Extensive ab Initio Study of the C_2O_2, C_2S_2, and C_2OS Systems: Stabilities and Singlet−Triplet Energy Gaps

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Ab initio molecular orbital theory has been used to study the three lowest open shell states of ethylenedione, C_2O_2, 2-thiooxoethen-1-one, C_2OS, and ethylenedithione, C_2S_2. To treat the singlet and triplet states in an even-handed manner, multiconfigurational self-consistent field theory (MCSCF), which included all the important configurations for a quantitative description of these states, was used as the basis of the investigation. Further correlation effects have been included using a multireference configuration interaction (MRCI) approach. Basis sets of triple-ζ quality with d- and f-polarization functions were employed. Equilibrium geometries were obtained from density functional theory (DFT) calculations using the B3LYP exchange correlation functional and are presented for the $^3\Sigma_g^-$, $^1\Delta_g$ states of all three molecules. Harmonic frequencies are also presented for these states and were calculated at the MCSCF and DFT levels. The reported relative energies for the states were obtained from MRCI calculations. As expected from previous work, the ground states are confirmed to be of $^3\Sigma_g^-$ symmetry for all molecules, but it is only for the C_2S_2 that this state lies below the energy of the dissociation products in their own ground states. For C_2OS, though, this energy gap is small (5.7 kcal/mol). In contrast to a number of other calculations, the $^1\Delta_g$ states for all three molecules are also shown to be minima on the MCSCF potential energy surfaces. The $^1\Delta_g$ states are all close to the ground states ($<$10 kcal/mol). Consequently, with C_2S_2, this singlet state also lies below the ground state of the dissociated products. The relative energies of the $^1\Sigma_g^+$ states at the optimized geometries for the $^1\Delta_g$ states have also been determined.

I. Introduction

Ethylenedione (O═C═C═O), 2-thioxoethen-1-one (O═C═C═S), and ethylenedithione (S═C═C═S) are the second members of the homologous series beginning with the well-characterized molecules CO_2, CS_2, and OCS, and having the general formulas $X(C)_nY$, where X and Y may be oxygen or sulfur. While others of the $n =$ odd members of the series are stable and have been known for a long time,[1] the $n =$ even members, which have open shell structures, have been much more difficult to synthesize. It is only recently that any of the second members of the homologous series have been made.[2]

There was a deliberate attempt by Staudiger and Anthes in 1913[3] to make C_2O_2. No further work was recorded until 1968, but thereafter followed a series of synthetic papers, which for the most part concentrated on other matters, but either mention C_2O_2 or describe attempts to trap it as an addendum to their main interest.[4−10] Around 1986, though, Birney and Berson made a deliberate attempt to find a synthetic pathway to ethylenedione.[11−14] They were unsuccessful, and all further experiments since have been unable to convincingly demonstrate that the neutral molecule exists.[15−21] Chen and Holmes[22] and Dawson et al.[23] made claims that they could infer the existence of C_2O_2 as a transient species in neutralization−reionization mass spectrometry experiments, but this claim is diputed by Schröder et al., who were unable to obtain any measurable evidence of its existence in a wider range of such experiments.[21] This is an extraordinary state of affairs, since the cation[24,25] $C_2O_2^+$, the anion[26] $C_2O_2^-$, the doubly charged anion[27] $C_2O_2^{2-}$, and the van der Waals molecule[28] $(CO)_2$, are all known, and evidence from IR spectroscopy for the existence of the doubly charged cation has been reported.[29,30] Furthermore, there have been many theoretical investigations of neutral ethylenedione, all of which have found a stable minimum on the potential energy surface corresponding to a covalently bound species.[31−45]

The valence shell configuration for C_2O_2 is

$$^3\Sigma_g^-,\ ^1\Delta_g,\ ^1\Sigma_g^+,\ 3\sigma_g^2\ 3\sigma_u^2\ 4\sigma_g^2\ 4\sigma_u^2\ 5\sigma_g^2\ 1\pi_u^4\ 1\pi_g^4\ 2\pi_u^2$$

and is formally like O_2. Here, though, there is the possibility of breaking the linear symmetry. Nevertheless, the predicted ground state for C_2O_2 is of $^3\Sigma_g^-$ symmetry.[37] An extensive study by Raine et al.,[40] which has been confirmed in the more recent work of Korkin et al.,[44] showed that the triplet state has a true minimum on the linear potential energy surface. This energy minimum was shown to be lower than the spin-allowed dissociation products of a pair of CO molecules, one in the ground state and the other in the lowest triplet state. However, this ground-state triplet is higher in energy than two ground-state CO molecules as has been emphasized, dissociation by this pathway is spin forbidden and, unless there is an efficient potential crossing, the molecule should be obtainable in a triplet ground state analogous to the ground state of O_2. The ease with which crossing from the singlet to the triplet surface might occur has been addressed by Schröder et al.,[21] who coupled another failure of a systematic attempt to produce C_2O_2 to a theoretical investigation of this issue. They located the minimum energy crossing point between the singlet and triplet surfaces and

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calculated the matrix element for the coupling between the two states at this point. Using this information, they showed the potential surface crossing is indeed efficient and obtained an estimate of the order of 0.5 ns for the lifetime of the triplet. Taking this estimate in conjunction with their experimental results, they concluded that ethylenedione is an intrinsically short-lived molecule.

In contrast to the continuing story of ethylenedione, almost no attention is paid in the older literature to ethylenedithione. There is a lone claim in 1940, by the Russians Kondriat'ev and Yakovlena, that they observed bands at 2300−2400 Å which could be attributed to C_2S_2.[46] As they were irradiating CS_2 and COS with an H_2 discharge tube to obtain CS radicals, it is possible they observed the intense C_2S_2 absorption beginning about 2400 Å.[47] What is more, the first attempt since to make the CS dimer was successful[48] using neutralization−reionization mass spectrometry. This preparation and detection of C_2S_2 was inspired by the theoretical work of Raine et al.,[40] who, as well as investigating C_2O_2, examined the sulfur molecule's potential energy surface and concluded that it too should be "a makeable molecule". It is, and since its first observation, several routes have been followed for its preparation.[47,49,50] Two groups have characterized the molecule by IR and UV spectroscopy,[47,50] and it has also been examined by mass spectrometry.[49] While ethylenedithione undergoes rapid reaction in the condensed phase or at higher pressures, it is stable over extended periods at low pressure (ca. 10^{-4} mbar), even to temperatures as high as1000 °C.[49]

Theoretically, ethylenedithione has been examined with the same rigor as C_2O_2, but earlier investigators did not choose to look at it, meaning that the semiempirical and lower level ab initio calculations are absent.

As with the dione, C_2S_2 is predicted to have a $^3\Sigma_g^-$ ground state which is lower in energy than the spin-allowed dissociation limit of separated $X^1\Sigma^+ + a^3\Pi$ CS molecules. However, $^3\Sigma_g^-$ ethylenedithione is also predicted to be an absolute minimum on the C_2S_2 potential energy surface at all levels of theory investigated.[40] Some experimental evidence that the ground state is a triplet comes from the work of Bohn et al.,[50] who used quenching to show that lowering the concentration of the triplet CS precursor to C_2S_2 also lowered the production of the dithione. However, from a CASSCF calculation, Maier et al.[47] claimed that the ground state for ethylenedithione should be $^1\Delta_g$. Later work with a larger basis set, by Ma and Wong,[51] failed to confirm this claim, and we have subjected this question to a further thorough examination in this paper. There has also been a recent density functional calculation,[52] which was only able to find a minimum for a triplet on the linear potential energy surface.

The last of the trio of molecules under discussion, OC_2S, was completely neglected by theoreticians, until its synthesis and detection by neutralization−reionization mass spectrometry by Sülzle et al. in 1990.[53] Subsequently, Maier et al. recorded the IR spectrum.[54]

In the paper announcing the observation of thioxoethylenone, Sülzle et al. also reported on single determinantal SCF calculations of the molecule for both the triplet and singlet states. The triplet was found to be the ground state and lower in energy than the spin-allowed dissociation products, but like C_2O_2 and unlike C_2S_2 it is higher in energy than the dissociation to two singlet ground-state molecules of CS and CO. Further single determinantal calculations, at various levels, with good basis sets, have consistently found the ground state to be a triplet.[54,55]

Apart from intrinsic interest in these molecules, because of their electronic structure and questions concerning their stability, they may also play some part in astrochemistry. CO, CS, and OCS are known in interstellar space,[56−58] and cumulenes, C_n, of which the XC_2Y molecules of this paper are an hetero example, have also been detected.[59] Thus it is possible that these XC_2Y molecules, either as stable molecules or as transient species, can be found in molecular clouds or have a part to play in reaction pathways in astrochemistry. The unsymmetric species, C_2S and C_3S, have also been detected,[60,61] and a transition which has been tentatively assigned to C_5S has been published.[62] Furthermore, the abundance of C_nS ($n \leq 5$) in the envelope surrounding one carbon star has been estimated to be similar to that of the cumulenes C_n ($n \leq 5$).[59] One might naively expect that SC_2S clusters would be present in such an environment. If detection of the symmetric species XC_2X is not possible by radioastronomy since they have no dipole moment, their detection is nevertheless possible through their IR spectra. It might even be that among the data collected by the ISO satellite there exist IR bands which can be attributed to these XC_2X molecules. Since their identification is only possible if available accurate theoretical spectra exist, it is obvious that there is a need for them. For the unsymmetrical species XC_2Y which have a dipole moment, radio detection is of course possible as long as their dipole moment is strong enough.

The main purpose of this study is 2-fold. In the first place we wish to use a uniformly high level of theory to examine the linear potential energy surfaces of the triplet and singlet states coming from the π_u^2 configuration for all the three molecules under examination. Since it is well-known that open shell singlet states require multideterminantal wave functions, we have constructed wave functions which treat the triplet state and the singlet states in a uniformly balanced way. The purpose of this treatment is to give a good estimate of the singlet−triplet gap for these molecules and to firmly establish that the triplet is indeed the ground state for all three systems. The singlet surfaces are not well established by the use of single determinantal approaches, and our methods should give a much more accurate description of these curves. We have also used our multideterminantal method to obtain good estimates of the position of the dissociation asymptotes, relative to the minima on the linear potential energy surface. As can be seen from previous investigations on ethylenedione, the fact that the triplet ground state is not an absolute minimum on the $(CO)_2$ surface has been used to explain the apparent intrinsic instability of this molecule. The one calculation on OC_2S which has addressed this issue finds that the triplet for this system is also not an absolute minimum on the (CO)(CS) surface, yet the molecule is stable enough to have been observed. It is important, then, to establish this asymptote more accurately than the Hartree−Fock calculations which have been used to date.[53]

The second purpose of this study, which will be the subject of a forthcoming paper, is to examine pathways to product C_2S_2 and OC_2S, in order to establish if there is a reaction path of a low enough barrier to make it a feasible reaction for the generation of these molecules in space.

II. Methodology

In terms of localized orbitals, the simplest electronic configuration which can be written for C_2O_2, C_2S_2 and C_2OS molecules is

$$^1\Sigma_g^+ \qquad \text{core...}sp_x^2\, sp_y^2\, \sigma_{CX}^2\, \sigma_{CY}^2\, \sigma_{CC}^2\, (1\pi_g)^4 (1\pi_u)^4 \sigma_{CC}{}^{*2}$$

(where X and Y are either O or S and sp_x, sp_y the corresponding lone pair orbitals).

This state in which an antibonding σ_{CC} orbital is doubly occupied has a repulsive character at short internuclear distances and is therefore very high in energy for C_2O_2, C_2S_2, or C_2OS equilibrium geometries. However, it correlates to the ground electronic states of the separated products (CO + CO, CO + CS, CS + CS), since both CC bonding and antibonding orbitals transform to the two carbon lone pairs with increasing CC distance.[5]

Instead, the ground electronic state of C_2O_2, C_2S_2, and C_2OS is contained in the following configuration:

$$\text{core...}\mathrm{sp}_x^{\,2}\ \mathrm{sp}_y^{\,2}\ \sigma_{\mathrm{CX}}^{\;2}\ \sigma_{\mathrm{CY}}^{\;2}\ \sigma_{\mathrm{CC}}^{\;2}\ (1\pi_{\mathrm{g}})^4(1\pi_{\mathrm{u}})^4(2\pi_{\mathrm{u}})^2$$

Since two electrons can occupy either one of the two orthogonal $2\pi_{\mathrm{u}}$ orbitals ($2\pi_{\mathrm{u}}(x)$ or $2\pi_{\mathrm{u}}(y)$, if z is the molecular axis), this configuration gives rise to the two lowest singlet Δ and Σ states of the above molecules:

$^1\Delta_{\mathrm{g}}$

$$\text{core...}\mathrm{sp}_x^{\,2}\ \mathrm{sp}_y^{\,2}\ \sigma_{\mathrm{CX}}^{\;2}\ \sigma_{\mathrm{CY}}^{\;2}\ \sigma_{\mathrm{CC}}^{\;2}\ (1\pi_{\mathrm{g}})^4(1\pi_{\mathrm{u}})^4(2\pi_{\mathrm{u}}(x)^2) - \text{core...}\mathrm{sp}_x^{\,2}\ \mathrm{sp}_y^{\,2}\ \sigma_{\mathrm{CX}}^{\;2}\ \sigma_{\mathrm{CY}}^{\;2}\ \sigma_{\mathrm{CC}}^{\;2}\ (1\pi_{\mathrm{g}})^4(1\pi_{\mathrm{u}})^4(2\pi_{\mathrm{u}}(\mathrm{y})^2)$$

$^1\Sigma_{\mathrm{g}}^{\;+}$

$$\text{core...}\mathrm{sp}_x^{\,2}\ \mathrm{sp}_y^{\,2}\ \sigma_{\mathrm{CX}}^{\;2}\ \sigma_{\mathrm{CY}}^{\;2}\ \sigma_{\mathrm{CC}}^{\;2}\ (1\pi_{\mathrm{g}})^4(1\pi_{\mathrm{u}})^4(2\pi_{\mathrm{u}}(x)^2) + \text{core...}\mathrm{sp}_x^{\,2}\ \mathrm{sp}_y^{\,2}\ \sigma_{\mathrm{CX}}^{\;2}\ \sigma_{\mathrm{CY}}^{\;2}\ \sigma_{\mathrm{CC}}^{\;2}\ (1\pi_{\mathrm{g}})^4(1\pi_{\mathrm{u}})^4(2\pi_{\mathrm{u}}(y)^2)$$

while the lowest triplet state is a single determinant of electronic configuration

$^3\Sigma_{\mathrm{g}}^{\;-}$

$$\text{core...}\mathrm{sp}_x^{\,2}\ \mathrm{sp}_y^{\,2}\ \sigma_{\mathrm{CX}}^{\;2}\ \sigma_{\mathrm{CY}}^{\;2}\ \sigma_{\mathrm{CC}}^{\;2}\ (1\pi_{\mathrm{g}})^4(1\pi_{\mathrm{u}})^4(2\pi_{\mathrm{u}}(x)^1)(2\pi_{\mathrm{u}}(y)^1)$$

In this study, we are interested in the lowest $^1\Delta_{\mathrm{g}}-^3\Sigma_{\mathrm{g}}^{-}$ energy gap of C_2O_2, C_2S_2, and C_2OS and the relative stability of these states with respect to their lowest dissociation limits ($\mathrm{CX}(\mathrm{X}^1\Sigma^+) + \mathrm{CY}(\mathrm{X}^1\Sigma^+)$ and $\mathrm{CX}(\mathrm{X}^1\Sigma^+) + \mathrm{CY}(\mathrm{a}^3\Pi)$) with

$$\mathrm{X}^1\Sigma^+ \qquad \text{core...}\mathrm{sp}_x^{\,2}\ \sigma_{\mathrm{CX}}^{\;2}\ \sigma_{\mathrm{CC}}^{\;2}\ \mathrm{spc}^2\ (1\pi)^4$$

$$\mathrm{a}^3\Pi \qquad \text{core...}\mathrm{sp}_x^{\,2}\ \sigma_{\mathrm{CX}}^{\;2}\ \sigma_{\mathrm{CC}}^{\;2}\ (1\pi)^4\ \mathrm{spc}^1\ (2\pi)^1$$

For this purpose configuration interaction (CI) calculations required for quantitative and qualitative results have to fulfill two conditions:

1. First, there must be a set of reference determinants able to correctly describe all singlet and triplet state configurations given above, at any point of the C−C potential energy surface. The correlation energy must be evaluated with respect to this set.

2. Second, an even-handed treatment is necessary for all these states throughout this potential energy surface, i.e., at equilibrium, intermediate, and infinite geometries.

To fulfill the first condition, the ideal procedure would use, as a multireference wave function, a set of reference configurations generated by distributing the 20 active electrons in the 16 available valence orbitals. However, the number of configurations generated with such a distribution is impossible to handle. Therefore, we have partitioned the active space, which we prefer to refer to as the internal space, into subsets. The number of electrons assigned to each of these sets, as shown in Table 1, is distributed in all possible ways among the orbitals belonging also to that subset. The various numbers of electrons put in each of the sets were chosen so that the electronic distributions were able to generate all important configurations needed for a quantitative description of the states of interest, at both equilibrium geometries and infinite separation, ensuring, by the degree of excitation allowed in the internal space, the treatment of all important valence correlation effects (see Table 1). Such a procedure was made possible by the flexibility of the ALCHEMY algorithm[63] used for the present study. In the set designated as “external” in Table 1, there are the remaining orbitals needed for the treatment of the x-order contributions to the correlation energy. Mainly first-order contributions with respect to all configurations generated by the electronic distributions of the internal space and second-order contributions with respect to all reference determinants needed to describe the $^3\Sigma_{\mathrm{g}}^{-}$, $^1\Delta_{\mathrm{g}}$, and $^1\Sigma_{\mathrm{g}}^{+}$ states at all geometries. The final CI n-particle space, given in Table 1, was designed after a series of test calculations where the orbitals were incorporated, one at a time, in the active space, and their importance tested. With such a CI n-particle space, the lowest singlet and triplet states are treated through the same even-handed CI calculations all along the C−C dissociation pathway toward the diatomic species.

TABLE 1: CI *n*-Particle Space Designed for Our MRCI Calculations

		electronic distributions			
		active space[b] or internal space			external[c] space
symmetry	core[a]	set 1	set 2	set 3	
a_1	core	$\mathrm{sp}_x\mathrm{sp}_y\sigma\mathrm{CX}\sigma\mathrm{CY}$	$\sigma\mathrm{CC}\sigma\mathrm{CC}^*$	$\sigma\mathrm{CX}^*\sigma\mathrm{CY}^*$	a1 MOs
b_2	core	$\pi\pi$	$\pi^*\pi^*$		b2 MOs
b_1	core	$\pi\pi$	$\pi^*\pi^*$		b1 MOs
a_2					a2 MOs
		Number of Electrons			
		16	4	0	0
		15	5	0	0
		14	6	0	0
		13	7	0	0
		15	4	1	0
		14	4	2	0
		16	3	1	0
		16	2	2	0
		15	3	2	0
		14	5	1	0
		16	3	0	1
		15	4	0	1
		Number of Electrons with Respect to References[d]			
		16	2	0	2
		14	4	0	2
		15	3	0	2

[a] For OCCO core is 1sC1sC1sO1sO; for OCCS core is 1sO1sC1sC1sS2sS2pS; for SCCS core is 1sS1sS1sC1sC2sS2sS2pS2pS. [b] X and Y are O and O for OCCO, S and S for SCCS, or O and S for OCCS. [c] The external set contains for OCCO 48 a1, 28b2 28b1, and 12a2 orbitals; for SCCS 44 a1, 26b2, 26b1 and 12a2 orbitals; and for OCCS 46 a1, 27b2, 27b1 and 12a2 orbitals. [d] For $^1\Delta_{\mathrm{g}}$ and $^1\Sigma_{\mathrm{g}}^{+}$ states the reference configurations are core...$(\mathrm{sp}_x)^2$ $(\mathrm{sp}_y)^2$ $\sigma\mathrm{CX}^2$ $\sigma\mathrm{CY}^2$ $\sigma\mathrm{CC}^2$ $\sigma\mathrm{CC}^{*0}$ $\sigma\mathrm{CX}^{*0}$ $\sigma\mathrm{CY}^{*0}$ π^2 π^2 π^{*2} π^{*0} π^2 π^2 π^{*0} π^{*0}, core...$(\mathrm{sp}_x)^2$ $(\mathrm{sp}_y)^2$ $\sigma\mathrm{CX}^2$ $\sigma\mathrm{CY}^2$ $\sigma\mathrm{CC}^2$ $\sigma\mathrm{CC}^{*0}$ $\sigma\mathrm{CX}^{*0}$ $\sigma\mathrm{CY}^{*0}$ π^2 π^2 π^{*0} π^{*0} π^2 π^2 π^{*2} π^{*0}, and core...$(\mathrm{sp}_x)^2$ $(\mathrm{sp}_y)^2$ $\sigma\mathrm{CX}^2$ $\sigma\mathrm{CY}^2$ $\sigma\mathrm{CC}^2$ $\sigma\mathrm{CC}^{*2}$ $\sigma\mathrm{CX}^{*0}$ $\sigma\mathrm{CY}^{*0}$ π^2 π^2 π^{*0} π^{*0} π^2 π^2 π^{*0} π^{*0}. For $^3\Sigma_{\mathrm{g}}^{-}$ the reference configuration is core...$(\mathrm{sp}_x)^2$ $(\mathrm{sp}_y)^2$ $\sigma\mathrm{CX}^2$ $\sigma\mathrm{CY}^2$ $\sigma\mathrm{CC}^2$ $\sigma\mathrm{CC}^{*0}$ $\sigma\mathrm{CX}^{*0}$ $\sigma\mathrm{CY}^{*0}$ π^2 π^2 π^{*1} π^{*0} π^2 π^2 π^{*1} π^{*0}. For $^3\Pi$ the reference configuration is core...$(\mathrm{sp}_x)^2$ $(\mathrm{sp}_y)^2$ $\sigma\mathrm{CX}^2$ $\sigma\mathrm{CY}^2$ $\sigma\mathrm{CC}^2$ $\sigma\mathrm{CC}^{*1}$ $\sigma\mathrm{CX}^{*0}$ $\sigma\mathrm{CY}^{*0}$ π^2 π^2 π^{*1} π^{*0} π^2 π^2 π^{*2} π^{*0} and core...$(\mathrm{sp}_x)^2$ $(\mathrm{sp}_y)^2$ $\sigma\mathrm{CX}^2$ $\sigma\mathrm{CY}^2$ $\sigma\mathrm{CC}^2$ $\sigma\mathrm{CC}^{*1}$ $\sigma\mathrm{CX}^{*0}$ $\sigma\mathrm{CY}^{*0}$ π^2 π^2 π^{*0} π^{*1} π^2 π^2 π^{*2} π^{*0}. Number of CSFs generated is 612 355 for OCCO($^1\Delta_{\mathrm{g}}$,$^1\Sigma_{\mathrm{g}}^{+}$), 841 794 for OCCO($^3\Sigma_{\mathrm{g}}^{-}$), 1 558 016 for OCCO($^3\Pi$), 573 557 for OCCS($^1\Delta_{\mathrm{g}}$,$^1\Sigma_{\mathrm{g}}^{+}$), 789 422 for OCCS($^3\Sigma_{\mathrm{g}}^{-}$), and 1 455 288 for OCCS($^3\Pi$), 536 123 for SCCS($^1\Delta_{\mathrm{g}}$,$^1\Sigma_{\mathrm{g}}^{+}$), 738 870 for SCCS($^3\Sigma_{\mathrm{g}}^{-}$), and 1 356 252 for SCCS($^3\Pi$).

At both equilibrium geometries and infinite CC separation, the core molecular orbitals (carbon, oxygen, sulfur 1s-like and sulfur 2s- and 2p-like) were held doubly occupied in all configurations and the corresponding highest lying virtual orbitals were deleted from the CI procedure. With the CI as given, for each point energy determination, an iterative procedure was adopted and the CI calculations were repeated using natural orbitals from the previous CI. Convergence was considered achieved when the energy stabilized at 1 kcal/mol. This use of natural orbitals for the CI calculations allowed an easy identification of the valence orbitals in terms of Lewis bonding pairs, an identification important for their assignment to the different internal sets.

We have also calculated the relative position of the second singlet state of the C_2O_2, C_2S_2, and C_2OS species, i.e., the $^1\Sigma_g^+$ state of the electronic configuration given above. This was achieved by using natural orbitals optimized for this second singlet state and following the iterative CI procedure above.

For the CI calculations, we used the Dunning correlation consistent triple-ζ basis set (cc-pVTZ) which includes 2d and 1f polarization functions for C, O, and S.[64,65]

The lowest singlet and triplet states of CO, CS, C_2O_2, C_2S_2, and C_2OS have been optimized at the Becke3LYP[66] level using a 6-311+G(2df) basis set (hereafter B3LYP/6-311+G(2df)). The singlet geometry was optimized from the $\pi_u(x)^2$ single determinantal configuration, in a restricted density functional calculation. B3LYP/6-311+G(2df) is a density functional method known to give reliable geometries close to the experimental one. Since a correct description of the lowest singlet states of C_2O_2, C_2S_2, and C_2OS needs at least a two configurational wave function, frequencies and zero-point energies were determined, for both singlet and triplet states at an MCSCF level, using the same cc-pVTZ basis set of the CI calculations. In this MCSCF treatment, a CASSCF(10,8), the 10 highest electrons were distributed in the 8 valence π-orbitals, i.e., the most important orbitals needed for a correct description of these singlet and triplet states, at their equilibrium geometries (hereafter MCSCF-(10,8)/cc-pVTZ). For comparison, the vibrational analysis has been undertaken at the same B3LYP/6-311+G(2df) level used for the geometry optimizations, and also at the B3LYP/cc-pVTZ level, to test the basis set influence on the IR spectra calculations. At this last level the vibrational analysis was only undertaken for the state of triplet multiplicity, since this is the only state for which this level of theory is meaningful. All frequency calculations were carried out using the analytic second derivative method.

III. Results

III.1. Structural Considerations. Our B3LYP/6-311+G(2df) optimized geometries for C_2OS, C_2O_2, and C_2S_2 in both triplet and singlet states are reported in Table 2. At this theoretical level, where the correlation energy is calculated from a one reference determinant, we have labeled the lowest singlet states "Σ" even if they are meant to be the "Δ" states. As can be seen from Table 2, B3LYP/6-311+G(2df) optimized geometries for CO($X^1\Sigma^+$), CO($a^3\Pi$), CS($X^1\Sigma^+$), and CS($a^3\Pi$) are in excellent agreement with the experimental values of Herzberg.[67] However, one might question the use of a B3LYP theoretical method to optimize geometries for states of $^1\Delta_g$ symmetry. As a justification, the Haddon et al. optimization[37] of the lowest $^1\Delta_g$ state of C_2O_2 using complex orbitals (hereafter /C) might be invoked. These authors have shown that the C−C bond optimized at the 4-31G/C level in $C_2O_2(^1\Delta_g)$ is almost identical to the C−C bond in the $C_2O_2(^3\Sigma_g^-)$ state optimized at the 4-31G/UHF one (i.e., 1.267 Å in $C_2O_2(^1\Delta_g)$ versus 1.261 Å in $C_2O_2(^3\Sigma_g^-)$). This is in agreement with our B3LYP optimized geometries for the lowest singlet and triplet states of C_2O_2. Even the 0.006 Å difference found by these authors between these two optimized C−C bonds is reproduced in our optimized structures (i.e., our values are C−C = 1.286 Å for $^1\Delta_g$ and 1.280 Å for $^3\Sigma_g^-$). Finally, these authors calculated identical CO bond lengths for both $^1\Delta_g$ and $^3\Sigma_g^-$ states (there is an insignificant difference of 0.002 Å) in agreement with our finding of equal CO bonds for both these states. We notice that our bond lengths for both $C_2O_2(^1\Delta_g)$ and $C_2O_2(^3\Sigma_g^-)$ are slightly shorter than the CCSD/DZP optimized ones from Korkin et al.[44] (for $^1\Delta_g$ CC = 1.296 Å and CO = 1.211 Å and for $^3\Sigma_g^-$ CC = 1.293 Å, CO = 1.204 Å). This is consistent with the fact that the CCSD method tends to overestimate bond lengths.

TABLE 2: B3LYP/6-311+G(2df) Optimized Geometries[a]

		experimental
CO($^1\Sigma^+$)	CO = 1.125	CO = 1.128
CO($^3\Pi$)	CO = 1.201	CO = 1.206
CS($^1\Sigma^+$)	CS = 1.534	CS = 1.535
CS($^3\Pi$)	CS = 1.571	CS = 1.569
$C_2O_2(^1\Sigma_g^+)$	CO = 1.185	
	CC = 1.286	
$C_2O_2(^3\Sigma_g^-)$	CO = 1.185	
	CC = 1.280	
$C_2S_2(^1\Sigma_g^+)$	CS = 1.573	
	CC = 1.275	
$C_2S_2(^3\Sigma_g^-)$	CS = 1.574	
	CC = 1.271	
$C_2OS(^1\Sigma_g^+)$	CS = 1.577	
	CO = 1.175	
	CC = 1.288	
$C_2OS(^3\Sigma_g^-)$	CS = 1.577	
	CO = 1.174	
	CC = 1.278	

[a] Lowest singlet states are labeled "$^1\Sigma$" in this table since they are calculated within a one reference determinant approach. Distances are in angstroms. Experimental geometries are from Herzberg.[67]

Our optimized C−C and C−S bond in $C_2S_2(^3\Sigma_g^-)$ are respectively 1.271 and 1.574 Å in agreement with the most recent values of 1.277 and 1.579 Å reported in the literature (QCISD/6-311+G(2d) calculations by Ma and Wong[51]). For $C_2S_2(^1\Delta_g)$, the only available multiconfigurational optimization existing in the literature is from Maier et al.[47] at the CAS(6,4)/3-21G(d) level. Their calculation found the C−C bond to be 1.562 Å and the C−S one to be 1.247 Å. These are shorter than our optimized B3LYP/6-311+G(2df) values of respectively 1.573 and 1.275 Å.

For $C_2OS(^3\Sigma_g^-)$ our values of 1.278, 1.174, and 1.577 Å for respectively C−C, C−O, and C−S bonds can be respectively compared to the values of 1.287, 1.191, and 1.287 Å determined at the B3LYP/6-311G* level by Lee et al.[55]

To the best of our knowledge, no reported optimized geometries obtained using a qualitatively satisfying multiconfigurational wave function exist for $C_2S_2(^1\Delta_g)$ and $C_2OS(^1\Delta_g)$. Nevertheless, our geometry results for these two systems are consistent with the bond behavior observed in C_2O_2. Thus for the same molecule, C−X (X = O, S) bonds in the $^1\Delta_g$ states are almost equal to C−X bonds in the corresponding $^3\Sigma_g^-$ states while C−C bonds are slightly shorter in triplet states compared to C−C bonds in the singlet states.

Frequencies determined (for C_{2v} symmetry) at the MCSCF/cc-pVTZ, B3LYP/6-311+G(2df), and B3LYP/cc-PVTZ levels can be seen in Table 3. At the MCSCF level all frequencies for the $C_2O_2(^1\Delta_g)$ state are real pointing to a linear arrangement, in agreement with Haddon et al.'s calculations[37] which found,

TABLE 3: Frequencies (in cm^{-1}) and Unscaled Zero-Point Vibrational Energies (e_0; in kcal/mol)

	B3LYP/6-311+G(2df)	B3LYP/cc-pVTZ	MCSCF/cc-PVTZ
$C_2O_2(^1\Delta_g)$	a1 = 942, 1806, 2372 b2 = *447i*, 273 b1 = 325, 690 e_0 = 9.16		a1 = 962, 1822, 2408 b2 = 343, 361 b1 = 343, 361 e_0 = 9.43
$C_2O_2(^3\Sigma_g^-)$	a1 = 949, 1786, 2379 b2 = 285, 304 b1 = 285, 304 e_0 = 8.99	a1 = 949, 1785, 2381 b2 = 247, 305 b1 = 247, 305	a1 = 971, 1827, 2429 b2 = 393, 396 b1 = 393, 396 e_0 = 9.44
$C_2S_2(^1\Delta_g)$	a1 = 544, 1191, 1959 b2 = 172, 185 b1 = 329, 557 e_0 = 7.08		a1 = 568, 1227, 1966 b2 = 168, 425 b1 = 168, 425 e_0 = 7.07
$C_2S_2(^3\Sigma_g^-)$	a1 = 555, 1188, 1970 b2 = 180, 443 b1 = 180, 443 e_0 = 7.10	a1 = 553, 1183, 1973 b2 = 179, 433 b1 = 179, 433	a1 = 568, 1226, 1995 b2 = 193, 452 b1 = 193, 452 e_0 = 7.26
$C_2OS(^1\Delta_g)$	a1 = 687, 1527, 2214 b2 = 64, 349 b1 = 212, 653 e_0 = 8.15		a1 = 719, 1556, 2206 b2 = 212, 527 b1 = 212, 527 e_0 = 8.21
$C_2OS(^3\Sigma_g^-)$	a1 = 693, 1537, 2236 b2 = 192, 481 b1 = 192, 481 e_0 = 8.31	a1 = 692, 1537, 2238 b2 = 186, 470 b1 = 186, 470	a1 = 713, 1578, 2285 b2 = 220, 552 a1= 220, 552 e_0 = 8.75
CO ($^1\Sigma^+$)	Σ_g = 2215 e_0 = 3.17		
CO ($^3\Pi$)	Σ_g = 1784 e_0 = 2.55		
CS ($^1\Sigma^+$)	Σ_g = 1306 e_0 = 1.87		
CS ($^3\Pi$)	Σ_g = 1137 e_0 = 1.62		

TABLE 4: Comparative Table between Our Calculated Frequencies and Literature Values[a]

	this work		from others			
	B3LYP/6-311+G(2df)	MCSCF/cc-PVTZ	QCISD/6-31G*[b]	SCF/DZ+P[c]	B3LYP/6-311G*[d]	expt[e]
$C_2O_2(^3\Sigma_g^-)$	2379 (0)	2429 (0)		2369		
	1786 (100)	1827 (100)		1745		
	949 (0)	971 (0)		913		
	304 (0)	396 (0)		308		
	285 (0)	393 (0)		247		
$C_2S_2(^3\Sigma_g^-)$	1970 (0)	1995 (0)	2036 (0)	1879	1908 (0)	1904
	1188 (100)	1226 (100)	1198 (100)	1127	1128 (100)	1179
	555 (0)	568 (0)	561 (0)	531	529 (0)	546
	443 (0)	452 (0)	364 (0)	434	366 (0)	
	180 (0)	193 (0)	175 (0)	178	168 (0)	

	this work		from others		
	B3LYP/6-311+G(2df)	MCSCF/cc-PVTZ	B3LYP/6-311G*[f]	B3LYP/6-311G*	expt[h]
$C_2OS(^3\Sigma_g^-)$	2236 (100)	2285 (100)	2158 (100)	2151 (100)	2156 (100)
	1537 (18)	1578 (14)	1446 (23)	1464 (23)	1505 (20)
	693 (0)	713 (0)	661 (0)	662 (0)	685
	481 (2)	553 (2)	447 (3)	437 (3)	452 (9)
	192 (0)	220 (0)	171 (0)	177 (0)	
CO($^1\Sigma^+$)	2115				2170[g]
CO($^3\Pi$)	1784				1743[g]
CS($^1\Sigma^+$)	1306				1285[g]
CS($^3\Pi$)	1137				1135[g]

[a] Frequencies are given in cm^{-1} and intensities relative to the strongest band are given in parentheses. Absolute intensities are at the MCSCF level (B3LYP): 389 (433) km/mol for C_2O_2, 92 (131) km/mol for C_2S_2 and 676 (603) km/mol for C_2OS. [b] Reference 51. [c] Reference 40. [d] Reference 52. [e] Reference 47. [f] Reference 55. [g] Reference 54. [h] Reference 67.

using complex orbitals, that the lowest singlet state of C_2O_2 is linear, even if lying in a shallow minimum. In fact these authors found that this state might not be stable with respect to a trans dissociation to 2 CO, but because of their limited theoretical level they were not able to decide whether there was a barrier for a trans bending distortion of $C_2O_2(^1\Delta_g)$. The B3LYP/6-311+G(2df) vibrational analysis of $C_2O_2(^1\Delta_g)$ shows one imaginary frequency of *447i* cm^{-1} corresponding to a trans bending motion of the molecule.This is a strong indication of the inadequacy of the single configurational wave function in describing this $^1\Delta_g$ state. It is also noteworthy that the vibrational degeneracy expected for this $^1\Delta_g$ state cannot be reproduced at the B3LYP level. As suspected, the $C_2O_2(^3\Sigma_g^-)$ state is correctly represented by a single determinant wave function; B3LYP/

6-311G+(2df) calculated frequencies are all real and are comparable to the MCSCF/cc-pVTZ ones (Table 3). They are also in excellent agreement with scaled frequencies determined by Raine et al.[40] at the SCF/DZ+P level (see Table 4). From this vibrational analysis we confirm the linearity of $C_2O_2(^3\Sigma_g^-)$ for which there was still some ambiguity after the bent structure found at the MBPT(2)/6-31+G(d) level.[44]

Frequencies for the $C_2S_2(^1\Delta_g)$ state calculated at both MCSCF and B3LYP/6-311+G(2df) levels are given Table 3. All frequencies are real when calculated at the MCSCF/cc-pVTZ level, confirming a $C_2S_2(^1\Delta_g)$ state of linear geometry. At the B3LYP/6-311+G(2df) level, the trans bending vibration is also associated with a positive frequency (while this frequency is imaginary at this level in $C_2O_2(^1\Delta_g)$). The vibrational frequencies for $C_2S_2(^3\Sigma_g^-)$ are given in Table 3. As expected, they are all real and are comparable whether calculated at the B3LYP/6-311+G(2df) or MCSCF/cc-pVTZ level.They are also compared (Table 4) to both experimental and calculated frequencies available from the literature and with which they all are in agreement.

For the lowest $C_2OS(^1\Delta_g)$ state, the MCSCF/cc-pVTZ vibrational analysis gives frequencies which are all real. At the B3LYP/6-311+G(2df) level, these frequencies are also real, even though we notice a rather small value of 64 cm^{-1} for the trans bending vibration of $C_2OS(^1\Delta_g)$. In their study at the B3LYP/6-311+G* level, Maier et al.[54] have optimized a transoidally bent structure for $C_2OS(^1\Delta_g)$. At this level of theory, we also find that constraining the molecule to be linear produces one imaginary frequency of *37i* cm^{-1} associated with the trans bending motion of the molecule. This is consistent with the slightly bent structure found by Maier et al.[54] However, once again, frequencies obtained at the B3LYP level are not meaningful for states of $^1\Delta_g$ symmetry, and since all calculated frequencies at the MCSCF/cc-pVTZ level are real, we can state that $C_2OS(^1\Delta_g)$ is linear. Our MCSCF/cc-pVTZ and B3LYP/6-311+G(2df) vibrational analysis for the $C_2OS(^3\Sigma_g^-)$ state is reported in Table 3. Corresponding frequencies are compared to previously calculated[54,55] and measured[54] ones in Table 4. They show good agreement.

The triple-ζ basis set of cc-pVTZ type used for our MCSCF and CI calculations is of the same size as the 6-311+G(2df) basis set used for the geometry optimizations but is of a different type. Because of this, we undertook a B3LYP/cc-pVTZ vibrational analysis of the lowest triplet states of C_2O_2, C_2S_2, and C_2OS, for geometries optimized at the same theoretical level, to be compared to B3LYP/6-311+G(2df) numbers. As can be seen from Table 3 they are identical, confirming the equivalence of these two extended basis sets.

Zero-point vibrational energies (ZPE) are reported Table 3. It is surprising to notice that for the lowest singlet states they are almost equal, whether calculated at the B3LYP or MCSCF level. The only logical explanation for such a resemblance is error compensations. With the triplet states ZPE are also extremely close when calculated at the two theoretical levels. For these states, the similarity of these values can be rationalized, even though the theoretical levels being used are rather different, so that different ZPE would be expected. For our final energy balances, MCSCF/cc-pVTZ zero-point energies, scaled by 0.95, have been used. This scaling factor was deduced by comparing experimental frequencies available for C_2S_2 and C_2OS (see Table 4) to our MCSCF values. For the diatomics, Table 4 shows that B3LYP/6-311+G(2df) frequencies are almost identical to the experimental frequencies given by Herzberg.[67] Hence the theoretical ZPE have been used without any scaling.

TABLE 5: Relative Intensities for the Lowest Single States of C_2O_2, C_2S_2, and C_2OS[a]

	MCSCF/cc-pVTZ
$C_2O_2(^1\Delta_g)$	2408 (0)
	1822 (100)
	962 (0)
	361 (2)
	343 (0)
$C_2S_2(^1\Delta_g)$	1966 (0)
	1227 (100)
	568 (0)
	425 (0)
	168 (0)
$C_2OS(^1\Delta_g)$	2206 (100)
	1556 (30)
	719 (2)
	527 (3)
	212 (0)

[a] Frequencies are in cm^{-1}. Absolute intensities for the strongest band are 300 km/mol for C_2O_2, 47 km/mol for C_2S_2, and 444 km/mol for the strongest C_2OS.

Our calculated relative intensities for $C_2O_2(^3\Sigma_g^-)$, $C_2S_2(^3\Sigma_g^-)$, and $C_2OS(^3\Sigma_g^-)$ are reported in parentheses in Table 4. They are identical whether calculated at the B3LYP or MCSCF level. For $C_2S_2(^3\Sigma_g^-)$ and $C_2OS(^3\Sigma_g^-)$, relative intensities are available from the literature, and it can be seen that there is good agreement between our values and both other calculations[51,54,55] and experimental measurements.[47,54] The absolute intensities for the dominant IR bands are very strong for the three species (Table 4). Therefore, if these molecules exist in the interstellar environment they should be detectable by IR spectroscopy, even if present in small abundance. Relative intensities for $C_2O_2(^1\Delta_g)$, $C_2S_2(^1\Delta_g)$, and $C_2OS(^1\Delta_g)$ calculated at the MCSCF/cc-pVTZ level are reported in Table 5. In a similar fashion, the absolute intensities of the dominant IR bands of the parent triplet molecules are also strong. It is important to notice that for the three species corresponding IR spectra for the lowest triplet and singlet states are almost identical in both band positions and relative intensities.

III.2. Singlet−Triplet Gap and Energy Stabilities with Respect to Dissociation Limits. *III.2.1. The Diatomic CO and CS.* Since there exist no experimental values on the energetics of C_2O_2, C_2S_2, and C_2OS to compare our CI calculations with, a comparison of our calculated first excitation energies for CO and CS with the well-known experimental values[67] is crucial to test the qualitative level of our CI treatment. Within the supermolecule approach energies of the lowest $^1\Sigma_g^+$ and $^3\Pi$ states of C_2O_2, C_2S_2, and C_2OS have been calculated by setting the C−C bond equal to 20 Å and the CO and CS distances equal to the B3LYP/6-311+G(2df) optimized geometries of the $CO(^1\Sigma^+)$, $CO(^3\Pi)$, $CS(^1\Sigma^+)$, and $CS(^3\Pi)$ fragments. At the MRCI level, with ZPE taken in account, a $CO(^1\Sigma^+) - CO(^3\Pi)$ energy difference of 139.3 kcal/mol was obtained, in excellent agreement with the experimental value of 139.2 kcal/mol given by Herzberg.[67] For CS, the calculated $CS(^1\Sigma^+) - CS(^3\Pi)$ energy difference is 77.8 kcal/mol, with ZPE considered. This value can also be considered in excellent agreement with the value of 79.1 kcal/mol given by Herzberg.[67] These results give confidence in both the qualitative and quantitative quality of our MRCI calculations.

III.2.2. The C_2O_2, C_2S_2, and C_2OS Species. Our energies, determined for C_2O_2, C_2S_2, and C_2OS with the MCSCF(10,8)/cc-pVTZ//B3LYP/6-311+G(2df) and MRCI/cc-pVTZ//B3LYP/6-311+G(2df) approaches, are reported in Table 6 and the corresponding energy diagrams Figures 1, 2, and 3, respectively. For lowest triplet states, we have also calculated at the

TABLE 6: Energies (in kcal/mol) of XC_2Y Excited States and Dissociation Limits Relative to the $^3\Sigma_g^-$ for Various Levels of Calculation[a]

	ΔE			ΔE_0	
	$^3\Sigma_g^-$	$^1\Delta_g$	$^1\Sigma_g^+$	$^1\Sigma^+ + {}^1\Sigma^+$	$^1\Sigma^+ + {}^3\Pi$
		X = Y = O			
MCSCF	0.0	8.6			
MRCI	0.0	9.1	21.4	−58.7	80.6
CCSD(T)				−58.8	79.5
ref 37	0.0	19.3		-53^b	57^b
ref 40				-68^b	71^b
ref 44	0.0	9.5	12.1	−66	73
		X = Y = S			
MCSCF	0.0	5.0			
MRCI	0.0	7.7	16.6	40.7	118
CCSD(T)				43.4	123
ref 40	0.0			36^b	115^b
ref 47	0.0	-0.7^c			
		-2.1^d			
ref 51	0.0	5.7	10.5	30^b	138^b
		X = O, Y = S			
MCSCF	0.0	7.6			
MRCI	0.0	9.9	19.8	−5.7	71.9
CCSD(T)				−3.7	76.1
ref 20	0.0	(5.4−16.3)			
ref 53	0.0	26		−4.3	45

[a] ΔE, singlet−triplet gap without ZPE; ΔE_0, energies for the dissociation limits relative to the $^3\Sigma_g^-$ considering ZPE corrections; MCSCF, our MCSCF(10,8)/cc-pVTZ//B3LYP/6-311+G(2df) calculations; MRCI, our MRCI/cc-pVTZ//B3LYP/6-311+G(2df) calculations; CCSD(T), our CCSD(T)/6-311+G(2df)//B3LYP/6-311+G(2df) calculations. [b] Relative energies given by corresponding authors did not take into account ZPE. We have therefore corrected their energies using our ZPE corrections. [c] CASSCF(6,6)/3-21G. [d] RHF-CISD/6-31G(d).

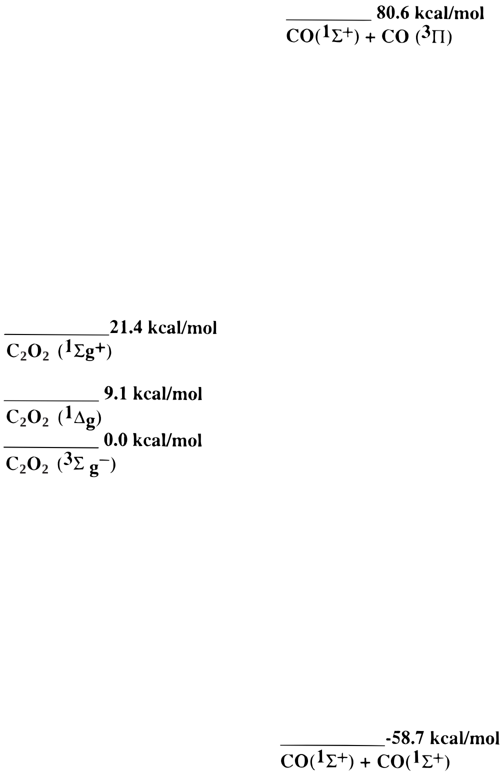

Figure 1. Energies for the C_2O_2 system.

CCSD(T)/6-311+G(2df)//B3LYP/6-311+G(2df) level the relative stability with respect to the diatomics in their ground electronic state. These numbers are also reported in Table 6. Finally, for comparison, energies available from the literature are also given.

C_2O_2. Even though the latest theoretical study[21] has shown that $C_2O_2(^3\Sigma_g^-)$ is a short-lived molecule and that both singlet and triplet states should dissociate rapidly to two ground state CO molecules, we have calculated energy balances for this molecule as a test of our theoretical method since there exists a comparable correct determination of the $C_2O_2(^1\Delta_g)$ energy obtained using a two determinant reference configuration.[44] Our triplet−singlet energy gap (hereafter ΔE(S−T) calculated at the MRCI/cc-pVTZ//B3LYP/6-311+G(2df) level is 9.1 kcal/mol (8.6 from MCSCF(10,8)/cc-PVTZ//B3LYP/6-311+G(2df), with the triplet state more stable than the singlet state as expected. Our MRCI calculated value is comparable to the value of 9.5 kcal/mol calculated by Korkin et al.[44] at the CCSD(T)/TZ2P level, using a two determinant reference configuration for the $^1\Delta_g$ state. At the CI/STO-3G level, and using complex orbitals, Haddon et al.[37] found a much higher value of 19.3kcal/mol for this ΔE(S−T), probably because of their limited basis set. At the MRCI/cc-pVTZ//B3LYP/6-311+G(2df) approximation we calculated the $^1\Sigma_g^+$ state, at the geometry of the $^1\Delta_g$ state, to be 21.4 kcal/mol above the $^3\Sigma_g^-$ state while Korkin et al.[44] have determined a value of 12.1 kcal/mol at the CCSD(T) level, using an ROHF wave function. We have also calculated $C_2O_2(^3\Sigma_g^-)$ to be 58.7 kcal/mol above the lowest $CO(^1\Sigma^+) + CO(^1\Sigma^+)$ dissociation limit but 80.6 kcal/mol below its spin-allowed one: $CO(^1\Sigma^+) + CO(^3\Pi)$ (see Figure 1). At the CCSD(T)/6-311+G(2df) level and for the B3LYP/6-311+G(2df) geometries, we calculated these dissociation limits to be respectively 58.8 and 79.5 kcal/mol, giving total agreement between the two calculations. At the same CCSD(T) level but using the smaller 6-311+G(2d) basis set (of the same size used in ref 44), we calculated $C_2O_2(^3\Sigma_g^-)$ to be 66.1 kcal/mol above $CO(^1\Sigma^+) + CO(^1\Sigma^+)$ and 72.1 kcal/mol below $CO(^1\Sigma^+) + CO(^3\Pi)$, numbers in total agreement with the values obtained by Korkin et al.[44] at the ROHF/CCSD(T)/TZ2P level (see Table 6). It is worth noticing here that the addition of an extra f-polarization function does increase the relative stability of the $C_2O_2(^3\Sigma_g^-)$. Values obtained by Raine et al.[40] in a CI/DZP calculation (see Table 6) are of the same order as numbers obtained by Korkin et al.[44]

C_2S_2. Maier et al.[47] have calculated, at the RCISD/6-31G* level, a $^1\Delta_g$ state 2 kcal/mol more stable than the $^3\Sigma_g^-$ state. We did not repeat these calculations since a single determinantal representation for the $^1\Delta_g$ state is not appropriate, but did repeat their MCSCF(6,6) calculation using our cc-pVTZ basis set, to test their statement of the $^1\Delta_g$ state being 0.7 kcal/mol more stable than the $^3\Sigma_g^-$ state. Using our B3LYP/6-311+G(2df) optimized geometry, we find the lowest state to be the $C_2S_2(^3\Sigma_g^-)$ with the $^1\Delta_g$ state 10.8 kcal/mol above it, in agreement with Ma and Wong,[51] who found a ΔE(S−T) of 10.7 kcal/mol at the CASSCF(6,6)/6-31G(d) level. At the CASSCF(10,8)/cc-pVTZ level we calculated this ΔE(S−T) to be 5.0 kcal/mol.

At our MRCI/cc-pVTZ//B3LYP/6-311+G(2df) approximation, the calculated singlet−triplet energy gap ΔE(S−T) for C_2S_2 is 7.7 kcal/mol, with, as expected, the $^3\Sigma_g^-$ state more stable than the $^1\Delta_g$ state, in qualitative agreement with the value of 5.7 kcal/mol calculated at the MRCI−CASSCF(10,8)/cc-pVQZ level by Ma and Wong.[51] The energy difference of 2 kcal/mol can be rationalized by considering the multiconfigurational wave function used for both CI calculations. While in our multiconfigurational wave function all valence sigma orbitals are correlated, they are not in the treatment of Ma and Wong.[51] In MCSCF test calculations not reported in this paper (but available upon request), we have shown that correlating the highest sigma orbital (i.e., CASSCF(12,10)) has almost no effect on the

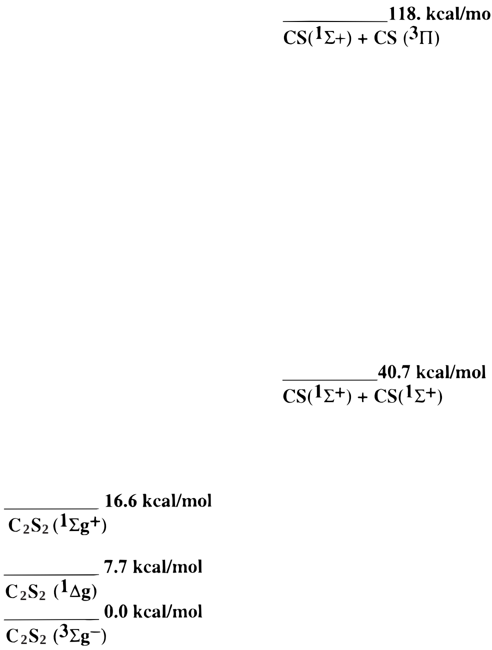

Figure 2. Energies for the C_2S_2 system.

ΔE(S−T) energy, in agreement with Ma and Wong's[51] results. However, increasing the size of the active space by correlating more sigma orbitals (i.e., CASSCF(16,12)) does affect the singlet−triplet gap which therefore increases (see notes under ref 68). At the ${}^1\Delta_g$ geometry, we calculated the energy of the next singlet, the ${}^1\Sigma_g{}^+$ state, to be 16.6 kcal/mol above the ${}^3\Sigma_g{}^-$. At the MRCI-CASSCF(10,8)/cc-pVQZ level Ma and Wong have calculated the ${}^1\Sigma_g{}^+$ state to be 10.5 kcal/mol above the ${}^3\Sigma_g{}^-$ state. This energy might have been underestimated in their treatment for the same reason invoked above for their ${}^1\Delta_g-{}^3\Sigma_g{}^-$ energy gap calculations.

At the MRCI/cc-pVTZ//B3LYP/6-311+G(2df) level we find $C_2S_2({}^3\Sigma_g{}^-)$ to be more stable than both the lowest $CS({}^1\Sigma^+) + CS({}^1\Sigma^+)$ and first excited $CS({}^1\Sigma^+) + CS({}^3\Pi)$ dissociation limits, being respectively 40.7 and 118 kcal/mol below (see Figure 2). At the CCSD(T)/6-311+G(2df)//B3LYP/6-311+G(2df) level we calculated these numbers to be respectively 43.4 and 123 kcal/mol, giving close agreement between the two calculations. At the CI/DZP level, Raine et al.[40] have calculated the same relative energies which they found to be respectively 39.4 and 118 kcal/mol, without considering ZPE corrections. Applying our scaled ZPE to these values lowers them to respectively 36.2 and 115 kcal/mol (Table 6). Ma and Wong,[51] using G2/QCI calculations, determined $C_2S_2({}^3\Sigma_g{}^-)$ to be repectively 33.2 and 141 kcal/mol below the two lowest dissociation limits. At this theoretical level their $CS({}^1\Sigma^+) - CS({}^3\Pi)$ excitation energy is 108 kcal/mol, much too high compared to the well-known value of 79.1 kcal/mol.[67] Thus, as found for C_2O_2, we determine the lowest triplet state of C_2S_2 to be more stable, with respect to the lowest dissociation limit, than any previous theoretical studies.

Finally, as can be seen from Figure 2, and confirming previous theoretical work,[51] we find all of $C_2S_2({}^3\Sigma_g{}^-)$, $C_2S_2({}^1\Delta_g)$, and $C_2S_2({}^1\Sigma_g{}^+)$ to be below the two lowest dissociation limits $CS({}^1\Sigma^+) + CS({}^1\Sigma^+)$ and $CS({}^1\Sigma^+) + CS({}^3\Pi)$.

C_2OS. As can be seen from Table 6, the singlet−triplet energy gap for C_2OS is 9.9 kcal/mol at the MRCI/cc-pVTZ//B3LYP/6-311+G(2df) level, with the $C_2OS({}^3\Sigma_g{}^-)$ more stable than the ${}^1\Delta_g$ state, confirming previous theoretical work. At the CASSCF(10,8)/cc-pVTZ level this energy is 7.6 kcal/mol. At the geometry of the ${}^1\Delta_g$ state, the corresponding ${}^1\Sigma_g{}^+$ state is determined to be 19.8 kcal/mol above $C_2OS({}^3\Sigma_g{}^-)$. The ${}^3\Sigma_g{}^-$ state is slightly higher than the lowest dissociation $CO({}^1\Sigma^+) + CS({}^1\Sigma^+)$ limit (5.7 kcal/mol above), but 71.9 kcal/mol lower than its spin-allowed dissociation limit $CO({}^1\Sigma^+) + CS({}^3\Pi)$ (see Figure 3). These numbers are consistent with those calculated at the CCSD(T)/6-311+G(2df) level (Table 6) and can be compared to the only available values from the literature, which were obtained at the SCF[53] level (see Table 6).

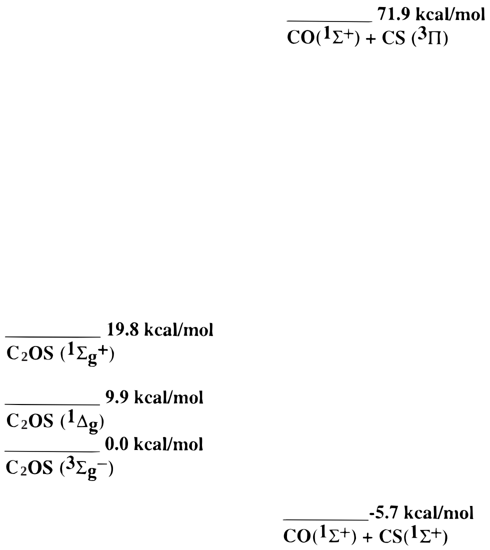

Figure 3. Energies for the C_2OS system.

IV. Conclusion

Our study of the C_2O_2, C_2S_2, and C_2OS entities at a highly correlated level confirms that in all cases the lowest states are of triplet multiplicity and of linear geometries, conforming therefore to Hund's rules. Our study has also shown that the lowest ${}^1\Delta_g$ states, when treated using a multiconfigurational wave function, are true minima for a linear arrangement while all previous studies using single determinantal wave functions have concluded that the minima are nonlinear. Both $C_2O_2({}^1\Delta_g)$ and $C_2OS({}^1\Delta_g)$ are above their lowest dissociation limit, but since (as has been shown for $C_2O_2({}^1\Delta_g)$[37]) their linear dissociation to the ground state diatomics is symmetry forbidden, a linear distortion along the CC coordinate should imply a very high potential energy barrier. However, since a trans bent dissociation is symmetry allowed, the stability of $C_2O_2({}^1\Delta_g)$ and $C_2OS({}^1\Delta_g)$ will depend on the amount of energy required for the molecule to be distorted from its linearity. Since neither of these singlet states have been isolated experimentally, it is likely that their barrier height to distortion is low enough to allow ready dissociation. The situation for $C_2S_2({}^1\Delta_g)$ is more optimistic, since this state is lower in energy than the $CS({}^1\Sigma^+) + CS({}^1\Sigma^+)$ products and therefore should be stable.

$C_2O_2({}^3\Sigma_g{}^-)$ and $C_2OS({}^3\Sigma_g{}^-)$, being much lower than their spin-allowed dissociation limit, but higher than two fragments in their ground electronic state, have their stability dependent on whether there is an efficient curve crossing with the ${}^1\Sigma$ repulsive state diabatically correlating to the two diatomics in their ground electronic state. This has been calculated to be the case for $C_2O_2({}^3\Sigma_g{}^-)$ by Shroeder et al.,[21] explaining therefore the failure of any experimental detection of $C_2O_2({}^3\Sigma_g{}^-)$. This might not be the case for $C_2OS({}^3\Sigma_g{}^-)$ since this molecule has reportedly been observed experimentally. Therefore, a search for the existence of such a curve crossing and an evaluation of the corresponding spin coupling is crucial to confirm the detectability of this molecule.

The stability of $C_2S_2(^3\Sigma_g^-)$ will not be affected by the existence of such a crossing since $C_2S_2(^3\Sigma_g^-)$ is below the $CS(^1\Sigma^+) + CS(^1\Sigma^+)$ dissociation limit. Therefore, since both $C_2S_2(^1\Delta_g)$ and $C_2S_2(^3\Sigma_g^-)$ are stable molecules, lying well below the two lowest dissociation limits, we suggest that both $C_2S_2(^1\Delta_g)$ and $C_2S_2(^3\Sigma_g^-)$ could be detected in carefully designed experiments. It might even be that in the experiments where $C_2S_2(^3\Sigma_g^-)$ has been thought to have been observed, $C_2S_2(^1\Delta_g)$ was also present but not distinguished because of the similarity of its IR spectrum with that of the triplet state (recall that our calculated IR spectra for both singlet and triplet states show that the main IR band occurs at the same wavelengths for both states i.e., around 1165 cm^{-1} at the MCSCF/cc-pVTZ level after scaling).

From an astrophysical point of view, the approach to understanding, if there is a possibility of producing any of the molecules under consideration in the interstellar environment, is completely different. Special conditions prevail in space. No extra energy is available to allow reactions to proceed over barriers, and species are in their ground electronic state. Although it appears quite clear that C_2O_2 is unlikely to be worth considering, the formation of both C_2S_2 and C_2OS in space seems possible. They could either be formed by association of the two diatomics or be formed by breakdown of a higher homologue in their respective series. For reasons described in the discussion the most likely molecule to be formed is C_2S_2.

For C_2OS, the endothermicity of the reaction with respect to $CS(^1\Sigma^+) + CO(^1\Sigma^+)$ reactants would seem to indicate that only a mechanism involving the breakdown of a higher homologue, such as OC_3S, could lead to its formation in these extreme conditions. However, in the case of a strong spin−orbit coupling between the $^1\Delta_g$ and $^3\Sigma_g^-$ state, $C_2OS(^3\Sigma_g^-)$ could be formed in a specific environment, such as in some parts of circumstellar envelopes, where the temperature can be much higher than generally assumed. This would allow reactions with a low barrier to proceed. The formation of $C_2OS(^3\Sigma_g^-)$ from $CS(^1\Sigma^+) + CO(^1\Sigma^+)$ is therefore worth the investigation.

From these considerations it appears that the logical following step from the present study is a search for reaction paths which might lead to the formation of C_2S_2 and C_2OS with a minimum energy cost.

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