



## Research paper

## Resonance enhanced multiphoton ionization and mass analyzed threshold ionization spectroscopy of 4-fluorobenzonitrile

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## HIGHLIGHTS

- 2C REMPI and MATI spectra of 4-fluorobenzonitrile are obtained.
- Vibronic spectra of 4-fluorobenzonitrile in  $S_1$  state are analyzed and assigned.
- Cationic vibrational features of 4-fluorobenzonitrile are analyzed and assigned.
- Most of the active vibrations are related to the in-plane ring deformation.

## ARTICLE INFO

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## ABSTRACT

The vibrational features of 4-fluorobenzonitrile in the first electronically excited state  $S_1$  and cationic ground state  $D_0$  have been studied by two-color resonance enhanced multiphoton ionization and mass analyzed threshold ionization spectroscopy. Most of observed vibrations in the  $S_1$  and  $D_0$  states are related to in-plane ring deformation and CN bending motions. The band origin of the  $S_1 \leftarrow S_0$  transition and adiabatic ionization energy of 4-fluorobenzonitrile are determined to be  $36,616 \pm 2$  and  $78,000 \pm 5 \text{ cm}^{-1}$ , respectively. These data provide insight into the substitution effect of fluorine atom and cyano group on the transition energy.

## 1. Introduction

Fluorinated organic molecules have been a subject of great interest due to their important applications in the agrochemical, medicinal, biological and material sciences [1–4]. In recent years, the chemical and physical properties of fluorinated aromatic compounds are investigated by various spectroscopic methods. The geometric changes of fluorination on fluorine-substituted compounds of benzene, benzonitrile, and pyridine have been studied by the high resolution microwave spectroscopy [5–7]. The vibrational features of fluorine-substituted derivatives of phenol, anisole, and aniline in the first electronically excited states  $S_1$  and cationic ground states  $D_0$  have also been studied by laser induced fluorescence (LIF), resonance enhanced multiphoton ionization (REMPI) and mass analyzed threshold ionization (MATI) spectroscopy [8–12]. Jiang and Levy performed the laser induced fluorescence and dispersed fluorescence experiments of 4-fluorobenzonitrile to analyze the internal vibration relaxation [13]. Arivazhagan et al. measured the vibrational properties of 4-fluorobenzonitrile in the electronic ground state  $S_0$  by infrared and Raman

spectroscopy [14]. To our best of knowledge, the detailed spectroscopic information of the  $S_1$  and  $D_0$  states of 4-fluorobenzonitrile are still unavailable in the literature.

In this paper, we study the two-color REMPI and MATI spectra of 4-fluorobenzonitrile. With the help of density functional theory (DFT) calculations, the active vibrations of 4-fluorobenzonitrile in the  $S_1$  and  $D_0$  states are assigned. The band origin of the  $S_1 \leftarrow S_0$  transition and the adiabatic ionization energy are determined. Comparing these experimental data with those of benzonitrile and *para*-fluoro substituted derivatives provides a better understanding of the substitution effect of fluorine atom and cyano group on the transition energy.

## 2. Experimental and computational details

## 2.1. Experimental method

The experimental apparatus consists of a time-of-flight (TOF) mass spectrometer and two tunable UV lasers as described in previous publication [15]. The sample of 4-fluorobenzonitrile, purchased from

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Sigma-Aldrich (99% purity) without further purification, was heated to 60 °C in order to obtain sufficient vapor pressure. A molecular beam was produced by expanding the vapor, seeded in 3 bar of argon, through a pulsed valve of 0.5 mm diameter nozzle into the vacuum. After passing through a 1 mm diameter skimmer, the molecular beam was crossed with the laser beams in the ionization region. The excitation and ionization lasers were generated by the frequency-doubled dye lasers (Sirah: CBR-D-24 and PrecisionScan-D), which were pumped by the third harmonics of two independent Nd:YAG lasers (Spectra Physics: INDI-40-10 and Quantel: Q-smart 850). The wavelengths of the dye lasers were calibrated using a wavemeter (HighFinesse WS-7). The REMPI spectrum was measured by scanning the excitation laser in the 260–274 nm range and fixing the ionization laser to 241 nm. The relative time between the two laser systems was controlled by a pulse delay generator (DG645) with 8 delay outputs.

For the MATI spectroscopy, molecules were excited to long-lived high  $n$  Rydberg states by the two tunable UV lasers. A weak pulse electric field of  $-1.3$  V/cm was switched on about 200 ns after the laser pulses to reject the prompt ions. This field resulted in the lowering of ionization energy, which can be estimated by  $4.0F^{1/2}$  cm $^{-1}$  ( $F$  is electric field in unit of V/cm). After a time delay of 21  $\mu$ s, a second pulse electric field of 140 V/cm was switch on to field-ionize the Rydberg neutrals. The produced threshold ions were accelerated and detected by a dual-stacked microchannel plates detector (Changcheng Microlight Equipment Co., 25 mm diameter) located at the end of a field-free flight tube. The mass spectra were collected and analyzed by a multichannel scaler (Stanford Research Systems, SR430), then transferred to a computer.

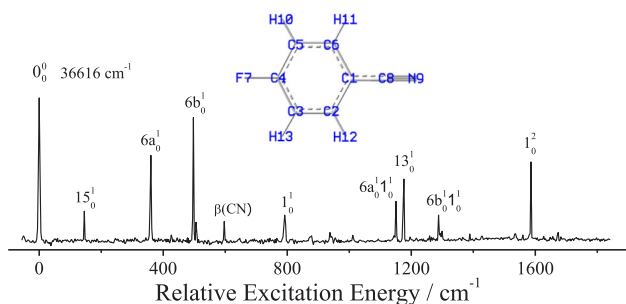
## 2.2. Computational method

In order to assign the observed bands in the REMPI and MATI spectra, we used the Gaussian 09 program package [16] to perform the geometry optimizations and frequency calculations of 4-fluorobenzonitrile. For the electronic ground state  $S_0$  and the cationic ground state  $D_0$ , the density functional theory (DFT) calculations using the B3LYP functional were carried out with the 6-311 + G (d,p) basis set. The first excited state  $S_1$  was calculated using the time-dependent density functional theory (TDDFT) with the 6-311 + G (d,p) basis set.

## 3. Results

### 3.1. Two-color REMPI spectrum of 4-fluorobenzonitrile

We recorded the vibronic spectrum of 4-fluorobenzonitrile in the  $S_1$  state by two-color REMPI experiment. No fragments were observed in the mass spectrum. Fig. 1 displays the two-color REMPI spectrum of 4-fluorobenzonitrile near the origin of the  $S_1 \leftarrow S_0$  transition. The result is in good agreement with the fluorescence excitation spectrum of 4-



**Fig. 1.** Two-color REMPI spectrum of 4-fluorobenzonitrile obtained by fixing the ionization laser at 241 nm and scanning the excitation laser. The spectrum is shifted by 36,616 cm $^{-1}$ . The insert shows the molecular structure and atom labels.

**Table 1**

Observed vibrational frequencies (cm $^{-1}$ ) of 4-fluorobenzonitrile in two-color REMPI spectrum and their assignments.<sup>a</sup> The predicted values obtained from the TD-B3LYP/6-311G++(d,p) calculation are scaled by 0.9766.

Ref. [34]	This work		Assignment <sup>b</sup>
	Exp. <sup>a</sup>	Exp. Rel. Int.	
	0	100	0 <sub>0</sub> <sup>0</sup> , band origin
	145	22	15 <sub>0</sub> <sup>1</sup> , β(C-CN)
	360	61	6a <sub>0</sub> <sup>1</sup> ,β(CCC)
497	497	86	6b <sub>0</sub> <sup>1</sup> ,β(CCC)
	506	15	4 <sub>0</sub> <sup>1</sup> , γ(CCC), γ(C-F)
	597	15	β(CN)
792	792	20	1 <sub>0</sub> <sup>1</sup> , breathing
	878	5	6a <sub>0</sub> <sup>1</sup> 4 <sub>0</sub> <sup>1</sup>
	938	8	15 <sub>0</sub> <sup>1</sup> 1 <sub>0</sub> <sup>1</sup>
	1011	6	4 <sub>0</sub> <sup>2</sup>
	1151	29	6a <sub>0</sub> <sup>1</sup> 1 <sub>0</sub> <sup>1</sup>
1176	1176	44	13 <sub>0</sub> <sup>1</sup> , ν(C-CN)
	1288	20	6b <sub>0</sub> <sup>1</sup> 1 <sub>0</sub> <sup>1</sup>
	1299	9	18b <sub>0</sub> <sup>1</sup> , β(CH)
1588	1586	56	1 <sub>0</sub> <sup>2</sup>
	1674	8	6b <sub>0</sub> <sup>1</sup> 13 <sub>0</sub> <sup>1</sup>

<sup>a</sup> The experimental values are shifts from 36,616 cm $^{-1}$ .

<sup>b</sup> ν, stretching; β, in-plane bending; γ, out-of-plane bending.

fluorobenzonitrile measured by Jiang and Levy [13]. The intense peak located at 36,616 cm $^{-1}$  is assigned as the origin of the  $S_1 \leftarrow S_0$  electronic transition. 4-fluorobenzonitrile is a planar molecule with 33 normal modes. Only the vibronic transitions with larger Franck-Condon factor can be observed in the REMPI spectrum [17,18]. Table 1 lists the frequencies of the observed vibronic bands of 4-fluorobenzonitrile, along with the computed values and their assignments. The assignments are based on the previous results [13] and our TDDFT calculation at B3LYP/6-311++G(d,p) level. The Varsanyi's numbering system [19] was adopted to approximately describe the normal modes of benzene-like vibrations, and the vibrational modes are expressed by Wilson's notation [20]. Most of active vibrations of 4-fluorobenzonitrile in the  $S_1$  state are related to the in-plane deformation of aromatic ring. The pronounced bands at 145, 360, 497 and 1176 cm $^{-1}$  are assigned to the transitions of 15<sub>0</sub><sup>1</sup>, 6a<sub>0</sub><sup>1</sup>, 6b<sub>0</sub><sup>1</sup>, and 13<sub>0</sub><sup>1</sup>, respectively. Modes 6a and 6b mainly involve the in-plane deformation of aromatic ring. Modes 15 and 13 are related to the substitute-sensitive in-plane ring-CN bending and ring-CN stretching vibrations, respectively. The bands at 792 and 1586 cm $^{-1}$  result from the ring breathing vibration 1<sup>1</sup> and its overtone 1<sup>2</sup>. The out-of-plane ring deformation vibration 4<sup>1</sup> appears at 506 cm $^{-1}$ . The weak band at 597 cm $^{-1}$  corresponds to CN in-plane bending β(CN). The high-frequency bands at 1151 and 1288 cm $^{-1}$  are assigned to the combination vibrations 6a<sup>1</sup>1<sup>1</sup> and 6b<sup>1</sup>1<sup>1</sup>, respectively.

### 3.2. PIE and MATI spectra of 4-fluorobenzonitrile

The photoionization efficiency (PIE) and MATI experiments are performed to determine the adiabatic ionization energy (IE) of 4-fluorobenzonitrile. The PIE curve (available on request) recorded by ionizing via the  $S_1$ 0<sup>0</sup> intermediate state indicates the IE of 4-fluorobenzonitrile to be 78,000 cm $^{-1}$  with an uncertainty of 10 cm $^{-1}$ . Because the MATI experiment only detects the threshold ions resulting from the field ionization of the high Rydberg molecules, it leads to a sharp peak at the ionization limit and yields a more precise IE. Figs. 2 and 3 show the MATI spectra of 4-fluorobenzonitrile recorded via the 0<sup>0</sup>, 15<sup>1</sup>, 6a<sup>1</sup>, 6b<sup>1</sup>, β(C-CN), and 1<sup>1</sup> levels of the  $S_1$  state. The most intense band 0<sup>+</sup> in Fig. 2a corresponds to the origin of the transition  $D_0 \leftarrow S_1$ . The resulting adiabatic IE, including the correction for Stark effect due to the pulsed electronic field, is determined to be

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