

The sulfur dioxide–water complex: CCSD(T)/CBS anharmonic vibrational spectroscopy of stacked and hydrogen-bonded dimers

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ABSTRACT

This study examines the structures, energies, and IR vibrational spectra of the sulfur dioxide–water $\text{SO}_2(\text{H}_2\text{O})$ complexes by employing coupled cluster theory CCSD(T) with Dunning style correlation consistent type basis sets aug-cc-pV($n+d$)Z ($n = \text{D}, \text{T}, \text{Q}, 5$). Complete basis set (CBS) extrapolations have been carried out to predict binding energies for two isomers of the $\text{SO}_2(\text{H}_2\text{O})$ complex: a stacked global minimum (1A) structure and a hydrogen-bonded local minimum (1B) structure. The CCSD(T)/CBS extrapolation predicts an intermolecular S–O distance $r_{\text{S} \cdots \text{O}} = 2.827 \text{ \AA}$ for the stacked isomer, which is in excellent agreement with an experimental measurement of 2.824 \AA [K. Matsumura *et al.*, *J. Chem. Phys.*, **91**, 5887 (1989)]. The CCSD(T)/CBS binding energy for the stacked dimer 1A and hydrogen-bonded form 1B is $D_e = -4.37 \text{ kcal/mol}$ and $D_e = -2.40 \text{ kcal/mol}$, respectively. This study also employs anharmonic VPT2 MP2/aug-cc-pV($n+d$)Z level corrections to CCSD(T)/aug-cc-pV($n+d$)Z vibrational frequencies in both forms of $\text{SO}_2(\text{H}_2\text{O})$. The anharmonic CCSD(T)/aug-cc-pV(Q+d)Z OH stretching frequencies in the stacked structure 1A are 3743 cm^{-1} (v_3) and 3647 cm^{-1} (v_1), and these align well with the recorded IR spectroscopic values of 3745 and 3643 cm^{-1} , respectively [C. Wang *et al.*, *J. Phys. Chem. Lett.*, **13**, 5654 (2022)]. If we combine CCSD(T)/aug-cc-pV($n+d$)Z D_e values with VPT2 vibrational frequencies, we obtain a new CCSD(T)/aug-cc-pV(Q+d)Z anharmonic dissociation energy $D_0 = -3.48 \text{ kcal/mol}$ for 1A and $D_0 = -1.74 \text{ kcal/mol}$ for 1B. In summary, the results presented here demonstrate that the application of CCSD(T) calculations with aug-cc-pV($n+d$)Z basis sets and CBS extrapolations is critical in probing the structure and IR spectroscopic properties of the sulfur dioxide–water complex.

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I. INTRODUCTION

The first experimental identification of the $\text{SO}_2(\text{H}_2\text{O})$ complex together with its rotational spectra was reported in 1989 by Matsumura and co-workers,¹ yielding a stacked configuration with $r_{\text{S} \cdots \text{O}} = 2.824 \text{ \AA}$ and a tilt angle of roughly 45° . The infrared (IR) spectra of the stacked $\text{SO}_2(\text{H}_2\text{O})$ complex have been measured in argon^{2,3} and nitrogen^{3,4} matrices, with a focus on intramolecular SO stretching frequencies, isotope shifts, and their dependence on the matrix environment. There are, to the best of our knowledge, no IR spectroscopic determinations of intermolecular vibrational frequencies for this dimer, nor any measured values for the corresponding dissociation energy D_0 . More recently, Wang and co-workers⁵ have reported on the gas-phase mid-IR spectra of mass-isolated $\text{SO}_2(\text{H}_2\text{O})_n$

clusters with $n = 1\text{--}16$ in the OH stretching region, together with band assignments from MP2/aVDZ frequency calculations. The authors focused on the stepwise structural transition of $\text{SO}_2(\text{H}_2\text{O})_n$ clusters, starting from a sandwich structure at $n = 1$, to cage-like water structures, with SO_2 on the surface of the clusters at $n > 4$. For the stacked $\text{SO}_2(\text{H}_2\text{O})$ complex, Wang and co-workers⁵ reported on the redshifts of 11 cm^{-1} (v_3) and 14 cm^{-1} (v_1), indicating a noticeable variation in the IR spectroscopic signature in this complex relative to free water. There have been several theoretical studies on the structures, stability, and IR spectroscopy of $\text{SO}_2(\text{H}_2\text{O})$, and examples of this work include DFT,^{6–10} MPN,^{7,9,11–18} CCSD,^{17,19} and CCSD(T)^{20–22} level calculations; however, anharmonic effects have not been considered in these studies. These effects have been examined in detail for $(\text{H}_2\text{S})_2$,²³ $(\text{H}_2\text{O})_2$,^{24,25} and $(\text{HF})_2$ ²⁵

using CCSD(T) theory, suggesting that a careful consideration of vibrational anharmonicity in these complexes should be given for the calculation of accurate vibrational frequencies and dissociation energies.

This work attempts to fill some of these knowledge gaps, by calculating CCSD(T) anharmonic vibrational frequencies and the values of D_0 for two isomers of $\text{SO}_2(\text{H}_2\text{O})$, a stacked (1A) structure and a hydrogen-bonded (1B) structure. In this study, we present new theoretical results for D_e , the zero-point energy (ZPE), and D_0 of the two $\text{SO}_2(\text{H}_2\text{O})$ isomers. These results have been calculated at the CCSD(T) level of theory with Dunning's augmented correlation consistent basis sets aug-cc-pV(n+d)Z [$n = \text{D}, \text{T}, \text{Q}, 5$, abbrev. aV(n+d)Z] up to the complete basis set (CBS) limit. This study also reports CCSD(T)/aV(n+d)Z level vibrational frequencies together with MP2/VPT2 anharmonic corrections, along with ZPE and new D_0 estimates.

II. COMPUTATIONAL DETAILS

Theoretical calculations have been carried out at the coupled cluster CCSD(T) level of theory, in combination with Dunning's augmented correlation-consistent basis sets aug-cc-pVnZ for H and O²⁶ and aug-cc-pV(n+d)Z for sulfur,²⁷ using the Gaussian 16 package.²⁸ Equilibrium geometry optimization of both $\text{SO}_2(\text{H}_2\text{O})$ dimers was undertaken at the CCSD(T)/aV(D+d)Z and CCSD(T)/aV(T+d)Z levels of theory. In addition, partial structure optimizations were carried out at the aV(Q+d)Z level with monomer distances and angles fixed at their estimated aV(Q+d)Z values, followed by single point energy calculations at the CCSD(T)/aV(5 + d)Z level of theory. No linear dependencies have been detected, with all eigenvalues in overlap matrices exceeding 10^{-6} in our dimer calculations. Basis set superposition errors (BSSEs) were accounted for using *post hoc* counterpoise (CP) corrections. We have employed an exponential CBS extrapolation scheme originally proposed by Feller,²⁹ written as

$$E(n) = E(\infty) + Be^{-Cn}, \quad (1)$$

where n is the cardinal number of the respective basis sets [aV(D+d)Z = 2, aV(T+d)Z = 3, aV(Q+d)Z = 4, aV(5 + d)Z = 5], $E(n)$ is the parameter of interest at the respective aV(n+d)Z basis set, and $E(\infty)$ is the CBS limit value, while B and C are constants. In addition, we have also undertaken a series of symmetry-adapted perturbation theory (SAPT) calculations to break down the individual components of the dimer binding energies, and these calculations have been carried out using the PSI4 code.³⁰

Anharmonic frequency estimates at the CCSD(T)/aV(n+d)Z level with $n = \text{D}, \text{T}, \text{Q}$ were obtained for SO_2 , H_2O , and $\text{SO}_2(\text{H}_2\text{O})$, using the following scheme:

$$\nu_{\text{CCSD}(\text{T})/\text{aV}(n+d)\text{Z}} = \omega_{\text{CCSD}(\text{T})/\text{aV}(n+d)\text{Z}} + (\nu_{\text{MP2}/\text{aV}(n+d)\text{Z}} - \omega_{\text{MP2}/\text{aV}(n+d)\text{Z}}), \quad (2)$$

where ν and ω represent the anharmonic and harmonic frequencies, respectively. Anharmonic corrections to vibrational frequencies were obtained using vibrational second-order perturbation theory (VPT2) at the MP2/aV(n+d)Z level of theory³¹ and applied to CCSD(T)/aV(n+d)Z ($n = \text{D}, \text{T}, \text{Q}$) harmonic frequencies.

III. RESULTS AND DISCUSSION

A. SO_2 monomer

Theoretical CCSD(T)/aV(n+d)Z energies, structural parameters $r_{\text{S-O}}$, bond angle $\theta_{\text{O-S-O}}$, and vibrational frequencies for the SO_2 monomer are listed in Table I, together with experimental measurements. Table I shows that the [T, Q, 5] extrapolation (Eq. (1)) yields a CBS limit of $-548.092\ 273\ \text{E}_h$, which is $9.87\ \text{mE}_h$ lower than the [D, T, Q] extrapolation ($-548.087\ 255\ \text{E}_h$). The four-point [D, T, Q, 5] extrapolation predicts a CCSD(T)/CBS energy of $-548.089\ 649\ \text{E}_h$, with the latter situated between the two corresponding three-point extrapolations, confirming the accuracy and correct ordering of the extrapolation method in calculating SO_2 energies at the CBS limit. As presented in Table I, the values of $r_{\text{S-O}}$ and $\theta_{\text{O-S-O}}$ converge systematically to CCSD(T)/CBS limit values of $1.435\ \text{\AA}$ and 119.24° , and these compare favorably with experimental determinations of $r_{\text{S-O}} = 1.4307 \pm 0.000\ 13\ \text{\AA}$ and $\theta_{\text{O-S-O}} = 119.19 \pm 0.7^\circ$,³² respectively. Anharmonic frequencies of SO_2 at CCSD(T)/aV(n+d)Z ($n = \text{D}, \text{T}, \text{Q}$) were calculated by applying VPT2 corrections at the MP2 level to CCSD(T) harmonic frequencies [Eq. (2)]. Our best estimates for the SO_2 vibrational frequencies are $515\ \text{cm}^{-1}$ (ν_2), $1154\ \text{cm}^{-1}$ (ν_1), and $1360\ \text{cm}^{-1}$ (ν_3) with CCSD(T)/aV(Q+d)Z, and these align well with the experimental values of 518 , 1152 , and $1362\ \text{cm}^{-1}$,³³ respectively.

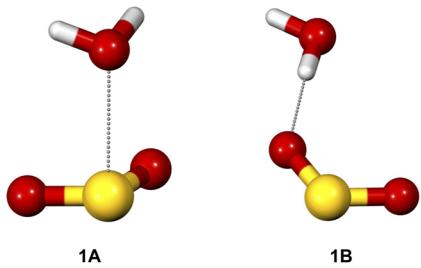
B. Dimer structures and D_e

Two structures of the $\text{SO}_2(\text{H}_2\text{O})$ dimer are reported here: a stacked form 1A, stabilized by one S···O and two O···H contacts, and a planar hydrogen-bonded complex (1B), bound by one O···H contact (see Fig. 1). Table II lists the binding energies D_e and structural parameters as a function of basis set size for both dimer complexes 1A and 1B, and these results have been extrapolated to the full CBS limit using Eq. (1). For the stacked structure 1A, the intermolecular distance $r_{\text{S...O}}$ spans from $2.835\ \text{\AA}$ [aV(D+d)Z], $2.830\ \text{\AA}$ [aV(T+d)Z] to $2.828\ \text{\AA}$ [aV(Q+d)Z] Å, and these values converge to $r_{\text{S...O}} = 2.827\ \text{\AA}$ at the CCSD(T)/CBS[D, T, Q] limit. The CCSD(T)/CBS distance $r_{\text{S...O}}$ reported here is in good agreement with the measured value of $2.824\ \text{\AA}$ obtained from microwave spectroscopy,¹ with the caveat that the measured value represents a vibrationally averaged distance r_0 rather than an equilibrium distance r_e . Our MP2 VPT2 calculations for the dimer 1A show a consistent shift toward a larger value of $r_{\text{S...O}}$, by roughly $0.06\ \text{\AA}$, when employing MP2/aV(n+d)Z with $n = \text{D}, \text{T}, \text{Q}$. By applying the $r_0 - r_e$ differences at the MP2/aV(T+d)Z and aV(Q+d)Z levels to the corresponding CCSD(T) r_e values, the CCSD(T) anharmonic distance r_0 is $2.896\ \text{\AA}$ [aV(T+d)Z] and $2.894\ \text{\AA}$ [aV(Q+d)Z], respectively, and these values are around $0.06\ \text{\AA}$ larger than the experimental value of $2.824\ \text{\AA}$. Thus, while the inclusion of anharmonic effects gives rise to slightly greater deviations from experiment, the predicted distances still remain within around 2.5% of the measured values. Results from CCSD(T)/aV(n+d)Z calculations for structure 1B predict an intermolecular distance $r_{\text{O...H}}$ of $2.127\ \text{\AA}$ [aV(D+d)Z], $2.131\ \text{\AA}$ [aV(T+d)Z], and $2.118\ \text{\AA}$ [aV(Q+d)Z], and these are slightly larger than the previously reported MP2/aVTZ $r_{\text{O...H}}$ distance of $2.115\ \text{\AA}$.¹⁸

Table II lists the CCSD(T)/aV(n+d)Z and CBS limit electronic energies (E_h) for both isomers, and as seen, E_h values for

TABLE I. Calculated CCSD(T) structural parameters and harmonic and anharmonic frequencies^a for SO₂.

Method	Basis set	Energy (E_h)	r_{S-O} (Å)	θ_{O-S-O} (deg)	ω_2 (cm ⁻¹)	ω_1 (cm ⁻¹)	ω_3 (cm ⁻¹)	v_2 (cm ⁻¹)	v_1 (cm ⁻¹)	v_3 (cm ⁻¹)
CCSD(T)	aV(D+d)Z	-547.815 249	1.469	119.07	489	1076	1273	485	1065	1259
	aV(T+d)Z	-548.006 270	1.443	119.24	511	1156	1366	507	1142	1349
	aV(Q+d)Z	-548.063 144	1.437	119.24	519	1168	1378	515	1154	1360
	aV(5+d)Z ^b	-548.082 407								
	CBS[D, T, Q]	-548.087 255	1.435	119.24						
	CBS[T, Q, 5]	-548.092 273								
	CBS[D, T, Q, 5]	-548.089 649								
CCSD(T) ^c	VQZ	-548.046 646	1.442	118.92	520	1162	1369	516	1146	1350
CCSD(T) ^d	aVQZ	-548.054 445	1.443	118.84	520	1166	1376	515	1151	1357
CCSD(T)-F12 ^e	aV5Z-F12		1.430	119.36						
MRCI-F12 ^e	aV5Z-F12		1.430	119.40						
Exp.			1.4307 ^f	119.19 ^f				518 ^g	1152 ^g	1362 ^g

^aCalculated with Eq. (2).^bSingle point energy calculation.^cReference 35.^dReference 34.^eReference 36.^fReference 32, errors in r_{S-O} and θ are at 0.000 13 Å and 0.7°, respectively.^gReference 33.**FIG. 1.** Structures of stacked (left) and hydrogen-bonded (right) SO₂(H₂O) isomers.

structures 1A and 1B converge systematically to their respective CBS limits, with 1A being ~1.9 kcal/mol more stable than 1B across the basis set range of aV(D+d)Z to aV(5+d)Z. The values of E_h at the CCSD(T)/aV($n+d$)Z level of theory have been extrapolated using two 3-point [D, T, Q] and [T, Q, 5] and one 4-point [D, T, Q, 5] CBS limit approaches via Eq. (1). For both isomers 1A and 1B, the [T, Q, 5] extrapolations yield lower CBS limit electronic energies E_h than the [D, T, Q] extrapolations, consistent with the results for the SO₂ monomer. All three CBS extrapolation schemes predict that isomer 1B is ~2.0 kcal/mol less stable than 1A. This feature indicates that the 3-point CBS[D, T, Q] extrapolation scheme itself can accurately reproduce energies retrieved by the extended 4-point [D,T,Q,5] CBS extrapolation scheme. Figure 2 shows the CCSD(T)/aV($n+d$)Z binding energies D_e , CP-corrected and uncorrected, as a function of basis set size up to the CBS limit. The values of D_e at the CCSD(T)/CBS limit are calculated by the differences in

CBS limit electronic energies of the dimer and the monomers, which follows $D_e(\text{CBS}) = E_{\text{CBS}}[(\text{SO}_2)(\text{H}_2\text{O})] - E_{\text{CBS}}[\text{SO}_2] - E_{\text{CBS}}[\text{H}_2\text{O}]$. Results from CP-uncorrected CCSD(T)/aV($n+d$)Z calculations predict D_e values for 1A at -4.88 kcal/mol [aV(D+d)Z], -4.55 kcal/mol [aV(T+d)Z], -4.48 kcal/mol [aV(Q+d)Z], and -4.43 [aV(5+d)Z] kcal/mol. For comparison, our CCSD(T)/aV(T+d)Z level binding energy D_e (-4.55 kcal/mol) is in excellent agreement with the previously reported CCSD(T)/aV(T+d)Z value of -4.6 kcal/mol.²⁰ The CBS extrapolation with $n = D, T, Q$ yields a CCSD(T)/CBS binding energy D_e value of -4.45 kcal/mol, whereas the CBS extrapolation with $n = T, Q, 5$ gives rise to a slightly reduced CCSD(T)/CBS binding energy D_e value of -4.37 kcal/mol. The 4-point CBS extrapolation scheme with $n = D, T, Q, 5$ yields a binding energy D_e value of -4.43 kcal/mol, and thus, despite adding considerable cost due to CCSD(T)/aV(5+d)Z single point energies, the [D, T, Q, 5] and [T, Q, 5] extrapolations provide little improvement compared to the 3-point [D, T, Q] CBS limit approach. The inclusion of CP-corrections yields CCSD(T)/aV($n+d$)Z binding energy D_e values of -3.64 kcal/mol [aV(D+d)Z], -4.06 kcal/mol [aV(T+d)Z], and -4.29 kcal/mol [aV(Q+d)Z]. As seen, the CCSD(T)/aV(T+d)Z CP-corrected D_e value of -4.06 kcal/mol aligns relatively well with a reported CCSD(T)/aV(T+d)Z D_e value of -4.1 kcal/mol,²⁰ despite being obtained from a geometry optimization on the CP-corrected CCSD(T)/aV(T+d)Z PES. This feature highlights that *post hoc* BSSE corrections are, indeed, sufficient in calculating accurate binding energies for SO₂(H₂O). Our CP-corrected D_e value at the CCSD(T)/aV(Q+d)Z level is -4.29 kcal/mol, and this value compares favorably with a recently reported estimate of -4.38 kcal/mol, which was obtained at the same level of theory.²¹ Finally, the CBS extrapolation of CP-corrected CCSD(T)/[T, Q, 5] binding energies gives a complete basis set limit value, $D_e = -4.37$ kcal/mol, and this value aligns well with a CBS value of -4.37 kcal/mol

TABLE II. Calculated CCSD(T) binding energies (D_e), scaled harmonic ZPE-corrected binding energies (D_0), uncorrected and counterpoise-corrected (shown in square brackets), and structural parameters for $\text{SO}_2(\text{H}_2\text{O})$.

Isomer	Basis set	Energy (E_h)	D_e (kcal/mol) ^a	D_0 (kcal/mol)	E_{def} (kcal/mol)	$r_{\text{S} \dots \text{O}}$ (Å)
1A	aV(D+d)Z	-624.096 935	-4.88 [-3.64]	-3.70	0.024	2.835
	aV(T+d)Z	-624.355 850	-4.55 [-4.06]	-3.41	0.025	2.830
	aV(Q+d)Z ^b	-624.433 867	-4.48 [-4.29]	-3.31	0.027	2.828
	aV(5+d)Z ^c	-624.459 764	-4.43 [-4.36]			
	CBS[D, T, Q]	-624.467 514	-4.45 [-4.44]			
	CBS[T, Q, 5]	-624.472 632	-4.37 [-4.37]			
	CBS[D, T, Q, 5]	-624.469 985	-4.43 [-4.43]			
1B	aV(D+d)Z	-624.093 890	-2.97 [-2.12]	-1.87	0.019	4.156
	aV(T+d)Z	-624.353 098	-2.82 [-2.31]	-1.74	0.014	4.273
	aV(Q+d)Z ^b	-624.430 899	-2.62 [-2.40]	-1.55	0.015	4.228
	aV(5+d)Z ^c	-624.456 698	-2.51 [-2.41]			
	CBS[D, T, Q]	-624.464 268	-2.41 [-2.42]			
	CBS[T, Q, 5]	-624.469 496	-2.40 [-2.41]			
	CBS[D, T, Q, 5]	-624.466 790	-2.42 [-2.42]			
Exp.					2.824 ^d	

^aCCSD(T)/CBS estimates of D_e are calculated by the differences in CBS electronic energies between the $\text{SO}_2(\text{H}_2\text{O})$ dimer and the sum of SO_2 and H_2O monomers.

^bPartial optimizations with monomer distances and angles fixed.

^cSingle point energy calculations.

^dReference 1.

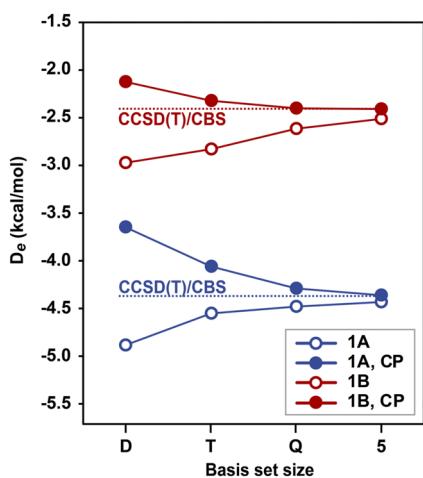


FIG. 2. Calculated CCSD(T)/aV($n+d$)Z and CBS limit binding energies D_e for stacked (blue) and hydrogen-bonded (red) $\text{SO}_2(\text{H}_2\text{O})$ isomers. The solid and hollow circles denote the CP-corrected and uncorrected D_e values, respectively.

that we obtained from CCSD(T) calculations using CP-uncorrected energies.

For the hydrogen-bonded structure 1B, the CCSD(T)/aV($n+d$)Z binding energies D_e are -2.97 kcal/mol [aV(D+d)Z], -2.82 kcal/mol [aV(T+d)Z], -2.62 kcal/mol [aV(Q+d)Z], and -2.51 kcal/mol [aV(5+d)Z] kcal/mol. It is

noteworthy that the [D, T, Q] series of D_e exhibits a non-convergence behavior (see Fig. 2) observed previously for similar dimer complexes.^{23,37–40} Despite these convergence inconsistencies, evaluating the differences in CBS electronic energies between dimer and monomers yields CCSD(T)/CBS D_e estimates of -2.41 kcal/mol [D, T, Q] and -2.42 kcal/mol [D, T, Q, 5]. We have also performed a 3-point [T, Q, 5] CBS extrapolation, which converges to a CCSD(T)/CBS level binding energy D_e value of -2.40 kcal/mol. The counterpoise-corrected values of D_e converge systematically for aV($n+d$)Z with $n = T - 5$ and yield a CCSD(T)/CBS[T, Q, 5] binding energy D_e value of -2.41 kcal/mol. An averaged value of $D_e = -2.406$ kcal/mol between the CP-uncorrected and corrected CBS values is chosen,⁴¹ representing our best estimate for the binding energy of isomer 1B. Our CCSD(T)/aV(T+d)Z binding energy for isomer 1B is -2.82 kcal/mol and is around 0.45 kcal/mol larger than the MP2/aVTZ//CCSD(T)/aVTZ D_e value of -2.37 kcal/mol reported by Cukras and Sadlej.¹² We have also calculated the deformation energies (E_{def}) of both monomers in $\text{SO}_2(\text{H}_2\text{O})$ following dimerization, and these results are presented in Table II. The values of E_{def} are in the range of 0.024–0.027 kcal/mol across CCSD(T)/aV($n+d$)Z for isomer 1A and 0.014–0.019 kcal/mol for isomer 1B. At the highest level CCSD(T)/aV(Q+d)Z, the values of E_{def} are at 0.027 kcal/mol and 0.015 kcal/mol for isomers 1A and 1B, respectively, and these are noticeably larger, by a factor of 10, than in the more weakly bound $(\text{H}_2\text{S})_2$ complex (0.004 kcal/mol²³). A brief review of these results appears to indicate that there is only minimal deformation occurring in SO_2 and H_2O following dimerization, and thus, binding in the system is rooted in the intrinsic electrostatic properties of both monomers and charge dispersion taking place upon dimerization.

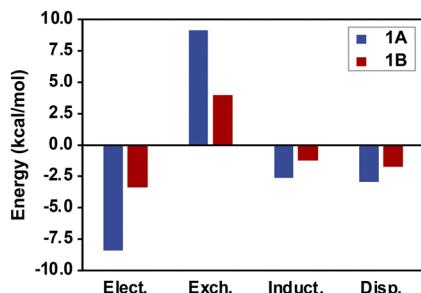


FIG. 3. SAPT/aV(D+d)Z energy decomposition of isomers 1A and 1B.

Expanding on this observation, we have performed a set of preliminary SAPT (symmetry-adapted perturbation theory) calculations at the SAPT2+3(CCD)/aV(D+d)Z level [abbreviated as SAPT/aV(D+d)Z] in order to address the nature of bonding in this dimer. These SAPT analyses decompose the intermolecular interactions between SO₂ and H₂O into electrostatic, exchange, induction, and dispersion contributions (see Fig. 3). For isomers 1A and 1B, electrostatic, induction, and dispersion interactions are negative, indicating that all three interaction types contribute toward the overall binding in SO₂(H₂O). For 1A, the electrostatic and exchange energies are predicted to be -8.39 kcal/mol and 9.15 kcal/mol, respectively, and these values align relatively well with the reported values of -7.71 and 8.31 kcal/mol [SAPT2/aV(D+d)Z¹²]. For 1B, these energetic contributions to D_e are -3.33 kcal/mol (electrostatic), -1.21 kcal/mol (induction), -1.72 kcal/mol (dispersion), and 3.93 kcal/mol (exchange).

C. Anharmonic frequencies and D₀

Tables III and IV list the CCSD(T)/aV(n+d)Z anharmonic VPT2 vibrational frequencies for SO₂(H₂O) 1A and 1B, respectively, together with experimental IR frequencies, covering the intramolecular vibrational frequency range from 500 to 3800 cm⁻¹. As given in Table III, the calculated HOH bending (v₂) and OH stretching frequencies (v₁ and v₃) in 1A all blueshift to higher energies as a function of basis set size. For instance, at the CCSD(T)/aV(D+d)Z level of theory, v₂ = 1592 cm⁻¹, v₁ = 3595 cm⁻¹, and v₃ = 3700 cm⁻¹, and these values shift upon a basis set expansion from n = D - T by +5 cm⁻¹ (v₂), +37 cm⁻¹ (v₁), and +28 cm⁻¹ (v₃) and from n = T - Q by +3 cm⁻¹ (v₂), +15 cm⁻¹ (v₁), and +15 cm⁻¹ (v₃). At the highest level of theory CCSD(T)/aV(Q+d)Z, the bending and stretching frequencies in H₂O are v₂ = 1600 cm⁻¹, v₁ = 3647 cm⁻¹, and v₃ = 3743 cm⁻¹. Our predicted CCSD(T)/aV(Q+d)Z values for v₁ and v₃ are in good agreement with those recorded from IR spectroscopic measurements with v₁ = 3643 cm⁻¹ and v₃ = 3745 cm⁻¹,⁵ respectively. These results demonstrate that the basis set expansion (from n = D, T, to Q) significantly enhances the agreement with gas-phase IR measurements. For instance, in the case of the water OH asymmetric stretching mode (v₃), differences between calculated CCSD(T)/aV(n+d)Z frequencies and experiment reduce from -45 to -17 to -2 cm⁻¹. The results of these frequencies have not been subjected to CBS extrapolation [Eq. (1)], due to their irregular convergence patterns, and thus, we have chosen to use anharmonic frequencies at CCSD(T)/aV(Q+d)Z as our most reliable estimates. Our CCSD(T)/aV(Q+d)Z calculations also predict that the water OH stretching frequencies in 1A are redshifted relative to those in the water monomer by 15 cm⁻¹ (v₃) and 13 cm⁻¹ (v₁), respectively. These results are in excellent agreement with the experimentally measured gas-phase shifts of 11 and 14 cm⁻¹.

TABLE III. Calculated CCSD(T) anharmonic^a (v_i, cm⁻¹) and experimental vibrational frequencies and anharmonic ZPE_F (kcal/mol) for SO₂(H₂O) isomer 1A.

Assignment	v _i			v _{Exp.}	v _i - v _{Exp.}		
	aV(D+d)Z	aV(T+d)Z	aV(Q+d)Z		aV(D+d)Z	aV(T+d)Z	aV(Q+d)Z
OH asym. stretch (v ₃)	3700	3728	3743	3745 ^b , 3723 ^c	-45, -23	-17, 5	-2, 20
OH sym. stretch (v ₁)	3595	3632	3647	3643 ^b , 3631 ^c	-48, -35	-11, 1	4, 16
H ₂ O bend (v ₂)	1592	1597	1600	1591 ^c	1	7	9
SO asym. stretch (v ₃)	1257	1342	1355	1344 ^c	-87	-2	11
SO sym. stretch (v ₁)	1072	1145	1160	1150 ^c	-78	-5	10
SO ₂ bend (v ₂)	494	514	522	522 ^d	-28	-8	0
H ₂ O twist	206	197	222				
H ₂ O wag	122	96	122				
S···O stretch	121	116	119				
H ₂ O rock	95	88	138				
SO ₂ wag	82	88	95				
SO ₂ twist	34	46	18				
ZPE _F	17.68	18.00	18.21				
D ₀	-3.95	-3.68	-3.48				

^aCalculated with Eq. (2).^bReference 5, in gas phase, at 200 K.^cReference 3, in Ar matrices, at 25 K.^dReference 2, in Ar matrices, at 19 K.

TABLE IV. Calculated CCSD(T) anharmonic^a (ν_i , cm^{-1}) and anharmonic ZPE_F (kcal/mol) for SO₂(H₂O) isomer 1B.

Assignment	ν_i		
	aV(D+d)Z	aV(T+d)Z	aV(Q+d)Z
OH asym. stretch (ν_3)	3701	3731	3748
OH sym. stretch (ν_1)	3598	3638	3653
H ₂ O bend (ν_2)	1599	1604	1606
SO asym. stretch (ν_3)	1256	1346	1358
SO sym. stretch (ν_1)	1066	1143	1155
SO ₂ bend (ν_2)	488	511	519
Bound OH wag	274	326	301
H ₂ O rock	174	165	145
O···H stretch	102	108	98
Free OH wag	61	35	35
SO ₂ rock	22	6	5
SO ₂ wag	7	38	34
ZPE _F	17.65	18.08	18.09
D ₀	-2.07	-1.86	-1.74

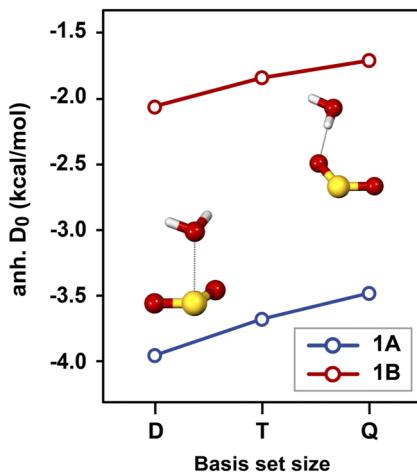
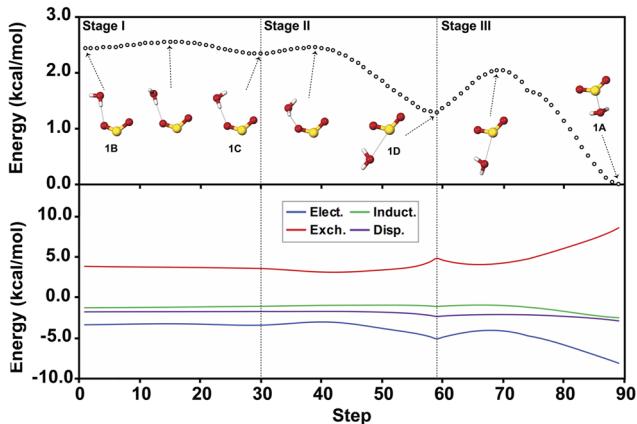
^aCalculated with Eq. (2).

reported by Wang and co-workers.⁵ Table III also demonstrates that the calculated intramolecular SO₂ vibrational frequencies in the stacked structure 1A all increase as a function of basis set size: for example, the SO stretching (ν_1 , and ν_3) and OSO bending (ν_2) modes are all blueshifted following the basis set expansion from $n = D - Q$ by +28 cm^{-1} (ν_2), +88 cm^{-1} (ν_1), and +98 cm^{-1} (ν_3). Our best estimates for SO₂ frequencies at CCSD(T)/aV(Q+d)Z are at $\nu_2 = 522 \text{ cm}^{-1}$, $\nu_1 = 1160 \text{ cm}^{-1}$, and $\nu_3 = 1355 \text{ cm}^{-1}$. It is also noteworthy that these CCSD(T)/aV(Q+d)Z results exhibit only minor deviations (0–11 cm^{-1}) from those reported for SO₂(H₂O) in Ar at 5 K.³ In the case of the hydrogen-bonded isomer 1B (see Table IV), the [D, T, Q] basis set expansion from $n = D - Q$ yields CCSD(T)/CBS values for the H₂O vibrational frequencies of $\nu_2 = 1606 \text{ cm}^{-1}$, $\nu_1 = 3653 \text{ cm}^{-1}$, and $\nu_3 = 3748 \text{ cm}^{-1}$ and for the SO₂ vibrational frequencies of 519 cm^{-1} (ν_2), 1155 cm^{-1} (ν_1), and 1358 (ν_3) cm^{-1} .

Building on the above theoretical CCSD(T) vibrational spectroscopy of 1A and 1B, we report on CCSD(T) zero-point-energies (ZPE_F) and ZPE-corrected anharmonic dissociation energies D₀ (see Tables III and IV). Our CCSD(T) calculations reveal an increase in the anharmonic ZPE_F with increasing basis set sizes. At the highest level of theory, CCSD(T)/aV(Q+d)Z, the predicted anharmonic ZPE_F values are 18.21 kcal/mol for 1A and 18.09 kcal/mol for 1B. If we combine these ZPE_F corrections with the CCSD(T)/aV(n+d)Z values of D_e, we obtain a new set of basis set-dependent dissociation energies D₀ of -3.95 kcal/mol [aV(D+d)Z], -3.68 kcal/mol [aV(T+d)Z], and -3.48 kcal/mol [aV(Q+d)Z] kcal/mol (see Fig. 4). In the case of isomer 1B, the anharmonic CCSD(T) values of D₀ are -2.07 [aV(D+d)Z], -1.86 [aV(T+d)Z], and -1.74 [aV(Q+d)Z] kcal/mol.

D. SAPT potential energy surface scan

We have supplemented our CCSD(T)/aV(n+d)Z energies with MP2/aV(D+d)Z potential energy surface calculations, employing

**FIG. 4.** Calculated CCSD(T)/aV(n+d)Z anharmonic D₀ [with MP2 VPT2 corrections using Eq. (2)] for stacked (blue) and hydrogen-bonded (red) SO₂(H₂O).**FIG. 5.** SAPT total energies along the reorientation trajectory from 1B to 1A (top) and SAPT component (electrostatic, exchange, induction, and dispersion) breakdown as a function of reorientation steps (bottom).

the quadratic synchronous transit (QST) method. The goal of these calculations is to energetic rank intermediate SO₂(H₂O) structures along the transition from isomer 1B to 1A. These MP2/aV(D+d)Z scans have been augmented with SAPT calculations, which will assist in elucidating the types of interaction (electrostatic, exchange, induction, and dispersion) involved in the binding of SO₂(H₂O). Figure 5 shows the variation in SAPT/aV(D+d)Z electronic energy upon reorientation from the hydrogen-bonded structure 1B (step 1) to the stacked form 1A (step 89). The transition from 1B to 1A involves three stages: in stage I, the water molecule rotates out-of-plane, resulting in a new structure 1C with a 2.158 Å OH···OS contact, and this structure is around 0.1 kcal/mol lower in energy than 1B. In stage II, a new intermediate structure 1D exists, featuring one reduced OH···OS (2.322 Å) contact and one extended HO···SO (3.132 Å) contact. Stage III is marked by a moderate shift

in total energy (0.8 kcal/mol) and a reduction in the S···O distance from 3.132 Å to 2.864 Å. This reorganization gives rise to an increase in the electrostatic interaction and a reduction in the dispersion contribution (Fig. 5). In conclusion, the restructuring of the hydrogen-bonded isomer 1B to the stacked form 1A involves a series of out-of-plane rotations and contact distance adjustments, resulting in an enhancement of the electrostatic contribution (7%) and a reduction in the dispersion contribution (6%).

IV. CONCLUSIONS

In this study, we have performed CCSD(T)/aV($n+d$)Z ($n = D, T, Q$) calculations for two isomers of the SO₂(H₂O) complex, a stacked global minimum (1A) and a hydrogen-bonded isomer (1B), with a particular focus on the molecular structures, IR vibrational spectroscopy, and binding energies D_e and D_0 . Our best CCSD(T)/CBS estimate for the intermolecular S···O distance ($r_{S\cdots O}$) in 1A is 2.827 Å, which is in good agreement with the experimental determination $r_{S\cdots O} = 2.824$ Å.¹ Using a CBS extrapolation scheme based on aV(D+d)Z, aV(T+d)Z, and aV(Q+d)Z geometry optimizations and binding energies, we arrive at a CCSD(T)/CBS value of $D_e = -4.37$ kcal/mol for isomer 1A and $D_e = -2.40$ kcal/mol for isomer 1B.

We have also undertaken VPT2 anharmonic frequency calculations for both structures and applied these results to estimate new values for the anharmonic dissociation energy D_0 . For the global minimum structure 1A, the CCSD(T)/aV(Q+d)Z vibrational frequencies for SO₂ are $\nu_2 = 522$ cm⁻¹, $\nu_1 = 1160$ cm⁻¹, and $\nu_3 = 1355$ cm⁻¹. In structure 1A, the water OH stretching frequencies are $\nu_1 = 3647$ cm⁻¹ and $\nu_3 = 3743$ cm⁻¹, and these align closely with the experimental values of $\nu_1 = 3643$ cm⁻¹ and $\nu_3 = 3745$ cm⁻¹ recorded using FEL IR spectroscopy on a proposed stacked isomer of SO₂(H₂O). If we combine results from our CCSD(T)/aV(Q+d)Z anharmonic frequency calculations with the corresponding binding energies D_e , we arrive at a new anharmonic estimate for the dissociation energy $D_0 = -3.48$ kcal/mol for 1A and -1.74 kcal/mol for 1B. Interestingly, the D_0 value for 1A reported here is quite close to the D_0 value reported for (H₂O)₂ ($D_0 = 3.15 \pm 0.03$ kcal/mol⁴²), and thus, SO₂(H₂O) would coexist with (H₂O)₂ as a stable and IR-spectroscopically detectable complex.

Finally, our VPT2 and CCSD(T)/CBS results have been supplemented with SAPT energy decomposition calculations, and these demonstrate that electrostatic interactions play a critical role in the stabilization of 1A, with around 60% of the dimer binding energy rooted in molecular electrostatics, and reduced contributions from dispersion (21%) and induction (19%). Electrostatic contributions to the dimer binding energy in the hydrogen-bonded form 1B, on the other hand, reduce slightly relative to 1A, to around 53%, while dispersion contributions in 1B increase by roughly 7% relative to the stacked structure 1A.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Wallace C. H. Hui: Writing – original draft (equal). Kono H. Lemke: Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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