[Article]

doi: 10.3866/PKU.WHXB201601293

www.whxb.pku.edu.cn

2,5-二氟苯酚分子之旋转异构物的质量分辨阈值电离光谱

吴沛颖^{1,2} 曾圣渊¹ 蔡青耘^{1,3} 曾文碧^{1,3,*}¹台湾中央研究院原子与分子科学研究所, 生化分子质谱与光谱学实验室, 台北 10617;²台湾大学化学系, 台北 10617; ³台湾师范大学化学系, 台北 11677)

摘要: 利用共振双光子电离(R2PI)技术和质量分辨阈值电离(MATI)技术来研究 2,5-二氟苯酚分子。实验所测得的顺式、反式 2,5-二氟苯酚分子电子激发能 E_1 分别为 36448 和 36743 cm^{-1} , 绝热电离能分别为 71164 和 71476 cm^{-1} 。这两个顺反转动同素异构分子在电子激发 S_1 态与离子 D_0 态活性振动主要是由于面内环变形和与取代基相关的弯曲振动。分析 2,5-二氟苯酚分子的振动光谱、 D_0 态离子光谱以及理论计算均表明这两个转动异构体在 D_0 态的几何构型与 S_1 态的中性几何构型相当相似。

关键词: 共振双光子电离技术; 阈值电离; 振动光谱; 离子态光谱; 2,5-二氟苯酚

中图分类号: O643

Rotamers of 2,5-Difluorophenol Studied Using Mass-Analyzed Threshold Ionization Spectroscopy

WU Pei-Ying^{1,2} TZENG Sheng-Yuan¹ TSAI Ching-Yun^{1,3} TZENG Wen-Bih^{1,3,*}¹Laboratory for Mass Spectrometric and Spectroscopic Studies of Biomolecules, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617; ²Department of Chemistry, National Taiwan University, Taipei 10617;³Department of Chemistry, National Taiwan Normal University, Taipei 11677)

Abstract: We applied resonant two-photon ionization (R2PI) and mass-analyzed threshold ionization (MATI) techniques to record the vibronic and cationic spectra of 2,5-difluorophenol. The distinct bands at 36448 and 36743 cm^{-1} were confirmed as the origins of the $S_1 \leftarrow S_0$ electronic transition of the cis and trans rotamers, respectively. The corresponding adiabatic ionization energies were found to be 71164 and 71476 cm^{-1} for these two rotameric species. The observed spectral features mainly result from the in-plane ring deformation and substituent-sensitive bending vibrations. Spectral analysis suggests that the molecular geometry and vibrational coordinates of the cation in the D_0 state resemble those of the neutral species in the S_1 state for both cis and trans rotamers.

Key Words: Resonant two-photon ionization technique; Threshold ionization; Vibronic spectrum; Cation spectrum; 2,5-Difluorophenol

1 Introduction

Multiply substituted benzenes may have various types of structural isomers, resulting from different locations and configurations of the substituents. The nature as well as the substituent–ring and substituent–substituent interactions cause the

structural isomers to have different molecular properties. One common type of structural isomers is positional isomer. For example, Silva and Ferreira¹ performed combustion calorimetric studies to determine the standard molar enthalpies of formation of the six positional isomers of difluorophenol. IR, Raman, and laser-

Received: November 30, 2015; Revised: January 28, 2016; Published on Web: January 29, 2016.

*Corresponding author. Email: wbt@sinica.edu.tw Tel: +886-2-23668236; Fax: +886-2-23620200.

The project was supported by the Ministry of Science and Technology of the Republic of China (MOST-103-2113-M-001-009, MOST-104-2113-M-001-014).

国家科技部(MOST-103-2113-M-001-009, MOST-104-2113-M-001-014)资助项目

© Editorial office of Acta Physico-Chimica Sinica

induced fluorescence (LIF) spectroscopies are important tools to investigate the molecular geometry, vibration, and other properties of positional isomers in the ground S_0 and electronically excited S_1 states²⁻⁷. Another type of structural isomers is rotational isomer (rotamer) or called configurational isomer. Molecular rotamers can be interconverted by rotation about a chemical bond and coexist in a chemical sample⁸. It has been reported that rotamers can involve in biological processes^{9,10}. Knowledge about molecular rotamers can help people to have more insights into some biological phenomena. Concerning positional isomers of difluorophenol, Chakrabarti and Jaman¹¹ applied radiofrequency-microwave double resonance and conventional microwave spectroscopy to study 2,4-difluorophenol in the gas phase. They proposed that the *cis* and *trans* rotamers coexist in the sample. However, the *cis* form is more abundant than the *trans* form. Shivatare and Tzeng¹² studied this molecule by using the one-color and two-color resonant two-photon ionization (1C-R2PI, 2C-R2PI), and mass-analyzed threshold ionization (MATI) techniques. They found that only the *cis* form involved in the two-photon photoexcitation and ionization processes. Tsai and Tzeng¹³ recorded the vibronic and cation spectra and reported the electronic excitation and ionization energies as well as the active vibrations of the *cis* and *trans* rotamers of 3,4-difluorophenol in the electronically excited S_1 and cationic ground D_0 states. In the present spectroscopic study, we choose 2,5-difluorophenol to learn the effects of substituent-ring and substituent-substituent interactions on molecular geometry, transition energy, and vibrational frequency. Although no optical spectrum of 2,5-difluorophenol has been reported, the existing experimental data of 2-fluorophenol¹⁴⁻¹⁶, 2,4-difluorophenol^{11,12}, 3-fluorophenol^{15,17,18}, 4-fluorophenol^{15,19}, 3,4-difluorophenol¹³, and 2,5-difluoroaniline²⁰ are useful for spectral assignment and interpretation.

Some molecular properties of specific rotamers in the S_0 and S_1 states can be obtained by combining supersonic jet-cooled expansion and LIF^{8,21}, resonance-enhanced multiphoton ionization (REMPI)^{22,23}, spectral hole-burning^{24,25} spectroscopic techniques, and theoretical calculations. However, these methods cannot give information about the ionic properties of each selected rotameric species. One may couple the resonant two photon excitation scheme²⁶ with either zero-kinetic energy (ZEKE) photoelectron²⁷⁻²⁹ or MATI spectroscopy³⁰⁻³³ to record vibrationally resolved cation spectra of the selected rotamers. Because the MATI technique provides mass information, it is suitable for spectroscopic studies of selected species in molecular systems which may have impurities³⁴.

In this paper, we report the vibronic, photoionization efficiency (PIE), and cation spectra of 2,5-difluorophenol, recorded by the 1C-R2PI, 2C-R2PI, and MATI techniques. In particular, the MATI spectra were recorded by ionizing *via* different vibronic intermediate states of the selected rotamers. This allowed us to detect more active cation vibrations and to investigate whether the molecular geometry changes upon $D_0 \leftarrow S_1$ transition. These new experimental data provide information about the precise excitation energies of the $S_1 \leftarrow S_0$ transition (E_1), adiabatic ionization ener-

gies (IE), and the active vibrations in the S_1 and D_0 states.

2 Experimental and computational methods

2.1 Experimental method

All experiments were performed by using a photoionization time-of-flight mass spectrometer described previously³⁵. The solid 2,5-difluorophenol (97%, Aldrich) sample was heated to about 77 °C to obtain sufficient vapor pressure. The vapors were seeded into 2–3 Pa of helium and expanded into the vacuum through a pulsed valve with a 0.15 mm diameter orifice. The molecular beam was collimated by a skimmer located 15 mm downstream from the nozzle orifice. The two-color resonant two-photon excitation process was achieved by utilizing two independent tunable UV lasers controlled by a delay/pulse generator. The excitation (pump) source is a Nd:YAG pumped dye laser (Quanta-Ray PRO-190-10/Lambda-Physik, Scanmate UV with BBO-III crystal; Coumarin-540A and Fluorocence-548dyes). The output visible radiation is frequency doubled to produce UV radiation. The ionization (probe) UV laser (Lambda-Physik, Scanmate UV with BBO-III crystal; Rhodamine-590 and Rhodamine-610 dyes) is pumped by a frequency-doubled Nd:YAG laser (Quanta-Ray LAB-150). The wavelengths of both lasers were calibrated by using a laser wavelength meter (Coherent, WaveMaster). These two counter-propagating laser beams were focused and intersected perpendicularly with the molecular beam at 50 mm downstream from the nozzle orifice.

In the MATI experiments, both prompt ions and Rydberg neutrals were formed simultaneously in the laser-molecular beam interaction zone. A pulsed electric field of $-1 \text{ V} \cdot \text{cm}^{-1}$ was applied to the laser-molecular beam interaction region to guide the prompt ions toward the opposite direction of the flight tube. So that the prompt ions were not detected by the particle detector. It follows that the Rydberg neutrals kept moving with molecular beam velocity of about $1500 \text{ m} \cdot \text{s}^{-1}$ towards the direction of the flight tube. After a time delay of about 11.8 μs , a second pulsed electric field of $+200 \text{ V} \cdot \text{cm}^{-1}$ was applied to field-ionize these Rydberg neutrals in the field-ionization region. The newly formed threshold ions were accelerated and passed through a 1.0 m field-free region flight tube before being detected by a microchannel plate (MCP) particle detector. The obtained optical spectra were normalized to the laser power in order to avoid spurious signals due to shot-to-shot laser fluctuation.

2.2 Computational method

All the calculations were performed by using the Gaussian 09 program package³⁶. The results predict the optimized structures, energies, vibrational frequencies, and many other molecular properties in the S_0 , S_1 , and D_0 states. These calculations give a total spin $\langle S^2 \rangle$ of about 0.75 for the cation. The computed vibrational frequencies are multiplied by a suitable factor (specified in the tables) and used to assign the bands in the spectra. The IE was deduced from the difference in the zero-point energy (ZPE) levels of the cation in the D_0 state and the corresponding neutral species in the S_0 state.

3 Results

3.1 Vibronic spectrum of 2,5-difluorophenol

Information about the E_1 of 2,5-difluorophenol is not available in literature. With the reported E_1 and IEs of 2-fluorophenol^{14–16} and 3-fluorophenol^{15,17,18} and additivity rule on the transition energy^{13,20}, we expect that the 1C-R2PI technique can be used to obtain the vibronic spectrum of 2,5-difluorophenol. As seen in Fig.1, the distinct features at 36448 and 36743 cm^{-1} are identified as the band origins of *cis*- and *trans*-2,5-difluorophenol, respectively. Table 1 lists the observed vibronic bands along with the excitation energy, relative intensity, energy shift with respect to the band origin, and possible assignment. The spectral assignment was accomplished by comparing these experimental data of 2,5-difluorophenol with those of 2-fluorophenol^{14–16}, 3-fluorophenol^{15,17,18}, 2,4-difluorophenol^{11,12}, 3,4-difluorophenol¹³, and 2,5-difluoroaniline²⁰ as well as the predicted vibrational frequencies from our time-dependent Becke three-parameter with the Lee-Yang-Parr functional (TD-B3LYP) calculations. We follow the GaussView³⁷ procedure to identify all normal vibrations. According to Varsanyi and Szoke^{38,39}, 2,5-difluorophenol is classified as a 1,2,5-tri-“light”-substituted benzene derivative. The numbering system of the normal vibrations is given in the corresponding nomenclature which is derived from Wilson’s notation of the benzene modes⁴⁰.

Fig.1 Vibronic spectrum of 2,5-difluorophenol obtained by the 1C-R2PI technique

The band origins of the *cis* and *trans* rotamers appear at 36448 and 36743 cm^{-1} , respectively. (c) = *cis* rotamer; (t) = *trans* rotamer

The spectral features in Fig.1 mainly result from vibronic transitions related to the in-plane ring deformation and substituent-sensitive bending vibrations. Modes 6a, 12, and 1 of *cis*-2,5-difluorophenol in the S_1 state have frequencies of 439, 705, and 718 cm^{-1} , whereas modes 6b and 6a of *trans*-2,5-difluorophenol have 396 and 446 cm^{-1} , respectively. The weak bands at 126 and 338 cm^{-1} are assigned to vibronic transitions $10b'_0$ and $15'_0$ of *cis*-2,5-difluorophenol, respectively. Mode $10b'_0$ mainly involves out-of-plane C—OH bending motion, whereas mode 15 corresponds to in-plane C—F bending vibrations. The band at 37007 cm^{-1} is tentatively assigned to vibronic transition $9a'_0$, which mainly involves in-plane C—OH bending vibration.

3.2 Cation spectra of *cis*- and *trans*-2,5-difluorophenol

We applied the 2C-R2PI technique to record the PIE spectra of *cis*- and *trans*-2,5-difluorophenol by ionizing *via* their respective S_10^0 levels. Because this method detects the total ion current, it leads to an abrupt change near the ionization limit in the photo-ionization curve, as seen in Fig.2. The abruptly rising step indicates the IE of the selected molecular species with an uncertainty of about 10 cm^{-1} .

Because the MATI experiment detects threshold ions, it yields a sharp peak at the ionization threshold and gives a more precise adiabatic IE. In addition, it reveals the active vibrations of the *cis*- and *trans*-2,5-difluorophenol cations, as seen in Fig.3. Analysis of the 0^+ bands with consideration of the uncertainty in the laser photon energy, spectral width, and Stark effect, yields the adiabatic IEs of *cis*- and *trans*-2,5-difluorophenol to be $(71164 \pm 5) \text{ cm}^{-1}$ ($(8.8232 \pm 0.0006) \text{ eV}$) and $(71476 \pm 5) \text{ cm}^{-1}$ ($(8.8619 \pm 0.0006) \text{ eV}$), respectively. It is evident that the MATI experiment gives more precise IEs than those estimated by the PIE experiment, mentioned previously.

The distinct MATI bands in Fig.3(a) shifted from the ionization threshold (denoted by 0^+) by 434, 501, 725, and 758 cm^{-1} result from the in-plane ring deformation vibrations $6b^1$, $6a^1$, 12^1 , and 1^1 of the *cis*-2,5-difluorophenol cation in the D_0 state, respectively, as listed in Table 2. These vibrations are also observed for the *trans*-2,5-difluorophenol cation. Fig.4(a–e) shows the MATI spectra of *cis*-2,5-difluorophenol, recorded by ionizing *via* the 0^0 (36448 cm^{-1}), $10b^1$ ($0^0 + 126 \text{ cm}^{-1}$), $6a^1$ ($0^0 + 439 \text{ cm}^{-1}$), 12^1 ($0^0 +$

Table 1 Observed bands in the vibronic spectrum of *cis*- and *trans*-2,5-difluorophenol^a

	Energy/ cm^{-1}	Relative intensity	Shift/ cm^{-1}	Cal. shift/ cm^{-1}	Assignment and approximate description ^b
<i>cis</i>	36448	87			0^0_0 , band origin
	36574	16	126	130	$10b^1_0$, $\gamma(\text{C—OH})$, $\gamma(\text{C—F})$
	36786	9	338	323	15^1_0 , $\beta(\text{C—F})$
	36887	27	439	448	$6a^1_0$, $\beta(\text{CCC})$
	37153	50	705	669	12^1_0 , $\beta(\text{CCC})$
	37166	68	718	722	1^1_0 , breathing
<i>trans</i>	36743	30			0^0_0 , band origin
	37007	10	264	288	$9a^1_0$, $\beta(\text{C—OH})$, $\beta(\text{C—F})$
	37139	22	396	387	$6b^1_0$, $\beta(\text{CCC})$
	37187	100	446	439	$6a^1_0$, $\beta(\text{CCC})$

^aThe predicted values are obtained from the TD-B3LYP/6-311++G(*d,p*) calculations, scaled by 0.97. ^b β , in-plane bending; γ , out-of-plane bending

Fig.2 PIE curves of (a) *cis*-2,5-difluorophenol and (b) *trans*-2,5-difluorophenol, recorded by ionizing via their respective S_10^0 states at 36448 and 36743 cm^{-1}

705 cm^{-1}), 1^1 ($0^0 + 718 \text{ cm}^{-1}$) levels in the S_1 state. All the observed MATI bands are listed in Table 2. When the S_110b^1 state is used as the intermediate level, a few MATI bands are observed. As stated previously, this mode mainly corresponds to the out-of-plane C—OH bending motion with some contribution of the out-of-plane substituent-sensitive C—F bending motion. It is expected that

Fig.3 MATI spectra of (a) *cis*-2,5-difluorophenol and (b) *trans*-2,5-difluorophenol, recorded by ionizing via their respective S_10^0 states at 36448 and 36743 cm^{-1}

Table 2 Observed bands (in cm^{-1}) in the MATI spectra of *cis*-2,5-difluorophenol^a

Intermediate level in the S_1 state						Assignment and approximate description ^b
0^0	$10b^1$	$6a^1$	12^1	1^1	Cal. shift ^c	
	260					$10b^2$, $\gamma(\text{C—OH})$, $\gamma(\text{C—F})$
331	331	331			308	$9a^1$, $\beta(\text{C—OH})$, $\beta(\text{C—F})$
389	388	386			354	15^1 , $\beta(\text{C—F})$
434					400	$6b^1$, $\beta(\text{CCC})$
501		501			510	$6a^1$, $\beta(\text{CCC})$
	519					$10b^4$
		659				$9a^2$
725			729	730	734	12^1 , $\beta(\text{CCC})$
758			763	766	771	1^1 , breathing
866						$6b^2$
				933		$6a^16b^1$
			982			12^110b^2
		999				$6a^2$
				1041		12^19a^1
				1149		1^115^1

^aThe experimental values are shifts from 71164 cm^{-1} , whereas the calculated ones are obtained from the UB3LYP/6-311++G(*d,p*) calculations (without being scaled). ^b β , in-plane bending; γ , out-of-plane bending.

most of the resulting active cation vibrations likely involve substituent-sensitive motions. The bands at 260, 331, 388, and 519 are tentatively assigned to the $10b^2$, $9a^1$, 15^1 , and $10b^4$ vibrations, respectively. In addition to these substituent-sensitive modes, many in-plane ring deformation vibrations of the *cis*-2,5-difluorophenol cation are observed. For example, vibrations $6b$, $6a$, 12 , and 1 are found to have frequencies of 434, 501, 729, and 766 cm^{-1} , respectively.

As shown in Fig.3(b) and Table 3, the active vibrations of the *trans*-2,5-difluorophenol cation include $6b^1$, $6a^1$, 12^1 , and 1^1 with frequencies of 434, 501, 725, and 758 cm^{-1} , respectively. For each of these in-plane ring deformation modes, the vibrational frequency of *trans*-2,5-difluorophenol is very close to that of *cis*-2,5-difluorophenol. This result indicates that relative configuration of the OH substituent with respect to the F atom has little effect on these normal vibrations of the 2,5-difluorophenol cation. In other words, the weak intramolecular OH...F through-space interaction has little influence on the frequency of the in-plane ring vibration.

4 Discussion

4.1 Energy level diagram and OH...F through-space interaction

Previous spectroscopic studies show that only the *cis* form involves in the photo-excitation and ionization processes of 2-fluorophenol^{14,15} and 2,4-difluorophenol^{11,12}. In the cases of 3-fluorophenol¹⁸ and 3,4-difluorophenol¹³, both *cis* and *trans* rotamers have been detected in the S_1 and D_0 states. The weak through-space intramolecular interaction between the F and OH substituents may be accountable for these experimental results. It is intuitively for one to expect a similar through-space OH...F substituent-sub-

Fig.4 MATI spectra of *cis*-2,5-difluorophenol recorded by ionizing via its (a) 0^0 , (b) $10b^1$, (c) $6a^1$, (d) 12^1 , and (e) 1^1 levels in the S_1 state

Table 3 Observed bands (in cm^{-1}) in the MATI spectra of *trans*-2,5-difluorophenol^a

Intermediate level in the S_1 state		Assignment and approximate description ^b
0^0	Cal. shift ^c	
434	407	$6b^1$, $\beta(\text{CCC})$
501	508	$6a^1$, $\beta(\text{CCC})$
725	737	12^1 , $\beta(\text{CCC})$
758	773	1^1 , breathing

^aThe experimental values are shifts from 71476 cm^{-1} , whereas the calculated ones are obtained from the UB3LYP/6-311++G(*d,p*) calculations (without being scaled). ^b β , in-plane bending; γ , out-of-plane bending.

stituent interaction to exist in 2,5-difluorophenol.

Our B3LYP/6-311++G(*d,p*) calculations show that in the S_0 state the ZPE of *cis*-2,5-difluorophenol is lower than that of *trans*-2,4-difluorophenol by 1012 cm^{-1} . As stated previously, the E_1 of *cis*- and *trans*-2,5-difluorophenol are measured to be 36448 and 36743 cm^{-1} , respectively. These experimental and calculated results suggest that the ZPE in the S_1 state of the *cis* rotamer is lower than that of the *trans* rotamer by 1307 cm^{-1} , as shown in Fig.5. This implies that the *cis* rotamer has a slightly stronger OH...F through-space interaction than the *trans* rotamer in the S_1

state as that in the S_0 state. In a similar fashion, Fujii and co-workers⁴¹ proposed an enhanced interaction of the NH_2 and OH substituents for the *cis* rotamer in their spectroscopic study of 3-aminophenol. With the measured IE and calculated values, one estimates that the *cis* rotamer lies in a lower energy level than that of the *trans* rotamer by 1324 cm^{-1} , as shown in Fig.5. These results suggest that in all S_0 , S_1 , and D_0 states *cis*-2,5-difluorophenol has an OH...F through-space interaction, where *trans*-2,5-difluorophenol does not have. Tsai and Tzeng¹³ reported that in the S_0 state *cis*-3,4-difluorophenol lies in a slightly higher energy level than *trans*-3,4-difluorophenol by 71 cm^{-1} . However, the *cis* rotamer lies in a slightly lower energy level than the *trans* rotamer in the S_1 and D_0 states by no more than 150 cm^{-1} . Because the two F atoms are far away from the OH substituent, the through-space interaction of the OH and F substituents of 3,4-difluorophenol is negligible. Therefore, the strength of through-space substituent-substituent interaction depends on the nature and location of the substituents as well as the electronic state of these rotameric species.

4.2 Transition energy and additivity rule

Table 4 lists the measured E_1 and IEs of phenol and its fluorine substituted derivatives on the basis of the LIF, REMPI, ZEKE, and MATI experiments^{14–18,42}. The E_1 of 2-fluorophenol is higher than that of phenol by 451 cm^{-1} , and those of *cis*- and *trans*-3-fluorophenol are greater by 274 and 480 cm^{-1} , respectively. The fluorine atom can interact with the aromatic ring through the σ bond by the inductive effect and via the π orbital overlap. The collective

Fig.5 Energy level diagram of the *cis* and *trans* rotamers of 2,5-difluorophenol in the S_0 , S_1 , and D_0 states

The energy is in unit of cm^{-1} . The relative energy of the two rotamers in the S_0 state is obtained from the B3LYP/6-311++G(*d,p*) calculations, whereas those in the S_1 and D_0 states are deduced from the measured values in our R2PI and MATI experiments.

Table 4 Measured transition energies (cm^{-1}) of phenol and its fluorine substituted derivatives^a

Molecule	E_1	δE_1	E_2	δE_2	IE	δIE
phenol ^b	36349	0	32276	0	68625	0
2-fluorophenol ^c	36800	451	33206	930	70006	1381
3-fluorophenol, <i>cis</i> ^d	36623	274	33565	1289	70188	1563
3-fluorophenol, <i>trans</i> ^d	36829	480	33620	1344	70449	1824
2,5-difluorophenol, <i>cis</i> ^e	36448	99	34716	2440	71164	2539
2,5-difluorophenol, <i>trans</i> ^e	36743	394	34733	2457	71476	2851

^a δE_1 , δE_2 , and δIE are energy shifts of E_1 , E_2 , and IE with respect to those of phenol. ^bRef.42, ^cRef.16, ^dRef.18, ^ethis work

result of this substituent-ring interaction leads to a blue shift in the E_1 for the F substitution at the *ortho* and *meta* positions of phenol, as seen in Table 4.

One may consider whether the additivity rule^{13,20} can be used to estimate the electronic excitation energy of 2,5-difluorophenol before performing the R2PI experiments for recording the vibronic spectrum as follows. The calculated energy shift (δE_1) of 274 cm^{-1} [for *cis*-3-fluorophenol] and 451 cm^{-1} [for 2-fluorophenol] is 725 cm^{-1} , which deviates from the experimental δE_1 of 99 cm^{-1} for *cis*-2,5-difluorophenol by as much as 626 cm^{-1} . Moreover, the δE_1 of *trans*-2,5-difluorophenol is estimated to be 931 cm^{-1} ($= 480 + 451 \text{ cm}^{-1}$). This value differs from the experimental δE_1 of 394 cm^{-1} by as much as 537 cm^{-1} for *trans*-2,5-difluorophenol. This additivity propensity allows us to predict the E_1 of 2,5-difluorophenol to no more than 4 nm. A previous study¹³ shows that the corresponding values for *cis*-3,4-difluorophenol and *trans*-3,4-difluorophenol are 95 and 107 cm^{-1} . The difference between the estimated E_1 and measured value is small for 3,4-difluorophenol.

The $D_0 \leftarrow S_1$ transition of the present two-photon R2PI and MATI experiments of 2,5-difluorophenol likely corresponds to the removal of one electron from the aromatic system. The electron-withdrawing F atom causes a decrease in the electron density on the aromatic ring as well as the OH group. Therefore, the energies of the $D_0 \leftarrow S_1$ transition (E_2) of 2-fluorophenol, *cis*- and *trans*-3-fluorophenol are greater than that of phenol, as seen in Table 4. Similar to that stated above, the calculated δE_2 of 2219 cm^{-1} ($= 930 + 1289 \text{ cm}^{-1}$) is different from the experimental value of 2440 cm^{-1} for *cis*-2,5-difluorophenol by as small as 221 cm^{-1} . Furthermore, the calculated δE_2 is 2274 cm^{-1} ($= 930 + 1344 \text{ cm}^{-1}$) which differs from the experimental δE_2 of 2457 cm^{-1} by only 183 cm^{-1} for *trans*-2,5-difluorophenol. This shows that the additivity rule propensity allows us to set the probe laser to monitor the $D_0 \leftarrow S_1$ transition of the *cis* and *trans* rotamers of 2,5-difluorophenol to no more than 2 nm.

4.3 *Cis-trans* isomerization energy barrier

Because the density functional theory (DFT) method does not give a convergent result for the S_1 state, we performed the Hartree-Fock (HF) calculations to investigate the *cis-trans* isomerizations of 2,5-difluorophenol in the S_0 , S_1 , and D_0 states. These calculations yield the total electronic energy (E_{total}) by scanning one-dimensional potential energy surface on the rotation of ring-hydroxyl bond while all other geometric parameters are fixed. The dihedral angle θ (or C2C1OH) defines the ring-hydroxyl bond with respect to the plane of the aromatic ring. Fig.6 shows the one-

dimensional potential energy surfaces of 2,5-difluorophenol in the D_0 , S_1 , and S_0 states, obtained from the unrestricted HF (UHF), configuration interaction singles (CIS), and restricted HF (RHF) calculations with the 6-311++G(*d,p*) basis set, respectively. It is noted that the obtained E_{total} is related to the bottom of potential well rather than the ZPE level. The calculated results indicate that the *cis* configuration is most stable in all these three states. They predict that the energy barrier for the *trans* rotamer to become the *cis* rotamer is 569 cm^{-1} in the S_0 state, 1787 cm^{-1} in the S_1 state, and 1795 cm^{-1} in the D_0 state. Clearly, the energy barriers of the S_1 and D_0 states are about three times of that of the S_0 state. A possible explanation is that the interaction between the hydroxyl group and

Fig.6 One-dimensional potential energy surfaces of 2,5-difluorophenol in the (a) D_0 , (b) S_1 , and (c) S_0 states, obtained from the UHF, CIS, RHF calculations with the 6-311++G(*d,p*) basis set

the ring of 2,5-difluorophenol in the S_1 or D_0 state is slightly stronger than that in the S_0 state. These calculated results support our experimental finding that isomerization of 2,5-difluorophenol does not occur in the UV photoexcitation and ionization processes.

4.4 Vibrational frequency and molecular geometry

2,5-Difluorophenol has 33 normal vibrational modes. The $S_1 \leftarrow S_0$ transition is likely subject to a $\pi^* \leftarrow \pi$ electronic excitation, leading to a ring expansion and significant change in molecular geometry. Because the intensity of the each vibronic band is related to Franck-Condon overlaps, not all transitions can be observed in the vibronic spectrum. Analysis of the vibronic spectrum in Fig.2 suggests that most of the observed active vibrations in the S_1 state are related to the in-plane ring deformation and substituent-sensitive bending modes. In the two-color resonant two-photon MATI experiments, the intensity of the observed MATI band is related to (1) the oscillator strength of the $S_1 \leftarrow S_0$ transition, (2) the transition cross section from the S_1 state to the Rydberg state, (3) the pulsed field ionization efficiency, and (4) the overlap integral between the vibrational coordinates of the neutral and the cation. Because of the above reasons, we could only record the MATI spectrum of *trans*-2,5-difluorophenol, by ionizing *via* the S_1^0 state, as seen in Fig.2(b). However, we were able to record the MATI spectra of *cis*-2,5-difluorophenol by ionizing *via* several intermediate vibronic states. When the $S_1 6a^1$, $S_1 12^1$, and $S_1 1^1$ states are used as the intermediate levels, the MATI bands resulting from the same in-plane vibrations of the *cis*-2,5-difluorophenol cation in the D_0 state appear to be very strong, as seen in Fig.4(c–e). This observed $\Delta v = 0$ propensity implies a good Franck-Condon correspondence associated with the $D_0 \leftarrow S_1$ transition. It indicates that the geometry and vibrational patterns of these modes of *cis*-2,5-difluorophenol are alike for both the S_1 and D_0 states. Similar observations have been reported for *cis*-3-fluorostyrene⁴³, 3-fluoroanisole⁴⁴, 3,4-difluoroanisole⁴⁵, and 3,4-difluorophenol¹³.

In-plane ring deformation vibrations $6a$, 12 , and 1 of *cis*-2,5-difluorophenol are measured to have respective frequencies of 439, 705, and 718 cm^{-1} in the neutral S_1 state and 501, 725, and 758 cm^{-1} in the cationic D_0 state. Similarly, modes $6b$, and $6a$ of *trans*-2,5-difluorophenol have respective frequencies of 396 and 446 cm^{-1} in the S_1 state and 434 and 501 cm^{-1} in the D_0 state. These experimental data show that frequencies of in-plane ring deformation vibrations in the D_0 state are slightly greater than those in the S_1 state for these two rotamers of 2,5-difluorophenol. It is known that frequency is proportional to the square root of force constant. The observed higher frequency of the ring deformation vibrations implies that the molecular geometry of 2,5-difluorophenol in the D_0 state is slightly tighter than that in the S_1 state.

5 Conclusions

We applied the R2PI and MATI techniques to record the vibronic and cation spectra of *cis*- and *trans*-2,5-difluorophenol in the S_1 and D_0 states. The E_1 values of the *cis* and *trans* rotamers are found to be 36448 and 36743 cm^{-1} , whereas the adiabatic IEs are determined to be 71164 and 71476 cm^{-1} , respectively. Our B3LYP/

6-311++G(*d,p*) calculations predict that in the S_0 state the ZPE of *cis*-2,5-difluorophenol is lower than that of *trans*-2,5-difluorophenol by 1012 cm^{-1} . Therefore, the ZPEs in the S_1 and D_0 states of the *cis* rotamer are deduced to be lower than those of the *trans* by 1307 and 1324 cm^{-1} , respectively. This implies that the *cis* rotamer in the S_0 , S_1 , and D_0 states may exhibit a intramolecular OH...F interaction.

With the available spectroscopic data of phenol, 2-fluorophenol, and *cis*- and *trans*-3-fluorophenol, we applied the additivity propensity to locate the band origin of the $S_1 \leftarrow S_0$ electronic transition and ionization threshold. This allows us to set the wavelengths of the pump and probe lasers for our R2PI and MATI experiments to record the vibronic and cation spectra of 2,5-difluorophenol in a very convenient way.

The observed active modes of *cis*- and *trans*-2,5-difluorophenol in the S_1 and D_0 states include the in-plane ring deformation and substituent-sensitive bending vibrations. Analysis of the MATI spectra recorded by ionizing *via* several intermediate levels shows that a propensity of maintaining the same vibration in the $D_0 \leftarrow S_1$ transition exists. This indicates that the molecular geometry and vibrational coordinates of the cation in the D_0 state resemble those of the neutral species in the S_1 state for *cis*-2,5-difluorophenol. In addition, investigations on the frequencies of in-plane ring deformation vibrations $6b^1$, $6a^1$, 12^1 , and 1^1 suggest that the geometries of *cis*- and *trans*-2,5-difluorophenol are more rigid in the cationic D_0 state than those in the neutral S_1 state.

References

- (1) Ribero da Silva, M. A. V.; Lobo Ferreira, A. I. M. C. *J. Chem. Thermodyn.* **2010**, *42*, 133. doi: 10.1016/j.jct.2009.07.021
- (2) Rao, R.; Aralakkanavar, M. K.; Rao, K. S.; Shashidhar, M. A. *Spectrochim. Acta A* **1989**, *45*, 103. doi: 10.1016/0584-8539(89)80110-2
- (3) Kolek, P.; Pirowska, K.; Gora, M.; Kozik, B.; Najbar, J. *Chem. Phys.* **2002**, *285*, 55. doi: 10.1016/S0301-0104(02)00689-4
- (4) Kolek, P.; Pirowska, K.; Chacaga, L.; Najbar, J. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4096. doi: 10.1039/B305797F
- (5) Itoh, T.; Tanaka, N.; Tsukada, Y.; Nishikiori, H.; Fujii, T. *J. Mol. Struct.* **2011**, *1000*, 35. doi: 10.1016/j.molstruc.2011.05.046
- (6) Yoon, Y. K.; Huh, C. S.; Lee, S. K. *Chem. Phys. Lett.* **2012**, *550*, 58. doi: 10.1016/j.cplett.2012.08.060
- (7) Huh, C. S.; Yoon, Y. W.; Lee, S. K. *J. Chem. Phys.* **2012**, *136*, 174306. doi: 10.1063/1.4708808
- (8) Ito, M.; Oikawa, A. *J. Mol. Struct.* **1985**, *126*, 133. doi: 10.1016/0022-2860(85)80109-5
- (9) Kazmierski, W. M.; Danehower, S.; Duan, M.; Ferris, R. G.; Elitzin, V.; Minick, D.; Sharp, M.; Stewart, E.; Villeneuve, M.; *Med. Chem. Lett.* **2014**, *5*, 1296. doi: 10.1021/ml5004124
- (10) Ortega, D. R.; Yang, C.; Ames, P.; Baudry, J.; Parkinson, J. S.; Zhulin, I. B. *Nat. Commun.* **2013**, *4*, 1. doi: 1038/ncomms3881
- (11) Chakrabarti, S.; Jaman, A. I. *J. Mol. Struct.* **2002**, *642*, 93. doi:

- 10.1016/S0022-2860(02) 00398-8
- (12) Shivatare, V.; Tzeng, W. B. *Bull. Korean Chem. Soc.* **2014**, *35*, 815. doi: 10.5012/bkcs.2014.35.3.815
- (13) Tsai, C. Y.; Tzeng, W. B. *J. Photochem. Photobiol. A* **2013**, *270*, 53. doi: 10.1016/j.jphotochem.2013.07.014
- (14) Fujii, A.; Iwasaki, A.; Mikami, N. *Chem. Lett.* **1997**, *11*, 1099. doi: 10.1246/cl.1997.1099
- (15) Fujimaki, E.; Fujii, A.; Ebata, T.; Mikami, N. *J. Chem. Phys.* **1999**, *110*, 4238. doi: 10.1063/1.478306
- (16) Yuan, L.; Li, C.; Lin, J. L.; Yang, S. C.; Tzeng, W. B. *Chem. Phys.* **2006**, *323*, 429. doi: 10.1016/j.chemphys.2005.10.004
- (17) Oikawa, A.; Abe, H.; Mikami, N.; Ito, M. *Chem. Phys. Lett.* **1985**, *116*, 50. doi: 10.1016/0009-2614(85) 80123-8
- (18) Yosida, K.; Suzuki, K.; Ishiuchi, S.; Sakai, M.; Fujii, M.; Dessent, C. E. H.; Muller-Dethlefs, K. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2534. doi: 10.1039/B201107G
- (19) Zhang, B.; Li, C.; Su, H.; Lin, J. L.; Tzeng, W. B. *Chem. Phys. Lett.* **2004**, *390*, 65. doi: 10.1016/j.cplett.2004.04.013
- (20) Huang, W. C.; Huang, P. S.; Hu, C. H.; Tzeng, W. B. *Chem. Phys. Lett.* **2013**, *580*, 28. doi: 10.1016/j.cplett.2013.06.053
- (21) Ribeiro-Claro, P. J. A.; Teixeira-Dias, J. J. C.; Hollas, J. M.; Milewski, M. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 197. doi: 10.1039/FT9959100197
- (22) Breen, P. J.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 1958. doi: 10.1021/ja00188a002
- (23) Li, C.; Lin, J. L.; Tzeng, W. B. *J. Chem. Phys.* **2005**, *122*, 044311. doi: 10.1063/1.1839863
- (24) Gerhards, M.; Perl, W.; Kleinermanns, K. *Chem. Phys. Lett.* **1995**, *240*, 506. doi: 10.1016/0009-2614(95) 00567-N
- (25) Patwari, G. N.; Doraiswamy, S.; Wategaonkar, S. *Chem. Phys. Lett.* **1998**, *289*, 8. doi: 10.1016/S0009-2614(98) 00398-4
- (26) Telle, H. H.; Urena, A. G.; Donovan, R. J. *Laser Chemistry*; John Wiley & Sons, Ltd.: West Sussex, England, 2007.
- (27) Müller-Dethlefs, K.; Sander, K. M.; Schlag, E. W. *Chem. Phys. Lett.* **1984**, *112*, 291. doi: 10.1016/0009-2614(84) 85743-7
- (28) Müller-Dethlefs, K.; Dopfer, O.; Wright, T. G. *Chem. Rev.* **1994**, *94*, 1845. doi: 10.1021/cr00031a006
- (29) Cockett, M. C. R. *Chem. Soc. Rev.* **2005**, *34*, 935. doi: 10.1039/b505794a
- (30) Zhu, L.; Johnson, P. J. *Chem. Phys.* **1991**, *94*, 5769. doi: 10.1063/1.460460
- (31) Dessent, C. E. H.; Haines, S.; Müller-Dethlefs, K. *Chem. Phys. Lett.* **1999**, *315*, 103. doi: 10.1016/S0009-2614(99) 01193-8
- (32) Georgiev, S.; Karaminkov, R.; Chervenkov, S.; Delchev, V.; Neusser, H. J. *J. Phys. Chem. A* **2009**, *113*, 12328. doi: 10.1021/jp908045k
- (33) Witte, F.; Riese, M.; Gunzer, F.; Grotemeyer, J. *Int. J. Mass Spectrom.* **2011**, *306*, 129. doi: 10.1016/j.ijms.2010.10.002
- (34) Lin, J. L.; Tzeng, W. B. *Appl. Spectrosc.* **2003**, *57*, 1178. doi: 10.1366/00037020360696062
- (35) Xu, Y.; Tzeng, S. Y.; Shivatare, V.; Takahashi, K.; Zhang, B.; Tzeng, W. B. *J. Chem. Phys.* **2015**, *142*, 124314. doi: 10.1063/1.4916052
- (36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; *et al.* *Gaussian 09*, Revision A.02; Gaussian Inc.: Wallingford, CT, 2009.
- (37) Dennington, R.; Keith, T.; Millam, J.; *GaussView*, Version 5; Semichem Inc.: Shawnee Mission KS, 2009.
- (38) Varsanyi, G.; Szoke, S. *Vibrational Spectra of Benzene Derivatives*; Academic Press: London, 1969.
- (39) Varsanyi, G. *Assignments of Vibrational Spectra of Seven Hundred Benzene Derivatives*; Wiley: New York, 1974.
- (40) Wilson, E. B. *Phys. Rev.* **1934**, *45*, 406. doi: 10.1103/PhysRev.45.706
- (41) Shinozaki, M.; Sakai, M.; Yamaguchi, S.; Fujioka, T.; Fujii, M. *Phys. Chem. Chem. Phys.* **2003**, *5*, 5044. doi: 10.1039/B309461H
- (42) Dopfer, O.; Müller-Dethlefs, K. *J. Chem. Phys.* **1994**, *101*, 8508. doi: 10.1063/1.468111
- (43) Wu, P. Y.; Tzeng, W. B. *J. Mol. Spectrosc.* **2015**, *316*, 72. doi: 10.1016/j.jms.2015.06.011
- (44) Shiung, K. S.; Yu, D.; Huang, H. C.; Tzeng, W. B. *J. Mol. Spectrosc.* **2012**, *274*, 43. doi: 10.1016/j.jms.2012.04.004
- (45) Xu, Y.; Tzeng, S. Y.; Zhang, B.; Tzeng, W. B. *Spectrochim. Acta A* **2013**, *102*, 365. doi: 10.1016/j.saa.2012.10.020