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REGULAR ARTICLE

Vertical excitation energies to valence states of DMS and DMSO

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Abstract Coupled cluster linear response formalism has been used to compute the vertical excitation energies and oscillator strengths of the lowest valence singlet states of dimethyl sulfide (DMS) and dimethyl sulphoxide (DMSO). Unless for one exception, the results are in very good agreement with experiment, but a new assignment of one DMSO transition is proposed.

1 Introduction

The role played by sulfur containing submicroparticles in the atmosphere behavior has been recognized for a long time. Although it was initially thought that the sources of atmospheric sulfur were volcano eruptions and anthropogenic emissions [1], such theory is unable to explain the concentration of sulfur in areas where the former causes cannot be invoked and, in particular, in oceanic regions. However, from the pioneering work by Lovelock et al. [2], it is nowadays well established that most of the sulfur present in the atmosphere has a biogenic origin. In this sense, dimethyl sulfide (DMS) has proved to be the main source of biogenic sulfur, required for the global balance of sulfur in the atmosphere.

Dimethyl sulfide is the result of the decomposition, by means of bacteria and marine algae, of dimethylsulfopropionate (DMSP), the largest source of DMS in the oceans. DMSP is an organic sulfured compound produced by a variety of halophytic plants and can be found in large quantities in phytoplankton as well as in the euphotic zone [3].

One of the most important features of the chemistry of DMS is its effect on climatic change. In this way, the so-called CLAW hypothesis [4] states the importance of sulfurous particles as cloud condensation nuclei (CCN) that favor albedo and therefore make temperature of the sea surface to decrease. This cooling, in turn, causes a diminution of DMS concentration and hence less CNN and a subsequent increase on albedo. As a result, climate and DMS emissions are intimately related.

Dimethyl sulfide has also a significant impact on acidic rain as it can be oxidized to produce sulfuric acid. The major oxidants of DMS are OH and NO_3 radicals [5], but reactions with halogen oxides, noteworthy with BrO, are also important. While the reaction with NO_3 proceeds exclusively via hydrogen abstraction, the OH radical can also oxidize DMS through an addition process [6,7]. Among the different products resulting from the OH radical initiated oxidation of DMS, dimethyl sulphoxide (DMSO) is the most abundant from the addition scheme [8]. Let us recall that reaction with OH is the most effective mechanism for the destruction of DMS under marine conditions as the low quantities of nitrogen oxides present makes reaction with NO_3 basically insignificant.

In this context, the study on the vertical excitation energies of DMS and DMSO might be of interest. To this aim, we have employed a response function approach using a coupled cluster reference function. In this formalism, the time evolution of the wavefunction is followed when a perturbation in applied. If the selected perturbation is an electric field, the poles and residues of the linear response function represent, respectively, the excitation energies and transition moments from the reference state to excited states [9]. Linear response functions have been derived and implemented for

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SCF [10], MCSCF [11], SOPPA [12] and CC [13,14] wavefunctions.

2 Calculation details

All coupled cluster calculations were carried out using Dalton program [15], in which it is implemented [16] a coupled cluster linear response using a linked triples corrected CCSD wavefunction as a reference function in a direct algorithm, in a similar manner to the energy code [17,18]. The employed CCSDR(3) method is correct to the third order in the fluctuation potential for states dominated by single excitations [19]. Core electrons were kept frozen in all calculations.

We have used Dunning's aug-cc-pVTZ [20] basis in all coupled cluster calculations. Previous experience demonstrates that this basis set is enough to properly describe the valence states in which we are interested. Let us note, however, that Rydberg states are not expected to be correctly reproduced because of the lack of sufficiently diffuse functions.

For DMSO, the molecular geometry was optimized, using Dunning's cc-pVTZ basis at the DFT level and employing Becke's 3-parameter functional B3LYP [21], by means of Gaussian 03 suite of programs [22]. A frequency analysis showed that the encountered structure was indeed a minimum of the potential energy surface. The computed geometry is in good agreement with the experimentally determined by Feder et al. [23] and Typke [24]. However, we have used the DMS experimental geometry as determined by Pierce et al. [25]. In order to estimate the difference between experimental and optimized geometries, we have also determined DMS geometry using the same procedure that for DMSO. The differences found were completely negligible and should not have any notable influence on the computed excitation properties. Also, the computed totally symmetric harmonic frequencies are similar to those determined by Scott et al. [26], showing a root mean deviation of 3.6 meV. In Table 1, we report some selected geometrical parameters of both species.

Table 1 Selected geometrical parameters of DMS and DMSO

	DMS exp	DMS opt	DMSO exp	DMSO opt [24]
R (C–S)	1.80	1.81	1.80	1.83
R (C–H)	1.09	1.09	1.10	1.09
R (S–O)	–	–	1.49	1.50
A (C–S–C)	98.9	99.7	96.6	96.5
A (H–C–H)	109.6	109.1	111.0	110.5
A (S–C–H)	109.4	109.7	107.9	108.4

Distances are expressed in Ångstroms and angles in degrees

3 Vertical excitation energies of DMS

Thompson et al. [27] published the first vacuum-ultra violet (VUV) spectrum of DMS in the range 190–250 nm and later on, Scott et al. [26] and McDiarmid [28] reported the spectrum starting in 125 nm. The absorption spectrum of dimethyl sulfide has also been investigated by Tokue et al. [29] and Hearn et al. [30]. Recently, Limão-Vieira et al. [31] carried out a high-resolution spectrum using synchrotron radiation, and Hynes and coworkers [32] published the gas phase UV absorption spectra for a series of alkyl sulfides including DMS.

In Table 2 we report the calculated vertical excitation energies of DMS calculated at the CCSD level both without and with triples correction included [the CCSDR(3) method]. All the reported states are described by wavefuctions clearly dominated by single excitations ($\%t_1 > 95$), what guaranties that the presented energies are close (around 0.1–0.2 eV) to the full CI limit.

The experimental studies coincide in that the first dipole allowed electronic excitation corresponds to the $1\,^1B_1 \leftarrow X\,^1A_1$ transition. In a single reference one-particle picture, this would represent an excitation from the sulfur lone pair $3b_1$ to the σ^* molecular orbital $9a_1$ of the DMS molecule. Our theoretical calculations agree with this result. The experimental 0–0 excitation has been identified with the transition appearing at 5.44 eV in the UV spectrum, while we have determined a vertical excitation energy of 5.58 eV. The 0.14 eV difference is a typical deviation from experiment and theory as theoretically we are computing vertical excitation energies, which obviously are not necessarily equivalent to

Table 2 Vertical excitation energies (eV) of DMS

Symmetry	State	$\%t_1$	ΔE CCSD	ΔE CCSDR(3)
$^1A_1$	1	95.5	6.50	6.45
	2	95.7	7.94	7.89
	3	95.0	8.37	8.28
	4	95.2	8.87	8.81
$^1B_2$	1	95.6	7.46	7.42
	2	95.1	8.36	8.29
	3	95.3	8.71	8.64
	4	95.3	9.61	9.52
$^1B_1$	1	95.3	5.65	5.58
	2	95.4	6.28	6.23
	3	95.3	6.95	6.89
	4	95.4	7.43	7.37
$^1A_2$	1	95.3	5.48	5.43
	2	95.4	6.98	6.93
	3	95.5	7.32	7.27
	4	95.5	8.61	8.56

the experimental 0–0 excitation. As a comparison, Fabian [33] determined it as 5.10 eV using TDDFT.

However, the lowest excited state of DMS is not the one just described, but corresponds to the transition $1\,^1A_2 \leftarrow X\,^1A_1$, which is symmetry forbidden. In a single-particle model, it is represented by an excitation from the same $3b_1$ lone pair of sulfur to the $8b_2$ molecular orbital of dimethyl sulfide. We have found this states 5.43 eV above the ground state.

The second valence band in the experimental spectrum exhibits a considerable vibrational structure extending in the 6.0–7.0 eV range. The 0–0 transition lies at 6.35 eV. From our computations we assign such band to the excitation $2\,^1A_1 \leftarrow X\,^1A_1$ with vertical excitation energy of 6.45 eV, again inside the characteristic margin of error of triples corrected coupled cluster response methods. Once more, the excitation is represented by a transition originating in the $3b_1$ lone pair of sulfur this time to the $4b_1$ molecular orbital of DMS.

The other computed excitations produce Rydberg states. As already mentioned, we are only interested in valence states and therefore we are using an atomic basis set that is not enough diffuse to account for Rydberg states. For instance, the simple inclusion of a 2s2p2d series of Rydberg functions built following Kaufman's technique [34] suffices for lowering the energy of the $3A_1$ state in more than 0.5 eV at the CCSD level. Nevertheless, the valence states like $2A_1$ are almost unaffected.

To estimate the intensity of the transitions, we have calculated the oscillator strength of the dipole allowed transitions at the CCSD level and these are summarized in Table 3. According to the experimental evidence, the transitions to valence states show intensities sensibly lower than that the transitions to Rydberg states.

Table 3 Transition moments (in a.u.) and oscillator strengths of lowest excitations in DMS

Symmetry	State	Transition moment	Oscillator strength	Polarization
$^1A_1$	1	0.2208	0.0352	*Y*
	2	0.1052	0.0204	*Y*
	3	0.0169	0.0035	*Y*
	4	0.8585	0.1867	*Y*
$^1B_2$	1	0.0133	0.0024	*X*
	2	0.0477	0.0098	*X*
	3	0.7610	0.1624	*X*
	4	0.2141	0.0504	*X*
$^1B_1$	1	0.0528	0.0073	*Z*
	2	0.2196	0.0338	*Z*
	3	0.0090	0.0015	*Z*
	4	0.1314	0.0239	*Z*

The CSC skeleton of the molecule (together with two methyl hydrogens) lies on the *XY* plane, with the sulfur atom along the *Y* axis

4 Vertical excitation energies of DMSO

Very recently, Drage et al. [35] have reported the high resolution VUV photoabsorption cross section of dimethyl sulphoxide (DMSO). Previously, Sze et al. [36] used electron energy loss spectroscopy combined with synchrotron radiation photoabsorption to measure the electronic spectra of inner shells and the valence shell of DMSO. In contrast to DMS, the experimental investigations have identified a variety of valence states in the spectrum, which is composed by several overlapping bands extending from 5.4 to 10.8–11 eV.

While DMS presents C_{2v} geometry, DMSO molecule belongs only to the C_s symmetry class. Together with its slightly bigger size, the lowering of symmetry makes coupled cluster calculations in DMSO sensibly more expensive than in DMS. Taking into account that for DMS triples contribution is not very important, less than 0.1 eV of all the cases considered in Table 2, we have restricted ourselves to only use the CCSD approach (not triples corrected) to study DMSO. In addition, the great number of Rydberg states makes the description of them unfeasible, as an extremely large basis set would be required. Our results for this system are collected in Table 4.

The first feature to note in the calculated values is the very low intensity of all the transitions as can be expected for a common solvent in UV spectroscopy. We will not discuss this aspect any more and will concentrate in the excitation energies to the states below 9 eV. Furthermore, as the employed atomic basis set it is not adequate for Rydberg states, we will restrict ourselves to valence states and leave apart the Rydberg states as, for instance, the $1^1A''$ state.

Experimentally, the lowest excited state appears at 5.53 eV and corresponds to the transition $14a' \rightarrow 8a''$. Surprisingly enough, and in despite the quality of the used method to represent single excitation dominated excitations like this, the same transition $1\,^1A'' \longleftarrow X\,^1A'$ is calculated using CCSD linear response at 6.09 eV, more than 0.5 eV above the experimental value. This great discrepancy reflects the fact that this transition has an important Rydberg contribution as shown by the weights of the excitations $14a' \rightarrow 11a''$ and $14a' \rightarrow 16a''$ that are also present in the coupled cluster description of this state. As mentioned before, the basis set we are using is not adequate to describe Rydberg states.

The second valence state is the $2^1A'$ state, which is originated from the $14a' \rightarrow 15a'$ transition and appears at 6.03 eV in the experiment and at 6.13 eV theoretically. We have assigned the next two valence states to transitions from the ground state to the $3^1A'$ (calculated at 6.73 eV) and $4^1A'$ (calculated at 6.97 eV) states, respectively. In an independent

Table 4 Vertical excitation energies (eV) and transition moments (a.u.) of DMSO

Symmetary	A'			A''		
State	% $t1$	ΔE CCSD	Oscillator strength	% $t1$	ΔE CCSD	Oscillator strength
1	94.6	5.90	0.0030	94.2	6.09	0.0584
2	94.4	6.13	0.0208	93.8	6.92	0.0105
3	94.6	6.73	0.0925	94.0	7.15	0.0078
4	94.6	6.97	0.0162	94.2	7.24	0.0102
5	94.3	7.18	0.0061	94.7	7.60	0.0110
6	93.6	7.33	0.0432	94.6	7.76	0.0037
7	94.8	7.98	0.0154	94.1	7.83	0.0101
8	93.9	8.27	0.0118	94.1	8.03	0.0009
9	94.4	8.38	0.0365	93.8	8.27	0.0769
10	94.7	8.40	0.0109	94.6	8.76	0.0032
11	94.1	8.69	0.0356	94.3	9.06	0.0038
12	94.3	8.83	0.0330	94.7	9.30	0.0034
13	94.2	8.91	0.0055	94.3	9.35	0.0008
14	94.5	9.23	0.0146	94.1	9.39	0.0101
15	94.4	9.32	0.0199	94.2	9.48	0.0055
16	94.6	9.43	0.0006	94.5	9.57	0.0004
17	94.2	9.59	0.0012	93.8	9.67	0.0106
18	93.9	9.69	0.0219	94.0	9.88	0.0499
19	93.8	9.77	0.1242	94.1	10.08	0.0004
20	94.1	9.86	0.0271	94.0	10.24	0.0097

particle model, these states are basically described by transitions from the $14a'$ occupied molecular orbital to the 16–$18a'$ virtual orbitals. Nevertheless, the assignment made for the experimentalists is not the same, as the third valence state (measured at 6.60 eV) is associated with the transition $7a'' \rightarrow 8a''$ and the fourth (measured at 6.90 eV) to the transition $14a' \rightarrow 16a'$.

Experiment and theory agree in the assignment of the fifth valence state, which is determined by Drage et al. at 7.12 eV and we have computed at 7.15 eV. It corresponds to the transition $3\,{}^1A'' \leftarrow X\,{}^1A'$, defined by excitation $7a'' \rightarrow 15a'$. The next valence state lies at 7.43 eV in the experimental spectrum and could not be interpreted by its authors. We propose to assign it to the $7a'' \rightarrow 8a''$ transition, the $6^1A'$ state, calculated at 7.33 eV.

The excitation $7a'' \rightarrow 16a'$ represents the seventh valence state. We have calculated it at 7.83 eV, 0.09 eV below the experimental value, and identified it as the $7^1A''$ state. The experimentalists were not able to assign the next valence state, which was found at 8.39 eV. We suggest to interpret it as the $8^1A'$ state, which has an important Rydberg contribution and lies 8.27 above the ground state at the CCSD level of calculation.

The last valence state below 9 eV appears in the experimental spectrum at 8.66 eV and results from the transition $7a'' \rightarrow 10a''$. Such transition defines the coupled cluster $11^1A'$ state characterized by an excitation energy of 8.69 eV. The rest of the computed states are of Rydberg type, although we must mention that a few more valence states were detected by Drage et al. outside the manifold of 40 states we have calculated.

5 Conclusions

We have theoretically investigated the vertical excitation energies to the lowest valence states of DMS and DMSO. We have got a very satisfactory agreement with the experimental value unless for the transition to the $1^1A''$ state of DMSO, which has an important Rydberg character. As a matter of fact, we have not considered Rydberg states because of the inadequacy of the employed atomic basis set. We have proposed the reassignment of the transitions occurring in the experimental spectrum of DMSO at 6.60 at 6.90 eV and suggested assignments of a couple of until now not interpreted transitions. With respect to valence states of DMS, there is full agreement between our computations and the experimental findings.

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