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Photodissociation of the CH₃O and CH₃S radical molecules: An *ab initio* electronic structure study

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Abstract

The electronic states and the spin-orbit couplings between them involved in the photodissociation process of the radical molecules CH_3X , $CH_3X \rightarrow CH_3 + X(X = O, S)$, taking place after the $(^2A_1) \leftarrow \bar{X}(^2E)$ transition, have been investigated using highly correlated *ab initio* techniques. A two-dimensional representation of both the potential-energy surfaces (PESs) and the couplings is generated. This description includes the C-X dissociative mode and the CH_3 umbrella mode. Spin-orbit effects are found to play a relevant role on the shape of the excited state potential-energy surfaces, particularly in the CH_3S case where the spin-orbit couplings are more than twice more intense than in CH_3O . The potential surfaces and couplings reported here for the present set of electronic states allow for the first complete description of the above photodissociation process. The different photodissociation mechanisms are analyzed and discussed in the light of the results obtained.

1 Introduction

The CH₃O and CH₃S radicals of the methoxy family are important intermediates in combustion and atmospheric chemistry.^{1–8} The methoxy radical CH₃O is an intermediate in the oxidation chemistry of hydrocarbons like methane, which is important to the ozone budget. In turn, the methylthio radical CH₃S is an intermediate in the atmospheric oxidation of organic sulfides of the type CH₃SCH₃, CH₃SSCH₃, and CH₃SH by OH and NO₃.^{9–12} Those processes contribute to a relevant portion of the acid precipitation in the atmosphere.

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Due to their atmospheric relevance, the spectroscopy and photofragmentation dynamics of the CH_3O 13–20 and CH_3S 21–31 radicals have been investigated by several authors in the last four decades. Photodissociation of CH_3X ($\text{X}=\text{O}, \text{S}$) takes place following excitation of the $(^2A_1) \leftarrow \bar{X}(\bar{^2E})$ transition. In the case of CH_3O three product channels have been identified experimentally17,18:

being (1) the dominant channel, which takes place through a predissociation mechanism. The branching ratio found experimentally for channels (1) and (2) was 3:1,17 and the probability of channel (3) is significantly smaller. While channel (1) could be considered a possible way to produce CH_3 radicals, it is noted that further predissociation of the CH_3 product may subsequently occur, which has recently been studied.32–34 For CH_3S only the $\text{CH}_3\text{S} \rightarrow \text{CH}_3 + \text{S}$ channel has been directly observed at the excitation energies investigated,30,31 although occurrence of the $\text{CH}_3\text{S} \rightarrow \text{CH}_2\text{S} + \text{H}$ channel has also been proposed based on indirect evidence.31 Thus, channel (1) is the major photofragmentation channel for both CH_3O and CH_3S radicals.

In the case of channel (1) for CH_3O , photodissociation experiments17,18 found two vibrational progressions (each of them split by the spin-orbit splitting of the $\bar{X}(\bar{^2E})$ state), namely a pure 3_0^v ($v = 6 - 13$) progression involving the ν_3 mode (essentially the C-O stretching mode) and a combination band $3_0^v 6_0^1$ ($v = 5 - 10$) involving the ν_3 and the ν_6 (the nontotally symmetric methyl rock vibration). The ν_6 mode has e symmetry and therefore is active due to the Jahn-Teller effect in the $\bar{X}$ state. Similar experiments on CH_3S photodissociation through channel (1) found also a pure 3_0^v progression (in the ranges $v = 2 - 15$ and $v = 3 - 14$ for the $^2E_{3/2}$ and $^2E_{1/2}$ doublet components of $\bar{X}(\bar{^2E})$, respectively), and a combination band $2_0^1 3_0^v$ (with $v = 3 - 12$ and $v = 4 - 6$ for the $^2E_{3/2}$ and $^2E_{1/2}$ components, respectively).30 These experiments, as well as previous spectra,28 indicate that the Jahn-Teller effect for CH_3S is small.

In addition to the experimental studies, some *ab initio* investigations on the ground and excited electronic states of CH_3O and CH_3S have been reported, starting with the pioneering work of Jackels for CH_3O .35,36 Several years later, *ab initio* calculations of the stationary points relevant for the different photodissociation pathways from the 2A_1 excited state of both CH_3O 37,38 and CH_3S 37 were reported. The ground electronic state 2E and its

associated Jahn-Teller effect have been investigated in a number of works for CH_3O ^{39,40} and CH_3S ,^{41–43} with and without spin-orbit (SO) coupling. Two-dimensional surfaces in the C-O distance and O-C-H bending angle were calculated for the ground and the three first repulsive excited states (i.e., excluding the bound 2A_1 excited state), in order to study the $\text{O}(^3\text{P}) + \text{CH}_3 \rightarrow \text{CH}_3\text{O}$ reactive scattering process.⁴⁴ More recently, *ab initio* full-dimensional calculations of the 2E and 2A_1 electronic states were carried out in the Franck-Condon region to simulate the light-induced fluorescence (LIF) $(^2A_1) \leftarrow \bar{X}(^2E)$ excitation spectrum of CH_3O and CD_3O .⁴⁵ Clearly CH_3O has been more extensively investigated than CH_3S from the theoretical point of view.

Despite the number of *ab initio* works reported in the literature for CH_3O , the picture of the potential-energy surfaces involved in the CH_3O photodissociation upon the $(^2A_1) \leftarrow \bar{X}(^2E)$ transition is still incomplete. Indeed, many of the previous studies have restricted to the Franck-Condon region because their focus was on investigating either the Jahn-Teller effect or the LIF excitation spectrum, and therefore the asymptotic region of the different electronic PESs was not sampled. Some other works sampled the whole spatial region, including both the interaction and the asymptotic regions, but they lack some of the electronic states involved in the photodissociation process (like the 2A_1 state) or they neglect the SO coupling. The situation for CH_3S regarding lack of *ab initio* information is even more dramatic. As a result, it is not possible at present to interpret the photodissociation of CH_3O and CH_3S in terms of the *ab initio* PESs of all the electronic states involved in the process.

The aim of the present work is to report the potential-energy surfaces of all the relevant electronic states involved in the $\text{CH}_3X \rightarrow \text{CH}_3 + X$ ($X = \text{O}, \text{S}$) photodissociation process that takes place upon the $(^2A_1) \leftarrow \bar{X}(^2E)$ transition, including the spin-orbit couplings between the corresponding states. Highly correlated *ab initio* methods are used in the calculation of the potential surfaces and couplings. A two-dimensional coordinate representation has been adopted, where the two main modes of the radical molecules, namely the C-X distance and the CH_3 umbrella mode (or the H-C-O angle), are considered. These two coordinates are denoted by R and θ , respectively, and are shown in Fig. 1. The C-H distance is denoted by the r coordinate in the figure, and this coordinate is related to the symmetric stretch mode of the CH_3 group. In the calculations only R and θ are varied, while r remains constant at its equilibrium value.

It would be desirable to use a three-dimensional representation including the three coordinates, but this turns out to be too demanding computationally. The reason to choose the R and θ coordinates in our two-dimensional representation instead of other possibilities, like the R and r representation, for instance, is that the coupling of the C-X stretch mode with the CH_3 umbrella mode is expected to be stronger than with the CH_3 symmetric stretch mode. In addition, the separation between the energy levels of the CH_3 umbrella mode is much smaller than that of the methyl group symmetric stretch mode. Thus, upon fragmentation of the C-X bond, the available energy is more likely to flow to the umbrella mode than to the symmetric stretch mode, producing an internal state distribution of the CH_3 fragment in the umbrella vibration that could be described by the R and θ two-dimensional representation currently chosen.

The paper is organized as follows. In Section 2 the theoretical methodology employed and the computational details are described. In Section 3 the results are presented and discussed. Conclusions are given in Section 4.

2 Theoretical background

The electronic structure calculations were performed using the MOLPRO suite of programs.^{46,47} In their ground electronic state, both CH_3O and CH_3S present C_{3v} symmetry, as displayed in Fig. 1. Since C_{3v} is not an Abelian group, the *ab initio* calculations were performed using the C_s group representation, which is valid for all the geometries considered in this work. The representations A_1 and A_2 of the C_{3v} symmetry group give rise to the A' and A'' representations in C_s , respectively, while the states in the E representation give rise to one A' and one A'' degenerate states. The aug-cc-pVQZ basis set of Dunning⁴⁸ was used in all the calculations of the surfaces, including *spdfg* basis functions for the C, O, and S atoms and *spdf* basis functions for the H atom.

We are primarily interested in the dissociation of the CH_3X ($\text{X}=\text{O}, \text{S}$) radical along the C-X stretching coordinate. In order to get the potential-energy curves along this coordinate, geometry optimizations in the ground state of CH_3X were carried out at different R values using the complete active space self-consistent field (CASSCF) method^{49,50} followed by the multireference perturbation theory CASPT2 method.⁵¹ Using the optimized geometries, the ground and excited electronic state energies were computed by means of state-average CASSCF followed by the internally contracted multireference configuration interaction (MRCI) approach.⁵² The orbitals included in the active space are 6 *a* (from 3rd to 8th) and 2 *a* (from 1st to 2nd) for CH_3O , and 6 *a* (from 6th to 11th) and 2 *a* (from 2nd to 3rd) for CH_3S . In order to consider all the states involved in the photodissociation process in the CASSCF wavefunction, the 3 doublet and the 3 quartet states correlating to $\text{O}/\text{S}(\bar{X}^3P) + \text{CH}_3(\bar{X}A_2)$ dissociation channel as well as the 5 doublet states correlating to $\text{O}/\text{S}(1^1D) + \text{CH}_3(\bar{X}A_2)$ products were included in the state average. Then, the electronic wave functions of the $4^2A'$, the $4^2A''$, the $4^4A'$, and the two $4^4A''$ states were calculated at MRCI level.

Spin-orbit matrix elements were calculated from the MRCI electronic wavefunctions using the Breit-Pauli method implemented in MOLPRO.⁵³ Taking into account the spin-orbit effects, the 11 states included in our electronic basis gave rise to 28 spin-orbit states which were considered in this work. Out of the 28 S-O states, 20 ones are relevant for the photodissociation process, namely 4 states associated with the electronic ground state $2E(2A' + 2A'')$, 2 states associated with the $2A_1$ bound electronic state, 2 states associated with the $2A_2(2A'')$ dissociative electronic states, 8 states associated with the $4E(4A' + 4A'')$ dissociative electronic state, and 4 states associated with the $4A_2(4A'')$ dissociative electronic state. The remaining 8 states associated with two $2E$ electronic states correlate to the $\text{O}/\text{S}(1^1D) + \text{CH}_3(\bar{X}A_2)$ dissociation channel and are not expected to play any role in the photodissociation process. They were included in the calculations in order to describe correctly the bound $2A_2$ state in the asymptotic region where they are degenerated.

In order to investigate the influence of the CH_3 umbrella mode on the photodissociation process, two-dimensional calculations of the spin-orbit states as a function of R and θ were

carried out. For CH₃O, the calculations sampled geometries over a 24×11 grid in R and θ , respectively, with the following values: $R = [0.5, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.5, 4.0, 4.5, 5.0, 20]$ Å and $\theta = [50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 145]$ degrees. For CH₃S, a grid of 22×11 was used, taking the shortest value of $R = 1$ Å, since sulfur is bigger than oxygen.

3 Results and discussion

The values of the R , θ , and r coordinates at the equilibrium configuration in 2E and 2A_1 were obtained in this work at the CCSD(T)-F12 (for 2E) and MRCI/CASSCF (for 2A_1) level of theory with the aug-cc-pVTZ (AVTZ) basis set,⁵⁴ using MOLPRO46 and the default options. In the MRCI/CASSCF calculations of the geometries, all the valence orbitals were employed to define the active space. Whereas the geometry of the 2A_1 non-degenerate electronic state was fully optimized without any restriction, the C_{3v} symmetry was imposed in the optimization process of the degenerated ground electronic state favor geometry. The calculated geometries are collected in Table 1, and compared to those reported in some previous works. The agreement with the previous results is excellent.

The equilibrium rotational constants of CH₃O and CH₃S were computed at the MRCI/CASSCF/AVTZ⁵² and RCCSD(T)-F12/AVTZ^{55,56} levels of theory, and compared to the experimental values when available. For the electronic ground state the B_e rotational constant was calculated with the equation^{57,58}

$$B_e = B_e(RCCSD(T) - F12) + \Delta B^{core}(RCCSD(T)), \quad (4)$$

and with similar equations for the constants A_e and C_e . In eqn (4) B^{core} is defined as

$$\Delta B^{core} = B_e(CV) - B_e(V), \quad (5)$$

where $B_e(CV)$ and $B_e(V)$ were calculated correlating both core and valence electrons (CV) or just the valence electrons (V) in the post SCF process. The effect of the core-electron correlation was determined at the RCCSD(T) level of theory.⁵⁹ In order to compare the calculated value with the experimental one of B_0 (and also of A_0 and C_0), the vibrational contribution must be taken into account,

$$B_0 = B_e + \Delta B^{vib}. \quad (6)$$

However, it was not possible to determine accurately the vibrational contribution due to the spin-orbit interaction (the $\bar{X}({}^2E)$ state is a degenerate doublet) and the Jahn-Teller effect. As a result, symmetry and the orbital degeneration are broken, and the optimization options of MOLPRO cannot be used, leading to a lower accuracy of the calculated values. An accurate calculation of the vibrational contribution is out of the scope of this work.

The calculated equilibrium rotational constants for the $\bar{X}(^2E)$ state of CH_3O at the RCCSD(T)-F12/AVTZ level are $A_e = 158183.50$ MHz and $B_e = C_e = 27671.60$ MHz, while the experimental¹⁹ values are $A_0 = 156068.96$ MHz and $B_0 = 27931.14$ MHz. An estimate of the vibrational contributions led to the result that $A^{vib} < 0$, $B^{vib} < 0$, and $C^{vib} > 0$. Taking into account these trends, the differences between the calculated and the experimental constants for CH_3O are not large. For CH_3S the calculated equilibrium rotational constants are $A_e = 159417.66$ MHz and $B_e = C_e = 13443.95$ MHz with the RCCSD(T)-F12 calculation. There are no experimental values available for CH_3S .

Excitation energies, rotational constants, and harmonic frequencies of the different modes have been calculated for the $(^2A_1)$ state of both CH_3O and CH_3S at the MRCI level. They are collected in Table 2 and compared to the available experimental data. Agreement between the calculated and the experimental magnitudes of Table 2 is very good in general for both radical molecules, particularly for the vertical excitation energies. The agreement is slightly better for CH_3O . It is found that the *ab initio* description of the experimental mode frequencies is quite accurate in general, which seems to indicate that the present level of theory used to calculate the potential-energy surfaces and the associated SO couplings is reliable enough. Those potential surfaces and couplings for CH_3O and CH_3S will be discussed in the following.

Potential-energy surfaces and SO couplings of CH_3O

The potential-energy curves of the ground and the first six excited electronic states of CH_3O as a function of the R distance are displayed in Fig. 2, with and without SO coupling. These are the relevant electronic states involved in the photodissociation process of eqn (1) upon the $(^2A_1) \leftarrow \bar{X}(^2E)$ transition. Indeed, after excitation of the 2A_1 state, it predissociates to the 4A_2 , 2A_2 , and 4E states through SO coupling.

Considering the SO coupling in the calculations has a remarkable effect in the shape of the potential-energy curves which is appreciable even at the large energy scale of Fig. 2. The insets in the two panels of Fig. 2 make possible a more detailed comparison of the shapes of the curves. The change in the shape of the different potential curves (and particularly the modification of the anharmonicity of the 2A_1 state) when the SO coupling is considered causes changes in the positions of the minima of the 2A_1 bound states, and of the crossing points of 2A_1 with the 4A_2 , 2A_2 , and 4E repulsive states. Table 3 summarizes the positions of those points when the SO coupling is considered or not.

Table 3 shows that the position of the ground state minimum does not practically change both in energy and C-O distance, upon consideration of the SO coupling. On the contrary, with SO coupling the energy position of the 2A_1 state minimum changes remarkably, appearing $\sim 1000\text{ cm}^{-1}$ higher, at a somewhat shorter, rather similar distance as without SO coupling. The crossing points between 2A_1 and the 4A_2 , 2A_2 , and 4E states are also modified, occurring at higher energies by $\sim 200\text{ cm}^{-1}$ and at shorter distances by $\sim 0.04\text{ \AA}$ when the SO coupling is considered.

The increase of the 2A_1 state minimum energy by $\sim 1000\text{ cm}^{-1}$ with SO coupling has the effect of increasing the corresponding vibrational energies by a similar amount. Since the

energy position of the crossing points between 2A_1 and the three repulsive states increases only by $\sim 200 \text{ cm}^{-1}$ with SO coupling, the net effect is a variation of $\sim 800 \text{ cm}^{-1}$ of the relative energies between the 2A_1 vibrational energies and the three crossing points. Such a variation is expected to have an impact on the predissociation dynamics of specific vibrational levels of 2A_1 , and particularly of those located at energies close to the positions of the crossing points.

A way to assess the quality of our *ab initio* calculations is to compare the calculated asymptotic spin-orbit splittings of $O(^3P)$ to those found experimentally. To this purpose we calculated the spin-orbit splittings of $O(^3P_J)$ at the distance $R = 50 \text{ \AA}$, and found the values 0, 157.40, and 239.98 cm^{-1} for $J = 2, 1$, and 0, respectively. Such values are to be compared with the experimental ones of 0, 158.265, and 226.977 cm^{-1} for $J = 2, 1$, and 0, respectively. The agreement between the calculated and the experimental splittings is indeed very good.

It is now interesting to analyze the SO couplings between the 2A_1 state and the 4A_2 , 2A_2 , and 4E repulsive states. Such couplings are depicted in Fig. 3 as a function of the R coordinate. The strongest coupling in the region of crossing between 2A_1 and the repulsive states is that with the 4E state. The coupling with the 4A_2 state is the second most intense one (although much weaker than the coupling with 4E), and the coupling with 2A_2 is the weakest one. A similar result was found in previous *ab initio* calculations.³⁷ The SO couplings of Fig. 3 provide very useful information about how the predissociation process from the 2A_1 state takes place. Indeed, since the first crossing of 2A_1 is with 4A_2 , when low-energy vibrational states are excited in 2A_1 predissociation to 4A_2 is expected to dominate. As the energy of the vibrational state initially excited increases, predissociation to the 4E state will be the dominant mechanism. Predissociation to 2A_2 is expected to be a quite minor mechanism at any excitation energy.

Contour plots of the potential-energy surfaces of the 2E , 2A_1 , 4A_2 , 2A_2 , and 4E states considering the SO coupling are displayed in Fig. 4 as a function of the radial and angular modes. Contour plots of the SO couplings between 2A_1 and the 4A_2 , 2A_2 , and 4E states are also shown in Fig. 5. As reflected in Table 1, the minimum of the 2E ground state is located at $\theta = 110.1^\circ$. The minimum of the excited bound state 2A_1 is located at a slightly smaller angle, $\theta \sim 104^\circ$. Thus, upon the $(^2A_1) \leftarrow \tilde{X}(^2E)$ transition CH_3O undergoes only a slight distortion of its geometry, both in the radial (see Table 3) and angular coordinates. It is also noted that the spreading of the well of the 2A_1 potential surface along the angular coordinate is more limited than that of the 2E state.

The three repulsive states 4A_2 , 2A_2 , and 4E display a very similar angular dependence, as expected. The angular spreading of the three surfaces is also very similar, and larger than that of the 2A_1 surface. The curves of intersection between the 2A_1 surface and those of the 4A_2 , 2A_2 , and 4E repulsive states are quite similar and rather constant ($R \sim 2 \text{ \AA}$) with θ , being the intersection curve between 2A_1 and 4A_2 slightly more separated from the other two (as expected from Fig. 2). The separation between the three curves becomes somewhat larger for angles $\theta < 80^\circ$ and $\theta > 120^\circ$, where the R values of the three intersections decrease slightly.

Regarding the SO couplings of Fig. 5, a rather weak angular dependence is found for the two couplings between 2A_1 and the 2A_2 and 4A_2 states (the two upper panels of Fig. 5), showing the same trend as the intersection curves of Fig. 4, namely the maximum intensity of the coupling occurs at somewhat smaller R values in the regions $\theta < 80^\circ$ and $\theta > 120^\circ$. The most relevant variation of these two couplings takes place along the radial coordinate (see Fig. 3). Interestingly, the most intense SO couplings, those between 2A_1 and the 4E states, present a more pronounced angular dependence. Indeed, the lower panels of Fig. 5 show that the maximum of the couplings occurs around $R = 1.8 \text{ \AA}$ and $\theta \sim 120^\circ$ for the couplings of the left bottom panel, and $R = 1.8 \text{ \AA}$ and $\theta \sim 130^\circ$ for the couplings of the right bottom panel. These angles are larger than the angle of the minimum of the 2A_1 potential surface ($\theta \sim 104^\circ$). The implication is that bending excitation of the vibrational state initially populated in 2A_1 would favor sampling the regions of maximum intensity of the $^2A_1 \rightarrow ^4E$ SO couplings, thus increasing substantially the efficiency of the $^2A_1 \rightarrow ^4E$ mechanism of predissociation.

Potential-energy surfaces and SO couplings of CH₃S

In the following the results obtained for CH₃S will be discussed and compared with those of CH₃O. The one-dimensional potential-energy surfaces of the ground and first excited electronic states of CH₃S vs. R are depicted in Fig. 6, with and without SO coupling. As in CH₃O, including the SO coupling in the calculations has a remarkable effect in the shape of the potential-energy curves. Not surprisingly, the spin-orbit effect on the potential curves of CH₃S is substantially larger than in CH₃O, as can be observed in the change of shape of the curves of the two panels of Fig. 6.

Table 4 summarizes the positions of the minima and crossing points of the different curves in the case of CH₃S when SO coupling is considered or not. Same as in CH₃O, the position of the potential minimum of the 2E ground state is practically unaffected upon consideration of the SO effect. Very similarly as in the case of CH₃O, for CH₃S the 2A_1 state minimum appears $\sim 1000 \text{ cm}^{-1}$ higher in energy when the SO coupling is considered, and also at a rather similar R distance as without SO coupling. The situation becomes different for the crossing points between 2A_1 and the 4A_2 , 2A_2 , and 4E states. Indeed, these points appear located $\sim 300 \text{ cm}^{-1}$ higher in energy (vs. $\sim 200 \text{ cm}^{-1}$ higher in CH₃O), and at shorter distances by $\sim 0.05 \text{ \AA}$ (vs. $\sim 0.04 \text{ \AA}$ in CH₃O), when the SO coupling is considered. In addition, a remarkable difference between CH₃O and CH₃S is that the 2E and 2A_1 bound states of CH₃O have substantially larger well depths than those of CH₃S. Same as in the case of CH₃O, we have calculated asymptotic SO splittings of the $S(^3P_J)$ atom at $R = 50 \text{ \AA}$. The calculated values of 0, 363.79, and 564.90 cm^{-1} are to be compared to the experimental ones⁶⁴ of 0, 396.055, and 573.640 cm^{-1} for $J = 2, 1$, and 0, respectively, showing again very good agreement.

The stronger SO effect found in CH₃S as compared to CH₃O is clearly reflected in the SO couplings between 2A_1 and the 4A_2 , 2A_2 , and 4E states displayed in Fig. 7 vs. R . While the shape of the different coupling curves is qualitatively similar as the corresponding ones in CH₃O, the intensity of the CH₃S spin-orbit couplings is more than twice that of the CH₃O couplings. Thus, to obtain a reasonably quantitative and reliable description of the electronic

states involved in the photodissociation induced by the $(^2A_1) \leftarrow \bar{X}(^2E)$ transition, including the SO effects appears to be important for both CH_3O and CH_3S , but particularly so for the latter system. The CH_3S SO couplings display the same trend as in CH_3O , with the $^2A_1 \rightarrow ^4E$ coupling being the most intense one, followed in intensity by the $^2A_1 \rightarrow ^4A_2$ coupling. Thus, again the $^2A_1 \rightarrow ^4E$ mechanism of predissociation is expected to be the dominant one in CH_3S .

In Fig. 8 contour plots associated with the potential surfaces of the 2E , 2A_1 , 4A_2 , 2A_2 , and 4E states considering the SO coupling are displayed as a function of R and θ . The shape of the surfaces is qualitatively very similar to that of the CH_3O surfaces of Fig. 4, leaving aside the above mentioned larger well depth of the 2E and 2A_1 surfaces in CH_3O . In CH_3S the minimum of the 2A_1 state occurs at even a smaller angle, $\theta \sim 99^\circ$, than the equilibrium angle $\theta \sim 110^\circ$ of the 2E ground state than in the case of CH_3O (see Table 1). This means a somewhat larger distortion of the CH_3S geometry upon the $(^2A_1) \leftarrow \bar{X}(^2E)$ transition as compared to CH_3O . The intersection curves between the 2A_1 state and the 4A_2 , 2A_2 , and 4E repulsive states display the same trend as in CH_3O , but showing a more pronounced angular dependence, particularly the intersection between 2A_1 and 4A_2 . Likewise, the separation of the three intersection curves at $\theta < 80^\circ$ and $\theta > 120^\circ$, is remarkably larger than in CH_3O . The implication is that bending excitation of the initial state excited in 2A_1 is expected to produce a larger discrimination between the two main mechanisms of predissociation, $^2A_1 \rightarrow ^4E$ and $^2A_1 \rightarrow ^4A_2$, than in CH_3O .

Contour plots of the different SO couplings of CH_3S are presented in Fig. 9. They are also similar in shape to those of CH_3O shown in Fig. 5, although more intense. Again, the couplings between 2A_1 and the 2A_2 and 4A_2 states display a rather weak angular dependence. The $^2A_1 \rightarrow ^4E$ SO couplings display two maxima, around $R = 2.2\text{\AA}$ and $\theta = 60^\circ$ and $R = 2.0\text{\AA}$ and $\theta = 134^\circ$ for the left bottom panel, and around $R = 2.2\text{\AA}$ and $\theta = 60^\circ$ and $R = 2.0\text{\AA}$ and $\theta = 130^\circ$ for the right bottom panel. As a result of this angular shift of the maxima of the SO couplings to remarkably higher and lower angles than the 2A_1 equilibrium angle, the effect of initial bending excitation in increasing the efficiency of the $^2A_1 \rightarrow ^4E$ mechanism of predissociation is expected to be even larger than in CH_3O .

Before concluding, it is interesting to point out that the excited electronic states of CH_3O and CH_3S present the same behavior as those of the diatomic radicals OH and SH.^{65,66} This is not surprising since both H and CH_3 present a single free electron that will lead to a similar covalent bond with the oxygen and sulfur atoms. This allows one to establish a direct correlation between the irreducible representations of C_{3v} and $\text{C}_{\infty v}$ symmetry groups. Through this correlation it appears clearly that the doubly degenerate $^2\Pi$ ground state of XH ($\text{X}=\text{O},\text{S}$) becomes a doubly degenerate 2E state for CH_3X . Similarly, the $^2\Sigma$ converts into 2A_1 , the $^4\Sigma^-$ and $^2\Sigma^-$ convert into 4A_2 and 2A_2 , respectively, and $^4\Pi$ becomes a 4E state. From this analogy we can expect qualitatively similar results for the dissociation of XH and CH_3X radicals. However, due to the larger number of degrees of freedom of CH_3X , more complex photodissociation dynamics is to be expected in this latter case.

4 Summary and conclusions

All the electronic states and the spin-orbit couplings between them involved in the photodissociation process $CH_3X \rightarrow CH_3 + X(X = O, S)$ that occurs upon the $(^2A_1) \leftarrow \bar{X}(^2E)$ transition, have been investigated through highly correlated *ab initio* methods. A coordinate representation including two degrees of freedom, namely the C-X dissociative coordinate and the O-C-H bending angle, was used. The present representation of all the electronic states and couplings involved allows for the first complete description of the above photodissociation process, and opens the possibility of carrying out dynamics simulations. It is found that spin-orbit effects have an important impact on the shape of the excited potential-energy surfaces. This is particularly true for CH_3S , which presents spin-orbit couplings with an intensity more than twice that of the CH_3O couplings. Therefore, spin-orbit effects need to be considered in the calculations in order to obtain a reliable representation of the states involved in the photodissociation. Based on the present potential-energy surfaces and on the intensity of the different couplings obtained, the mechanisms of photodissociation are discussed. In particular, bending excitation of the vibrational state initially excited in $(^2A_1)$ may favor the specific $^2A_1 \rightarrow ^4E$ mechanism of predissociation vs. the other ones.

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Fig. 1. Schematic picture of the equilibrium geometry of both CH_3O and CH_3S that displays C_{3v} symmetry. The coordinate representation used in the *ab initio* calculations is also shown in the figure.

Fig. 2.

(a) Potential-energy curves vs. R of the ground and first excited electronic states involved in the CH_3O photodissociation process that takes place upon the $(^2A_1) \leftarrow \tilde{X}(^2E)$ transition, when the SO coupling between the 2A_1 bound state and the 4A_2 , 2A_2 , and 4E repulsive states is considered. (b) The same potential-energy curves as in (a) when the SO coupling is not considered. An inset within each panel shows in more detail the excited electronic states.

Fig. 3.

Spin-orbit couplings between the 2A_1 state and the 4A_2 , 2A_2 , and 4E repulsive states vs. R for CH_3O . The figure shows the calculated *ab initio* points along with the curves joining them. Only the nonzero couplings between the 2A_1 state and the corresponding ${}^4A_2^{J,M_J}$, ${}^2A_2^{J,M_J}$, and ${}^4E^{J,M_J}$ components are shown. The couplings to the degenerate components ${}^4E^{3/2,3/2}$ and ${}^4E^{3/2,1/2}$ (and similarly with the degenerate components ${}^4E^{3/2,-3/2}$ and ${}^4E^{3/2,-1/2}$) are identical.

Fig. 4.

Contour plots of the CH_3O potential-energy surfaces associated with the 2E ground state, and the 2A_1 , 2A_2 , 4E , and 4A_2 excited states as a function of the R and θ coordinates, when the SO coupling is considered. The intersections of the 2A_1 state with the 2A_2 (solid line), 4E (dashed line), and 4A_2 (dotted line) states are also shown in the panels.

Fig. 5.

Contour plots of the spin-orbit couplings between 2A_1 and the ${}^2A_2^{1/2, 1/2}$ state, the ${}^4A_2^{3/2, 1/2}$ state, the ${}^4E^{3/2, 3/2}$ and ${}^4E^{3/2, 1/2}$ states, and the ${}^4E^{3/2, -3/2}$ and ${}^4E^{3/2, -1/2}$ states, as a function of the R and θ coordinates for CH_3O .

Fig. 6.
Same as Fig. 2 but for CH_3S .

Fig. 7.
Same as Fig. 3 but for CH₃S.

Fig. 8.
Same as Fig. 4 but for CH_3S .

Fig. 9.
Same as Fig. 5 but for CH_3S .

Table 1

Equilibrium geometries obtained in this work for the minima associated with the $\bar{X}(^2E)$ and $(^2A_1)$ bound states, and compared with those found in previous works. See the text for details.

System	State	R (Å)	r (Å)	θ (deg)
CH_3O^a	$\bar{X}(^2E)$	1.378	1.096	110.1
CH_3O^b	$\bar{X}(^2E)$	1.374	1.094	110.3
CH_3O^a	$(^2A_1)$	1.574	1.086	103.1
CH_3O^c	$(^2A_1)$	1.573	1.085	103.1
CH_3S^a	$\bar{X}(^2E)$	1.798	1.089	109.7
CH_3S^d	$\bar{X}(^2E)$	1.794	1.088	109.8
CH_3S^a	$(^2A_1)$	2.114	1.083	98.9
CH_3S^d	$(^2A_1)$	2.064	1.079	99.8

^aThis work.

^bRef. [40].

^cRef. [45].

^dRef. [43].

Table 2

Vertical excitation energies, E (from the 2E state), rotational constants, and fundamental frequencies of the different modes calculated at the CASSCF/AVTZ level for the 2A_1 state of CH_3O and CH_3S . The corresponding available experimental values are also collected in the table for comparison.

CH_3O			CH_3S		
	MRCI	Exp.		MRCI	Exp.
E (cm^{-1})	31777	31644.2 ^a	E (cm^{-1})	26841	26396.8 ^c
A_e (MHz)	149320.52		A_e (MHz)	146124.35	
$B_e=C_e$ (MHz)	22710.58		$B_e=C_e$ (MHz)	10327.23	
$\nu_1(a_1)$ CH_3 st (cm^{-1})	3055	2947.8 ^b	$\nu_1(a_1)$ CH_3 st (cm^{-1})	3092	2940 ^c
$\nu_2(a_1)$ umb (cm^{-1})	1351	1289.3 ^b	$\nu_2(a_1)$ umb (cm^{-1})	1155	1095.9 ^c
$\nu_3(a_1)$ CO st (cm^{-1})	710	662.4 ^b	$\nu_3(a_1)$ CS st (cm^{-1})	418	401 $\pm$ 2 ^c
$\nu_4(E)$ CH_3 st (cm^{-1})	3203	3077.8 ^b	$\nu_4(E)$ CH_3 st (cm^{-1})	3263	3006 ^d
$\nu_5(E)$ CH_2 sc (cm^{-1})	1464	1403.0 ^b	$\nu_5(E)$ CH_2 sc (cm^{-1})	1444	
$\nu_6(E)$ HCO def (cm^{-1})	996	929.5 ^b	$\nu_6(E)$ HCS def (cm^{-1})	670	635 $\pm$ 10 ^e

(st= stretch, umb=umbrella, sc=scissors, def=deformation)

^aRef. [60].

^bRef. [19].

^cRef. [61].

^dRef. [62].

^eRef. [28].

Table 3

Energies and R distances associated with the minima of the 2E and 2A_1 bound states and with the crossing points between the 2A_1 state and the repulsive 4A_2 , 2A_2 , and 4E states for CH_3O , both with and without SO coupling.

With SO coupling		
State	Energy (cm^{-1})	R ($\text{\AA}$)
2E	-30900	1.378
2A_1	1058	1.520
4A_2	7371	2.010
4E	8490	2.077
2A_2	8644	2.087

Without SO coupling		
State	Energy (cm^{-1})	R ($\text{\AA}$)
2E	-30859	1.378
2A_1	73	1.549
4A_2	7125	2.056
4E	8300	2.121
2A_2	8456	2.130

Table 4Same as Table 3, but for CH₃S.

With SO coupling		
State	Energy (cm ⁻¹)	<i>R</i> (Å)
² <i>E</i>	-25131	1.798
² <i>A</i> ₁	2327	2.120
⁴ <i>A</i> ₂	4295	2.486
² <i>A</i> ₂	5091	2.593
⁴ <i>E</i>	5.114	2.597

Without SO coupling		
State	Energy (cm ⁻¹)	<i>R</i> (Å)
² <i>E</i>	-25140	1.798
² <i>A</i> ₁	1340	2.100
⁴ <i>A</i> ₂	4016	2.535
² <i>A</i> ₂	4798	2.637
⁴ <i>E</i>	4922	2.656