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Multi-reference calculations of the photodissociation of $HSCH_3$ molecule*

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This paper performs multi-reference second-order perturbation theory calculations on the ground state and a number of low-lying excited states of $HSCH_3$ molecule, and calculates the vertical excitation energies and low-energy potential-energy curves, based on which the photodissociation channels of $HSCH_3$ at 193,222,248 nm are clarified.

Keywords: photodissociation, potential-energy curve, $HSCH_3$ molecule
PACC: 8250E, 8250F

1. Introduction

Methyl mercaptan ($HSCH_3$) is one kind of primary sulfur-containing molecule emitted into the atmosphere. The properties of its excited states have received much attention in experimental and theoretical studies.[1,2]

Experimental observation of molecular fragments is a method to understand the bond dissociation nature of molecule. The recent experimental investigations have focused on the fission of C–S bond and S–H bond of methyl mercaptan.[3−7] The ultraviolet absorption spectra have been measured,[5] and two important processes are given as follows:[8]

$$CH_3SH + h\gamma \rightarrow CH_3S + H, \quad (1)$$

$$CH_3SH + h\gamma \rightarrow CH_3 + SH, \quad (2)$$

the first one being dominant.[3,4] Fission of the C–S bond occurs only to a small degree at 222 nm and is not observable at 248 nm.[4] The primary quantum yields of H atom produced at 222 nm and 193 nm by fission of S–H bond have been determined to be 0.95±0.10 and 0.49±0.08 relative to CH_3SH at 248 nm at 296 K.[5] At 193 nm the selective bond fission of stronger S–H bond over weaker C–S bond were observed, but excitation of CH_3SH at 193 nm reached a bound state for S–H bond, which has been attributed to the nonadiabatic coupling between the upper and lower states by Keller[3] and Jensen[4] *et al*, and further theoretical works were suggested.

High-quality potential-energy curves (PECs) are required to investigate the dissociation processes theoretically. And to our knowledge, the *ab initio* PECs of $HSCH_3$ have been given by Mouflih *et al* for S–H fission[8] and by Jensen *et al* for S–C fission using effective valence shell Hamiltonian method.[4] However, both these two calculations are not accurate enough to well interpret the experimental results, especially the photodissociation of $HSCH_3$ molecule at 193 nm.To construct the PECs, adequate description for the excited states of $HSCH_3$ molecule should be given. In previous work, pretty good calculations for the characters of the excited states were achieved except the relative big errors (above 0.4 eV).[9] The main objective of this paper is to give more accurate calculation of the excited states and provide high-quality PECs, which give us a clear and detailed understanding of the photodissociation dynamics of $HSCH_3$ at different specific wavelength.

2. Computational methods

The atomic natural orbital (ANO) basis sets designated by Roos *et al*[10] are used in energy calculations of this paper, and for different atoms we have chosen the contractions $(17s, 12p, 5d)$ / $[5s, 4p, 2d]$(S), $(14s, 9p, 4d)/[4s, 3p, 2d]$ (C), $(8s, 4p)/[3s, 2p]$(H). To describe correctly not only valence states but also the low-energy Rydberg states, Rydberg basis sets[11] $2s'2p'1d'$ are added to S and C atom.

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The geometry of the ground states was optimized by using completed active space self-consistent-field (CASSCF) method in C_s symmetry. Multi-reference second-order Moller–Plesset (MRMP2) methods[12] were then used to calculate the vertical excitation energies. The PECs along the reaction coordinates described by S–C and S–H bond distance were calculated by using MRMP2 methods. And the same shift was used in the calculation of all PECs to avoid the intruder states.[13] In the CASSCF calculations, the active space included the σ and σ^* orbital of S–C and S–H bond, the remaining $3p$ orbital of sulfur, and the Rydberg orbitals $4s$, $4p_x$, $4p_y$, $4p_z$ of S atom. That is to say, the active space is 6 electrons in 9 orbitals. The $1s$ cores of carbon and sulfur were frozen in all MRMP2 calculations. All calculations were performed by using GAMESS (General Atomic and Molecular Electronic Structure System) program package.[14]

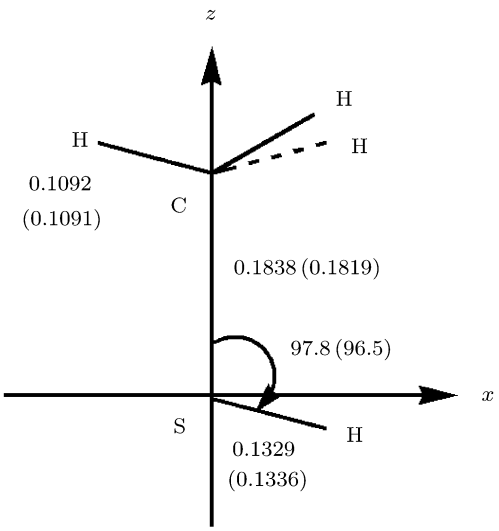


Fig.1. Optimized structure parameters and the values from Ref.[9] (in parentheses), nm for bond length and degree for angle.

3. Results and discussion

3.1. Ground state

We optimized the ground state geometry of methyl mercaptan at CASSCF/aug-ccpvtz level, and the harmonic vibrational frequencies are calculated at the same level. The main optimized geometrical parameters of the ground state are given in Fig.1, in which we list the corresponding values obtained in Ref.[9] by Hartree–Fock method for comparison. The unscaled harmonic vibrational frequencies are listed in Table 1. The S–C bond and S–H bond stretch motions correspond to mode 11(948 cm^{-1}) and mode 4 (3040 cm^{-1})

Table 1. The calculated frequencies (in cm^{-1}) of methyl mercaptan in ground state.

Mode	Symmetry	CASSCF
1	a''	3214
2	a'	3192
3	a'	3153
4	a'	3040
5	a'	2688
6	a''	1605
7	a'	1361
8	a'	1269
9	a''	1219
10	a'	1146
11	a'	948
12	a''	738

3.2. Vertical excitation energies

Employing C_s symmetry, the vertical excitation energies T_v is calculated with the MRMP2 theory, which are compared with the related theoretical[9] and experimental[1] results, as shown in Table 2. It can be found that the transitions in Table 2 present prominent Rydberg characters, and the present calculations agree much better with the measurements[1] in comparison with the calculations of Rauk and Collins.[9] For the dominant photodissociation channel at 204 nm corresponding to the Rydberg transition $3p_y \rightarrow 4s, \sigma^*_{sc}$ at 6.13 eV, our calculation agrees well with the measurement with an error about 0.05 eV, which is much less than the calculation error of Rauk and Collins.

Table 2. The comparison of the vertical excitation energy between the present work and related references, in which the corresponding transitions are given in the second column.

states	transition	T_v/eV		
		Theory[a]	Theory [b]	Expt.[c]
$1^1A'$	Ground state	0	0	0
$1^1A''$	$3p_y \rightarrow (\sigma^*_{SH,SC})^-$	5.55	5.98	5.45
$2^1A''$	$3p_y \rightarrow 4s, \sigma^*_{SC}$	6.13	6.67	6.07
$2^1A'$	$3p_y \rightarrow 4p_y$	6.98	7.33	6.76
$3^1A''$	$3p_y \rightarrow 4p_x$	6.91	7.35	6.76

[a] present MRMP2 calculation.

[b] the calculation of Rauk and Collins.

[c] measurement data from Ref.[1].

3.3. The MRMP2 PECs

The MRMP2 method is one of good methods to calculate the PECs. Firstly the energies of methyl mercaptan were calculated at different bond distance of S–H or S–C, and then the vertical excitation energies of excited states at every point were calculated. Thus, the adiabatic PECs along S–C and S–H bond were constructed, as shown in Figs.2 and 3. The zero-point of potential energy is the MRMP2 energy of the optimized ground state of methyl mercaptan. In Fig.2, there are some 'avoided crossing 'points between the PECs with same symmetries, such as1-2 $^3A''$, 1-2 $^1A''$, and 2 -3$^3A'$ etc. In Fig.4, some chosen PECs are illustrated diabatically in order to discuss the dissociation of S–C bond. The single photon energies corresponding to 248 nm, 222 nm and 193 nm are given by using horizontal lines in Figs.3 and 4. The lowest vibrational energy levels for the stretch motion of S–C and S–H bonds, with the corresponding Franck–Condon regions, are also drawn in Figs.3 and 4.

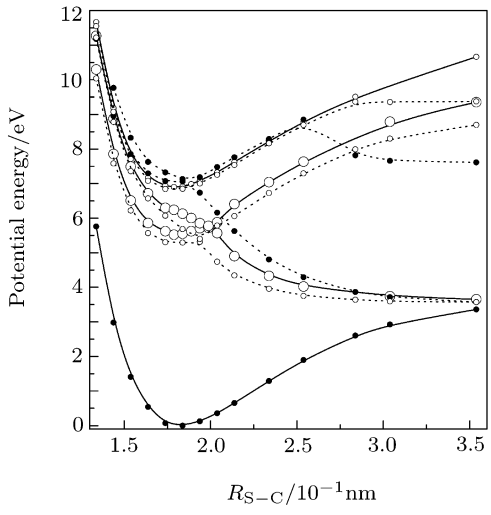


Fig.2. The potential-energy curves along S–C bond. The solid lines are used for singlet states and the dotted lines for triplet states; the solid cycles are for A′ states, and the hollow cycles for A″ states.

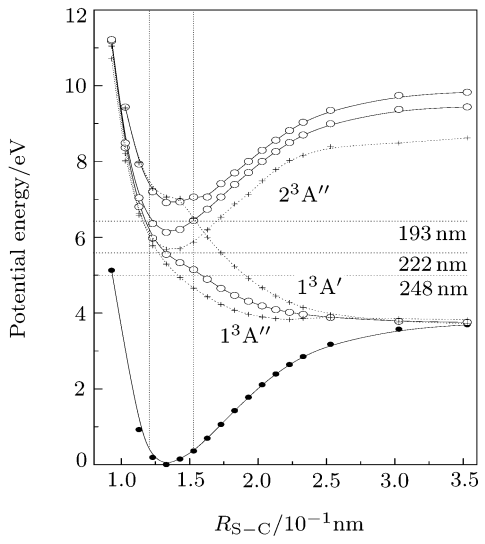


Fig.3. The potential energy curves along S–H bond. The solid lines with solid cycles are used for singlet A′ states, the solid lines with hollow cycles are for singlet A″ states and the dotted lines with hollow squares are for triplet states.

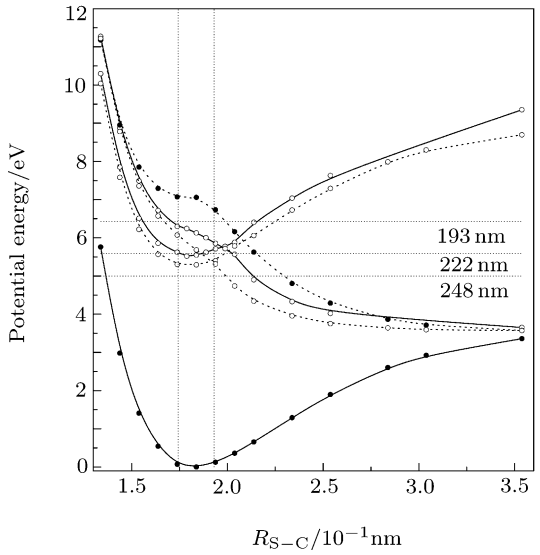


Fig.4. The diabolical dissociation curves along S–C bond. Same as Fig.2.

3.4. The dissociation dynamics of $HSCH_3$ molecule

The corresponding energies of 248 nm, 222 nm and 193 nm laser are illustrated by using oriental lines in both Figs.3 and 4. In Fig.3, the molecule can be excited into the lowest singlet A″ state with 222 nm laser, which is repulsive along S–H bond and quasi-bound along S–C bond (see Figs.2 and 4). The excitation with 222 nm laser then leads to the dissociation of the molecule into H atom and SCH_3 molecule automatically. Consider the error in calculation and the probability in higher vibrational level, the molecule can be excited to the 1A″ by using 248 nm laser in F–C region at different S–H bond length during its stretch motion. Consequently, the S–H bond would dissociate automatically. Since it is the same mechanism in the dissociation processes with 248 nm and 222 nm laser according to our calculation, the quantum yields for the above two dissociation processes would be similar, this result coincides with that of the previous experiment.[5] According to Fig.3, the molecule is excited with 193 nm laser into a bound electronic excited state $1^1A''$, which is a bound state. This agrees with the experimental result by Keller *et al* in Ref.[3], that is the 193 nm excitation corresponding to a bound state along S–H bond. The bound singlet state $1^1A''$ crosses with a repulsive triplet state $1^3A'$, the vertical energy height of the crossing point is almost 6.42 eV (193 nm).The molecule is at a certain vibrational level in the bound $1^1A''$ state with the excitation of 193 nm laser, the superposition between the bound vibrational wave of $1^1A''$ state and continuum wave of repulsive $1^3A'$ state near the crossing point leads the electron state transit from $1^1A''$ to $1^3A'$. This radiationless process is a diabatic one followed by the dissociation along the S–H bond in the $1^3A'$ state. Comparing to the direct dissociation along the repulsive potential energy curves, this process is less efficient and makes the quantum yields observed in experiment decrease.[5]

No previous experimental reports on S–C bond photodynamic of $HSCH_3$ molecule at 193 nm is found in our knowledge. And in Fig.4, according to present work, the resonance excitation hardly occurs at this wavelength. This also makes the SCH_3 fragment stable at 193 nm while simultaneously the S–H bond is broken. Obviously, the S–C bond keeps bonding at 248 nm because of its corresponding energy is below the smallest electronic excitation energy in Franck–Condon region, and no S–C fission observed in experiment.[4] A small degree S–C fission was observed in experiment at 222 nm.[4] This phenomenon is mostly due to the crossing between the $1^1A''$ state and the repulsive $2^3A''$ in F–C region. The less efficient dissociation observed in experiment is owing to the two diabatic "non-crossing points" (in Fig.2) found in this region. And the direct S–H dissociation also reduces the efficiency of S–C dissociation at 222 nm.

4. Summary

The photodissociation dynamic of $HSCH_3$ molecule are investigated based on multi-reference calculations in this work. A fairly good interpretation of phenomenon observed in previous experiments is present in this paper. The dissociation mechanics is discussed in comparison with experiments at different specific wavelength. The direct dissociation of S–H bond occurs along repulsive 1A″ state at 248 nm and 222 nm, and the molecule also dissociates into SCH_3 radical and H atom at 193 nm through a radiationless process, which makes the dissociation less efficient. The dissociation of S–C bond at 222 nm is an inefficient diabatic process according to our calculation. All the results agree qualitatively with the experiments.

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