(3df,2p)]-E[MP2/6-311G(2df,p)]-E[MP2/6-311+G(d,p)]+E[PMP2/6-311G(d,p)].$$

$\Delta(HLC,RCC2)$ is the "higher level correction", equal to $-xn_\beta-0.19n_\alpha$ in mhartree, where n_α and n_β are the numbers of α and β valence electrons, respectively. For G2M(RCC2) and G2M(CC2) x is 5.71 and 5.78, respectively.

All quantum chemistry ab initio calculations were performed with Gaussian 03 programs (Frisch *et al.*, 2003). Rate constants were calculated using the transition state theory (TST) (Barrow, 1966).

RESULTS AND DISCUSSION

Structures of reactants, products and transition states optimized at the B3LYP/6-311G+(3df,2p) level are shown in Fig.1, and vibrational frequencies for species are summarized in Table 1. Table 2 sums up relative energies for reactants, products and transition states calculated at B3LYP/6-311G+(3df,2p), MP2/6-311+G(3df,2p), MP4/6-311G(2df,p), CCSD(T)/6-311G(d) and G2M levels on the optimized structures at B3LYP/6-311G+(3df,2p) level. ZPE corrections (kcal/mol) at the B3LYP/6-311G+(3df,2p) level of theory for species
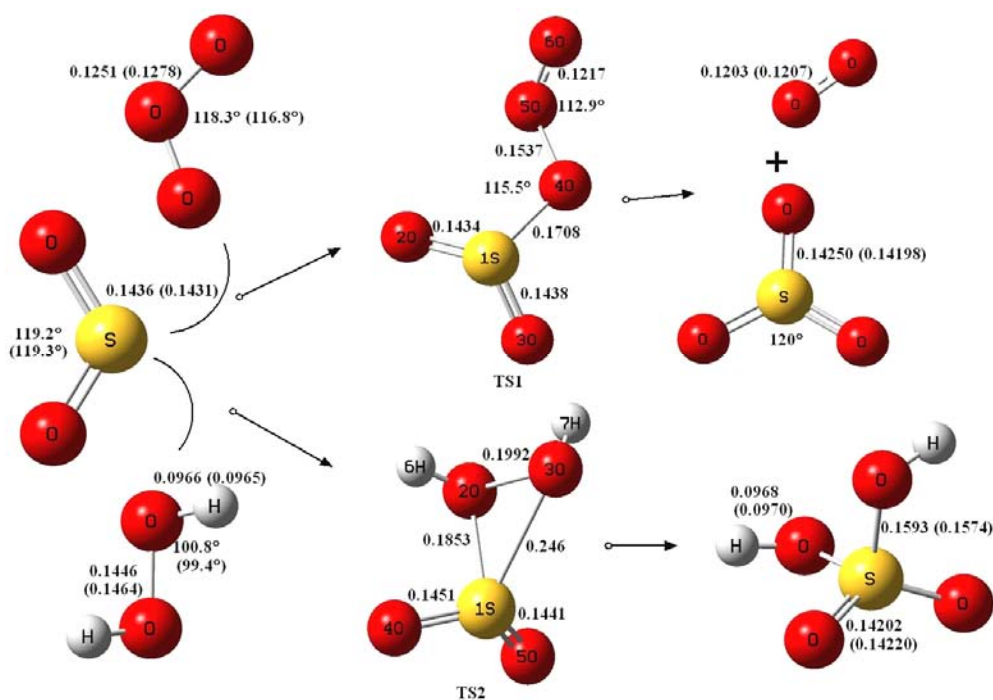
Fig.1 Optimized structures of various species involved in R1 and R2
Bond distances are in nm, values in parentheses are experimental data

are involved. On account of a higher accuracy of the G2M method relative energies cited in the rest of this study are the ones obtained at this level except for special explanations. Adiabatic potential energies at stationary points for reactions R1 and R2 relative to the reactants obtained at the G2M level are shown in Fig.2. Although ozone is a notorious multireference system, no spin-contamination has been found during our calculations. This may be attributed to the ability of DFT methods to overcome this problem and the multiplicity of the system studied involving ozone is 1.

Reactants and products

As shown in Fig.1, structures optimized at B3LYP/6-311G+(3df,2p) are in reasonable agreement with related experimental data (Matsumura *et al.*, 1989; Fournier and DePristo, 1992; Larson and Tao, 2001; Peiró-García and Nebot-Gil, 2002; Natsheh *et al.*, 2004). Some deviations are discussed as follows. For O_3, the deviation is 0.0027 nm for bond length, and 1.5° for angle. The structures of SO_2, SO_3, H_2SO_4 and H_2O_2 are in good accordance with related experimental data. Bond length deviations are small for H_2O_2 and H_2SO_4. The deviation is 0.0018

Table 1 Vibrational frequencies (cm^{-1}) and species involved in title reactions

| Specie	Frequency
SO_2	519, 1179, 1377
O_3	753, 1213, 1265
SO_3	495, 524, 524, 1076, 1340, 1340
O_2	1645
H_2O_2	395, 951,1337, 1444, 3780, 3781
H_2SO_4	248, 326, 371, 434, 493,5 38, 551, 812, 862, 1150, 1167, 1221, 1467, 3774, 3779
TS1	559i[*], 92, 108, 173, 280, 442, 490, 506, 754, 1132, 1340, 1379,
TS2	658i, 71, 203, 267, 298, 333, 496, 528, 558, 942, 1009, 1119, 1300, 3710, 3768

[*] i: imaginary frequency

nm and 0.0019 nm for O—O in H_2O_2 and S—OH in H_2SO_4, respectively. Deviations from these values also appeared in the existing references on the reactions involving such species and nice theoretical results have been obtained (Chen and Plummer, 1985; Bishenden and Donaldson, 1998; Lu *et al.*, 2000; Larson and Tao, 2001; Peiró-García and Nebot-Gil, 2002; Ignatov, 2004; Natsheh *et al.*, 2004). Our deviations are not large. Optimized B3LYP/6-311G+ (3df,2p) structures should be good enough to research the mechanism of title reactions.

Table 2 Relative energie(kcal/mol) of the reactants, products and transition states for R1 and R2

Species	Relative energy					
	ZPE	1	2	3	4	5
SO_2+O_3	9.01	0	0	0	0	0
TS1	9.58	23.19	43.58	32.80	21.44	9.68
SO_3+O_2	10.10	−58.15	−53.65	−53.58	−45.99	−53.67
$SO_2+H_2O_2$	20.85	0	0	0	0	0
TS2	20.64	58.15	74.06	62.89	68.33	62.39
H_2SO_4	20.12	−60.13	−69.94	−64.41	−44.24	−65.94

1: B3LYP/6-311G+(3df,2p); 2: MP2/6-311+G(3df,2p); 3: MP4/6-311G(2df,p); 4: CCSD(T)/6-311G(d); 5: G2M
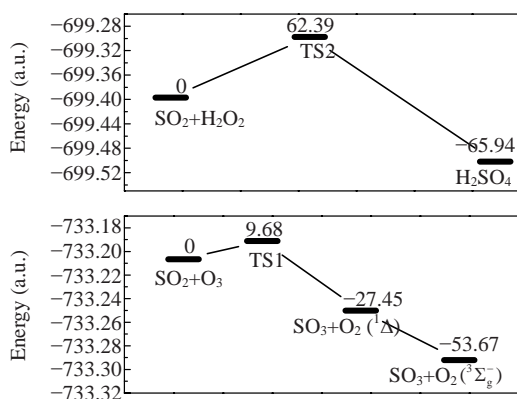
Fig.2 Adiabatic potential energies at stationary points for reactions R2 and R1 relative to reactants obtained at the G2M level. Relative energies are given in kcal/mol

**Potential energy surface and reaction mechanism**

　　1. SO_2+O_3 reaction

　　Calculated results show this reaction is a one-step process of O-abstraction. Reactants and products are connected by the transition state denoted as TS1 (Fig.1). To reach TS1, SO_2 and O_3 molecules draw close and SO_2 attacks the terminal O_3 oxygen atom. As a result, the 1S—6O bond distance formed is 0.1708 nm, 0.0283 nm longer than the S—O bond of SO_3. The 5O—6O bond is 0.1217 nm, 0.0034 nm shorter than O—O bond of O_3, which is close to the O—O bond distance (0.1203 nm) of O_2. The relative energy calculated for TS1 is 9.68 kcal/mol. To reach products, the 1S—4O bond of TS1 becomes shorter and the 4O—5O bond gets longer so that the product O_2 distracts from SO_3. According to the result of our IRC calculations the initial spin-allowed products of the reaction are SO_3+O_2 ($^1\Delta$) and the final product is SO_3+O_2 ($^3\Sigma_g^-$), consistent with the HONO+O_3 reaction (Lu *et al.*, 2000). The relative energy of

$SO_3+O_2(^1\Delta)$ and SO_3+O_2 ($^3\Sigma_g^-$), is −27.45 kcal/mol and −53.67 kcal/mol, respectively.

　　2. $SO_2+H_2O_2$ reaction

　　This reaction is seemingly a one-step process, in which the reactants and product are connected by the transition state denoted as TS2 (Fig.1). SO_2 and H_2O_2 approach each other to form TS2; its 1S—2O bond is 0.1853 nm, 0.026 nm longer than the S—O bond in H_2SO_4, while its 2O—3O bond is 0.1992 nm, which is 37.8% longer than the O—O in H_2O_2, indicating that the two OH radicals of H_2O_2 stay apart. To get product H_2SO_4, the 1S—2O bond and the 1S—3O bond of TS2 become shorter. From our IRC calculations of the product direction, bond distances of 1S—2O and 1S—3O were obtained. Fig.3 shows that the bond distances of 1S—2O and 1S—3O vary along the reaction coordinate towards the H_2SO_4 direction. The horizontal axis stands for points along the reaction path. The 1S—2O bond distance becomes significantly shorter in the beginning and when it is shortened to around 0.163 nm the bond distance undergoes gentle changes subsequently. Correspondingly, the 1S—3O bound becomes mildly shorter at the outset and then displays great variations. IRC calculations demonstrate that 2O5H is the first to be appended to SO_2, forming a radical whose structure is similar to HSO_3. Three S—O bonds of this radical obtained from IRC calculations is 0.16258 nm, 0.14460 nm, 0.14346 nm; the difference is only 0.0003 nm, 0.00023 nm and 0.00057 nm, as compared to the three bonds of HSO_3 (0.16288 nm, 0.14483 nm, 0.14403 nm) which is optimized at UB3LYP/6-311G+(3df,2p) level. The 3O—7H bond
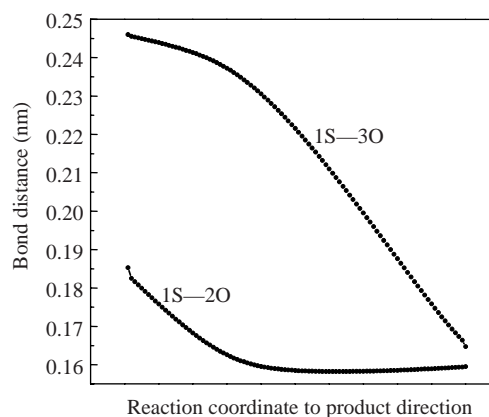
Fig.3 Variational bond distance of 1S—2O and 1S—3O vs reaction coordinate towards the product direction

is 0.0968 nm at that time, 0.0006 nm shorter than the O—H of OH radicals (0.0974 nm) optimized at UB3LYP/6-311G+(3df,2p); meanwhile, it is 0.224 nm away from the radical of SO_2—OH. Two radicals whose structures are similar to HSO_3 and OH, respectively, draw close to each other and as a result 3O7H is finally appended to HSO_3 to produce H_2SO_4. TS2 changes to H_2SO_4 may be strictly regarded as two processes. First HSO_3 and OH are formed by TS2, and then two radicals react with each other to form H_2SO_4. The whole process of the SO_2 reaction with H_2O_2 can be expressed as follows in a rigorous viewpoint:

$$SO_2+H_2O_2 \rightarrow TS2,$$
$$TS2 \rightarrow HSO_3+OH,$$
$$HSO_3+OH \rightarrow H_2SO_4.$$
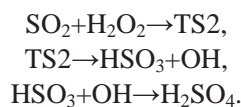
It is also reasonable to assume TS2 being directly converted to H_2SO_4 as our IRC calculations confirmed that TS2 connects $SO_2+H_2O_2$ and H_2SO_4.

The relative energy of TS2 (Fig.2) and H_2SO_4 is 62.39 and −65.94 kcal/mol, respectively. We can infer that the reaction of SO_2 with H_2O_2 should be more slowly than O_3 in gas phase by comparing the relative energies of TS1 and TS2.

Reaction enthalpy

Table 3 lists reaction enthalpies of the two reactions calculated at different levels based on the geometries which has been optimized at the B3LYP/6-311G+(3df,2p) level. Thermal corrections to enthalpy calculated at the B3LYP/6-311+G(3df,2p) level have been included. Both reactions are exothermic; the values calculated at the MP2/6-311 +G(3df,2p) and MP4/6-311G(2df,p) levels are closer to G2M results, while those obtained at the CCSD(T)/6-311G(d) level are below G2M results. Reaction enthalpies calculated at the G2M level are taken as the better prediction, which are −53.76 kcal/mol for R1 and −67.24 kcal/mol for R2.

Reaction rate constant

Reaction rate constants for the two reactions: $SO_2+O_3 \rightarrow SO_3+O_2$ ($^3\Sigma_g^-$), and $SO_2+H_2O_2 \rightarrow H_2SO_4$ have been calculated by means of the TST formulation (Barrow, 1966):

$$k(T) = \frac{k_B T}{hc^\circ} \exp(-\Delta^{\neq}G^\circ / (RT)),$$

where k_B is the Boltzmann constant, h the Planck constant, c° the reference concentration with a value 1, and R the gas constant. $\Delta^{\neq}G^\circ$ is the standard free energy of activation, whose value is 19.85 and 72.23 kcal/mol for R1 and R2, respectively, including thermal correction to Gibbs free energy at the B3LYP/ 6-311+G(3df,2p) level. Fig.4 shows the predicted rate constants with k_1 for R1 and k_2 for R2. A two-parameter Arrhenius expression for R1 has been provided by National Institute for Standards and Technology (NIST, 2008) as $3.01 \times 10^{-12} \exp(-7000.5/T)$. This rate constant is also shown in Fig.4 marked as k_{1_NIST}. From Fig.4, k_1 is greater than k_2, indicating that the energy barrier of R2 is higher than that of R1; this is more obvious in low temperatures than in the high temperature range. The rate constants for both R1 and R2 have positive temperature dependence in the temperature range of 250~2500 K. k_1 is in fairly good accordance with k_{1_NIST} in 250~500 K, but the predicted rate constant by NIST is a little underestimated in higher temperatures.

Table 3 Reaction enthalpy for R1 and R2 calculated at different levels

Method	Reaction enthalpy (kcal/mol)	
	R1	R2
B3LYP/6-311G+(3df,2p)	−62.93	−61.44
MP2/6-311+G(3df,2p)	−53.74	−71.25
MP4/6-311G(2df,p)	−53.67	−65.71
CCSD(T)/6-311G(d)	−46.08	−45.54
G2M	−53.76	−67.24
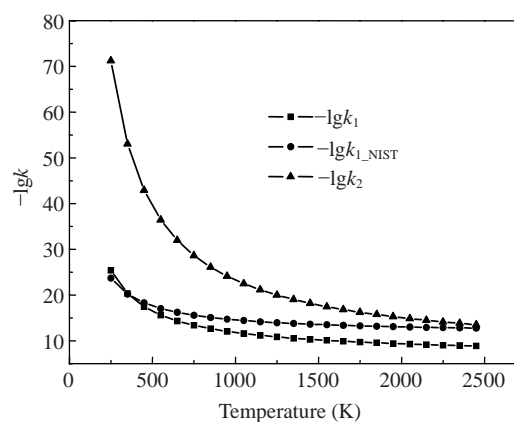
Fig.4 Rate constant plots of the predicted k_1, k_2 and k_{1_NIST}

Our calculated rate constant for R1 is 3.61×10^{-23} cm^3/(molecule·s) at 300 K, below the experimental upper limit of 2.0×10^{-22} cm^3/(molecule·s) (Davis *et al.*, 1974). The *k* at 300 K for R2 is 2.48×10^{-61} cm^3/(molecule·s), much smaller than that for R1. No experimental data have been yet available about the rate constant for R2, and our predicted rate constant may thus be useful information for experimentalists on the kinetic study of this reaction in the future.

CONCLUSION

Reaction mechanisms of SO_2+O_3 and $SO_2+H_2O_2$ have been studied by means of the quantum chemistry ab initio method using the G2M(RCC2 or CC2)/B3LYP/6-311+G(3df,2p) level of theory. The reaction of SO_2 with O_3 is an O-abstraction process. The terminal O atom of O_3 is abstracted by SO_2 and transferred from O_3 to SO_2 forming SO_3 and O_2. The barrier height is 9.68 kcal/mol; and the predicted rate constant is 3.61×10^{-23} cm^3/(molecule·s) at 300 K, which is below the upper experimental limit. The reaction of SO_2 with H_2O_2 can be treated as an OH-abstraction reaction. Two OH radicals of H_2O_2 are appended to SO_2 to form H_2SO_4. The barrier height predicted is 62.39 kcal/mol, and the rate constant is 2.48×10^{-61} cm^3/(molecule·s) at 300 K. Our results would be of great interest to atmosphere chemistry researchers.

References

Albrecht, M., Gossage, R.A., Frey, U., Ehlers, A.W., Baerends, E.J., Merbach, A.E., van Koten, G., 2001. Mechanistic aspects of the reversible binding of SO_2 on arylplatinum complexes: experimental and ab initio studies. *Inorganic Chemistry*, **40**(5):850-855. [doi:10.1021/ic0009019]

Barrow, G.M., 1966. Physical Chemistry. McGraw-Hill, New York.

Becke, A.D., 1992a. Density-functional thermochemistry. I. the effect of the exchange-only gradient correction. *Journal of Chemical Physics*, **96**(3):2155-2160. [doi:10.1063/1.462066]

Becke, A.D., 1992b. Density-functional thermochemistry. II. the effect of the Perdew-wang generalized-gradient correlation correction. *Journal of Chemical Physics*, **97**(12):9173-9177. [doi:10.1063/1.463343]

Becke, A.D., 1993. Density-functional thermochemistry. III. the role of exact exchange. *Journal of Chemical Physics*, **98**(7):5648-5852. [doi:10.1063/1.464913]

Berthe-Gaujac, N., Jean, Y., Volatron, F., 1995. Ab initio study

of the $(SO_2)(SO_2^-)$ dimer: structures involving a two-electron S—O bond. *Chemical Physics Letters*, **243**(1-2):165-170. [doi:10.1016/0009-2614(95)00805-E]

Bishenden, E., Donaldson, D.J., 1998. Ab initio study of SO_2+H_2O. *Journal of Physical Chemistry A*, **102**(24): 4638-4642. [doi:10.1021/jp980160l]

Chen, T.S., Plummer, P.L.M., 1985. Ab initio mo investigation of the gas-phase reaction $SO_3+H_2O \rightarrow H_2SO_4$. *Journal of Physical Chemistry A*, **89**(17):3689-3693.

Choo, J., Kimb, S., Kwon, Y., 2002. Theoretical molecular structures for partially bonded complexes of trimethyl-amine with SO_2 and SO_3: ab initio and density functional. *Journal of Molecular Structure: Theochem*, **594**(3): 147-156. [doi:10.1016/S0166-1280(02)00262-2]

Davis, D.D., Prusazcy, J., Dwyer, M., Klm, P., 1974. A stop-flow time-of-flight mass spectrometry kinetics study. reaction of ozone with nitrogen dioxide and sulfur dioxide. *Journal of Physical Chemistry*, **78**(18):1775-1779. [doi:10.1021/j100611a001]

Eggleton, A.E.J., Cox, R.A., 1978. Homogeneous oxidation of sulphur compounds in the atmosphere. *Atmospheric Environment (1967)*, **12**(1-3):227-230. [doi:10.1016/0004-6981(78)90202-0]

Fournier, R., DePristo, A.E., 1992. Predicted bond energies in peroxides and disulfides by density functional methods. *Journal of Chemical Physics*, **96**(2):1183-1193. [doi:10.1063/1.462206]

Friedlander, M.E., Howell, J.M., Sapse, A.M., 1983. SO_2…HF. An ab initio study. *Inorganic Chemistry*, **22**(1):100-103. [doi:10.1021/ic00143a022]

Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Vreven, T., Kudin, K.N., Burant, J.C., *et al.*, 2003. Gaussian 03. Gaussian, Inc., Pittsburgh, PA.

Gonzalez, C., Schlegel, H.B., 1989. An improved algorithm for reaction path following. *Journal of Chemical Physics*, **90**(4):2154-2161. [doi:10.1063/1.456010]

Groves, C., Lewars, E., 2000. Dimers, trimers and oligomers of sulfur oxides: an ab initio and density functional study. *Journal of Molecular Structure: Theochem*, **530**(3): 265-279. [doi:10.1016/S0166-1280(99)00384-X]

Ignatov, S.K., 2004. Ab-initio and DFT study of the molecular mechanisms of SO_3 and $SOCl_2$ reactions with water in the gas phase. *Journal of Physical Chemistry A*, **108**(16):3642-3649. [doi:10.1021/jp038041f]

Larson, L.J., Tao, F.M., 2001. Interactions and reactions of sulfur trioxide, water, and ammonia: an ab initio and density functional theory study. *Journal of Physical Chemistry A*, **105**(17):4344-4350. [doi:10.1021/jp004354o]

Lee, C., Yang, W., Parr, R.G., 1988. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B*, **37**(2):785-789. [doi:10.1103/PhysRevB.37.785]

Lu, X., Park, J., Lin, M.C., 2000. Gas phase reactions of HONO with NO_2, O_3, and HCl: ab initio and TST study. *Journal of Physical Chemistry A*, **104**(38):8730-8738.

[doi:10.1021/ jp001610o]

Matsumura, K., Lovas, F.J., Suenram, R.D., 1989. The microwave spectrum and structure of the H_2O—SO_2 complex. *Journal of Chemical Physics*, **91**(10):5887-5894. [doi:10.1063/1.457457]

Mebel, A.M., Morokuma, K., Lin, M.C., 1995. Modification of the GAUSSIAN-2 theoretical model: the use of coupled-cluster energies density-functional geometries and frequencies. *Journal of Chemical Physics*, **103**(17):7414-7421. [doi:10.1063/1.470313]

Mok, Y.S., Lee, H.J., 2006. Removal of sulfur dioxide and nitrogen oxides by using ozone injection and absorption-reduction technique. *Fuel Processing Technology*, **87**(7):591-597. [doi:10.1016/j.fuproc.2005.10.007]

Möller, D., 1980. Kinetic model of atmospheric SO_2 oxidation based on published data. *Atmospheric Environment (1967)*, **14**(9):1067-1076. [doi:10.1016/0004-6981(80)90037-2]

National Institute for Standards and Technology (NIST), 2008. Chemical Kinetics Database on the Web, Standard Reference Database 17. Available from: http://kinetics.nist.gov/kinetics/Detail?id=1997DEM/SAN1-266:385 [Accessed 2008-05-01]

Natsheh, A.A., Nadykto, A.B., Mikkelsen, K.V., Yu, F., Ruuskanen, J., 2004. Sulfuric acid and sulfuric acid hydrates in the gas phase: a DFT investigation. *Journal of Physical Chemistry A*, **108**(41):8914-8929. [doi:10.1021/jp048858o]

Peiró-García, J., Nebot-Gil, I., 2002. Ab initio study of the

mechanism and thermochemistry of the atmospheric reaction $NO+O_3 \rightarrow NO_2+O_2$. *Journal of Physical Chemistry A*, **106**(43):10302-10310. [doi:10.1021/jp020422q]

Sander, S.P., Ravishankara, A.R., Fried, R.R., Golden, D.M., Kolb, C.E., Kurylo, M.J., Molina, M.J., Moortgat, G.K., Keller-Rudek, H., Finlayson-Pitts, B.J., *et al.*, 2006. Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies Evaluation Number 15, **2**:1-26. Available from: http://jpldataeval.jpl.nasa.gov/.JPL Publication [Accessed 2008-05]

Tachikawa, H., Abe, S., Iyama, T., 2001. An ab initio MO study on the structures and electronic states of hydrogen-bonded O_3—HF and SO_2—HF Complexes. *Inorganic Chemistry*, **40**(6):1167-1171. [doi:10.1021/ic000880i]

Urone, P., Schroeder, W.H., 1969. SO_2 in the atmosphere: a wealth of monitoring data, but few reaction rate studies. *Environmental Science & Technology*, **3**(5):436-445. [doi:10.1021/es60028a006]

Wang, Z.H., Zhou, J.H., Zhu, Y.Q., Wen, Z.C., Liu, J.Z., Cen, K.F., 2007. Simultaneous removal of NO_x, SO_2 and Hg in nitrogen flow in a narrow reactor by ozone injection: experimental results. *Fuel Processing Technology*, **88**(8):817-823. [doi:10.1016/j.fuproc.2007.04.001]

Zheng, C., Liu, J., Liu, Z., Xu, M., Liu, Y., 2005. Kinetic mechanism studies on reactions of mercury and oxidizing species in coal combustion. *Fuel*, **84**(10):1215-1220. [doi:10.1016/j.fuel.2004.09.027]