Theor Chem Acc (2001) 107:33–37
DOI 10.1007/s002140100298

Theoretical
Chemistry Accounts

Regular article

A theoretical study on the ionization of OCS with an analysis of vibrational structures of the photoelectron spectrum

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Received: 20 January 2001 / Accepted: 22 August 2001 /

Abstract. Ab initio calculations have been performed to study the molecular structures and vibrational levels of the four low-lying ionic states (1, $2^2\Pi$, and 1, $2^2\Sigma^+$) of carbonyl sulfide. The global regions of the potential-energy surfaces have been obtained by multireference single and double excitation configuration interaction calculations. Vibrational calculations using explicit vibrational Hamiltonians have been used for vibrational analysis. The equilibrium molecular structures and a vibrational analysis of the four ionic states are presented. The theoretical ionization intensity curves including the vibrational structures of the ionic states are also presented and are compared with the photoelectron spectrum.

Key words: Low – lying ionic states of OCS – Vibrational analysis – Franck–Condon factor – Theoretical intensity curve of ionization

1 Introduction

The electronic configuration of the ground state of carbonyl sulfide is represented by $\ldots(9\sigma)^2\ (3\pi)^4$ with the $C_{\infty v}$ symmetry group.

He(I) photoelectron spectroscopy investigations of OCS have been reported by Turner et al. [1] and Delwiche et al. [2] and the four ionic states have been observed below 19 eV, where well-resolved vibrational structure was found and an assignment of the structure was reported.

As far as we are aware, there has been neither a theoretical study of the molecular structures with a vibrational analysis of the ionic states nor a theoretical study on the vibrational structures of the photoelectron spectrum (PES). In this work, we examine theoretically the molecular and the vibrational structures of the PES.

We undertook vibrational analysis using the explicit vibrational Hamiltonians, which have the global regions of the potential-energy surfaces calculated at the multireference single and double excitation configuration interaction (MRSDCI) levels, and the exact **G** matrix. Using these calculations, we obtained vibrational wave functions, Franck–Condon factors (FCFs), and intensity curves. The vibrational structure of the PES is discussed using the properties calculated.

2 Method of calculations

We used the split-valence-type basis sets of MIDI-4-type prepared by Sakai et al. [3] and Tatewaki and Huzinaga [4]. These were augmented by one d-type polarization function for C, O, and S; the exponents of the polarization functions for C, O, and S being 0.61, 1.16, and 0.46, respectively.

The MRSDCI method was used to get the global region of the potential-energy surface. The molecular orbitals for the MRSDCI calculations of the ionic states were obtained by the open-shell Roothaan's restricted Hartree–Fock method. In the MRSDCI calculations, the singly and doubly excited configuration state functions (CSFs) forming reference CSFs were generated while C_{1s}, O_{1s}, S_{1s}, S_{2s}, and S_{2p} were kept frozen. We determined the reference CSFs which had weights of more than 1% in a preliminary CI calculation for each state. The number of reference CSFs of the $^1\Sigma^+$, $^2\Pi$, and $^2\Sigma^+$ states were 2, 6, and 4, respectively.

In the MRSDCI calculations, we used C_{2v} symmetry instead of the $C_{\infty v}$ symmetry group. The electronic configuration of $\ldots(9\sigma)^2$ $(3\pi)^4$ in the $C_{\infty v}$ symmetry group correlates to $\ldots(9a_1)^2\ (3b_1)^2\ (3b_2)^2$ in the C_{2v} symmetry group.

The vibrational energies and eigenfunctions were obtained by the basis set expansion method and the methods of calculation of the FCFs and the theoretical intensity curves (TICs) were the same as used in our previous work [5].

The study was carried out using the ALCHEMY II [6–8] program for the MRSDCI calculations. The VIBR4 [9] program was used for vibrational analysis calculations of the global region of the potential-energy surface.

3 Results and discussion

The optimized geometrical parameters of the ground and the four ionic states ($1^2\Pi$, $2^2\Pi$, $1^2\Sigma^+$, and $2^2\Sigma^+$)

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are listed in Table 1, which also shows the magnitude of the changes in the C–S and C–O bond lengths upon ionization. The magnitude of the change in the C–S bond length in the $1^2\Pi$ state is larger than that of the other states and that in the C–O bond length in the $2^2\Pi$ state is as large as 0.1 Å.

Table 1. Optimized structure and magnitude of the changes in the bond lengths (angstroms) upon ionization. The values in *parentheses* are the magnitudes of the changes in geometry upon ionization. The experimental values [10] of $R_{C\text{-}S}$ and $R_{C\text{-}O}$ of $^1\Sigma^+$ are 1.560 Å and 1.160°, respectively

State	$R_{C\text{-}S}$	$(\Delta R_{C\text{-}S})$	$R_{C\text{-}O}$	$(\Delta R_{C\text{-}O})$
$^1\Sigma^+$	1.571		1.157	
$1^2\Pi$	1.657	(0.086)	1.129	(−0.028)
$2^2\Pi$	1.589	(0.018)	1.267	(0.110)
$1^2\Sigma^+$	1.578	(0.007)	1.154	(−0.003)
$2^2\Sigma^+$	1.519	(−0.052)	1.183	(0.026)

Table 2. The ionization energies (*IE*) and the Frank–Condon factors (*FCF*) of the 0–0 transitional state. The experimental values are from Ref. [1]

State	IE (eV)	Experimental (eV)	FCF	Experimental
$1^2\Pi$	10.54	11.18	0.33	0.48
$2^2\Pi$	14.56	15.08	0.04	0.04
$1^2\Sigma^+$	15.77	16.04	0.99	0.95
$2^2\Sigma^+$	17.84	17.96	0.60	0.48

Table 3. Reference functions of the multireference single and double excitation configuration interaction (*MRSDCI*) calculations. The total energy of the $^1\Sigma^+$ state is −510.117008 a.u. In the MRSDCI calculations, we used the C_{2v} symmetry group instead of the $C_{\infty v}$ symmetry group

State	Reference function	Weight (%)
$^1\Sigma^+$	$...(8a_1)^2(9a_1)^2(3b_1)^2(3b_2)^2$	86.7
	$...(8a_1)^2(9a_1)^2(3b_1)^1(4b_1)^1(3b_2)^1(4b_2)^1$	1.4
$1^2\Pi$	$...(9a_1)^2(2b_1)^2(3b_1)^1(2b_2)^2(3b_2)^2$	86.4
	$...(9a_1)^2(2b_1)^1(3b_1)^2(2b_2)^2(3b_2)^2$	0.4
	$...(9a_1)^2(2b_1)^1(3b_1)^1(4b_1)^1(2b_2)^2(3b_2)^2$	–
	$...(9a_1)^2(2b_1)^1(3b_1)^2(2b_2)^2(3b_2)^1(4b_2)^1$	0.3
	$...(9a_1)^2(2b_1)^2(4b_1)^1(2b_2)^2(3b_2)^2$	–
	$...(9a_1)^2(2b_1)^1(3b_1)^2(2b_2)^1(3b_2)^2(4b_2)^1$	–
$2^2\Pi$	$...(9a_1)^2(2b_1)^2(3b_1)^2(2b_2)^2(3b_2)^2$	5.3
	$...(9a_1)^2(2b_1)^1(3b_1)^2(2b_2)^2(3b_2)^2$	53.3
	$...(9a_1)^2(2b_1)^1(3b_1)^1(4b_1)^1(2b_2)^2(3b_2)^2$	17.2
	$...(9a_1)^2(2b_1)^1(3b_1)^2(2b_2)^2(3b_2)^1(4b_2)^1$	4.5
	$...(9a_1)^2(2b_1)^2(4b_1)^1(2b_2)^2(3b_2)^2$	4.9
	$...(9a_1)^2(2b_1)^1(3b_1)^2(2b_2)^1(3b_2)^2(4b_2)^1$	0.3
$1^2\Sigma^+$	$...(8a_1)^2(9a_1)^1(3b_1)^2(3b_2)^2$	78.2
	$...(8a_1)^1(9a_1)^2(3b_1)^2(3b_2)^2$	5.0
	$...(8a_1)^1(9a_1)^2(3b_1)^1(4b_1)^1(3b_2)^2$	1.7
	$...(8a_1)^1(9a_1)^2(3b_1)^2(3b_2)^1(4b_2)^1$	1.7
$2^2\Sigma^+$	$...(8a_1)^2(9a_1)^1(3b_1)^2(3b_2)^2$	12.9
	$...(8a_1)^1(9a_1)^2(3b_1)^2(3b_2)^2$	54.8
	$...(8a_1)^1(9a_1)^2(3b_1)^1(4b_1)^1(3b_2)^2$	8.4
	$...(8a_1)^1(9a_1)^2(3b_1)^2(3b_2)^1(4b_2)^1$	8.4

The 0–0 ionization energies and the FCFs of the 0–0 transitions are given in Table 2, which shows that the FCF of the 0–0 transitional of the $1^2\Sigma^+$ state is almost 1.

The reference functions and the weight of the reference function of the MRSDCI calculations at the optimized geometry are given in Table 3. The main configurations of the $1^2\Pi$ and $2^2\Pi$ states are $...(9a_1)^2$ $(2b_1)^2$ $(3b_1)^1$ $(2b_2)^2$ $(3b_2)^2$ and $...(9a_1)^2$ $(2b_1)^1$ $(3b_1)^2$ $(2b_2)^2$ $(3b_2)^2$, respectively. For the $2^2\Pi$ state, the weight of the smain configuration is 53.3%. The total weight of the other configurations corresponding to the single excitations of $(3b_1)^{-1} \rightarrow (2b_1)^1$, $(3b_1)^{-1} \rightarrow (4b_1)^1$ and $(3b_2)^{-1} \rightarrow (4b_2)^1$ is 27%. The weight of the configuration with the double excitation of $(3b_1)^{-2} \rightarrow (2b_1)^1$ $(4b_1)^1$ is 4.9%. The main configurations of the $1^2\Sigma^+$ and $2^2\Sigma^+$ states are $...(8a_1)^2$ $(9a_1)^1$ $(3b_1)^2$ $(3b_2)^2$ and $...(8a_1)^1$ $(9a_1)^2$ $(3b_1)^2$ $(3b_2)^2$, respectively. For the $2^2\Sigma^+$ state, the weight of the main configuration is 54.8%. The total weight of the other configurations corresponding to the single

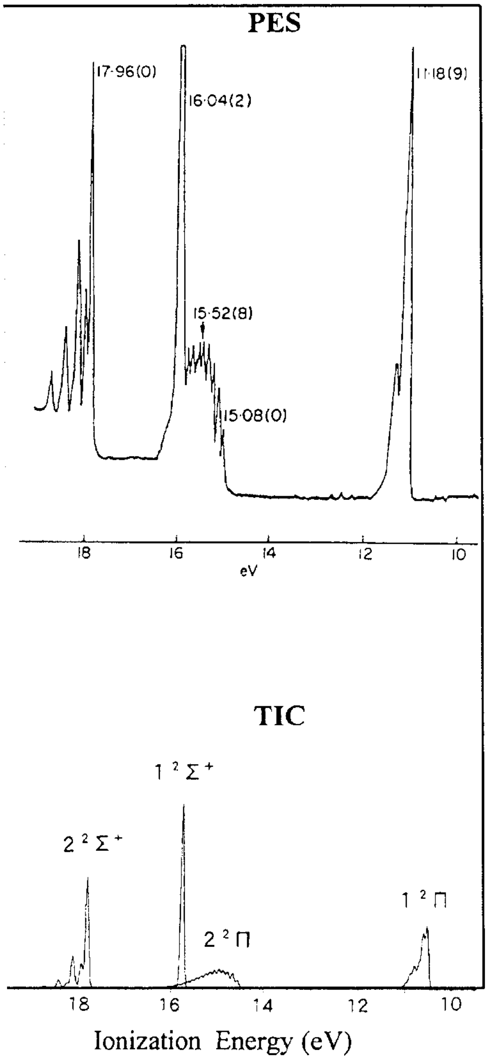

Fig. 1. Overall features of the theoretical intensity curve (TIC) of ionization with a half width of 0.08 eV and the observed photoelectron spectrum (PES) from Ref. [1]

excitations of $(8a_1)^{-1} \rightarrow (7a_1)^1$, $(3b_1)^{-1} \rightarrow (4b_1)^1$ and $(3b_2)^{-1} \rightarrow (4b_2)^1$ is 29.7%.

The vibrational frequencies of the totally symmetric stretching mode of the ground and ionic states are shown in Table 4. The ν_1 and ν_2 modes are characterized as the C–S and C–O stretching modes, respectively.

The overall features of the TIC with a half width of 0.08 eV are compared with the PES observed by Turner et al. [1] in Fig. 1. The TIC reproduces the vibrational structure of the PES except for the first ionic state.

A more resolved vibrational structure of the first ionic state ($1^2\Pi$) and an assignment of the vibrational structure are shown in Fig. 2. The vibrational structure of the PES was assigned as the (0 0), (1 0), (2 0), (0 1), and (1 1) transitions as given by Turner et al. [1]. They reported that the FCFs of the (0 0), (1 0), (2 0), (0 1), and (1 1) transitions were 0.48, 0.28, 0.08, 0.12, and 0.06, respectively, whereas in the present calculations, the FCFs are 0.326, 0.285, 0.125, 0.093, and 0.076, respectively; The FCF of the (0 0) transition is underestimated compared

Table 4. Vibrational frequency (cm^{-1}) of the totally symmetric stretching mode. The experimental values of $^1\Sigma^+$ are from Ref. [10]. The experimental values of the ionic states are from Ref. [1]

State	ν_1 (C–S)		ν_2 (C–O)	
	Calculated	Experimental	Calculated	Experimental
$^1\Sigma^+$	904	859	2161	2062
$1^2\Pi$	697	650 ± 50	2166	2000 ± 50
$2^2\Pi$	843	790 ± 50	2282	2050 ± 50
$1^2\Sigma^+$	870	–	1934	–
$2^2\Sigma^+$	996	970 ± 50	2490	2170 ± 50

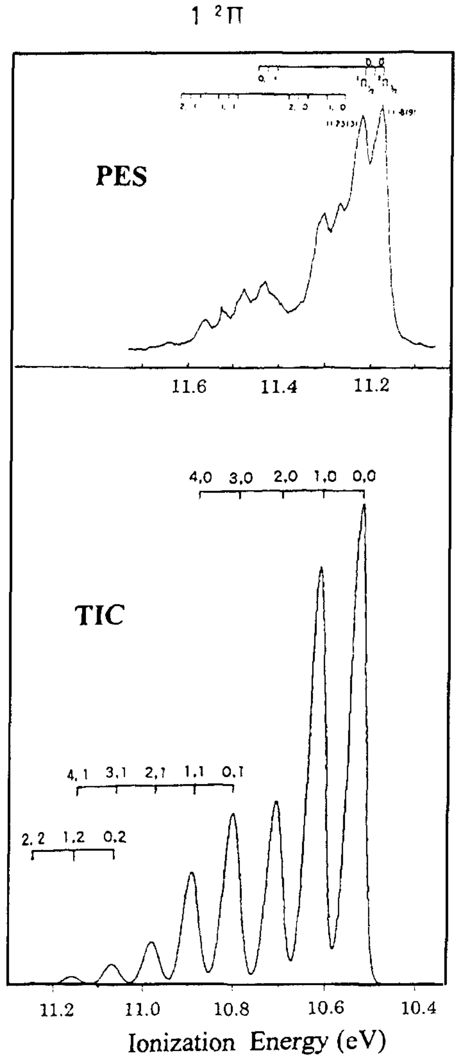

Fig. 2. TIC of the $1^2\Pi$ state with a half width of 0.02 eV and the PES from Ref. [1]

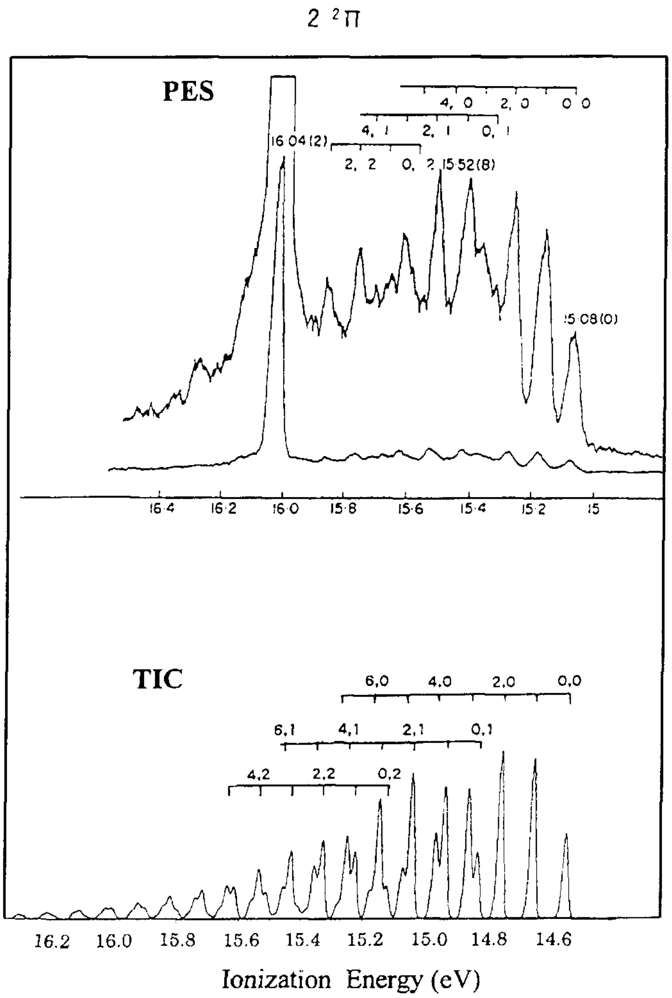

Fig. 3. TIC of the $2^2\Pi$ state with a half width of 0.02 eV and the PES from Ref. [1]

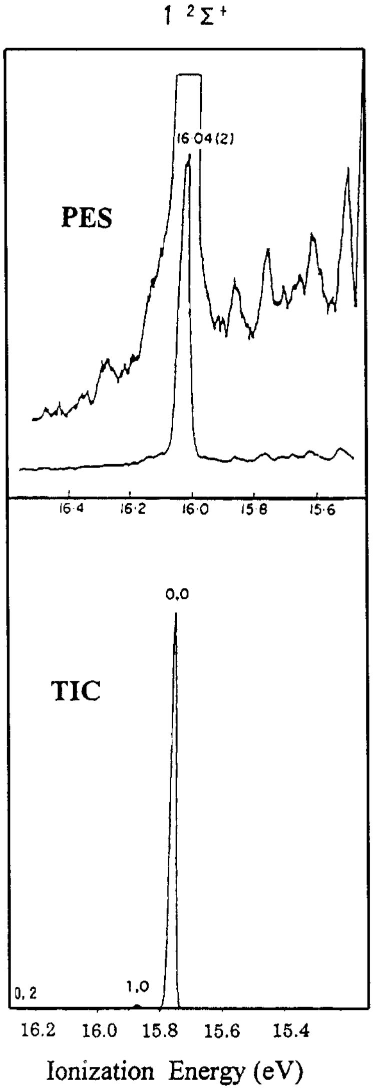

Fig. 4. TIC of the $1^2\Sigma^+$ state with a half width of 0.02 eV and the PES from Ref. [1]

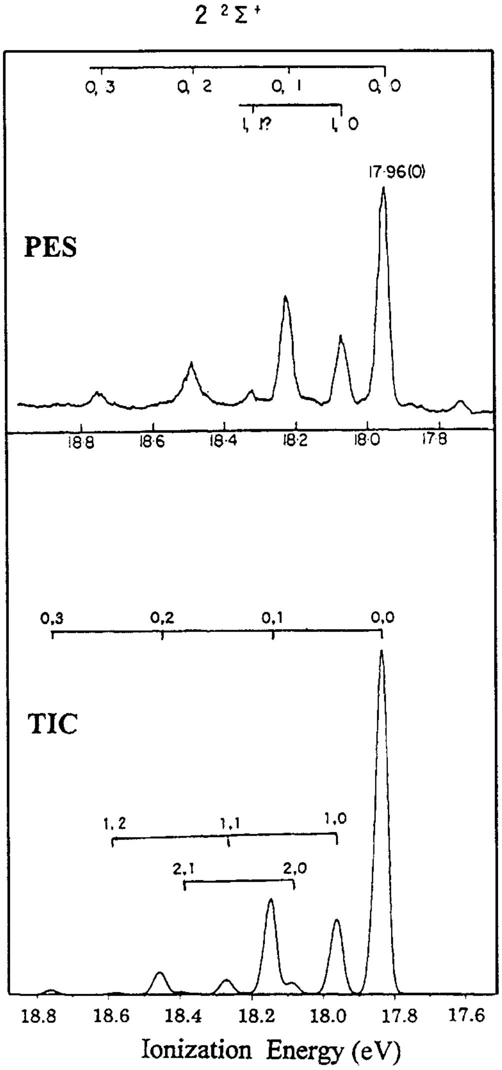

Fig. 5. TIC of the $2^2\Sigma^+$ state with a half width of 0.02 eV and the PES from Ref. [1]

with the observed one, a situation connected with the fact that the magnitude of the changes of the geometrical parameters upon ionization may be overestimated. Table 1 shows that the magnitude of the changes in the C–S and C–O bond lengths are 0.086 and −0.028 Å, respectively. The present calculation, in which the C–S bond length may have been overestimated, suggests the possibility of (3 0), (4 0), (2 1), (3 1), (4 1), (1 2), and (2 2) transitions; however, these transitions were not found in the PES observed. This may also be connected to the fact of the overestimation of the magnitude of the change in the C–S bond length. The vibrational excitation of the ν_1 and ν_2 modes contributes to the intensity. The calculated values of the ν_1 and ν_2 frequencies are 697 and 2166 cm^{-1}, respectively, while the observed values were 650 ± 50 and 2000 ± 50 cm^{-1}, respectively.

The vibrational structure of the second ionic state ($2\,^2\Pi$) is shown in Fig. 3. The vibrational structure of the TIC with a half width of 0.02 eV reproduces that of the PES well. The strong peak at 16.04 eV in the PES is due to the third ionic state ($1^2\Sigma^+$). Three vibrational progressions are found in the TIC: the (n 0, n = 0–7), (n 1, n = 0–6), and (n 2, n = 0–5) transitions. The FCFs of the (0 0)–(7 0) transitions are 0.042, 0.080, 0.083, 0.065, 0.043, 0.025, 0.014, and 0.007. The FCFs of the (0 1)–(6 1) transitions are 0.033, 0.066, 0.073, 0.060, 0.042, 0.026, and 0.015. The FCFs of the (0 2)–(5 2) transitions are 0.016, 0.033, 0.039, 0.034, 0.025, and 0.016. Delwiche et al. [2] obtained a well-resolved He(I) PES of the second ionic state and the vibrational structure of the present TIC reproduces well that of Delwiche et al. except for the spin–orbit splitting. The present assignment of the vibrational structure is consistent with their assignment. The vibrational excitation of the ν_1 and ν_2 modes contributes to the intensity. The calculated values of the ν_1 and ν_2 frequencies are 843 and 2282 cm^{-1}, respectively, while the observed values were 790 ± 50 and 2050 ± 50 cm^{-1}, respectively.

A more resolved vibrational structure of the third ionic state ($1^2\Sigma^+$) of the TIC with a half width of 0.02 eV is shown in Fig. 4. The three vibrational transitions of the (0 0), (1 0), and (0 2) levels are recognized.

The FCFs of the (0 0), (1 0), and (0 2) transitions are 0.990, 0.007, and 0.001, respectively, with the intensity of the (0 0) transition being almost 1. The (1 0) transition has some intensity, but this peak would not be distinguishable from other peaks as it should overlap the peaks of the higher–energy region of the $2^2\Pi$ states that have the same order of intensity as the (1 0) transition of the $1^2\Sigma^+$ state.

The vibrational structure of the fourth ionic state ($2\ {}^2\Sigma^+$) is shown in Fig. 5. The vibrational structure of the TIC with a half width of 0.02 eV reproduces well that of the PES. In the TIC, three vibrational progressions are found: the (0 n, $n = 0$–3), (1 n, $n = 0$–2), and (2 n, $n = 0$–1) transitions. The assignment of the vibrational structure agrees well with that of Delwiche et al., except for the (1 2) transition. The FCFs of the (0 0)–(0 3) transitions are 0.597, 0.167, 0.040, and 0.008. The FCFs of the (1 0), (1 1), and (1 2) transitions are 0.132, 0.025, and 0.004, respectively. The FCFs of the (2 0) and (2 1) transitions are 0.019 and 0.003, respectively. Turner et al. assigned the vibrational progression to the (0 n, $n = 0$–3) and (1 n, $n = 0$–1) transitions. The present calculation reveals that the (2 n, $n = 0$–1) and (1 2) transitions also contribute to the spectrum. Delwiche et al. referred to the (2 n, $n = 0$–1) transition and assigned the weak peak at 18.6 eV as the excitation of the bending mode. The present calculations suggest that the (1 2) transition has intensity at 18.6 eV and that they should correspond. The vibrational excitation of the v_1 and v_2 modes contribute to the intensity. The calculated values of the v_1 and v_2 frequencies are 996 and 2490 cm^{-1}, respectively, while the observed values of the v_1 and v_2 frequencies were 970 ± 50 and 2490 ± 50 cm^{-1}, respectively.

4 Conclusion

We studied the vibrational eigenfunctions, the FCFs, and the approximate TICs of the four ionic states ($1^2\Pi$, $2^2\Pi$, $1^2\Sigma^+$, and $2^2\Sigma^+$) of OCS by explicit vibrational calculations using the global region of the potential-energy surface at the MRSDCI level.

The theoretical intensity curves reproduced the PES well except for the spin–orbit splitting and the first ionic state. The present calculations support the assignments of the vibrational structures by Turner et al. Delwiche et al. reported a more resolved PES, and our assignment of the vibrational structures is almost in congruence with their assignment.

The present calculations indicate the following additional assignment: the weak peak at 18.6 eV of the fourth ionic state should be assigned to the (1 2) transition.

The present calculation of the first ionic state gives an underestimation of the FCF of the (0 0) transition compared with the observed value. This may be connected with the overestimation of the magnitude of the change in the C–S bond lengths upon ionization. We expect that a more advanced theoretical study, which includes the spin–orbit energy, will present a clearer picture of this problem.

Acknowledgements. This work was supported by the Joint Studies Program (1995–1996) of the Institute for Molecular Science (IMS). Some of the calculations were performed using the IBM RS/6000 SP2 cluster in the Computer Center of the IMS.

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