Optical Excitation and Absorption Spectra of C_{2v} and D_{2d} Isomers of CO_4

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Z. Naturforsch. **63a,** 170 – 174 (2008); received September 29, 2007

Recently the CO_4 isomer with C_{2v} symmetry has been detected in an experiment [C. S. Jamieson et al., Chem. Phys. Lett. **440**, 105 (2007)]. To further characterize this isomer, we report its optical excitation and absorption spectra calculated by the time-dependent density functional theory. Its rich spectral features are compared with those of another stable isomer having D_{2d} symmetry. Their spectral difference can be an evidence to distinguish the isomers in experiments.

Key words: CO_4; Vibrational Frequencies; Optical Excitation; Absorption Spectra.

1. Introduction

In the past few decades high-order carboxides, CO_n ($n > 2$), have received considerable attention [1 – 9]. One of the high-order carboxides, carbon tetraoxide (CO_4), has been calculated to have two lowest energy isomers with the symmetry C_{2v} and D_{2d} [3 – 5], respectively. Their geometries can be seen in Figure 1. Theoretical calculations show the C_{2v} structure lying by 138 kJ mol^{-1} below the D_{2d} structure [3]. The CO_4 molecule has been assumed to be a key intermediate that is formed in irradiated molecular oxygen-carbon dioxide (O_2-CO_2) mixtures as a prerequisite for ozone formation and in explaining the disappearance of oxygen atoms [6]. The CO_4 molecule has also been suggested as a potential high energy molecule due to the large amount of energy that would accompany its dissociation [4, 7]. Cacace et al. [8] indicated the existence of the CO_4 neutral molecule, although they could not tell which structural isomers were produced. Recently, Jamieson et al. [9] reported the first detection of the C_{2v} isomer of CO_4, using infrared spectroscopy in low temperature carbon dioxide ice.

A quantitative understanding of the optical excitations and absorptions of molecules, clusters, and nanocrystals is important in many areas, for example, spectroscopy, photochemistry, and the design of optical materials [10 – 17]. The measurement, prediction, and interpretation of the discrete excitonic spectra of these systems is a demanding and time consuming task. To further characterize the C_{2v} isomer of CO_4, we report its optical absorption spectrum calculated by the time-dependent density functional theory (TD-DFT). The results are compared with another stable isomer with D_{2d} symmetry.

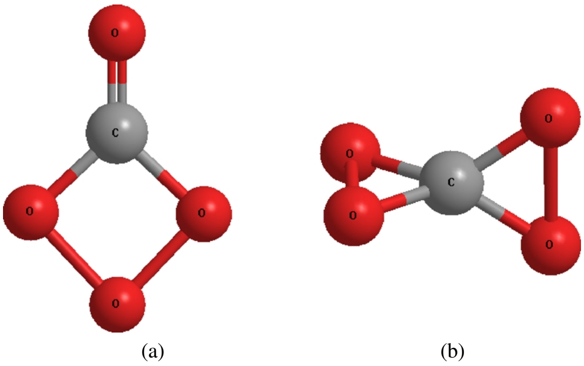

Fig. 1. Optimized B3LYP/6-311+G(2df,2pd) structures of (a) C_{2v} and (b) D_{2d} isomers of CO_4.

TD-DFT [18 – 21] is a common computational technique for computing the excitation energies and photoabsorption spectra of atoms, molecules, and clusters. This technique incorporates electronic screening and relevant correlation effects of electronic excitations and has been successfully applied to atoms, molecules, and clusters [18 – 26]. Therefore we apply the TD-DFT to compute the optical excitation and absorption spectra of the C_{2v} and D_{2d} isomers of CO_4.

2. Computational Details

All calculations were performed using the GAUSSIAN 03 package [27]. We first optimized the ground-state structures of the two CO_4 isomers with the hybrid B3LYP functional [28] and a 6-311+G(2df,2pd)

0932–0784 / 08 / 0300–0170 \$ 06.00

Table 1. Vibrational frequencies (unscaled, scaled and experimental), symmetries, and infrared intensities of the C_{2v} isomer of CO_4 calculated at the B3LYP/6-311+G(2df,2pd) level of theory. The scaling factor is 0.9679.

	$w_1(a_1)$	$w_2(a_1)$	$w_3(a_1)$	$w_4(a_1)$	$w_5(b_2)$	$w_6(b_2)$	$w_7(b_2)$	$w_8(b_1)$	$w_9(b_1)$
Wavenumber (cm^{-1}) (unscaled)	1991	1035	932	791	1121	884	510	729	306
Wavenumber (cm^{-1}) (scaled)	1927	1002	902	766	1085	856	494	706	296
Wavenumber (cm^{-1}) [9]	1941	–	–	–	–	–	–	–	–
Infrared intensity ($km\,mol^{-1}$)	584.0	39.2	1.2	12.5	104.9	1.0	3.5	23.5	1.6

Table 2. Vibrational frequencies (unscaled and scaled), symmetries, and infrared intensities of the D_{2d} isomer of CO_4 calculated at the B3LYP/6-311+G(2df,2pd) level of the theory. The scaling factor is 0.9679.

	$w_1(b_2)$	$w_2(b_2)$	$w_3(a_1)$	$w_4(a_1)$	$w_5(e)$	$w_6(e)$	$w_7(b_1)$
Wavenumber (cm^{-1}) (unscaled)	1663	782	1045	620	1004	539	345
Wavenumber (cm^{-1}) (scaled)	1610	757	1011	600	972	522	334
Infrared intensity ($km\,mol^{-1}$)	455.7	17.4	0.0	0.0	44.4	10.3	0.0

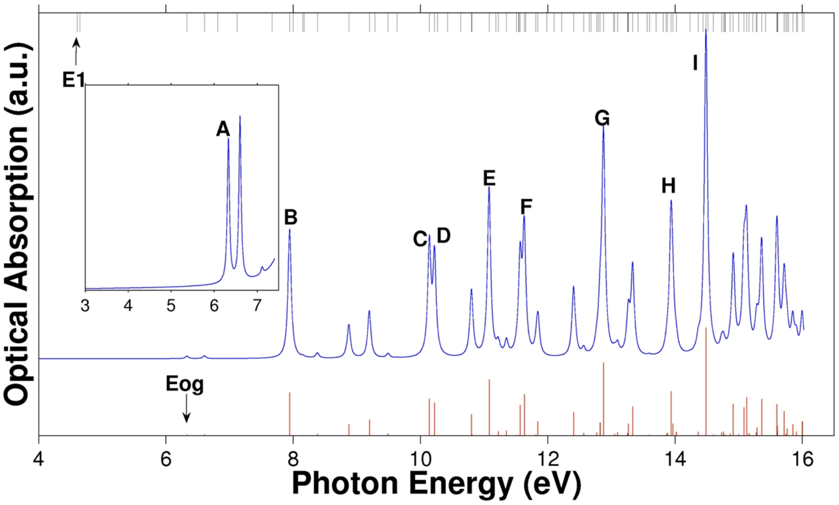

Fig. 2. Optical absorption spectrum of the C_{2v} isomer of CO_4. The vertical lines at the top denote the singlet excitation energies ${}^{(1)}E_i$, and the vertical lines at the bottom represent the oscillator strength f_{osc}. The inset is the enlarged part around the optical gap.

basis set. The basis set we used here is larger than inprevious calculations [18, 19] 6-311G* and 6-311+G* basis sets employed. To compare the vibrational frequencies with previous calculated [3, 9] and experimental results [9], we calculated the vibrational frequencies of the C_{2v} and D_{2d} isomers of CO_4. Based on the optimized ground-state structure, we computed the energy ${}^{(1)}E_i$ [${}^{(3)}E_i$] of the ith singlet (triplet) excited state, the oscillator strengths f_{osc}, and the optical absorption gap E_{og} (defined in general as the exciation energy of the first dipole-allowed transition of atoms and molecules [22 – 26]). To understand the optical excitation, we also computed the excitation participation contribution [24 – 26], P_n^v (i.e., probability P, in percent), of an exciton pair (n,v) to be in a specified excited state, where n and v represent the (HOMO $- n$)th occupied and (LUMO $+ v$)th unoccupied single-electron states of a molecule. For example, (1,3) is a pair state formed by exciting one electron in HOMO $-$ 1 to LUMO $+$ 3 single-electron states.

3. Results and Discussion

3.1. Vibrational Frequency

The calculated vibrational frequencies of the C_{2v} and D_{2d} isomers of CO_4 are listed in Tables 1 and 2, respectively. Since the calculated frequencies are often larger than the observed frequencies, scaling factors are needed. The scaling factors account for anharmonicity effects that are neglected in the theoretical calculations, an inadequate description of electron correlation, and the use of finite basis sets. The recommended value of the scaling factor depends on the level of the theory [29]. In this article, we choose the scaling factor to be 0.9679, which was suggested by Andersson and Uvdal [30]. They claimed that their optimum

Table 3. Exciton pair contribution P_n^v to the first five triplet states, the first and second singlet states and nine dipole-allowed singlet states with largest oscillator strength for the C_{2v} isomer of CO_4 calculated by TD-B3LYP/6-311+G(2df,2pd). E, λ, f_{osc} and $\prod$ denote the energy, wavelength, oscillator strength and degeneracy, respectively. The symmetry is also listed.

State	Symmetry	E (eV)	λ (nm)	$\prod$	f_{osc}	P_n^v
$^{(3)}E_1$	B1	3.542	350.0	1	0.0000	$55_0^0+2_3^0+2_2^1$
$^{(3)}E_2$	A2	3.555	348.8	1	0.0000	$54_0^1+3_3^1+2_2^0$
$^{(3)}E_3$	B2	5.955	208.2	1	0.0000	$45_1^0+7_4^0$
$^{(3)}E_4$	A1	6.002	206.6	1	0.0000	$45_1^1+5_0^2+2_4^1$
$^{(3)}E_5$	A2	6.123	202.5	1	0.0000	$48_2^0+3_3^1+2_7^1$
$^{(1)}E_1$	A2	4.604	269.3	1	0.0000	45_0^1
$^{(1)}E_2$	B1	4.650	266.6	1	0.0000	45_0^0
$^{(1)}E_3$	B2	6.331	195.8	1	0.0021	49_1^0
$^{(1)}E_8$	A1	7.945	156.1	1	0.1112	$34_0^2+5_4^1+3_1^1+1_3^2$
$^{(1)}E_{19}$	A1	10.140	122.3	1	0.0956	$32_5^0+7_4^1+3_6^0+2_9^1$
$^{(1)}E_{20}$	B2	10.22	121.3	1	0.0850	$19_5^1+18_2^2+2_9^0+2_6^1+2_4^0+2_1^3$
$^{(1)}E_{26}$	A1	11.08	111.9	1	0.1455	$30_3^2+9_1^5+3_1^16$
$^{(1)}E_{34}$	B2	11.63	106.6	1	0.1069	$27_6^1+11_2^4+6_4^3+1_9^0$
$^{(1)}E_{48}$	A1	12.88	96.3	1	0.1899	$45_1^8+4_4^5$
$^{(1)}E_{63}$	A1	13.94	89.0	1	0.1148	$33_5^6+12_6^3+3_9^1$
$^{(1)}E_{70}$	B2	14.49	85.6	1	0.2802	$18_9^0+7_1^{11}+6_4^7+4_2^{10}+3_4^{11}+1_4^9+1_6^1$

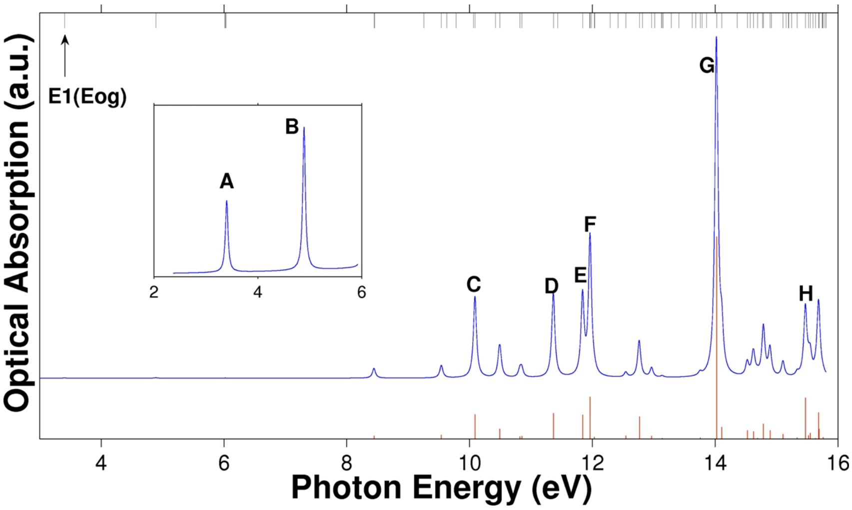

Fig. 3. Optical absorption spectrum of the D_{2d} isomer of CO_4. The vertical lines at the top denote the singlet excitation energies $^{(1)}E_i$, and the vertical lines at the bottom represent the oscillator strength f_{osc}. The inset is the enlarged part around the optical gap.

scaling factors are valid for the basis sets 6-311G(d,p) to 6-311++G(3df,3pd). Vibrational frequencies of the C_{2v} and D_{2d} isomers of CO_4 after being scaled are also listed in Tables 1 and 2, respectively. The observed wavenumber of the w_1 vibration of $^{12}C^{16}O_4$ (C_{2v}) in a former experiment [9] is 1941 cm^{-1}, as shown in Table 1. Our calculated result (1927 cm^{-1}) agrees well with the experimental result. Due to their low intensities and the noise level in the experiment, other vibrational frequencies were not detected in Jamieson et al.'s experiment [9]. It should be noted that there are only 7 normal vibrational modes for the D_{2d} isomer of CO_4, while 9 for the C_{2v} isomer of CO_4, since the vibrational frequencies of w_5 (1004 cm^{-1}) and w_6 (539 cm^{-1}) of the D_{2d} isomer of CO_4 are both doubly degenerate.

3.2. *Optical Excitation and Absorption Spectra*

We show in Figs. 2 and 3 the singlet excitation energy spectrum $^{(1)}E_i$, the corresponding oscillator strength f_{osc}, and the optical absorption spectrum of the C_{2v} and D_{2d} isomers of CO_4, respectively. We first discuss the C_{2v} isomer of CO_4.

Table 3 lists the exciton pair contribution P_n^v for several representative excited states of the C_{2v} isomer of CO_4. As shown in Table 3, the first singlet excited state, with $^{(1)}E_1$ equal to 4.604 eV (269.3 nm), is mainly due to the contribution of the (0,1) excited pair, i. e., the excitation of one electron from HOMO to LUMO + 1, and it is nondegenerate but dipole-forbidden. The second singlet excited state, with $^{(1)}E_2$ = 266.6 nm, is also nondegenerate and

Table 4. Exciton pair contribution P_n^v to the first five triplet states, the first singlet state and seven other dipole-allowed singlet states for the D_{2d} isomer of CO_4 calculated by TD-B3LYP/6-311+G(2df,2pd). E, λ, f_{osc} and $\prod$ denote the energy, wavelength, oscillator strength and degeneracy, respectively. The symmetry is also listed.

State	Symmetry	E (eV)	λ (nm)	$\prod$	f_{osc}	P_n^v
$^{(3)}E_1$	E	2.132	581.5	2	0.0000	$41_0^0+21_1^0+5_0^1+2_1^1$
$^{(3)}E_2$	E	4.821	257.2	2	0.0000	$34_1^0+15_0^0$
$^{(3)}E_3$	E	5.039	246.0	2	0.0000	$39_4^1+27_5^1+6_4^0+4_5^0+1_8^1$
$^{(3)}E_4$	E	5.100	243.1	1	0.0000	$26_2^0+26_3^1+2_7^0+2_6^1$
$^{(3)}E_5$	E	5.104	242.9	1	0.0000	$26_2^0+26_3^1+2_7^0+2_6^1$
$^{(1)}E_1$	E	3.404	364.2	2	0.0002	$20_0^0+15_0^1+5_1^0+4_1^1$
$^{(1)}E_2$	E	4.890	253.5	2	0.0004	$39_1^1+11_0^1$
$^{(1)}E_{16}$	E	10.09	122.9	2	0.0803	$18_5^0+8_0^5+6_1^5+5_8^0+5_0^7+1_1^7+1_4^0+1_0^{12}$
$^{(1)}E_{21}$	E	11.37	109.1	2	0.0838	$17_1^7+12_8^0+4_0^7+3_1^6+2_8^1+2_1^5+2_5^0+1_1^{12}$
$^{(1)}E_{23}$	E	11.84	104.7	2	0.0791	$16_3^3+10_2^3+8_1^6+6_1^7+1_8^1+1_0^6$
$^{(1)}E_{25}$	E	11.96	103.6	2	0.1377	$23_3^3+11_1^6+3_0^{11}+2_0^6+2_8^1+2_5^1$
$^{(1)}E_{45}$	E	14.02	88.4	1	0.6638	$18_2^6+18_3^7+2_3^{12}+2_2^{11}+2_0^{10}$
$^{(1)}E_{62}$	B2	15.47	80.2	1	0.1348	$34_8^2+12_4^8+1_7^4+1_6^5$

dipole-forbidden. The first dipole-allowed transition is the third singlet excitation occurring at 195.8 nm (6.331 eV), and it is mainly due to the contribution of the (1,0) excited pair. This can be seen in Fig. 2, peak A in the inset (note that the oscillator strength f_{osc} of the first dipole-allowed excited state is very small). So the optical absorption gap (E_{og}) of the C_{2v} isomer of CO_4 is 6.331 eV. Other dipole-allowed transitions can be seen in Figure 2. We just list the dipole-allowed transitions with the largest oscillator strength in Table 3. They are the peaks B, C, D, E, F, G, H and I, located at 156.1, 122.3, 121.3, 111.9, 106.6, 96.3, 89.0 and 85.6 nm, respectively. These peaks arise mainly from the contributions of the (0,2), (5,0), (5,1), (3,2), (6,1), (1,8), (5,6), (9,0) pairs, respectively. As listed in Table 3, the eight strongest dipole-allowed singlet states are all nondegenerate. The detailed excitation processes for those dipole-allowed transitions (A, B, C, D, E, F, G, H, I) are listed in Table 3. The symmetries of these excited states are also listed in Table 3.

In the following, we discuss the optical excitation and absorption spectra of the D_{2d} isomer of CO_4. Since the LUMO and HOMO − 2 of this isomer are both doubly degenerate, it implies the degeneracy of the $^{(1)}E_i$ and $^{(3)}E_i$ excited states we calculated. Detailed excitation processes and symmetries of excited states of the D_{2d} isomer of CO_4 are listed in Table 4. We find that the first singlet state, with $^{(1)}E_1 = 3.404$ eV (364.2 nm), is mainly due to the contribution of the (0,0) excited pair and is doubly degenerate. This state is dipole-allowed, although the oscillator strength is only 0.0002 (see peak A in the inset of Fig. 3). So the optical absorption gap (E_{og}) is 3.404 eV, redshifted by about 3 eV relative to that of the C_{2v} isomer of CO_4. The peak B near peak A in Fig. 3 is also listed in Table 4, although it is very weak. Other dipole-allowed transitions can be seen in Figure 3. In Table 4, we list the six strongest dipole-allowed transitions (C, D, E, F, G, H), which are located at 122.9, 109.1, 104.7, 103.6, 88.4 and 80.2 nm, respectively. These peaks (C, D, E, F, H) stem mainly from the contribution of the (5,0), (1,7), (3,3), (3,3), (8,2) pairs, respectively, while peak G is mainly due to the contribution of (2,6) and (3,7) pairs. Excited states $^{(1)}E_{16}$, $^{(1)}E_{21}$, $^{(1)}E_{23}$, $^{(1)}E_{25}$ are all doubly degenerate, while $^{(1)}E_{45}$, $^{(1)}E_{62}$ are both nondegenerate.

Transient absorption spectroscopy [24, 25] of a molecule can be used to study and characterize the triplet-triplet absorption bands, for example, the bleaching maximum and the isosbestic points. Thus, in Table 3, we list the lowest five triplet states of the C_{2v} isomer of CO_4. These triplet states are all nondegenerate, and come mainly from the contribution of (0,0), (0,1), (1,0), (1,1) and (2,0), respectively. The exchange-splitting, defined by $^{(1)}E_1 - {}^{(3)}E_1$, is 1.062 eV. Similar to Table 3, we list the lowest five triplet states of the D_{2d} isomer of CO_4 in Table 4. These triplet states are mainly due to the contribution of (0,0), (1,0), (4,1), (2,0), (2,0), respectively. The exchange-splitting of the D_{2d} isomer of CO_4 is 1.272 eV.

4. Conclusion

In conclusion, we have calculated the excitation states and optical absorption spectra of both C_{2v} and D_{2d} isomers of CO_4. The optical absorption gap (E_{og}) of the C_{2v} isomer of CO_4 is 6.331 eV (195.8 nm), while the E_{og} of the D_{2d} isomer of CO_4 is 3.404 eV (364.2 nm). They are both in the ultraviolet region. The first singlet excitation of the C_{2v} isomer of CO_4 is optically forbidden, while the first singlet excitation of the D_{2d} isomer of CO_4 is dipole-allowed. The difference between these two isomers' optical absorption spectra can be an evidence to distinguish them in the experiment.

Acknowledgement

This work was supported by the Teng Fei Program of Xi'an Jiaotong University and the Nature Science Foundation of China (Grant Nos. 10674106 and 60778021).

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