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**Bound Electron Molecule Interaction**

# Rydberg electron-transfer spectroscopy and ab initio studies of dimethylsulfoxide–water neutral and anion dimers

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## Abstract

Very low energy electron attachment to DMSO and DMSO–water clusters is studied by means of the Rydberg electron-transfer spectroscopy method. Only $DMSO^-$ and $(DMSO\text{-}H_2O)^-$ anions, with excess electrons in diffuse orbitals, are observed, and the corresponding excess electron-binding energies are, respectively, 12.7 and 3.6 meV. The relative energies and equilibrium geometries of DMSO, DMSO-$H_2O$, and their anions are determined by means of MP2 and DFT calculations and compared to experimental results. (Int J Mass Spectrom 205 (2001) 227–232) © 2001 Elsevier Science B.V.

*Keywords:* Rydberg electron-transfer spectroscopy

## 1. Introduction

Different experimental techniques are currently used for the study of slow electron attachment to molecular systems [1–3] in the gas phase. Among them, the Rydberg electron-transfer (RET) technique offers the possibility of performing mass-spectrometry experiments that can, under certain circumstances, provide structural information [4] and even select between isomers [5]. In order to interpret experimental data and to extract this geometrical information, model structure calculations or, even better, accurate quantum calculations are required. We here consider dimethylsulfoxide ($(CH_3)_2$ S-O, DMSO) and its hydrated complex, which we study by means of RET spectroscopy and ab initio calculations. DMSO and its aqueous solutions are important solvents in organic chemistry and protein structure studies. The physical and chemical properties of the DMSO–water mixture present strong deviations from ideal behavior and have been widely investigated by molecular dynamics simulations [6–16]. In these mixtures, the local structural order is strongly influenced by the competition between the strong hydrogen bonding of the highly polar $S = O$ group to water and the hydrophobic character of the two methyl

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Dedicated to Professor Aleksandar Stamatovic on the occasion of his 60th birthday.

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groups. The analysis of pair distribution functions has lead to the conclusion that long-lived aggregates characterize molecular association between DMSO and water in solution [16] and has motivated the present investigation of those complexes in the gas phase. We take advantage of the large polarity of both DMSO and water to use RET spectroscopy of dipole-bound anion formation, which provides geometrical configurations of neutral complexes directly comparable to quantum chemistry calculations. We first describe the procedure that allows us to produce complex anions and to determine the nature of the excess electron binding. We then analyze the obtained experimental results by means of ab initio and model calculations.

## 2. Experimental

In RET spectroscopy experiments, very weakly bound anions are produced under well-defined single-collision conditions by charge transfer between laser-excited Rydberg atoms and cold neutral polar species [17]. In this experimental setup, a supersonic neutral molecular cluster beam is created by means of a pulsed valve (General Valve, 0.15-mm conical nozzle) followed by a 1-mm skimmer. We expand neat DMSO into few bars of helium for the production of the DMSO monomer. For the production of mixed DMSO–water complex, we flow helium over a first reservoir containing water, followed downstream by a second reservoir containing DMSO. By changing the pressure of the helium carrier gas, both reservoir temperatures, and the time delay between the opening of the valve and the Rydberg atom creation, we can vary the composition of the DMSO–water neutral cluster beam. In a second beam, xenon atoms are first excited into metastable states by electron bombardment and then excited further into Rydberg Xe**(nf) states by means of a tunable dye laser pumped by a pulsed Nd/YAG laser. This beam of laser-excited xenon atoms crosses the molecular cluster beam and charge-exchange takes place in a range of values of the principal quantum number of the Rydberg atoms. The created anions are further mass analyzed in a time-of-flight tube [18] and detected by a set of microchannel plates. The dependencies of the rate constants for the formation of created anions as a function of the principal quantum number $n$ of the xenon Rydberg atoms ($n$-dependencies) are determined by comparison with $SF_6{}^-$ rate constants caused by collisions with a thermal beam [19].

## 3. Dipole binding to isolated DMSO molecules and to DMSO–water complexes

Although we varied the composition of the supersonic neutral beam, using either pure DMSO or different vapor mixtures of DMSO and water at different reservoir temperatures, the only observed negative ions were DMSO$^-$ and the (DMSO..H$_2$O)$^-$ dimer. The best results were obtained for DMSO heated at ~60°C while keeping the water reservoir at room temperature. We looked carefully for larger mixed cluster anions but could not observe clearly any ion corresponding to DMSO$(H_2O)_N^-$ or $(DMSO)_N^-$ with $N > 1$. For the two observed anions, we recorded the Rydberg $n$-dependencies that are displayed in Fig. 1. We have previously shown that these very peaked variations are characteristic of the formation of anions with diffuse orbitals corresponding to the creation of molecular dipole- [20] or quadrupole-bound [21] anions. The Rydberg selectivity of the anion production can be understood within the framework of a multiple curve–crossing model, and an empirical law relates the very weak excess electron-binding energies $E_b$ to the value $n_{max}$, at which the rate constants are maximum [22]: $E_b \approx 23$ eV/$n_{max}^{2.8}$. From this law, we deduce the excess electron-binding energies of the bare DMSO anion and the mixed DMSO- H$_2$O dimer anion that are close to 13 and 3.5 meV, respectively. There is no straightforward one-to-one relationship between dipole-bound electron-binding energies and dipole moments because of the influence of other electrostatic properties (quadrupole, polarizability, etc.) of the neutral complex. A comparison between the measured values and those obtained with similar systems, such as those containing acetonitrile [4], however, indicates that the dipole moments of DMSO molecules and DMSO-H$_2$O complexes should, re-

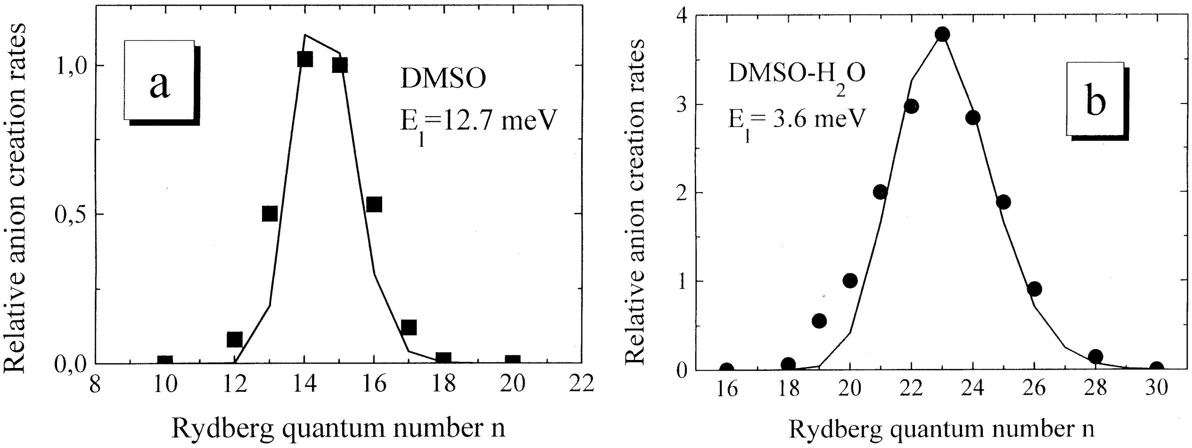

Fig. 1. Relative rate constants for the formation of DMSO$^-$ anions (a) and (DMSO ... $H_2O$)$^-$ (b) in Rydberg electron-transfer collisions as a function of the Rydberg atom principal quantum number *n*.

spectively, lie in the 3.5–4-D and 2.5–3-D ranges. We thus interpret the absence of any observed larger mixed or homogeneous dipole-bound anion clusters as caused by dipole moment values of corresponding neutral parents smaller than the critical value of ~2.5 D for electron binding [20].

The above-measured electron-binding energies correspond to electron attachment in diffuse orbitals and should not be confused with the vertical and adiabatic electron affinities that will be considered in the following section and that correspond to electron capture into valence orbitals. From the absence of any observed valence anion clusters, too, we can already deduce that the valence electron affinity of DMSO is highly negative, as few water or DMSO molecules are not sufficient to stabilize the valence anion within the clusters [23].

## 4. Quantum calculations of DMSO and DMSO–water valence electron affinities

It is known that examination of hydrogen bonding between molecules and that calculation of energetic properties of radical complexes require high levels of calculations. We thus performed full optimization of the DMSO molecule and the DMSO-$H_2O$ and their valence anions in the gas phase using large basis sets. We used calculations with functional density B3LYP and the basis set 6-31+G*. Both the DMSO molecule and its anion were also optimized with the 6-311+G(2d,2p) basis set at the MP2 level. All ab initio calculations were performed with the Gaussian 94 molecular orbital packages [24] on the Cray C98 and on the RISC 6000 at the IDRIS computer center

Table 1
Energies and geometrical parameters of neutral DMSO and DMSO$^-$ anion

| | DMSO | | DMSO$^-$ | |
|---|---|---|---|---|
| Species | B3LYP/6-31+G* | MP2/6-311+G(2d,2p) | B3LYP/6-31+G* | MP2/6-311+G(2d,2p) |
| d(S-O) (Å) | 1.5189 | 1.5022 | 1.5369 | 1.5134 |
| d(S-C) (Å) | 1.8386 | 1.81232 | 1.8344 | 1.8073 |
| Energy (a.u.) | −553.19950 | −552.33994 | −553.15971 | −552.31403 |
| $EA_{ad}$ (eV)[a] | −1.08 | −0.71 | | |

[a] $EA_{ad}$ is the adiabatic electron affinity of the DMSO molecule.

Table 2
B3LYP/6-31+G* energies of DMSO-$H_2O$ neutral and anion complexes

| | DMSO-$H_2O$ | (DMSO-$H_2O$)$^-$ |
|---|---|---|
| Total energy (a.u.) | −629.63789 | −629.59896 |
| Interaction energy (kcal/mol) | −10.1 | −10.7 |
| EA (eV)[a] | −1.06 | ⋯ |

[a] EA is the electron affinity of the complex when the anion initial geometry is the equilibrium geometry of the neutral.

in Orsay (France). Energies and geometrical parameters of fully optimized bare DMSO molecules and anions are reported in Table 1. The geometry of DMSO is in agreement with that reported in the literature [9], and it changes very little on reduction. Actually, examination of the lowest unoccupied molecular orbital (LUMO) of DMSO and of the singly occupied molecular orbital (SOMO) of DMSO$^-$ indicates localization of the electron mostly on the methyl groups and on the sulfur atom. The adiabatic electron affinity reported in Table 1 is strongly negative, in agreement with the experiment (solvation by several water molecules does not lead to any observable valence anion). Calculations with MP2/6-311+G(2d,2p) give similar results, and we thus concentrated on partial optimization of water and intermolecular parameters in DMSO-$H_2O$ and (DMSO-$H_2O$)$^-$ complexes using the B3LYP/6-31+G* method. Results are reported in Table 2 and in Fig. 2. Even if the neutral complex geometry calculated here is very different (see discussion in the next section) from that of Zheng and Ornstein [9], both intermolecular interaction energies are of the same order of magnitude; that is, 9–10 kcal/mol. Starting from the neutral equilibrium geometry, the (DMSO-$H_2O$)$^-$ complex anion undergoes a minor rearrangement, leading to an interaction energy only slightly higher than the neutral. On solvation with one water molecule, the energy stabilization of the valence negative ion, formed from zero-energy electron attachment to the neutral configuration, is then very small and the calculated electron affinity is only slightly less negative than for neat DMSO. These results could provide an explanation for the absence of stable cluster valence anions in the experiments: because of a large negative electron affinity of the bare molecule and an ineffective solvation stabilizing effect, DMSO anions could be unstable even within clusters containing several polar molecules. This interpretation should, however, be ascertained by additional calculations of electron affinities of larger clusters.

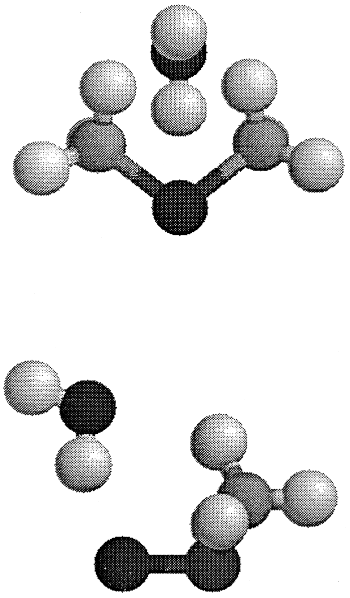

Fig. 2. Optimized structure of the DMSO … $H_2O$ neutral complex calculated by means of ab initio calculations (see text).

## 5. Equilibrium geometry of the DMSO–water complex

The calculated dipole moment of DMSO alone is equal to 4.43 D and is slightly larger than the literature experimental value of 3.96 D [25]. The calculated value for the DMSO-$H_2O$ complex is found equal to 2.85 D, in qualitative agreement with the experimental observation. More quantitatively, the solid curves of Fig. 1 are the results of model calculations of the charge transfer cross sections [22]. In both cases, for both the DMSO monomer and the DMSO-$H_2O$ dimer, the only adjustable parameter is the excess electron-binding energy $E_b$. The resulting values corresponding to best fits (12.7 and 3.6 meV) are fully consistent with the above-calculated dipole moment values. From an electrostatic model of weakly bound anions [21] and from the other electrostatic parameters of the neutrals (quadrupole, polarizability) that can be easily evaluated, we can independently estimate $E_b$ values. In the case of the DMSO monomer, this leads to $E_b = 20 \pm 6$ meV; that is, larger than the experimental value. However, if we adjust (increase) the repulsion parameter of the model so that we now fit the experimental value of about 13 meV, and if we use the same repulsion parameter for the DMSO-$H_2O$ complex, with the calculated dipole moment of 2.85 D and the other evaluated electrostatic parameters, we then obtain $E_b \approx 3.5$ meV; that is, the experimental value.

The present geometry of the DMSO-$H_2O$ complex is, however, substantially different from that reported in previous calculations [9]. In our results, as displayed in Fig. 2, the water molecule lies in the symmetry plane of DMSO, with the $S = O \ldots H$ hydrogen bond bent so that the water oxygen atom interacts with both methyl groups of DMSO. In the previously reported calculations, the water molecule was almost perpendicular to the symmetry plane of DMSO, the water oxygen atom interacting with only one of the two methyl groups of DMSO. As quoted above, both calculations, however, lead to similar intermolecular interaction energies (9–10 kcal/mol). To elucidate this contradiction, we first performed a complete exploration of the structures and dipole moments of the DMSO-$H_2O$ complex by using a genetic algorithm with a semiempirical intermolecular potential model consisting of partial atomic charges, van der Waals interactions, and specific hydrogen-bond terms [26]. This last set of parameters for the $S = O \ldots$ H-O H-bond was not known from previous studies, and we thus tried different sets of values. In most cases, we obtained two low-lying equilibrium structures, the lowest one being similar to that published by Zheng and Ornstein [9] with a high total dipole moment of about 4.5–5 D and the highest one being similar to the present ab initio result with a lower total dipole moment of 2.5–3 D. Depending on the set of H-bond parameters used, the interaction energies range from 9 to 11.5 kcal/mol and the energy difference between the two configurations ranges from 0 to 1.3 kcal/mol. These semiempirical results thus agree with the previous ab initio studies [9], with the lowest equilibrium geometry corresponding to the high total-dipole moment. They are, however, in contradiction with the present experimental results, as this geometry should correspond to a dipole-bound anion whose electron-binding energy should be $E_b \geq$ 50 meV; that is, to a maximum anion formation at low Rydberg quantum numbers ($<9$) where no anions were observed.

Coming back to ab initio calculations, we have then verified that, starting from this high dipole configuration and performing a full optimization without any geometrical constraint at both MP2/6-311+G(2d,2p) and B3LYP/6-31+G* levels, we recover the same low dipole moment equilibrium geometry. Moreover, by adding a second water molecule, we have obtained an equilibrium geometry of the neutral DMSO$(H_2O)_2$ complex, within which each water molecule is in a configuration either similar to that of the high dipole configuration or similar to that of the low dipole configuration of the 1-1 complex. In this calculated DMSO$(H_2O)_2$ complex, both water molecules have a similar interaction energy with DMSO; that is, 8.5 and 9.7 kcal/mol. From this work, it seems that the previously reported geometry is thus not a minimum unless a second water molecule is added to stabilize it.

## 6. Conclusion

In this article, we have shown, using both Rydberg electron-transfer spectroscopy of dipole-bound anions and quantum mechanical calculations, that the lowest equilibrium geometry of the neutral DMSO–water complex corresponds to a rather low total–dipole moment configuration (2.5–3 D) and a high hydrogen-bonding interaction energy ($\approx 10$ kcal/mol). Low-energy electron attachment to the DMSO molecule of this complex in this equilibrium configuration does not lead to a stable valence complex anion because the adiabatic electron affinity of neat DMSO is strongly negative ($\approx -25$ kcal/mol or 1.1 eV) and the interaction energy is about the same as in the neutral species. Further experiments and calculations would be needed to elucidate whether larger mixed DMSO$(H_2O)_N$ clusters would be able to give birth to stable solvated valence anions.

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