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Photoinduced rotational isomerization mechanism of 2-chlorobenzaldehyde in low-temperature rare-gas matrices by vibrational and electronic spectroscopies

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Abstract

Rotational isomerization of 2-chlorobenzaldehyde in low-temperature rare-gas matrices has been investigated by vibrational and electronic spectroscopies with aids of the density functional theory (DFT) and configuration interaction single (CIS) calculations. Infrared spectrum of the less stable *O-cis* isomer, produced from the more stable *O-trans* isomer upon UV irradiation, is measured with an FT-IR spectrophotometer. The enthalpy difference between the *O-cis* and *O-trans* isomers is estimated to be $9.7 \pm 0.2\,\mathrm{kJ\,mol^{-1}}$ from the temperature dependence of the infrared band intensities. Analyses of the infrared and electronic absorption spectral changes after UV irradiation and the phosphorescence spectra measured at various excitation wavelengths suggest that the rotational isomerization occurs via the intersystem crossing from S_1 to T_1. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 2-Chlorobenzaldehyde; Matrix isolation; Infrared spectra; Molecular orbital calculations; Electronic absorption and emission spectra

1. Introduction

ortho- and *meta*-substituted benzaldehydes have two possible rotational isomers around the bond between phenyl and formyl groups, *O-trans* and *O-cis*. The population ratio of the isomers of 2-chlorobenzaldehyde was investigated by NMR [1], resulting in that only the *O-trans* isomer exists at room temperature. This finding implies that *O-trans* is stabilized by an intramolecular hydrogen bond between the hydrogen atom of formyl group and the chlorine atom, while the *O-cis* isomer has a weak repulsive force between the chlorine and oxygen atoms, as shown in Scheme 1.

On the other hand, Green and Harrison [2] analyzed the IR and Raman spectra in the liquid phase and suggested the existence of the two isomers, although their spectra were too broad to distinguish them.

The torsional barriers for several 2-hologenated benzaldehydes were estimated from the assignment of the torsional bands measured by far-infrared spectroscopy [3,4]; the barrier height and the energy difference between the two isomers of 2-chlorobenzaldehyde were estimated to be 17.61 and $2.93\,\mathrm{kJ\,mol^{-1}}$, respectively [4]. However, this energy difference seems to be unreasonable because they may have underestimated the effect of the intramolecular hydrogen bond.

One of the purposes of the present study is to estimate the energy difference more precisely from the temperature dependence of the matrix-isolation infrared spectra of this molecule, where the isomer bands can be identified more clearly.

Another purpose of this study is to elucidate the mechanism of photoinduced rotational isomerization of 2-chlorobenzaldehyde using electronic transition spectra. The energy curves for the ground and excited states of the parent molecule, benzaldehyde, have been extensively studied experimentally and theoretically [5,6]. However, many fewer studies have been reported on the excited states of substituted benzaldehydes. For example, Ito et al. [7,8] investigated the isomerization through the electronically excited states by supersonic molecular-beam and sensitized phosphorescence excitation spectroscopy techniques. They concluded that the isomerization for 2-methylbenzaldehyde occurred on the double-minimum potential surface of the lowest triplet excited state, although direct observation of the $T_1 \rightarrow S_0$ transition was impossible. On the other hand, the vibrational analysis of electronic absorption and emission spectra for *O-trans* 2-chlorobenzaldehyde in the gas phase was made by Haque and Thakur [9,10], who observed the 0–0 bands of fluorescence and phosphorescence spectra

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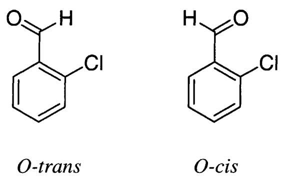

Scheme 1.

at 25901.7 and 24178.0 cm^{-1}, respectively. They concluded that *O-trans* was also more stable in the S_1 and T_1 states than *O-cis*.

The analyses of photoinduced isomerizations and conformations for several molecules in low-temperature matrices have been reported [11–15]. However, their mechanisms were not discussed in detail except for *o*-hydroxybenzaldehyde studied by Morgan et al. [15] by IR, UV and emission spectroscopies; they concluded that photoisomerization occurs below the torsional barrier of the S_1 state, while reverse photoisomerization occurs in the S_1 or S_2 states. However, they could not make it clear whether the former process occurs via intersystem crossing or internal conversion. The present paper reports on the photoinduced isomerization of matrix isolated 2-chlorobenzaldehyde by infrared and ultraviolet spectroscopic methods with the aid of molecular orbital calculations. The potential energy surfaces of the ground and excited electronic states are estimated from the observed spectra and the results of the calculations, and the *trans–cis* rotational isomerization mechanism is proposed. To our knowledge, no matrix-isolation spectra of 2-chlorobenzaldehyde have yet been published.

2. Experimental and calculation methods

2-Chlorobenzaldehyde was purchased form Wako Pure Chemical Industries and used after vacuum distillation. The sample gas was diluted with argon (Nippon Sanso, 99.9999% purity) or xenon (Tokyo Gas Chemical, 99.999% purity) in glass cylinders. The mixing ratio of the sample was about 1/2000. For IR measurements, premixed gases were expanded through a stainless steel pipe (1/8 inch o.d.) and deposited in a vacuum chamber on a CsI plate, cooled at 15 K by a closed cycle helium refrigeration (CTI Cryogenics, Model M-22). UV radiation from a super high-pressure mercury lamp was used to induce photoreaction through a water filter to remove thermal reactions and cutoff filters, UV-32, UV-31, UV-30 and UV-28 (HOYA), to choose the wavelength. Infrared spectra of the matrix samples were measured with an FT-IR spectrophotometer (JEOL, Model JIR-7000). The spectral resolution was 0.5 cm^{-1}, and the number of accumulation was 64. Other experimental details were reported elsewhere [16,17]. To measure dependence of the population ratio on nozzle temperature, a heating system composed of a stainless steel pipe nozzle and a 1/4 in. sample reserver equipped with a heater was used.

Electronic absorption and emission spectra were measured with a UV/Vis spectrophotometer (JASCO, Ubest50) and an emission spectrophotometer (SHIMADZU, RF-5300PC), respectively. To measure electronic spectra, a quartz plate cooled at about 18 K by a closed cycle helium refrigeration (IWATANI, compressor PA 101) was used instead of a CsI plate.

Density functional theory (DFT) and configuration interaction single (CIS) calculations were performed by using the GAUSSIAN 98 program [18] with the 6-31++G** basis set. The hybrid density functional [19], in combination with the Lee–Yang–Parr correlation functional (B3LYP) [20], was used to optimize the geometrical structures in the ground and the lowest triplet excited states, while the CIS/6-31++G** method was used to calculate vertical electronic transition energies.

3. Results and discussion

3.1. Infrared spectra of O-trans and O-cis isomers

An infrared spectrum of 2-chlorobenzaldehyde is shown in Fig. 1 with a calculated *O-trans* spectral pattern obtained by the DFT method, where a scaling factor of 0.98 was used. The observed wavenumbers are summarized and compared with the calculated values in Table 1. The C=O stretching mode was observed at 1710 and 1706 cm^{-1} as a doublet. The bands appearing around 1390 cm^{-1} also show splitting as well as the bands of 1295/1292, 1059/1056 and 719/717 cm^{-1} pairs. Some of the remaining bands are assignable to combination modes.

After the spectral measurement, the sample was irradiated by UV radiation through a UV-30 cutoff filter. Fig. 2

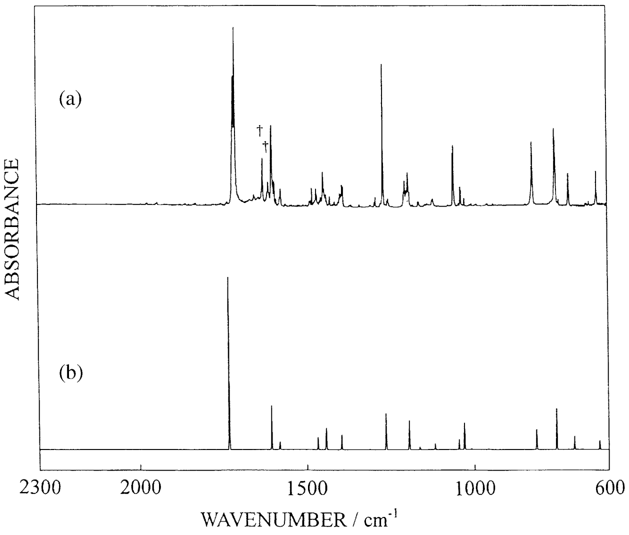

Fig. 1. Infrared spectra of 2-chlorobenzaldehyde: (a) observed matrix spectrum; (†) H_2O in the matrix, (b) calculated spectral pattern for *O-trans* obtained by DFT/B3LYP/6-31++G**, where a scaling factor of 0.98 was used.

Table 1
Observed and calculated vibrational wavenumbers (cm^{-1}) and relative intensities for *O-trans* and *O-cis* rotational isomers of 2-chlorobenzaldehyde

O-trans				*O-cis*			
Observed[a]		Calculated[b]		Observed[a]		Calculated[b]	
ν	Intensity	ν	Intensity	ν	Intensity	ν	Intensity
3098	1.2	3157	1.9	3067	1.1	3157	1.4
3092	1.0	3151	2.2			3147	4.2
3079	2.7	3141	1.7			3131	1.5
3070	1.4	3129	0.9			3114	1.5
2884	8.4	2947	18.4	2852	3.2	2848	42.3
2757	2.1			2826	3.7		
2724	1.7			2742	5.3		
2709	1.6			2734	10.1		
2639	1.9						
1710	72.7						
1706	100	1729	100	1730	100	1751	100
1597	42.3	1604	25.7	1596	16.0	1605	20.3
1571	9.6	1580	4.5	1576	5.3	1578	9.1
1480	11.6						
1468	10.2	1468	7.1	1474	22.3	1474	11.4
1454	4.8						
1447	19.3	1444	12.6	1445	16.0	1445	3.8
1428	6.6						
1414	2.0						
1399	6.7	1399	8.6	1404	10.6	1411	6.2
1395	6.4						
1393	12.4						
1389	11.2						
1295	2.7	1315	0.3	1300	6.4	1322	7.3
1292	5.6			1298	9.6		
1269	88.6	1265	21.3	1257	4.3	1258	3.4
1203	13.6	1195	16.9	1195	12.8	1186	24.1
1194	19.4			1184	5.1		
1161	2.3	1163	1.6	1164	0.3	1166	1.0
1119	4.1	1117	3.6	1133	3.2	1132	2.4
1059	30.5	1046	5.9	1074	25.5	1055	11.4
1056	34.5						
1037	11.1	1030	15.6	1044	4.0	1041	9.8
1025	4.5						
1003	1.1	1009	0.5	999	0.8	1004	0.4
		987	0			982	0
958	1.0	960	0.4	949	1.1	948	0.5
		868	0			865	0
826	37.4	818	11.8	846	37.2	839	13.2
760	43.9	759	23.9	755	19.1	755	24.8
747	3.2					700	0.1
719	18.9	705	7.7	682	6.2	676	8.6
717	17.6						
		696	0	654	23.4	650	6.4
633	20.1	628	5.3				

[a] Observed in argon matrices.

[b] Calculated by DFT/B3LYP/6-31++G**. A scaling factor of 0.98 was used.

shows a difference spectrum between those measured before and after the UV irradiation for 10 min, where decreasing and increasing bands represent a reactant and a photoproduct, respectively. A calculated spectral pattern of *O-trans* (down-side) and *O-cis* (up-side) obtained by the DFT method is also shown there. It is clear that the calculated spectral pattern reproduces the observed difference spectrum satisfactorily. As shown in Table 1, the observed vibrational wavenumbers of the *O-cis* isomer are consistent with the corresponding calculated values as well as the *O-trans* isomer.

3.2. Nozzle-temperature dependence of infrared spectra

It is known that the population ratio of conformational isomers in the gas phase is maintained in low-temperature

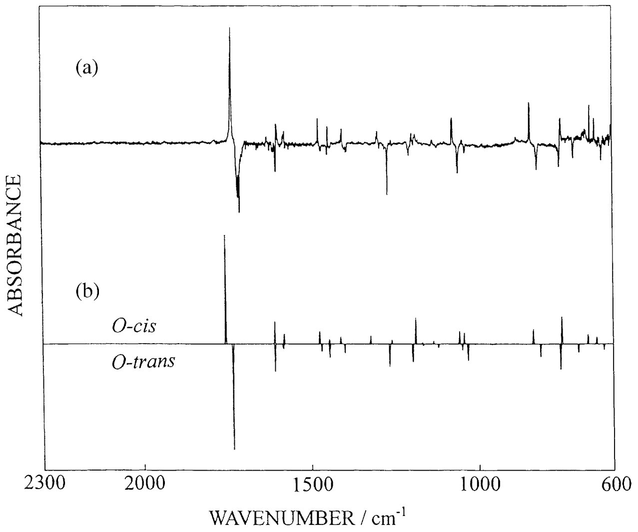

Fig. 2. A comparison between observed difference spectrum and calculated spectral pattern: (a) measured before and after UV irradiation through a UV-30 cut-off filter for 10 min; product and reactant bands are shown above and below, respectively, (b) calculated spectral patterns for *O-cis* (up) and *O-trans* isomers (down) obtained by DFT/B3LYP/6-31++G**, where a scaling factor of 0.98 was used.

matrices without redistribution [21]. To estimate the energy difference between the two isomers, nozzle-temperature dependence of infrared spectra was examined. Fig. 3 shows the infrared spectra of 2-chlorobenzaldehyde in argon matrices in the region between 800 and 900 cm^{-1}. The nozzle temperature was varied from 298 to 483 K. When the nozzle temperature was 298 K, only the *O-tarns* band was observed at 826 cm^{-1}, but the *O-cis* band was too weak to be observed clearly. As the nozzle temperature increased, the intensity of the *O-cis* band appearing at 846 cm^{-1} increased.

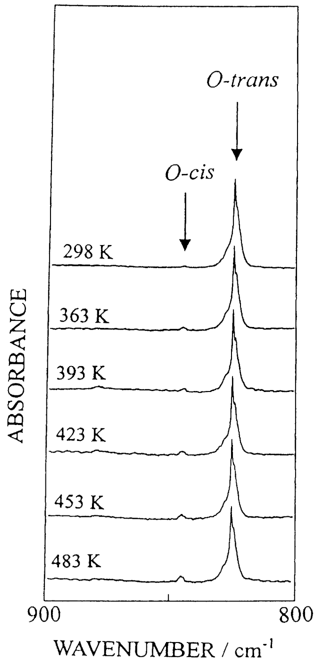

Fig. 3. Dependence of infrared spectra of 2-chlorobenzaldehyde in argon matrices on nozzle temperature.

In order to estimate the energy difference between the two isomers, the logarithm of the ratio of the absorbances of the 846 cm^{-1} (*O-cis*) and the 826 cm^{-1} (*O-trans*) bands was plotted versus the inverse of the nozzle temperature in Fig. 4. The enthalpy difference between the isomers is estimated to be 9.7 ± 0.2 kJ mol^{-1} from the plot by a least-squares fitting. This value is nearly equal to our calculated value, 11.2 kJ mol^{-1}, obtained by the DFT method, but more than three times larger (2.9 kJ mol^{-1}) than the energy difference reported by Miller et al. [4]. Since our matrix-isolation

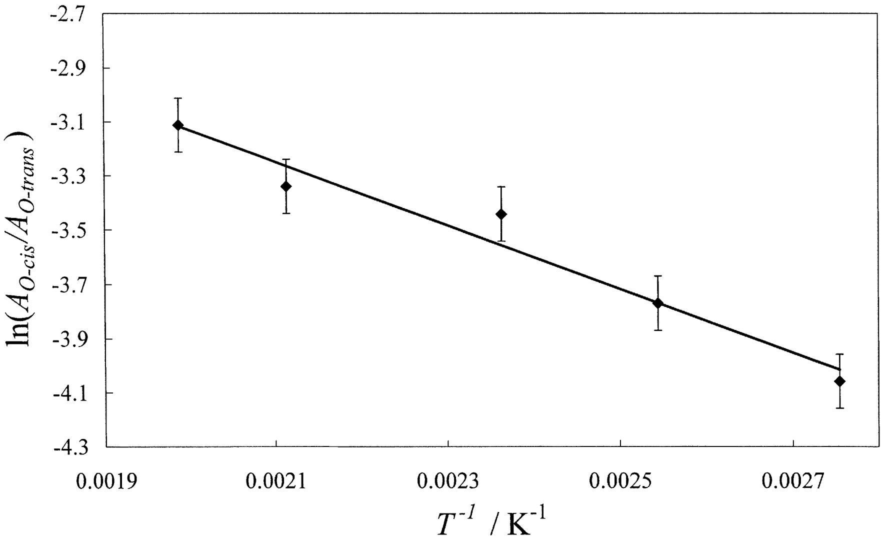

Fig. 4. Logarithmic plot of absorbance ratio versus inverse of nozzle temperature. $A_{O\text{-}cis}$ and $A_{O\text{-}trans}$ represent the absorbances of *O-cis* (846 cm^{-1} band) and *O-trans* (826 cm^{-1} band), respectively. Solid line represents the values calculated by a least-squares fitting.

spectra can clearly distinguish the two isomer bands, our present estimate is considered to be more accurate than that reported previously. This result is supported by the fact that the corresponding value for 2-fluorobenzaldehyde was reported to be about 13.4 kJ mol^{-1} by an ab initio calculation, where the Hartree–Fock method with the 6-31G** basis set was used [22].

We have also estimated the torsional barrier height scaled from an energy minimum for the more stable *O-trans* isomer to be 33.0 kJ mol^{-1} by a calculation at the DFT/B3LYP/6-31++G** level. This value is 13 kJ mol^{-1} higher than the experimental value for non-substituted benzaldehyde, 20 kJ mol^{-1}, determined by electron diffraction and ab initio calculation [23]. This implies that the *O-trans* isomer of 2-chlorobenzaldehyde is stabilized by a hydrogen bond between the chlorine atom and the hydrogen atom of the formyl group. The height of the torsional barrier at the ground state, 33.0 kJ mol^{-1}, may be so high that isomerization cannot occur thermodynamically at the matrix temperature, 15 K. A schematic representation of the potential surface of the ground electronic state is shown in Fig. 5.

3.3. Electronic transition spectra

Fig. 6 shows the electronic absorption spectra of matrix isolated 2-chlorobenzaldehyde measured before and after UV irradiation. The absorption band in the region between 280 and 320 nm is assigned to the $S_1(n, \pi^*) \leftarrow S_0$ transition, where the vibronic structure is composed of bands appearing at 302.7, 298.8, 295.7, 292.0 and 289.3 nm. When the matrix sample was irradiated by UV light through a UV-30 cutoff filter, a spectral change was observed although the absorption of *O-cis* is mostly overlapped with that of *O-trans*; the intensities of the 302.7, 298.8 and 292.0 nm bands decreased, while the shorter-wavelength absorption in the region between 265 and 290 nm increased slightly. Thus, the absorption coefficient of *O-cis* in this shorter-wavelength region seems to be larger than that of *O-trans*. This result will be used to explain the reverse

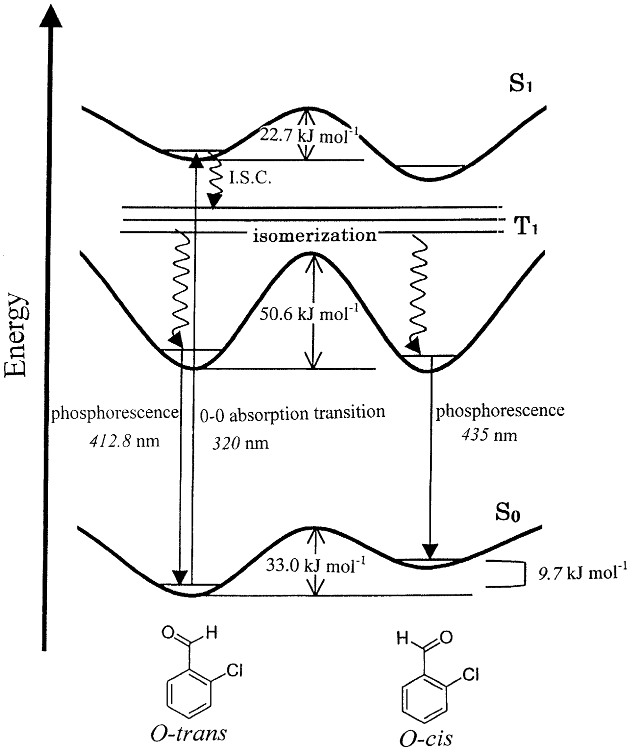

Fig. 5. Schematic potential energy surfaces of 2-chlorobenzaldehyde for photoinduced rotational isomerization. The barrier heights of S_0 and T_1 states are calculated by DFT/B3LYP/6-31++G**, while that of S_1 state is calculated by CIS/6-31++G**. Energy differences determined experimentally are shown in italic.

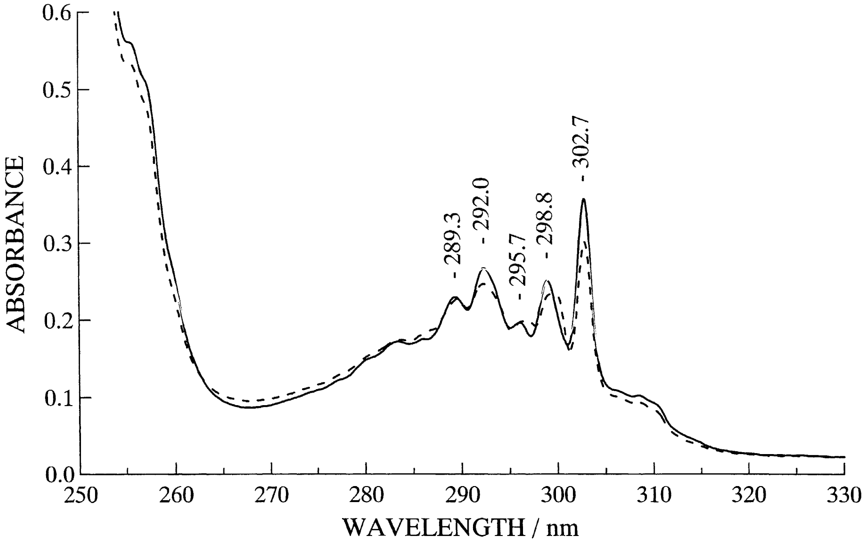

Fig. 6. UV absorption spectra of 2-chlorobenzaldehyde in argon matrices measured before (solid line) and after (dotted line) irradiation, where UV light from super high-pressure mercury lamp through a UV-30 cutoff filter and a water filter was used.

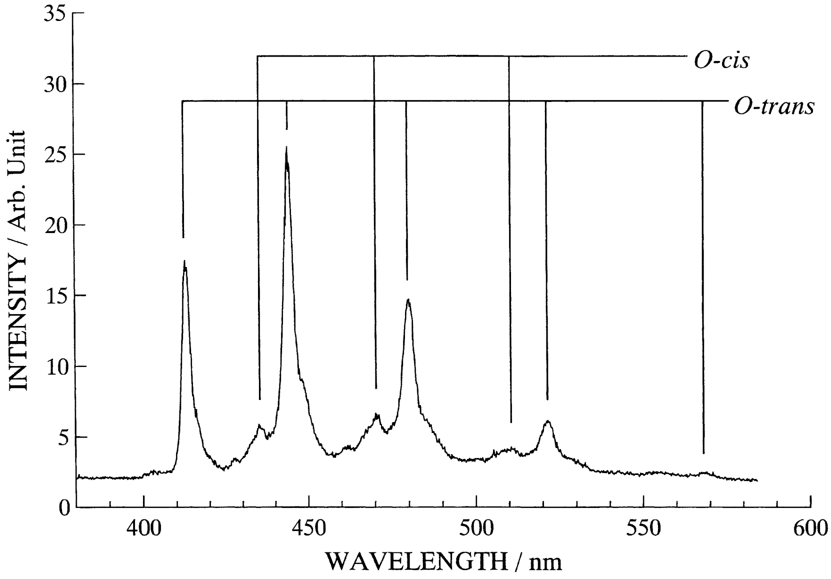

Fig. 7. Emission spectrum of 2-chlorobenzaldehyde in argon matrices. Excitation wavelength was 300 nm.

photoisomerization from *O-cis* to *O-trans* upon UV irradiation with a shorter wavelength described in the next section.

An emission spectrum of 2-chlorobenzaldehyde measured by 300 nm excitation is shown in Fig. 7, where phosphorescence was observed clearly but no fluorescence. The similar emission patterns were obtained by 310, 300, 280 and 260 nm excitation. The emission peaks can be divided into two kinds of progressions due to the $T_1 \rightarrow S_0$ transition. We assign the stronger progression composed of 412.8, 444.0, 480.2, 521.6 and 569.0 nm to the *O-trans* isomer. The 412.8 nm band, which is consistent with the phosphorescence value reported by Haque and Thakur [10], is assigned to the 0–0 transition, where the energy difference between 412.8 and 444.0 nm is 1702 cm^{-1}. The other progression has the 0–0 transition at 435.0 nm, where the first vibrational transition energy is 1721 cm^{-1}. We assigned the weaker progression to the *O-cis* isomer because the energy difference, 1721 cm^{-1}, is 19 cm^{-1} higher than that of *O-trans*, 1702 cm^{-1}, where this finding is consistent with the calculated values for *O-cis* (1751 cm^{-1}) and *O-trans* (1729 cm^{-1}). Our assignment that the longer-wavelength progression is due to *O-cis* is also supported by the CIS calculation on the vertical transition energies from T_1 to S_0; the calculated transition energy for *O-trans*, 497.5 nm, is higher than that for *O-cis*, 502.6 nm. The progression wavelengths and energy differences are summarized in Table 2.

3.4. Irradiation-wavelength dependence of infrared spectra

In order to study the photoinduced isomerization and its reverse process, the dependence of the population ratio on the irradiation wavelength was examined. The *O-cis*/*O-trans* relative populations of the matrix sample were found to reach equilibrium within a few minutes after the UV irradiation started. The population ratio increased as the shorter-wavelength irradiation, UV-32, UV-31 or UV-30, was used. This is consistent with the fact that the

Table 2
Observed phosphorescence emission bands (nm) and energy differences (cm^{-1})

Progression 1 (*O-trans*)			Progression 2 (*O-cis*)		
Emission	Assignment	Energy difference	Emission	Assignment	Energy difference
412.8	$0 \rightarrow 0$		435.0	$0 \rightarrow 0$	
		1702			1721
444.0	$0 \rightarrow 1$		470.2	$0 \rightarrow 1$	
		1698			1683
480.2	$0 \rightarrow 2$		510.6	$0 \rightarrow 2$	
		1653			
521.6	$0 \rightarrow 3$				
		1597			
569.0	$0 \rightarrow 4$				

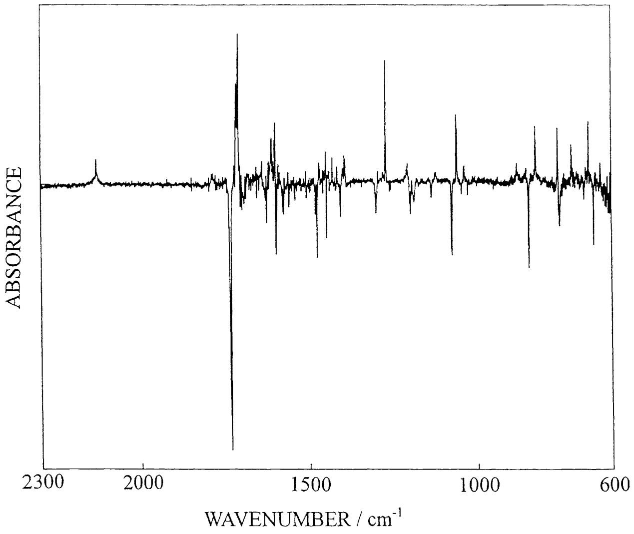

Fig. 8. Difference spectrum of 2-chlorobenzaldehyde upon the UV irradiation through a UV-28 cutoff filter for 10 min subsequent to the UV irradiation through a UV-30 cutoff filter for 20 min. *O-trans* bands increase and *O-cis* bands decrease.

absorption maximum of the $S_1(n, \pi^*) \leftarrow S_0$ electric transition is 302 nm, as shown in Fig. 6.

The matrix sample was irradiated through a UV-30 cutoff filter until the relative intensities of the bands for both *O-trans* and *O-cis* isomers were no longer changed. When the UV-30 cutoff filter was replaced with a UV-28 filter, the intensities of the *O-cis* bands decreased and those of the *O-trans* bands increased, as shown in Fig. 8. This difference spectrum was obtained by the UV irradiation through the UV-28 filter for 10 min subsequent to the UV irradiation through the UV-30 filter for 20 min. The increasing bands are completely identical to the initial spectrum of *O-trans* shown in Fig. 1 except for the 880 and 2134 cm^{-1} bands. Therefore, the photoinduced reverse process occurs more effectively upon UV-28 irradiation than UV-30 irradiation. This fact is consistent with the results of the UV absorption spectra described in Section 3.3 that the absorption coefficient of *O-cis* around 280 nm is larger than that of *O-trans*, in contrast to the absorption around 300 nm.

It is known that non-substituted benzaldehyde dissociates into carbon monoxide and benzene upon UV-irradiation via the S_2 state [24]. If a similar photoreaction occurs for 2-chlorobenzaldehyde, carbon monoxide and chlorobenzene could be photoproduced through the S_2 state; the $S_2(\pi, \pi^*) \leftarrow S_0$ absorption starts at about 265 nm as shown in Fig. 6. The 2134 cm^{-1} band of the product caused by UV-28 irradiation is assignable to carbon monoxide. However, the new peak appearing at 880 cm^{-1} is unassignable to any infrared bands of chlorobenzene. Identification of the co-product remains to be unsolved in the present study.

3.5. Isomerization mechanism

A schematic representation for the isomerization mechanism of 2-chlorobenzaldehyde is shown in Fig. 5. As described in Section 3.2, the rotational barrier height in the ground state was estimated to be about 33 kJ mol^{-1}. This means that the thermal isomerization in the ground state is hard to occur at the matrix temperature, 15 K. We estimated the torsional barrier height scaled from the energy minimum of the *O-trans* isomer in the S_1 state to be about 22.7 kJ mol^{-1} by the CIS/6-31++G** method. As shown above, the photoisomerization from *O-trans* to *O-cis* occurs at least upon UV-32 irradiation. The energy is larger enough to excite the molecules to the S_1 state but not beyond the torsional barrier height on the potential. Thus, we conclude that the isomerization does not occur at the S_1 state. As discussed in Section 3.3, no fluorescence was observed for the matrix isolated *O-trans* isomer, while the phosphorescence was observed clearly. The observed phosphorescence includes two progressions assignable to the $T_1 \rightarrow S_0$ vertical transition of the *O-trans* and *O-cis* isomers. Then, both isomers must exist at the minima of the T_1 potential surface. The DFT calculation predicts that *O-cis* is more stable than *O-trans* by about 1.1 kJ mol^{-1} in the T_1 state. The torsional barrier height scaled from the minimum of *O-trans* in the T_1 state is calculated to be 50.6 kJ mol^{-1}. Then, we conclude that the rotational isomerization occurs at vibrational excited states of T_1 after the intersystem crossing from S_1 to T_1. Since the potential energy surface of the T_1 state has the high barrier for the isomerization, the species relaxed to the bottom of the T_1 state cannot take over the barrier. However, the second isomerization may occur at vibrational excited states of S_0 during the intersystem crossing from T_1 to S_0. Ito et al. [7] reached a similar conclusion for the isomerization mechanism of 2-methylbenzaldehyde.

When the matrix material is changed from argon to xenon, intersystem crossing is expected to be accelerated by the external heavy atom effect [25]. We carried out similar experiments using xenon instead of argon. However, the observed spectra in a xenon matrix were essentially similar to those observed in an argon matrix. Thus, the heavy atom effect has not been found in this study, which may be due to that the intersystem crossing to the triplet states for 2-chlorobenzaldehyde occurs significantly even in an argon matrix, where an alternative pathway, that is internal conversion, seems to be negligible. Acceleration of the intersystem crossing pathway by matrix materials, both xenon and argon, makes it hard to observe the fluorescence reported in the gas phase [9,10].

4. Summary

Infrared spectra of the less stable rotational isomer, *O-cis*, produced from the more stable one, *O-trans*, have been assigned with the aid of DFT/B3LYP/6-31++G**. The enthalpy difference between the two isomers is estimated to be 9.7 ± 0.2 kJ mol^{-1}. The torsional barrier heights on the S_0, T_1 and S_1 potential surfaces are obtained to be 33.0, 50.6 and 22.7 kJ mol^{-1}, respectively, by the DFT and CIS calculations. The electronic absorption and phosphorescence spectra have been observed, where the 0–0 transition energies from S_0 to T_1 and S_1 are consistent with the vertical electronic transition energies obtained by the CIS/6-31++G** calculation. It is concluded that photoisomerization occurs at the vibrational excited states of T_1 during the intersystem crossing from S_1 to T_1.

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