A theoretical study on the ionization of CO$_2$ and CS$_2$ with analysis of the vibrational structure of the photoelectron spectra

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Ab initio calculations have been performed to study the molecular structures and the vibrational levels of the low-lying ionic states ($^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_u^+$, and $^2\Sigma_g^+$) of CO$_2$ and CS$_2$. The global regions of the potential energy surfaces have been obtained by multireference single and double excitation configuration interaction calculations. The vibrational calculations using the explicit vibrational Hamiltonians have been used for the vibrational analysis. The equilibrium molecular structures and the vibrational analysis of the 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 spectra. © *2000 American Institute of Physics.* [S0021-9606(00)30324-5]

I. INTRODUCTION

The electronic configuration of the ground state of carbon dioxide and carbon disulphide are represented by $\cdots(4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^4$ and $\cdots(6\sigma_g)^2(5\sigma_u)^2(2\pi_u)^4(2\pi_g)^4$ with the D_{*h} symmetry group, respectively. The two molecules have the same type of the electronic configuration of the valence electrons.

The He(I) photoelectron spectroscopy investigation of CO$_2$ and CS$_2$ has been published by Turner *et al.*[1] The four ionic states were observed below 19 eV. The spectrum shows a well-resolved vibrational structure and an assignment of the structure has been reported.

The theoretical study of the photoelectron spectrum has been reported by Kimura *et al.*[2] They have obtained the vertical ionization energies.

As far as we are aware, there is no theoretical study of the molecular structures and vibrational analysis of the ionic states. There is also no theoretical study on the vibrational structures of photoelectron spectra. In this paper, we examine theoretically the molecular structures and the vibrational structure of the photoelectron spectra.

In this work, we use vibrational analysis using the explicit vibrational Hamiltonians, which have the global region of the potential energy surface calculated at the multireference single and double excitation configuration interaction (MRSDCI) level, and the exact G matrix. Using these calculations, we obtained the vibrational wave functions, the Franck–Condon factors (FCFs), and the intensity curves of ionization. The vibrational structure of the photoelectron spectrum is discussed by using the calculated properties.

II. METHOD OF CALCULATIONS

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

The multireference single and double excitation configuration interaction (MRSDCI) method was used to get the global regions of the potential energy surfaces. The basis functions for the MRSDCI calculations of the ionic states were obtained by the open shell Roothaan's restricted Hartree–Fock method. In the MRSDCI method, the singly and doubly excited configuration state functions (CSFs) from 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 $^1\Sigma_g^+$, $^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_u^+$, and $^2\Sigma_g^+$ states of CO$_2$ are 1, 4, 3, 3, and 3, respectively. The number of reference CSFs of the $^1\Sigma_g^+$, $^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_u^+$, and $^2\Sigma_g^+$ states of CS$_2$ are 1, 4, 4, 5, and 3, respectively.

In the MRSDCI calculations, we used the D_{2h} symmetry group instead of the D_{*h} symmetry group. For the CO$_2$ molecule, the electronic configuration $\cdots(4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^4$ in the D_{*h} symmetry group correlates to $\cdots(4a_g)^2(3b_{1u})^2(1b_{2u})^2(1b_{3u})^2(1b_{3g})^2(1b_{2g})^2$ in the D_{2h} symmetry group. For the CS$_2$ molecule, the electronic configuration $\cdots(6\sigma_g)^2(5\sigma_u)^2(2\pi_u)^4(2\pi_g)^4$ in the D_{*h} symmetry group correlates to $\cdots(6a_g)^2(5b_{1u})^2(2b_{2u})^2(2b_{3u})^2(2b_{3g})^2(2b_{2g})^2$ in the D_{2h} symmetry group.

The vibrational energies and eigenfunctions were obtained by the basis set expansion method.[5] The method of

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TABLE I. Optimized structure of CO$_2$ and magnitude of the change in the bond length upon ionization. The bond lengths are in angstroms. The values in parentheses are the magnitude of the change in geometry upon ionization. The experimental value is from Herzberg (Ref. 10).

State	$R_{\text{C-O}}$	$(\Delta R_{\text{C-O}})$
$^1\Sigma_g^+$	1.159	
Expt	1.162	
$^2\Pi_g$	1.177	$(+0.018)$
$^2\Pi_u$	1.219	$(+0.060)$
$^2\Sigma_u^+$	1.174	$(+0.015)$
$^2\Sigma_g^+$	1.150	(-0.009)

calculation of the FCFs and theoretical intensity curves was the same as we used in the above-mentioned paper.

This work was carried out by using the computer program system ALCHEMY II[6–8] for the MRSDCI calculations. The program system VIBR4[9] was used for the calculations of the vibrational analysis considering the global region of the potential energy surface.

III. RESULTS AND DISCUSSION

A. CO$_2$

The optimized geometrical parameters of the ground and four ionic states ($^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_u^+$, and $^2\Sigma_g^+$) are listed in Table I, which also shows a magnitude of the change in the C–O bond length upon ionization. The magnitude of the change for the $^2\Pi_u$ state is larger than that of the other states.

Table II gives the 0–0 ionization energies (I.Es) and the Franck–Condon factors (FCFs) of the 0–0 transitions compared with the experimental values. The 0–0 transitions of the $^2\Pi_g$, $^2\Sigma_u^+$, and $^2\Sigma_g^+$ states have maximum intensity in their vibrational levels.

Table III gives the reference functions and the weight of the reference function of the MRSDCI calculations at the optimized geometry. The main configurations of the $^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_u^+$, and $^2\Sigma_g^+$ states correspond to the single electron ionization of $(1b_{3g})^{-1}$, $(1b_{2u})^{-1}$, $(3b_{1u})^{-1}$, and $(4a_g)^{-1}$ from the main configuration of the ground state, respectively. For the $^2\Pi_u$ state, the other configurations with the double excitations of $(1b_{3g})^{-2} \rightarrow (1b_{2u})^1 (2b_{2u})^1$ and $(1b_{2g})^{-1}(1b_{3g})^{-1} \rightarrow (1b_{2u})^1(2b_{3u})^1$ compared with the main configuration of $^2\Pi_u$ are important. For the $^2\Sigma_u^+$ state, the configurations with the double excitations of $(4a_g)^{-1}(1b_{3g})^{-1} \rightarrow (3b_{1u})^1(2b_{2u})^1$, and $(4a_g)^{-1}(1b_{2g})^{-1} \rightarrow (3b_{1u})^1(2b_{3u})^1$ contribute to energy lowering. For the

TABLE III. The reference functions of the MRSDCI calculation of CO$_2$. The total energies of the $^1\Sigma_g^+$ state is $-187.724\,19$ a.u. In the MRSDCI calculations, we used the D_{2h} symmetry group instead of the D_v symmetry group.

State	Reference function	Weight (%)
$^1\Sigma_g^+$	$\cdots (4a_g)^2(3b_{1u})^2(1b_{2u})^2(1b_{3u})^2(1b_{2g})^2(1b_{3g})^2$	89.8
$^2\Pi_g$	$\cdots (4a_g)^2(3b_{1u})^2(1b_{2u})^2(1b_{3u})^2(1b_{2g})^2(1b_{3g})^1$	84.5
	$\cdots (4a_g)^2(3b_{1u})^2(1b_{2u})^1(2b_{2u})^1(1b_{3u})^2(1b_{2g})^2(1b_{3g})^1$	2.9
	$\cdots (4a_g)^2(3b_{1u})^2(2b_{2u})^2(1b_{3u})^2(1b_{2g})^2(1b_{3g})^1$	1.5
	$\cdots (4a_g)^2(3b_{1u})^2(1b_{2u})^2(1b_{3u})^2(2b_{3u})^1(1b_{2g})^1(1b_{3g})^2$	0.7
$^2\Pi_u$	$\cdots (4a_g)^2(3b_{1u})^2(1b_{2u})^1(1b_{3u})^2(1b_{2g})^2(1b_{3g})^2$	76.0
	$\cdots (4a_g)^2(3b_{1u})^2(1b_{2u})^2(2b_{2u})^1(1b_{3u})^2(1b_{2g})^2$	6.8
	$\cdots (4a_g)^2(3b_{1u})^2(1b_{2u})^2(1b_{3u})^2(2b_{3u})^1(1b_{2g})^1(1b_{3g})^1$	5.1
$^2\Sigma_u^+$	$\cdots (4a_g)^2(3b_{1u})^1(1b_{2u})^2(1b_{3u})^2(1b_{2g})^2(1b_{3g})^2$	82.5
	$\cdots (4a_g)^1(3b_{1u})^2(1b_{2u})^2(2b_{2u})^1(1b_{3u})^2(1b_{2g})^2(1b_{3g})^1$	3.2
	$\cdots (4a_g)^1(3b_{1u})^2(1b_{2u})^2(1b_{3u})^2(2b_{3u})^1(1b_{2g})^1(1b_{3g})^2$	3.2
$^2\Sigma_g^+$	$\cdots (4a_g)^1(3b_{1u})^2(1b_{2u})^2(1b_{3u})^2(1b_{2g})^2(1b_{3g})^2$	80.1
	$\cdots (4a_g)^2(3b_{1u})^1(1b_{2u})^2(2b_{2u})^1(1b_{3u})^2(1b_{2g})^2(1b_{3g})^1$	4.4
	$\cdots (4a_g)^2(3b_{1u})^1(1b_{2u})^2(1b_{3u})^2(2b_{3u})^1(1b_{2g})^1(1b_{3g})^2$	4.4

$^2\Sigma_g^+$ state, the configurations with the double excitations of $(3b_{1u})^{-1}(1b_{3g})^{-1} \rightarrow (4a_g)^1(2b_{2u})^1$ and $(3b_{1u})^{-1}(1b_{2g})^{-1} \rightarrow (4a_g)^1(2b_{3u})^1$ are important.

Vibrational frequencies of the totally symmetric streching mode for the ground and ionic states are shown in Table IV.

Figure 1 illustrates the overall feature of the theoretical intensity curve (TIC) with a half width of 0.08 eV compared with the observed photoelectron spectrum (PES). The theoretical intensity curve reproduces the vibrational structure of the photoelectron spectrum. The spectrum of the second ionic state ($^2\Pi_u$) has a broad appearance which is attributed to the large change in C–O bond length upon ionization; the change is more than three times as large as that of the other states.

Figure 2 shows a more resolved PES of the first ionic state ($^2\Pi_g$) from Turner et al., where the (0 0 2) peak is observed. It was assigned to the vibrational excitation of the antisymmetric stretching mode. We used vibrational analysis including the antisymmetric modes. The theoretical intensity curve with a half width of 0.02 eV is illustrated in Fig. 2. The vibrational structure of the theoretical intensity curve reproduces well that of the photoelectron spectrum. The Franck–Condon factor of the vibrational excitation of the antisymmetric mode usually has a negligibly small value. However, it has considerable value if the difference of the

TABLE II. The 0–0 transitional state of CO$_2$. The experimental values are from Turner et al. (Ref. 1). The calculated value of FCF is obtained by considering only the symmetric stretching mode.

State	I.E. (eV)	Expt (eV)	FCF	Expt
$^2\Pi_g$	12.72	13.78	0.81	0.81
$^2\Pi_u$	16.55	17.32	0.10	0.08
$^2\Sigma_u^+$	17.36	18.08	0.86	0.85
$^2\Sigma_g^+$	18.55	19.40	0.95	0.91

TABLE IV. Vibrational frequency of the totally symmetric stretching mode (cm^{-1}) of CO$_2$. The experimental value of $^1\Sigma_g^+$ is from Herzberg (Ref. 10). The experimental values of the ionic states are from Turner et al. (Ref. 1).

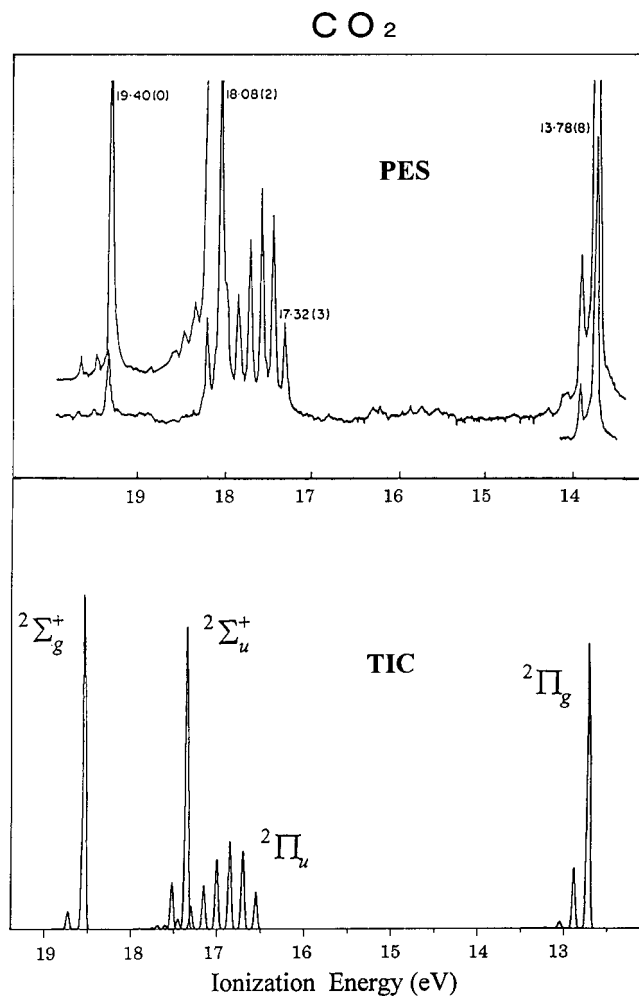| State	Calc	Expt
$^1\Sigma_g^+$	1425	1337
$^2\Pi_g$	1324	1210 ± 50
$^2\Pi_u$	1217	1100 ± 50
$^2\Sigma_u^+$	1336	1270 ± 50
$^2\Sigma_g^+$	1458	1390 ± 50

FIG. 1. The overall feature of the theoretical intensity curve of ionization of CO_2 half width of 0.08 eV and the observed photoelectron spectrum from Turner *et al.* (Ref. 1). TIC: Theoretical intensity curve; PES: photoelectron spectrum.
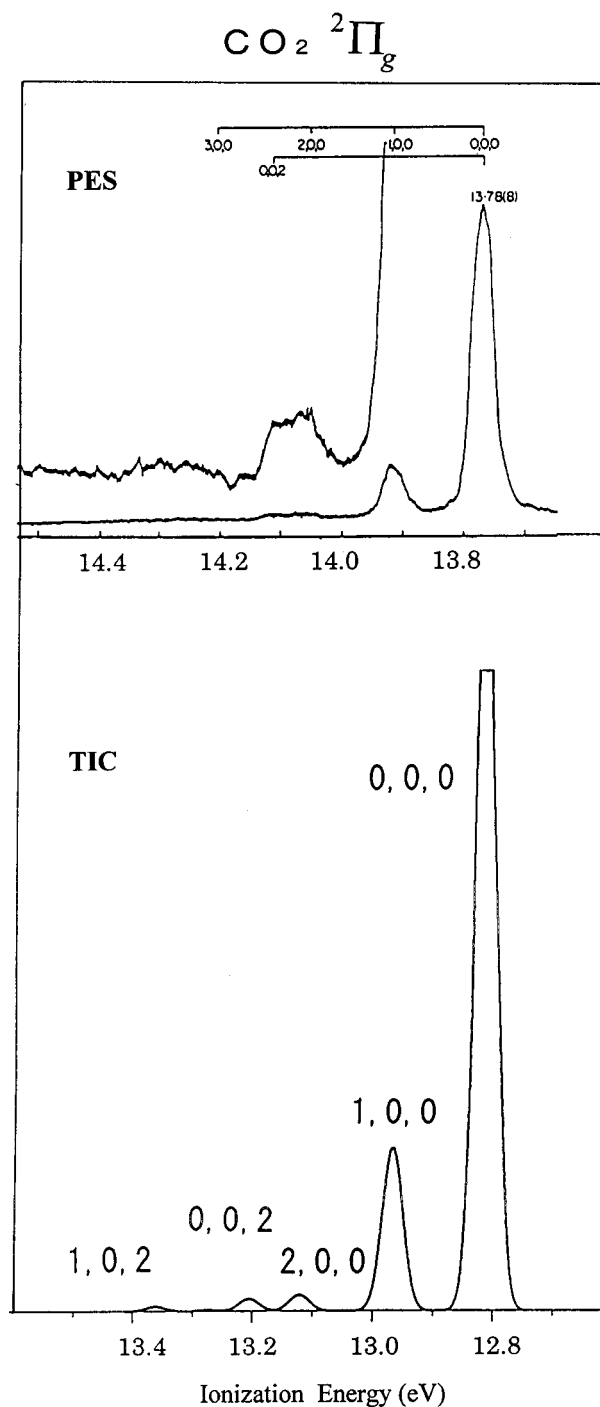

FIG. 2. The theoretical intensity curve of the $^2\Pi_g$ state of CO_2 with a half width of 0.02 eV and the PE spectrum from Turner *et al.* (Ref. 1).

vibrational frequencies between the final and initial states is large. In this case, vibrational transitions with an even quantum number are possible. Table V gives the vibrational levels including the antisymmetric stretching mode of the initial ($^1\Sigma_g^+$) and final ($^2\Pi_g$) states. The frequencies of the (0 0 1) antisymmetric stretching mode of the initial and final states are 2468 and 1405 cm^{-1}, respectively. The difference between the two is 1063 cm^{-1}. Table V reveals that the FCFs of the (0 0 2) and (1 0 2) transitions have considerable values. Turner *et al.* have assigned the (3 0 0) transition. The calculated value of FCF of the (3 0 0) transition is 0.001. The peak should be found at 13.28 eV. However, this transition is not recognized in the theoretical intensity curve. The calculated values of the ν_1 and ν_3 frequencies are 1243 and 1405 cm^{-1}, respectively. The observed values of the ν_1 and ν_3 frequencies are 1210 ± 50 and $1420\pm50\,cm^{-1}$, respectively.

Figure 3 shows the vibrational structure of the second and third ionic states ($^2\Pi_u$ and $^2\Sigma_u^+$). The vibrational structure of the TIC with a half width of 0.02 eV reproduces well that of the PES. The vibrational structure of the $^2\Pi_u$ state is assigned to the (n 0 0, $n=0-10$) transitions. The FCFs of the (0 0 0)–(10 0 0) transitions are 0.095, 0.204, 0.236, 0.195,

0.130, 0.074, 0.037, 0.017, 0.007, 0.003, and 0.001. The vibrational structure of the $^2\Sigma_u^+$ state is assigned to the (n 0 0, $n=0-3$) transitions. The FCFs of the (0 0 0), (1 0 0), and (2 0 0) transitions are 0.857, 0.132, and 0.011, respectively. These assignments are consistent with that of Turner *et al.*, who proposed the possibility of the observation of the (0 0 2) transition. We examined the possibility of this transition. We could not, however, recognize this transition. The calculated and observed values of the ν_1 frequencies of $^2\Pi_u$ are 1217 and $1100\pm50\,cm^{-1}$, respectively. The calculated and ob-

TABLE V. Vibrational levels including antisymmetric stretching mode of CO_2.

Level	$^1\Sigma_g^+$ state		$^2\Pi_g$ state		
	cm^{-1}	Mode	cm^{-1}	Mode	FCF
1	0	0 0 0	0	0 0 0	0.793
2	1417	1 0 0	1243	1 0 0	0.169
3	2468	0 0 1	1405	0 0 1	
4	2829	2 0 0	2484	2 0 0	0.017
5	3866	1 0 1	2665	1 0 1	
6	4235	3 0 0	3163	0 0 2	0.013
7	4912	0 0 2	3727	3 0 0	0.001
8	5259	2 0 1	3934	2 0 1	
9	5636	4 0 0	4422	1 0 2	0.005
10	6292	2 0 2	4976	4 0 0	

served values of the ν_1 frequencies of $^2\Sigma_u^+$ are 1336 and 1270 ± 50 cm^{-1}, respectively.

The fourth ionic state is the $^2\Sigma_g^+$ state. The vibrational structure of the TIC in Fig. 1 is assigned to the $(n\ 0\ 0,\ n = 0-1)$ transitions. The FCFs of the $(0\ 0\ 0)$ and $(1\ 0\ 0)$ transitions are 0.950 and 0.050, respectively. The calculated value of the ν_1 frequency is 1458 cm^{-1}. The observed value is 1390 ± 50 cm^{-1}.

B. CS₂

The optimized geometrical parameters of the ground and four ionic states ($^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_u^+$, and $^2\Sigma_g^+$) are listed in Table VI. It gives a magnitude of the change in the C–S bond length upon ionization. The magnitude of the change in the bond length of the $^2\Pi_u$ state is larger than that of the other states.

Table VII gives the 0–0 ionization energies and the Franck–Condon factors of the 0–0 transitions. It indicates that the 0–0 transitions of the $^2\Pi_g$, $^2\Sigma_u^+$, and $^2\Sigma_g^+$ states have the maximum intensity.

Table VIII gives the reference functions and the weight of the reference function of the MRSDCI calculations at the optimized geometry. The main configurations of the $^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_u^+$, and $^2\Sigma_g^+$ states correspond, respectively, to the single electron ionization of $(2b_{3g})^{-1}$, $(2b_{2u})^{-1}$, $(5b_{1u})^{-1}$, and $(6a_g)^{-1}$ from the main configuration of the ground state. For the $^2\Pi_u$ state, the weight of the configuration of the double excitation of $(2b_{3g})^{-2} \rightarrow (2b_{2u})(3b_{2u})$ compared with the main configuration of $^2\Pi_u$ is 12.7%. The configurations with the double excitations of $(2b_{3g})^{-2} \rightarrow (3b_{2u})^2$ and $(2b_{2g})^{-1}(2b_{3g})^{-1} \rightarrow (2b_{2u})^1(3b_{3u})^1$ also contribute to this state. For the $^2\Sigma_u^+$ state, the configurations with the double excitations of $(6a_g)^{-1}(2b_{3g})^{-1} \rightarrow (5b_{1u})^1(3b_{2u})^1$ and $(6a_g)^{-1}(2b_{2g})^{-1} \rightarrow (5b_{1u})^1(3b_{3u})^1$ are important. For the $^2\Sigma_g^+$ state, the total weight of the configurations of the double excitations of $(5b_{1u})^{-1}(2b_{3g})^{-1} \rightarrow (6a_g)^1(3b_{2u})^1$ and $(5b_{1u})^{-1}(2b_{2g})^{-1} \rightarrow (6a_g)^1(3b_{3u})^1$ is 18%.

Vibrational frequencies of the totally symmetric streching mode for the ground and ionic states are shown in Table IX.

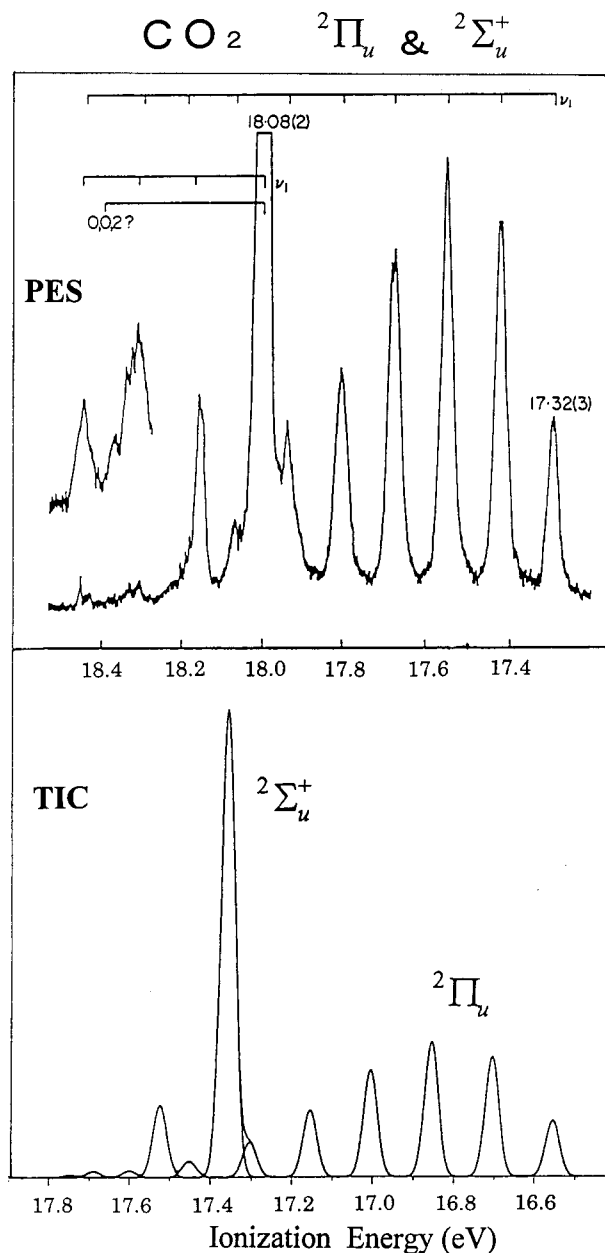Figure 4 illustrates an overall feature of the theoretical intensity curve with a half width of 0.08 eV compared with

FIG. 3. The theoretical intensity curve of the $^2\Pi_u$ and $^2\Sigma_u^+$ states of CO₂ with a half width of 0.02 eV and the PE spectrum from Turner *et al.* (Ref. 1).

the observed photoelectron spectrum. The theoretical intensity curve reproduces well the vibrational structure of the photoelectron spectrum. The spectrum of the second ionic state ($^2\Pi_u$) has a broad appearance, which is attributed to the

TABLE VI. Optimized structure of CS₂ and magnitude of the change in the bond length upon ionization. Bond lengths are in angstroms. The values in parentheses are the magnitude of the change in geometry upon ionization. The experimental value is from Herzberg (Ref. 10).

State	$R_{C\text{-}S}$	$(\Delta R_{C\text{-}S})$
$^1\Sigma_g^+$	1.560	
Expt	1.554	
$^2\Pi_g$	1.570	(+0.010)
$^2\Pi_u$	1.624	(+0.064)
$^2\Sigma_u^+$	1.571	(+0.011)
$^2\Sigma_g^+$	1.544	(−0.017)

TABLE VII. The 0–0 transitional state of CS_2. The experimental values are from Turner *et al.* (Ref. 1). The calculated value of FCF is obtained by considering only the symmetric stretching mode.

State	I. E. (eV)	Expt (eV)	FCF	Expt
$^2\Pi_g$	9.16	10.06	0.94	1.0
$^2\Pi_u$	11.92	12.69	0.08	0.11
$^2\Sigma_u^+$	13.77	14.47	0.93	0.89
$^2\Sigma_g^+$	15.69	16.19	0.83	0.92

TABLE IX. Vibrational frequency of the totally symmetric stretching mode (cm^{-1}) of CS_2. The experimental value of $^1\Sigma_g^+$ is from Herzberg (Ref. 10). The experimental values of the ionic states are from Turner *et al.* (Ref. 1).

State	Calc	Expt
$^1\Sigma_g^+$	704	657
$^2\Pi_g$	672	⋯
$^2\Pi_u$	617	560 ± 50
$^2\Sigma_u^+$	658	600 ± 50
$^2\Sigma_g^+$	721	600 ± 50

large change in the C–S bond length upon ionization, as in the case of CO_2.

Figure 5 shows a more resolved vibrational structure of the first ionic state ($^2\Pi_g$). The vibrational structure of TIC with a half width of 0.02 eV reproduces that of the PES except for the spin–orbit splitting. In the first peak of PES, the spin–orbit splitting is observed. Turner *et al.* have proposed that the shoulder of the first peak should be assigned to the (0 2 0) and (0 4 0) transitions. The present result of the FCF calculation suggests that it should be the (1 0 0) transition. Turner *et al.* have also proposed that the (0 0 2) transition should be observed. Table X gives the vibrational levels, including the antisymmetric stretching mode of the $^1\Sigma_g^+$ and $^2\Pi_g$ states. The frequencies of the (0 0 1) antisymmetric stretching mode of the initial and final states are 1597 and 1377 cm^{-1}, respectively. The difference between the two is 220 cm^{-1}, which is a fifth of that for CO_2. The FCF of the (0 0 2) transition is 0.002 and the (0 0 2) transition with weak intensity is recognizable in the TIC.

Figure 6 shows a more resolved vibrational structure of the second ionic state ($^2\Pi_u$). The vibrational structure of the TIC with a half width of 0.02 eV reproduces well that of the PES. The vibrational progression observed in the TIC is as-

signed to (n 0 0, $n=0-11$) transition. The (0 0 0) transition of the TIC should correspond to the peak at 12.69 eV of the PES. The FCFs of the (0 0 0)–(11 0 0) transitions are 0.043, 0.128, 0.197, 0.209, 0.172, 0.117, 0.069, 0.036, 0.017, 0.007, 0.003 and 0.001. The calculated value of the ν_1 frequency is 617 cm^{-1}. Turner *et al.* have assigned the vibrational structure to the (n 0 0, $n=0-7$) transitions. The observed frequency of ν_1 is 560 ± 50 cm^{-1}.

The third ionic state is the $^2\Sigma_u^+$ state. The 0–0 transition has a maximum intensity. The vibrational structure found in the TIC is assigned to the (n 0 0, $n=0-2$) transitions. The
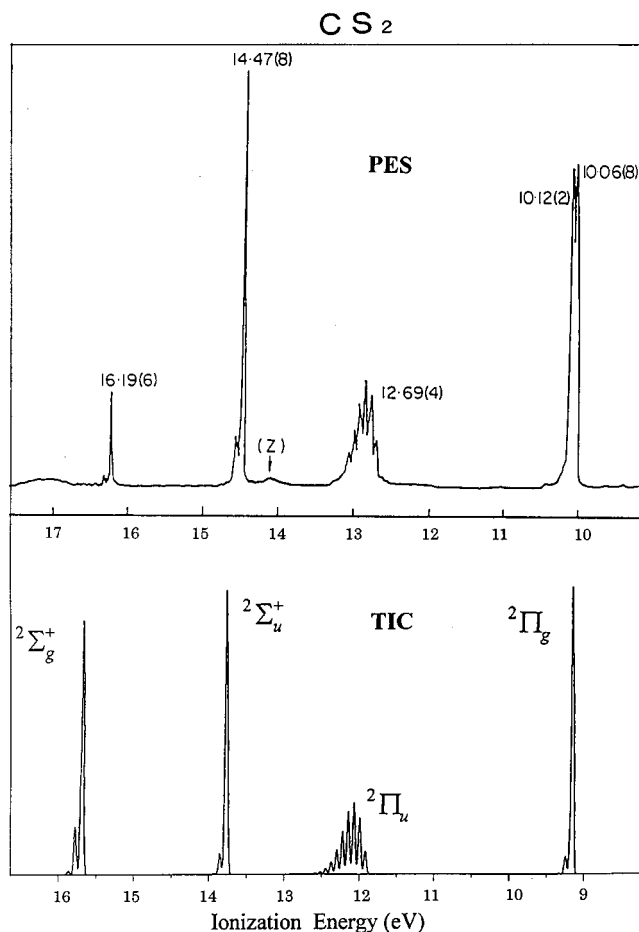
TABLE VIII. The reference functions of the MRSDCI calculation of CS_2. The total energies of the $^1\Sigma_g^+$ state is $-832.341\,173$ a.u. In the MRSDCI calculations, we used the D_{2h} symmetry group instead of the $D_{\infty v}$ symmetry group.

State	Reference function	Weight (%)
$^1\Sigma_g^+$	$\cdots (6a_g)^2 (5b_{1u})^2 (2b_{2u})^2 (2b_{3u})^2 (2b_{2g})^2 (2b_{3g})^2$	86.5
$^2\Pi_g$	$\cdots (6a_g)^2 (5b_{1u})^2 (2b_{2u})^2 (2b_{3u})^2 (2b_{2g})^2 (2b_{3g})^1$	81.4
	$\cdots (6a_g)^2 (5b_{1u})^2 (2b_{2u})^1 (3b_{2u})^1 (2b_{3u})^2 (2b_{2g})^2 (2b_{3g})^1$	2.8
	$\cdots (6a_g)^2 (5b_{1u})^2 (3b_{2u})^2 (2b_{3u})^2 (2b_{2g})^2 (2b_{3g})^1$	1.2
	$\cdots (6a_g)^2 (5b_{1u})^2 (2b_{2u})^1 (2b_{3u})^1 (3b_{3u})^1 (2b_{2g})^2 (2b_{3g})^2$	1.0
$^2\Pi_u$	$\cdots (6a_g)^2 (5b_{1u})^2 (2b_{2u})^1 (2b_{3u})^2 (2b_{2g})^2 (2b_{3g})^2$	65.9
	$\cdots (6a_g)^2 (5b_{1u})^2 (2b_{2u})^2 (3b_{2u})^1 (2b_{3u})^2 (2b_{2g})^2$	12.7
	$\cdots (6a_g)^2 (5b_{1u})^2 (2b_{2u})^1 (3b_{2u})^1 (2b_{3u})^2 (2b_{2g})^2$	4.3
	$\cdots (6a_g)^2 (5b_{1u})^2 (2b_{2u})^2 (2b_{3u})^2 (3b_{3u})^1 (2b_{2g})^1 (2b_{3g})^1$	2.5
$^2\Sigma_u^+$	$\cdots (6a_g)^2 (5b_{1u})^1 (2b_{2u})^2 (2b_{3u})^2 (2b_{2g})^2 (2b_{3g})^2$	78.0
	$\cdots (6a_g)^1 (5b_{1u})^2 (2b_{2u})^2 (3b_{2u})^1 (2b_{3u})^2 (2b_{2g})^2 (2b_{3g})^1$	2.8
	$\cdots (6a_g)^1 (5b_{1u})^2 (2b_{2u})^2 (2b_{3u})^2 (3b_{3u})^1 (2b_{2g})^2 (2b_{3g})^2$	2.8
	$\cdots (6a_g)^2 (5b_{1u})^1 (2b_{2u})^2 (2b_{3u})^2 (3b_{3u})^1 (2b_{2g})^2$	0.9
	$\cdots (6a_g)^2 (5b_{1u})^1 (2b_{2u})^2 (3b_{2u})^2 (2b_{3u})^2 (2b_{2g})^2$	0.9
$^2\Sigma_g^+$	$\cdots (6a_g)^1 (5b_{1u})^2 (2b_{2u})^2 (2b_{3u})^2 (2b_{2g})^2 (2b_{3g})^2$	66.3
	$\cdots (6a_g)^1 (5b_{1u})^2 (2b_{2u})^2 (3b_{2u})^1 (2b_{3u})^2 (2b_{2g})^2 (2b_{3g})^1$	9.1
	$\cdots (6a_g)^2 (5b_{1u})^1 (2b_{2u})^2 (2b_{3u})^2 (3b_{3u})^1 (2b_{2g})^1 (2b_{3g})^2$	9.1

FIG. 4. The overall feature of the theoretical intensity curve of ionization of CS_2 half width of 0.08 eV and the observed photoelectron spectrum from Turner *et al.* (Ref. 1).
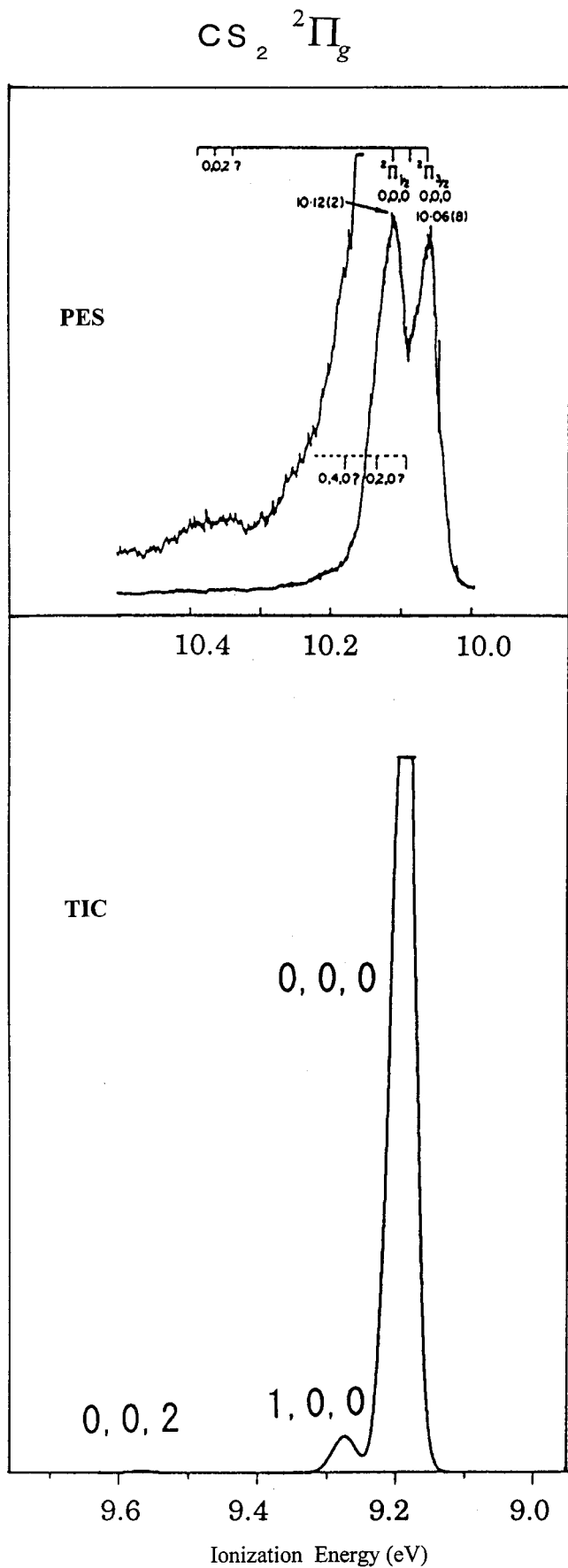
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CS_2 $^2\Pi_g$

TABLE X. Vibrational levels including antisymmetric stretching mode of CS_2.

Level	$^1\Sigma_g^+$ state		$^2\Pi_g$ state		
	cm^{-1}	Mode	cm^{-1}	Mode	FCF
1	0	0 0 0	0	0 0 0	0.956
2	699	1 0 0	648	1 0 0	0.041
3	1396	2 0 0	1287	2 0 0	
4	1597	0 0 1	1377	0 0 1	
5	2091	3 0 0	1919	3 0 0	
6	2288	1 0 1	2048	1 0 1	
7	2785	4 0 0	2540	4 0 0	
8	2977	2 0 1	2693	2 0 1	
9	3180	0 0 2	3012	0 0 2	0.002
10	3477	5 0 0	3136	5 0 0	

FCFs of the (0 0 0), (1 0 0), and (2 0 0) transitions are 0.930, 0.068, and 0.002, respectively. The calculated value of the ν_1 frequency is 658 cm^{-1}. The observed value is 600 $\pm 50\, cm^{-1}$.

CS_2 $^2\Pi_u$

FIG. 5. The theoretical intensity curve of the $^2\Pi_g$ state of CS_2 with a half width of 0.02 eV and the PE spectrum from Turner et al. (Ref. 1).
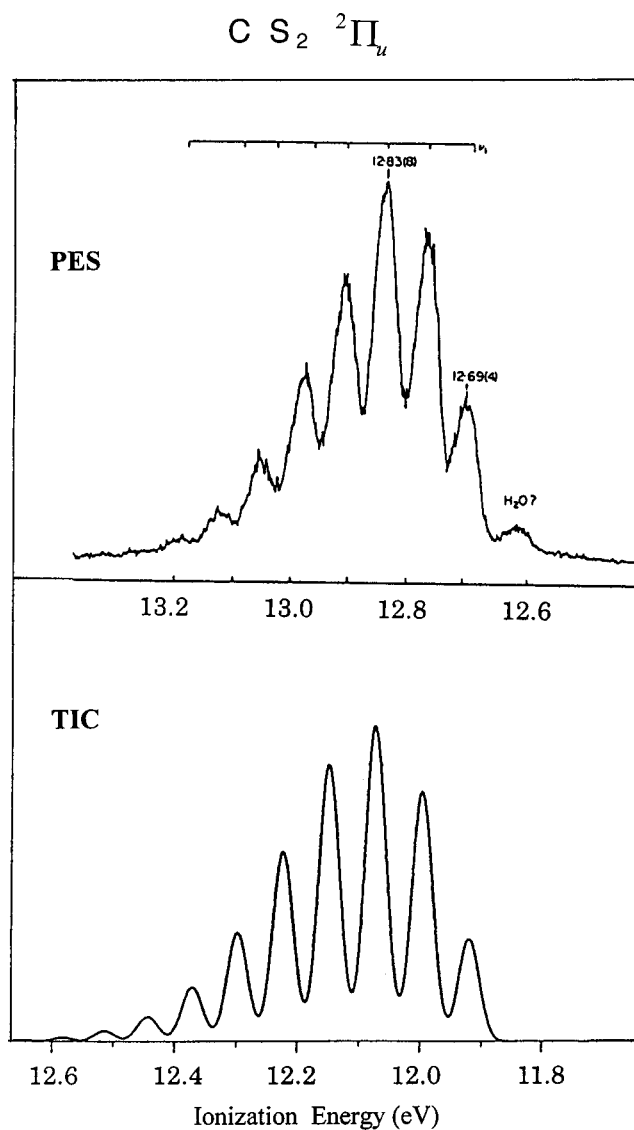
FIG. 6. The theoretical intensity curve of the $^2\Pi_u$ state of CS_2 with a half width of 0.02 eV and the PE spectrum from Turner et al. (Ref. 1).

The fourth ionic state is the $^2\Sigma_g^+$ state. The vibrational structure in Fig. 4 is assigned to the $(n\,0\,0, n=0-2)$ transitions. The FCFs of the $(0\,0\,0)$, $(1\,0\,0)$, and $(2\,0\,0)$ transitions are 0.831, 0.157, and 0.012, respectively. The calculated value of the ν_1 frequency is 721 cm^{-1}. The observed value is 600 ± 50 cm^{-1}.

IV. CONCLUSIONS

We have studied the vibrational eigenfunctions, the Franck–Condon factors, and the theoretical intensity curves of the four ionic states ($^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_u^+$ and $^2\Sigma_g^+$) of CO_2 and CS_2 by explicit vibrational calculations using the global region of the potential energy surface at the MRSDCI level.

The theoretical intensity curves reproduce well the PE spectra. An assignment of the vibrational structures agrees in most cases with that by Turner *et al.*

For the first ionic state ($^2\Pi_g$) of CO_2, the vibrational excitations of the antisymmetric stretching mode should be observed. This situation is connected with the fact that the difference of the vibrational frequencies of the antisymmetric stretching mode between the final and initial states is large. The difference between the two is 1063 cm^{-1}. The FCFs of the $(0\,0\,2)$ and $(1\,0\,2)$ transitions are 0.013 and 0.005, respectively. For the first ionic state ($^2\Pi_g$) of CS_2, the difference between the two is 220 cm^{-1}, which is a fifth of that for CO_2. The FCF of the $(0\,0\,2)$ transition is 0.002.

The spectra of the second ionic states ($^2\Pi_u$) of CO_2 and CS_2 have broad features compared with the other states. This is attributed to the large change (~0.06 Å) in the bond length upon ionization. The change of the $^2\Pi_u$ state is more than three times as large as that of the other states.

ACKNOWLEDGMENTS

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