Computational studies of the potential energy surface for $O(^1D)+H_2S$: Characterization of pathways involving H_2SO , $HOSH$, and H_2OS

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(Received 19 July 1994; accepted 16 August 1994)

Structures and vibrational frequencies for minima and transition states on the $O(^1D)+H_2S$ potential energy surface have been characterized at the unrestricted second-order Møller–Plesset (UMP2)=full/6-31G(*d*) level. The results for the thioperoxide $HOSH$ agree with experimental IR spectra. Gaussian-2 theory was employed to calculate $\Delta H_{f,298}$ for $HOSH$ of $-119.3\text{ kJ mol}^{-1}$, -47.1 kJ mol^{-1} for the sulfoxide H_2SO , and 47.0 kJ mol^{-1} for the thiooxonium ylide H_2OS . We also derived $\Delta H_{f,0}$ for HOS and HSO of -2.7 and -17.0 kJ mol^{-1} , respectively. Comparisons with ΔH_f for known asymptotes on the potential energy surface gave good agreement, except in the case of HSO . Rice–Ramsperger–Kassel–Marcus (RRKM) analysis suggests that in most environments, except at low pressures and temperatures, H_2OS will be short lived, and rate constants for isomerization of the three bound adducts under thermally equilibrated conditions are derived. The potential energy surface is discussed in the context of single-collision experiments, and pathways leading to $SH+OH$, $^1SO+H_2$, $HSO+H$, $HOS+H$, and $^1S+H_2O$ have been analyzed. © 1994 American Institute of Physics.

I. INTRODUCTION

Molecular beam studies of collisions between $O(^1D)$ and H_2S show that both $H+(HSO\text{ or }HOS)$ and $OH+SH$ are produced, with no evidence for the other exothermic channel to H_2+SO (Refs. 1–3 and references therein). The suggested mechanism is insertion into a S–H bond to form a highly excited molecule that fragments rapidly.² Candidates for this bound intermediate include the thioperoxide $HOSH$, the sulfoxide H_2SO with both H atoms bonded to S, and the thiooxonium ylide H_2OS with both H atoms bonded to O. $HOSH$ is known from matrix-isolation experiments,⁴ and $HOSH$ and H_2OS have very recently been identified in the gas phase by neutralization–reionization mass spectrometry,⁵ while H_2SO remains unobserved.

There have been several computational studies of $HOSH$,^{6–13} but fewer of H_2SO (Refs. 6 and 11–13) and H_2OS .¹¹ Wolfe and Schlegel made the only study of the relative stability of all three isomers, at up to the fourth-order Møller–Plesset (MP4)/6-31G(*d,p*) level of theory,¹⁴ and of the barriers to isomerization between them.¹¹ Because of the importance of sulfur species to atmospheric and combustion chemistry, where numerous but poorly characterized sulfur-containing molecules play significant roles, we have investigated the singlet $O+H_2S$ potential energy surface (PES) at a uniform and high level of *ab initio* theory. We employ the Gaussian-2 (G2) methodology, which has a target accuracy of $\pm 8\text{ kJ mol}^{-1}$ for atomization enthalpies and an average absolute deviation of 5 kJ mol^{-1} ,^{15–17} to obtain approximate quadratic single and double configuration interactions with triple substitutions [QCISD(T)]/6-311+G(3*df*,2*p*) energies. The results are used to predict the thermochemistry of $HOSH$, H_2SO , and H_2OS and to analyze pathways for their isomerization and dissociation to $O(^1D)+H_2S$, H_2+^1SO , $H+HOS$ and HSO , $S(^1D)+H_2O$, and $OH+SH$.

II. AB INITIO METHODOLOGY

The general principles of quantitative molecular orbital theory have been described elsewhere,^{18,19} and the *ab initio* calculations were carried out with the Gaussian 90 and 92 programs.^{20,21} Preliminary searches of the singlet PES were made at the self-consistent field or Hartree–Fock (HF) and second-order Møller–Plesset (MP2) levels of theory with the 3-21G(*d*) and 6-31G(*d*) basis sets, which are of double zeta plus polarization (DZ+P) quality. The MP2 calculations incorporate a partial correction for the effects of electron correlation. Each stationary point was characterized as a true minimum (all vibrational frequencies real) or a transition state (a single imaginary frequency) at the MP2=full/6-31G(*d*) level.¹⁴ The reactants and products connected by each transition state (TS) were confirmed by visualization of the imaginary vibrational normal mode and/or by following the intrinsic reaction coordinate. The calculated harmonic frequencies are scaled by a standard factor of 0.95 to account for effects of basis set deficiency and anharmonicity, and are used to derive the zero-point vibrational energy $\Delta E(ZPE)$ and various thermodynamic quantities. Spin-restricted Hartree–Fock (RHF) wave functions are typically appropriate for singlet species, but as is well known, RHF wave functions do not properly describe PESs for dissociation; the classic example is H_2 whose RHF wave function tends towards H^++H^- as the bond length is increased, whereas the spin-unrestricted Hartree–Fock (UHF) wave function leads correctly to 2 H.²² Accordingly stationary points were all optimized at the unrestricted UMP2=full/6-31G(*d*) level of theory (of which spin-restricted RMP2 is a special case with identical orbitals for α and β electrons). Often the lowest energy wave function appeared to be RHF; this was tested at each stationary point by examination of the stability of the wave function with respect to relaxation of internal constraints.²³ Exceptions are H_2OS and the TS to $HOSH$, where RHF wave functions are employed because the UHF

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TABLE I. A comparison of singlet-triplet energy gaps for atomic oxygen and sulfur (in kJ mol^{-1}).

Method	$O(^3P) \rightarrow O(^1D)$	$S(^3P) \rightarrow S(^1D)$
Experiment ^a	190	110
UMP2=full/6-31G(d)	98	65
RMP2=full/6-31G(d)	284	187
UMP4/6-311G(d,p)	97	61
RMP4/6-311G(d,p)	267	171
PMP4/6-311G(d,p)	197	119
UQCISD(T)/6-311G(d,p)	40	36
RQCISD(T)/6-311G(d,p)	221	140
UMP4/6-311G(2df,p)	93	56
RMP4/6-311G(2df,p)	261	160
U-G2	24	19
R-G2	200	116
P-G2	124	75

^aReference 29.

wave functions with $\langle S^2 \rangle \approx 0.1$ are only about 0.0002 a.u. below the RHF solutions, and when correlation is taken into account, the UMP2 energy lies *above* the RMP2 energy.

The next step is to obtain the energy at each stationary point, at a much higher level of theory. Approximate QCISD(T)/6-311+G(3df,2p) energies are calculated at the UMP2=full/6-31G(d) geometries by means of the G2 methodology.¹⁷ Briefly, the MP4/6-311G(d,p) energy is modified with a series of additive corrections defined as follows: $\Delta E(+)=E[\text{MP4/6-311+G}(d,p)]-E[\text{MP4/6-311G}(d,p)]$, $\Delta E(2df)=E[\text{MP4/6-311G}(2df,p)]-E[\text{MP4/6-311G}(d,p)]$, $\Delta E(\text{QCI})=E[\text{QCISD(T)/6-311G}(d,p)]-E[\text{MP4/6-311G}(d,p)]$, and $\Delta E(\text{HLC})=(-0.00019n_{\text{unpair}}-0.00614n_{\text{pair}})$ a.u. (1 a.u. $\approx 2625 \text{ kJ mol}^{-1}$), where n_{unpair} and n_{pair} represent the numbers of unpaired valence electrons and valence pairs, respectively. The G1 energy is defined as $E(\text{G1})=E[\text{MP4/6-311G}(d,p)]+\Delta E(+)+\Delta E(2df)+\Delta E(\text{QCI})+\Delta E(\text{HLC})+\Delta E(\text{ZPE})$. The further term $\Delta E=E[\text{MP2/6-311+G}(3df,2p)]-E[\text{MP2/6-311G}(2df,p)]-E[\text{MP2/6-311+G}(d,p)]+E[\text{MP2/6-311G}(d,p)]$ leads to the G2 energy as $E(\text{G2})=E(\text{G1})+\Delta+0.00114n_{\text{pair}}$ a.u. Our use of MP2 rather than HF frequencies to obtain $\Delta E(\text{ZPE})$ is a modification of the original G2 method; we have summarized the small changes in energy for the published G2 energies of relevant one-, two-, and three-atom species elsewhere.²⁴

A complication arises in the case of singlet diradical species such as $O(^1D)$, where the near degeneracy of occupied and unoccupied orbitals leads to instability in the RHF wave function and a lower energy UHF solution which is heavily spin contaminated ($\langle S^2 \rangle \approx 1$). This has been discussed by Yamaguchi *et al.*,²⁵ who found poor accord with experimental singlet-triplet energy gaps for such species at the RHF level, but good accord with the UHF wave function provided a correction was made for spin contamination at the MP4/6-311(d) and MP4/6-311G(d,p) levels of theory. Computed $^3P \rightarrow ^1D$ energy gaps for atomic oxygen and sulfur at various levels of the theory are summarized in Table I.

It may be seen that neither UMP4 nor RMP4 results are in satisfactory accord with experimental data, although the RMP4 results are slightly closer with larger basis sets. As

FIG. 1. UMP2=full/6-31G(d) geometries for bound minima (a) OHSH; (b) H₂SO; (c) HOSH; (d) H₂OS. Distances are in Angstroms and angles are in degrees.

noted by Yamaguchi *et al.*, the spin-projected PMP4 data are in good agreement (here we used Schlegel's spin-projection algorithm,²⁶ which yields slightly better accord). For a given basis set, QCISD(T) gives better results than MP4 with the RHF wave function, but worse with the UHF wave function. These factors combine in the R-G2 method (the default G2 approach for singlet species), which employs QCISD(T) and large basis sets, to give good agreement with experiment. By contrast, G2 using UHF wave functions shows very bad performance, which is not fully mitigated at the "P-G2" level, where a spin correction equal to the difference between PMP4 and MP4 energies is applied.

In summary, UHF/6-31G(d) wave functions with MP2 correlation corrections were used in searches of the PES, but RHF wave functions were employed in the high-level G2 calculations at each singlet stationary point with basis sets up to 6-311+G(3df,2p).

III. RESULTS AND DISCUSSION

Geometries for HOSH, H₂SO, and H₂OS calculated with MP2=full/6-31G(d) theory are shown in Fig. 1, and transition states for the following processes:

where OHSH refers to a very loose adduct between $O(^1D)$ and H₂S,

FIG. 2. UMP2=full/6-31G(*d*) geometries for transition states (a) TS1 for OHSH→SH+OH; (b) TS2 for H₂SO→H₂+SO; (c) TS3 for H₂SO→HOSH; (d) TS4 for HOSH→HSO+H; (e) TS5 for H₂OS→HOSH. Distances are in Angstroms and angles are in degrees.

are shown in Fig. 2. The scaled UMP2=full/6-31G(*d*) vibrational frequencies are summarized in Tables II and III. Based on total energies that exclude ZPE, Fig. 3 shows the PES that was actually searched at the UMP2=full/6-31G(*d*) level. It may be seen that the chemistry of the singlet O/H/H/S system is dominated by unimolecular processes. No evidence was found for barriers to the following insertion and association reactions:

TABLE II. A comparison of computed and measured frequencies for HOSH and DOSD (in cm⁻¹).

Mode	HOSH		Isotopic shift	
	Theory ^a	Expt. ^b	Theory ^a	Expt. ^b
OH stretch	3555	3425	965	764
SH stretch	2600	...	731	...
HOS bend	1205	1177	324	311
HSO bend	984	...	239	...
SO stretch	745	763	29	12
Torsion	486	449	130	117

^aMP2=full/6-31G(*d*) scaled by 0.95.

^bReference 4.

^cUnobserved. DSO bending was measured at 737 cm⁻¹ (cf. 745 cm⁻¹ computed).

A. Geometries and vibrational frequencies

There are no experimental data for comparison with the geometries shown in Fig. 1. The results for HOSH are similar to those obtained in other theoretical studies. In particular, the S–O distance of 1.69 Å, while greater than the experimental value of 1.57 Å for the single S–O bonds in H₂SO₄,²⁷ is very close to the CISD/DZ+P result of Lee *et al.*¹⁰ Calculated vibrational frequencies for HOSH and DOSD (Ref. 28) are compared with the matrix measurements of Smardzewski and Lin (Table II)⁴ and agreement is seen to be satisfactory. The *cis* and *trans* transition states for internal rotation about the S–O bond were characterized at the G2 level to yield torsional barriers of 26.3 and 18.2 kJ mol⁻¹, respectively, before inclusion of ZPE. These values are extremely close to the HF/4-31G(*d*) results of 26.3 and 16.6 kJ mol⁻¹ obtained by Magnusson.⁹

Our structure for H₂SO agrees with results from two previous computational studies.^{6,12} There appear to be no published data to compare with the calculated frequencies summarized in Table III. The S–O bond length of 1.50 Å suggests only minor multiple bond character and may be compared to the experimental value of 1.43 Å for SO₂.²⁹ There is extensive charge separation in H₂SO, where the

TABLE III. Scaled UMP2=full/6-31G(*d*) frequencies (in cm⁻¹) for stationary points in the O(¹D)+H₂S PES.

H ₂ SO		H ₂ OS		OHSH		TS1		TS2		TS3		TS4		TS5	
Symmetry	ν	Symmetry	ν	Symmetry	ν	Symmetry	ν	Symmetry	ν	Symmetry	ν	Symmetry	ν	Symmetry	ν
A''	970	A'	482	A'	66	A'	1772i	A'	1563i	A	1688i	A	903i	A	1599i
A'	1055	A'	733	A'	87	A'	221	A'	611	A	846	A	363	A	552
A'	1119	A''	779	A''	137	A''	254	A''	1053	A	918	A	442	A	928
A'	1252	A'	1601	A'	1220	A'	672	A'	1125	A	1010	A	891	A	1162
A''	2349	A'	3496	A'	2660	A'	1100	A''	1168	A	2445	A	1069	A	1967
A'	2351	A''	3614	A'	2688	A'	2665	A'	2033	A	2504	A	2480	A	3487

FIG. 3. Potential energy surface calculated at the UMP2=full/6-31G(d) level, showing energies (excluding ZPE) relative to $O(^1D)+H_2S$.

Mulliken charge on O [based on the HF/6-311+G(3df,2p) wave function] is -0.63 and the dipole moment is 3.94 D (1 D $\approx 3.336 \times 10^{-29}$ C m).

The geometry and frequencies (Table III) obtained for H_2OS appear to be the first published values for this species. There is a very large S–O separation of 1.93 Å and an ylide structure has been written as $H_2O^+S^-$. The HF/6-311+G(3df,2p) wave function yields a Mulliken charge on S of only -0.20 , although the dipole moment is high at 4.58 D, and much larger than, e.g., the value of 1.74 D for HOSH.

B. Thermochemistry

Components of the G2 energies for stationary points on the UMP2=full/6-31G(d) PES are listed in Table IV. For each bound molecule, the change in G2 energy for the hydrogenation reaction

equals the enthalpy change at 0 K, ΔH_0 . $\Delta H_{f,0}$ (molecule) is obtained from ΔH_0 and the measured $\Delta H_{f,0}$ of H_2O and H_2S .²⁹ As a test of this thermochemical approach, we used “molecule” = OH + SH to obtain a computed combined $\Delta H_{f,0}$ of 178.8 kJ mol⁻¹ (thermochemical data are quoted to one decimal place to avoid rounding errors; we do not imply this degree of accuracy), in excellent accord with the sum of the experimental $\Delta H_{f,0}$ for OH (Ref. 29) and SH (Ref. 30) of 180.9 kJ mol⁻¹. The results for the unknown molecules are

$\Delta H_{f,0}(\text{HOSH}) = -108.8$, $\Delta H_{f,0}(H_2SO) = -35.7$, and $\Delta H_{f,0}(H_2OS) = 57.5$ kJ mol⁻¹. Enthalpy corrections to other temperatures, S and C_p are calculated via statistical mechanics, with the torsional mode in HOSH treated as a hindered internal rotor and thermochemical properties interpolated from tables.³¹ To use these tables, which apply only to symmetrical barriers, the barriers for HOSH are averaged to 22.2 kJ mol⁻¹ and twofold symmetry imposed. Sets of derived thermochemical properties for the three molecules over 200 – 2000 K are given in Tables V–VII. There are no experimental values against which to compare our estimates, though we note moderate accord with bond additivity correction (BAC)-MP4 results for $\Delta H_{f,298}$ of HOSH and H_2SO of -128.1 ± 6.0 and -28.6 ± 5.4 kJ mol⁻¹, respectively.¹³ An earlier group-additivity estimate for the latter quantity is -67 ± 17 kJ mol⁻¹.³² Our stability ordering, with HOSH having the lowest $\Delta H_{f,0}$ followed by H_2SO and then H_2OS , is the same as that found by Wolfe and Schlegel who used MP4/6-31G(d,p)+ZPE data.¹¹ They derived ΔH_0 for HOSH isomerizations to H_2SO and H_2OS to be 116.9 and 142.9 kJ mol⁻¹, whereas we estimate values of 73.1 and 166.3 kJ mol⁻¹, respectively. The larger basis sets and QCISD(T) correlation correction in the G2 method should make the G2 results more accurate.

Excluding zero-point energies, at the G2 level, $SO(^1\Delta)$ is predicted to be excited by 124 kJ mol⁻¹ relative to $SO(^3\Sigma)$. This energy, although higher than a previous estimate of 76 kJ mol⁻¹, more plausibly lies between the analogous transition energies for O_2 (95 kJ mol⁻¹) and S_2 (rough estimate 263 kJ mol⁻¹).³³

$\Delta H_{f,298}$ for HOSH, H_2SO and H_2OS can be used to derive S–O bond dissociation enthalpies DH_{298} (leading to ground state products, i.e., triplet O and S atoms). The results are 296.9 , 271.4 , and -16.1 kJ mol⁻¹, respectively. Interestingly, although the S–O bond in HOSH is significantly longer than in H_2SO , DH_{298} is actually slightly greater in HOSH. Benson used group-additivity methods to predict $DH_{298}(H_2S-O) = 297 \pm 17$ kJ mol⁻¹,³² in good accord with the present data. The results also reveal that H_2OS is thermodynamically unstable with respect to $H_2O + S(^3P)$, although this dissociation may be slow because it is spin forbidden.

Equation (13) combined with $\Delta H_{f,0}(H)$ ²⁹ yields $\Delta H_{f,0}(\text{HOS}) = -2.7$ kJ mol⁻¹, in excellent agreement with a

TABLE IV. Absolute G2 energies of stationary points on the $O(^1D)+H_2S$ PES calculated at the UMP2=full/6-31G* optimized geometries.

Species	Symmetry	State	MP4/6-311G(d,p) ^a	$\Delta E(+)^b$	$\Delta E(2df)^b$	$\Delta E(QCI)^b$	$\Delta E(ZPE)^b$	Δ^b	$E(G2)^a$	H_{rel}^c
HOSH	C_1	1A	-473.912 79	-10.09	-93.38	-0.34	21.81	-10.58	-474.040 37	-535.6
H_2SO	C_s	$^1A'$	-473.869 33	-11.64	-105.05	+1.24	20.72	-13.46	-474.012 52	-462.5
H_2OS	C_s	$^1A'$	-473.861 58	-6.25	-90.28	-1.10	24.38	-7.20	-473.977 03	-369.3
OHSH	C_s	$^1A'$	-473.704 28	-5.27	-78.79	-18.93	15.62	-9.99	-473.836 64	-0.8
TS1	C_s	$^1A'$	-473.673 92	-7.48	-81.72	-4.56	11.21	-10.11	-473.801 58	91.2
TS2	C_s	$^1A'$	-473.802 13	-12.31	-104.67	+2.58	13.64	-10.63	-473.948 52	-294.5
TS3	C_1	1A	-473.801 60	-16.65	-102.15	+0.46	17.59	-11.06	-473.948 41	-294.2
TS4	C_1	1A	-473.784 80	-10.31	-98.13	-6.87	11.95	-11.26	-473.934 42	-239.7
TS5	C_1	1A	-473.836 63	-8.19	-91.61	+0.45	18.44	-9.76	-473.962 30	-330.6

^aIn atomic units.

^bComponent of G2 energy in 10^{-3} a.u. $n_{\text{pair}}=7$ and $n_{\text{unpair}}=0$, so that $\Delta E(\text{HLC}) = -0.042 98$ a.u. for all isomers.

^cEnthalpy relative to $O(^1D)+H_2S$ at 0 K in kJ mol⁻¹.

TABLE V. Thermochemical data for HOSH.

T (K)	C_p (J K ⁻¹ mol ⁻¹)	S (J K ⁻¹ mol ⁻¹)	H_T-H_0 (kJ mol ⁻¹)	$\Delta_f H^0$ (kJ mol ⁻¹)	$\Delta_f G^0$ (kJ mol ⁻¹)
200	39.0	228.2	7.0	-112.8	-110.4
298.15	45.4	245.0	11.1	-114.9	-108.8
400	51.3	259.2	16.0	-119.1	-106.4
500	55.7	271.2	21.4	-122.1	-102.9
700	61.5	291.0	33.2	-126.3	-94.4
1000	66.6	313.8	52.5	-182.4	-72.8
1300	69.8	331.7	73.0	-182.1	-39.9
2000	74.1	362.7	123.5	-181.3	36.4

recent measurement by O'Hair *et al.* of -2.1 ± 8.4 kJ mol⁻¹.³⁴ For comparison, previous *ab initio* work by Luke and McLean³⁵ and Xantheas and Dunning³⁶ yielded $\Delta H_{f,0}(\text{HOS}) = -12.1$ and 0 kJ mol⁻¹, respectively. The G2 $\Delta H_{f,0}$ for HSO is -17.0 kJ mol⁻¹, which may be compared with recent *ab initio* estimates by Luke and McLean,³⁵ Xantheas and Dunning,³⁶ and Espinosa-Garcia and Corchado³⁷ of -1.7 , -22.6 , and -8.8 kJ mol⁻¹, respectively, and the most recent experiments by Balucani *et al.*³ which yielded -3.8 ± 2.9 kJ mol⁻¹. These controversial enthalpies are discussed elsewhere in the context of the triplet PES,³⁸ with a focus on resolving the disagreement between the G2 $\Delta H_{f,0}(\text{HSO})$ and the value from experiments based on the $O(^3P)+H_2S$ system. Here we use the G2 model chemistry to derive S-H and O-H bond dissociation enthalpies at 0 K, DH_0 , for HOSH, H₂SO, and H₂OS. $DH_0(\text{O-H})$ in HOSH is predicted to be 307.8 kJ mol⁻¹, considerably reduced from 493.3 kJ mol⁻¹ found for H₂O and 350.8 kJ mol⁻¹ found for H₂O₂,²⁹ and it is reduced further to 155.8 kJ mol⁻¹ in H₂OS. $DH_0(\text{S-H})$ is 376.1 kJ mol⁻¹ in H₂S,^{29,30} which is lowered to 321.3 kJ mol⁻¹ in HOSH and 234.7 kJ mol⁻¹ in H₂SO. In accord with these calculations, O'Hair *et al.*³⁴ obtained $DH_{298}(\text{HOS-H}) = 330.5 \pm 14.6$ kJ mol⁻¹ with a combination of experiment and theory. An unexpected feature is that while O-H bonds are normally stronger than S-H bonds, this situation is reversed in the case of HOSH. The generally weak bonding to H atoms in the three molecules implies facile abstraction and dissociation pathways, and a rich chemistry in both combustion and atmospheric environments.

C. Kinetics

G2 enthalpies at 0 K, relative to $O(^1D)+H_2S$, for stationary points on the vibrationally adiabatic PES are shown in Fig. 4. This diagram may be contrasted to Fig. 3, based on a much smaller basis set and lower level of correlation correction. There are two main qualitative differences. First, the energy of TS2 is now extremely close to that of $^1\text{SO}+H_2$ and suggests that there may not really be a true energy barrier to reaction (2) beyond the endothermicity. Second, the energy of TS4 now falls between that of $\text{HSO}+H$ and HOSH, consistent with the idea that there is no barrier to reaction (4) as well. The G2 barriers to isomerization of HOSH are in line with those predicted by Wolfe and Schlegel.¹¹ For the reverse of reactions (3) and (5), they found barriers of 149.5 and 49.6 kJ mol⁻¹, while the G2 values are 168.3 and 38.7 kJ mol⁻¹, respectively.

The two lowest energy pathways for the decomposition of H₂SO [reactions (2) and (3) that lead to H_2+SO and HOSH] have very similar calculated barriers. The unimolecular kinetics are now analyzed in terms of Rice-Ramsperger-Kassel-Marcus (RRKM) theory as outlined by Gilbert and co-workers.^{39,40} Rate constants are derived for an Ar bath gas, on the assumption of a weak collision "exponential down" model for energy transfer between the bath gas and H₂SO. $\sigma = 3.85$ Å and $\epsilon = 177$ K were chosen as the Lennard-Jones parameters that describe Ar+H₂SO collisions based on the values known for Ar+SO₂ collisions.⁴¹ Angular momentum effects for the molecule and TS are taken into account by allowing the energy of the rotational mode with

TABLE VI. Thermochemical data for H₂SO.

T (K)	C_p (J K ⁻¹ mol ⁻¹)	S (J K ⁻¹ mol ⁻¹)	H_T-H_0 (kJ mol ⁻¹)	$\Delta_f H^0$ (kJ mol ⁻¹)	$\Delta_f G^0$ (kJ mol ⁻¹)
200	34.1	225.5	6.7	-40.0	-37.1
298.15	38.2	239.8	10.2	-42.7	-35.1
400	44.0	251.8	14.4	-47.6	-32.0
500	49.6	262.3	19.1	-51.3	-27.7
700	58.5	280.4	29.9	-56.5	-17.2
1000	67.3	302.9	48.9	-112.9	7.6
1300	72.2	321.3	69.9	-112.1	43.7
2000	78.0	353.8	122.9	-108.8	126.8

TABLE VII. Thermochemical data for H_2OS .

T (K)	C_p ($J K^{-1} mol^{-1}$)	S ($J K^{-1} mol^{-1}$)	H_T-H_0 ($kJ mol^{-1}$)	$\Delta_f H^0$ ($kJ mol^{-1}$)	$\Delta_f G^0$ ($kJ mol^{-1}$)
200	38.8	228.6	6.9	53.5	55.7
298.15	45.0	245.2	11.0	51.3	57.3
400	49.9	259.2	15.9	47.0	59.8
500	53.6	270.7	21.1	43.8	63.3
700	58.8	289.6	32.3	39.1	72.0
1000	64.4	311.6	50.9	-17.7	94.1
1300	68.8	329.1	70.9	-17.9	127.7
2000	75.1	360.1	121.5	-17.0	205.9

the unique moment of inertia to be active,³⁹ i.e., to be available to help cross the potential barrier, while the other two rotations with similar moments of inertia were taken to be inactive. It should be noted that the derived rate constants are upper limits in the sense that variational TS theory has not been applied; on the other hand, tunneling effects will tend to increase reaction rates.

At 298 K, the fall-off pressures for reactions (2) and (3) are predicted to be of the order of 1000 Torr (1 Torr $\approx$ 133.3 Pa), but the reactions will be far too slow to observe. Thus at room temperature, H_2SO should be stable with respect to gas-phase unimolecular decomposition. At higher temperatures, the kinetics lie close to the low-pressure limit for pressures below 2000 Torr and can be characterized in terms of the second-order rate constant k_0 . Figure 5 shows Arrhenius plots of $k_{0,2}$, $k_{0,3}$, and the reverse reaction $k_{0,-3}$. Data for the reverse reaction are derived via the relationship $k_{0,3}/k_{0,-3} = K_{eq}$, with equilibrium constants K_{eq} derived from ΔG_f data in Tables V–VII. Also shown in Fig. 5 are $k_{0,5}$ and $k_{0,-5}$, the rate constants that describe $H_2OS \rightleftharpoons HOSH$, which were obtained with the same kind of RRKM analysis. We find reaction (5) to be close to the low-pressure limit for pressures below 2000 Torr at 298 K. It may be seen that H_2OS is not only thermodynamically unstable, as discussed in the previous section, but also labile. At 298 K, $k_{0,5} \approx 1.7 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$, so that in 1 atm of Ar, the average lifetime of H_2OS before isomerization to $HOSH$ is about 240 μs . At, e.g., 1500 K and 1 atm, all the isomerization reactions become fast, and an equilibrium distribution of H_2SO , $HOSH$, and H_2OS might be expected. However, dissociation channels to, e.g., $OH+SH$ and $H+HSO$ and HOS

will also be accessible, and these fragments will probably react readily with the parent adducts in subsequent bimolecular steps. We are continuing work on these systems to obtain the information needed to carry out kinetic modeling of sulfur-containing flames.

The G2 PES is now discussed in the context of single-collision $O(^1D)+H_2S$ experiments carried out in molecular beams. The extremely loose OHSH adduct identified at the UMP2=full/6-31G(d) level is negligibly bound by 0.8 $kJ mol^{-1}$ at the G2 level and therefore is not a distinct species. A significant barrier to “direct” abstraction [reaction (1)] to form $OH+SH$ is predicted, and insertion and addition to form $HOSH$ and H_2SO are favored and appear to be barrierless. This is consistent with a recent experimental study of $O(^1D)+CH_4$, where it was concluded, contrary to some earlier work, that most reactive collisions initially created excited methanol.⁴² Other recent experiments showed that overall removal of $O(^1D)$ by H_2S is very fast, with a room temperature rate constant of $2.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$,² i.e., gas kinetic as expected for a barrierless process. The $HOSH$ and H_2SO molecules will be formed with $\sim 500 \text{ kJ mol}^{-1}$ of internal energy (Table IV). In principle, at sufficiently high densities, these molecules could be collisionally stabilized, but under single-collision conditions, they will certainly isomerize and ultimately fragment. OH was an observed product that accounted for about 26% of the consumption of $O(^1D)$.² Species at $m/e=49$ that could be HSO , HOS , or both have also been detected.¹ Interestingly, Balucani *et al.*¹ did not observe SO formation and attributed this to a very

FIG. 4. Potential energy surface calculated at the G2 level, showing enthalpies at 0 K relative to $O(^1D)+H_2S$.

FIG. 5. Arrhenius plot of low-pressure second-order rate constants k_0 for isomerization and decomposition reactions (2) $H_2SO+Ar \rightarrow H_2+^1SO+Ar$; (3, -3) $H_2SO+Ar \rightleftharpoons HOSH+Ar$; (5, -5) $H_2OS+Ar \rightleftharpoons HOSH+Ar$.

high barrier to H_2 elimination,⁴³ although we do not calculate a high barrier. Their observation might mean that excited HOSH is formed preferentially. The channel leading to H_2O+^1S appears not to have been considered previously and there are no experimental data for comparison. Finally, we note that formation of bound adducts may provide opportunities for intersystem crossings to the triplet PES and, because triplet H_2SO and HOSH are not strongly bound,³⁸ $O(^3P)+H_2S$ and $OH+SH$ could be formed via this kind of formally spin-forbidden mechanism.

IV. CONCLUSIONS

Structures and vibrational frequencies for minima and transition states on the $O(^1D)+H_2S$ potential energy surface have been characterized at the UMP2=full/6-31G(d) level. The results for HOSH agree with experimental IR spectra, and the data for H_2SO and H_2OS may aid their detection. Gaussian-2 theory was employed to calculate the thermochemistry of these species. Comparisons with ΔH_f for known asymptotes on the PES gave good agreement, except in the case of HSO. HOSH is the most stable isomer, followed by H_2SO and then H_2OS . The results suggest that in most contexts, except low pressures and temperatures, H_2OS will be short lived. Rate constants for isomerization of the three bound adducts under thermally equilibrated conditions are derived. Most aspects of the theoretical PES are consistent with information from single-collision experiments, and pathways leading to $SH+OH$, $^1SO+H_2$, $HSO+H$, $HOS+H$, and $^1S+H_2O$ have been analyzed.

ACKNOWLEDGMENTS

We thank J. T.-C. Chow and K. E. Holmes for assisting with some of the diagrams. J.-D.R.R. thanks the Ronald E. McNair Post-Baccalaureate Achievement Program for a scholarship. This work was supported by the Robert A. Welch Foundation (Grant No. B-1174) and computer time was provided through the NSF Pittsburgh Supercomputing Center (Grant No. CHE900059P) and the UNT Faculty Research Fund.

- ¹N. Balucani, L. Beneventi, P. Casavecchia, D. Stranges, and G. G. Volpi, *J. Chem. Phys.* **94**, 8611 (1991).
- ²A. A. Iogansen, O. M. Sarkisov, E. V. Simont, J. A. Seetula, R. S. Timonen, and S. Cheskiš, *Chem. Phys. Lett.* **212**, 604 (1993).
- ³N. Balucani, P. Casavecchia, D. Stranges, and G. G. Volpi, *Chem. Phys. Lett.* **211**, 469 (1993).
- ⁴R. R. Smardzewski and M. C. Lin, *J. Chem. Phys.* **66**, 3197 (1977).
- ⁵M. Iraqi and H. Schwarz, *Chem. Phys. Lett.* **221**, 359 (1994).
- ⁶H. Wallmeier and W. Kutzelnigg, *J. Am. Chem. Soc.* **101**, 2084 (1979).
- ⁷E. Magnusson, *Tetrahedron* **41**, 2939 (1985).
- ⁸E. Magnusson, *J. Comput. Chem.* **5**, 612 (1984).
- ⁹E. Magnusson, *Aust. J. Chem.* **39**, 735 (1986).
- ¹⁰T. J. Lee, N. C. Handy, J. E. Rice, A. C. Scheiner, and H. F. Schaefer III, *J. Chem. Phys.* **85**, 3930 (1986).
- ¹¹S. Wolfe and H. B. Schlegel, *Gazz. Chim. Ital.* **120**, 285 (1990).
- ¹²M. Solà, C. Gonzalez, G. Tonachini, and H. B. Schlegel, *Theor. Chim. Acta* **77**, 281 (1990).
- ¹³C. F. Melius (unpublished work communicated July, 1993).

- ¹⁴In this notation, the acronym before the "/" denotes the theory applied, and the basis set description follows the /. Some commonly applied levels of theory include Hartree-Fock (HF), Møller-Plesset perturbation theory to n th order (MP n), spin-restricted and unrestricted theory (prefixed by U or R), configuration interaction with single and double substitutions (CISD), and quadratic CISD with triple substitutions as well [QCISD(T)]. Full means all electrons are involved in the correlation treatment, otherwise only valence electrons are included.
- ¹⁵J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, *J. Chem. Phys.* **90**, 5622 (1989).
- ¹⁶L. A. Curtiss, C. Jones, G. W. Trucks, K. Raghavachari, and J. A. Pople, *J. Chem. Phys.* **93**, 2537 (1990).
- ¹⁷L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991).
- ¹⁸W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986).
- ¹⁹J. B. Foresman and A. Frisch, *Exploring Chemistry with Electronic Structure Methods* (Gaussian, Pittsburgh, 1993).
- ²⁰M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, *GAUSSIAN 90*, Gaussian, Pittsburgh, 1990.
- ²¹M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, *GAUSSIAN 92*, Gaussian, Pittsburgh, 1992.
- ²²A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (Macmillan, New York, 1982), Chap. 3.
- ²³R. Seeger and J. A. Pople, *J. Chem. Phys.* **66**, 3045 (1977).
- ²⁴D. Laakso, C. E. Smith, A. Goumri, J.-D. R. Rocha, and P. Marshall, *Chem. Phys. Lett.* **227**, 377 (1994).
- ²⁵K. Yamaguchi, F. Jensen, A. Dorigo, and K. N. Houk, *Chem. Phys. Lett.* **149**, 537 (1988).
- ²⁶H. B. Schlegel, *J. Chem. Phys.* **84**, 4530 (1986).
- ²⁷R. B. Kuczkowski, R. D. Suenram, and F. J. Lovas, *J. Am. Chem. Soc.* **103**, 2561 (1981).
- ²⁸Frequencies for all deuterated molecules and transition states have been calculated and may be obtained from the authors.
- ²⁹M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *J. Phys. Chem. Ref. Data* **14**, 1211, 1248, 1274, 1280, 1290 (1985).
- ³⁰J. M. Nicovich, K. D. Kreutter, C. A. van Dijk, and P. H. Wine, *J. Phys. Chem.* **96**, 2518 (1992).
- ³¹G. N. Lewis and M. Randall, *Thermodynamics*, 2nd ed., revised by K. S. Pitzer and L. Brewer (McGraw-Hill, New York, 1961), Chap. 27.
- ³²S. W. Benson, *Chem. Rev.* **78**, 23 (1978).
- ³³K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand Reinhold, New York, 1979), Vol. 4.
- ³⁴R. A. O'Hair, C. H. DePuy, and V. M. Bierbaum, *J. Phys. Chem.* **97**, 7955 (1993).
- ³⁵B. T. Luke and A. D. McLean, *J. Phys. Chem.* **89**, 4592 (1985).
- ³⁶S. S. Xantheas and T. H. Dunning, Jr., *J. Phys. Chem.* **97**, 6616 (1993).
- ³⁷J. Espinosa-García and J. C. Corchado, *Chem. Phys. Lett.* **218**, 128 (1994).
- ³⁸A. Goumri, D. Laakso, C. E. Smith, J.-D. R. Rocha, and P. Marshall (to be published).
- ³⁹R. G. Gilbert and S. C. Smith, *Theory of Unimolecular and Recombination Reactions* (Blackwell, Oxford, 1990).
- ⁴⁰R. G. Gilbert, M. J. T. Jordan, and S. C. Smith, UNIMOL program (see Ref. 39), 1990.
- ⁴¹R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids* (McGraw-Hill, New York, 1958).
- ⁴²J. M. Parnis, L. E. Hoover, T. D. Fridgen, and R. D. Laflaur, *J. Phys. Chem.* **97**, 10708 (1993).
- ⁴³P. Casavecchia, N. Balucani, L. Beneventi, D. Stranges, and G. G. Volpi, *Faraday Discuss. Chem. Soc.* **91**, 147 (1991).