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4-Chloro-3-fluoroaniline studied by resonant two-photon ionization and mass-analyzed threshold ionization spectroscopy

Yi Hsuan Huang, Wei Chih Huang, Wen Bih Tzeng *

Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, 1, Sec. 4, Roosevelt Road, Taipei 10617, Taiwan
Department of Chemistry, National Taiwan Normal University, 88, Sec. 4, Tingzhou Road, Taipei 11677, Taiwan

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ABSTRACT

The excitation energy of the $S_1 \leftarrow S_0$ transition (E_1) and the adiabatic ionization energy (IE) of 4-chloro-3-fluoroaniline (4C3FA) are found to be 33 242 and 63 868 cm^{-1}, respectively. Comparing these data with those of 4-chloroaniline, 3-fluoroaniline, and aniline, we find an additivity rule associated with the E_1 and IE. This implies that the interaction among the Cl, F, and NH_2 substituents is weak. The new vibronic and cation spectra 4C3FA can be used as fingerprints for molecular identification.

1. Introduction

Spectroscopic studies of tri-substituted benzenes [1–5] are not rich because they involve challenging spectral assignment. To resolve this problem, scientists investigate a series of structural and positional isomers by using high resolution spectroscopic techniques. Recently, Tzeng and coworkers reported the vibronic and cation spectra of 3,4-difluoroaniline [6], 2,4-difluoroaniline [7], 2,5-difluoroaniline [8], 3-chloro-4-fluoroaniline [9], 3,4-difluorophenol [10], and 3,4-difluoroanisole [11]. These experimental data provide information about precise electronic excitation and ionization energies as well as active vibrations in the electronically excited S_1 and cationic ground D_0 states. Here, we choose 4-chloro-3-fluoroaniline (4C3FA) for the present studies because no spectroscopic information is currently available in the literature. By comparing these with the existing data, we can learn more about photochemistry and photophysics of structural and positional isomers. In addition, we can examine whether an additivity rule regarding the transition energy exists for 4C3FA, as those found in some tri-substituted benzenes [6–11].

Excitation laser-induced fluorescence (LIF) [12,13] and zero kinetic energy (ZEKE) photoelectron [14–16] spectroscopy are effective methods to record the vibronic and cation spectra. These techniques detect photons or electrons with high sensitivity and spectral resolution. As alternative approaches, the resonance enhanced multiphoton ionization (REMPI) [17,18] and mass-analyzed threshold ionization (MATI) spectroscopic methods [19–22] can give the same experimental data with unambiguous mass information. We adopt the REMPI and MATI techniques for the present studies to distinguish isotopologues and to avoid spectral complication from impurities in the chemical sample.

In this Letter, we report the vibronic and cation spectra of 4C3FA, which provide new data of excitation energy of the $S_1 \leftarrow S_0$ electronic transition (E_1), adiabatic ionization energy (IE) and active vibrations in the S_1 and D_0 states. Comparing these data with those of aniline [23,24], 4-chloroaniline [25], 3-fluoroaniline [26], 3,4-difluoroaniline [6] and 3-chloro-4-fluoroaniline [9], we gain knowledge about the halogen substitution effect on the electronic transition, ionization, and molecular vibration.

2. Experimental and computational methods

2.1. Experimental method

The REMPI and MATI experiments were performed by using a laser-based time-of-flight (TOF) mass spectrometer described in our previous publication [27]. 4C3FA (99% purity) was purchased from Alfa Aesar and used without further purification. The vapor of this solid sample is seeded into 2–3 bar of helium and expanded into the vacuum through a pulsed valve with a 0.15 mm diameter orifice. The free jet passes through a skimmer (1.0 mm diameter) located about 10 mm from the nozzle orifice. The skimmed molecular beam is intersected perpendicularly with two counter-propagating laser beams in the laser-molecular beam interaction zone which is at about 50 mm downstream from the nozzle orifice. During the experiments, the gas expansion, laser-molecular beam interaction, and ion detection regions were maintained at a pressure of about $1 \text{ x } 10^{-3}$, $1 \text{ x } 10^{-5}$, and 1×10^{-6} Pa (i.e. 1×10^{-5}, 1×10^{-7}, and 1×10^{-8} mbar), respectively.

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* Corresponding author at: Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, 1, Sec. 4, Roosevelt Road, Taipei 10617, Taiwan. Fax: +886 2 23620200.

E-mail address: wbt@sinica.edu.tw (W.B. Tzeng).

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We initiate the two-color resonant two-photon excitation process by utilizing two independent tunable UV laser systems controlled by a delay/pulse generator (Stanford Research Systems DG535). The excitation source is a Nd:YAG pumped dye laser (Quanta-Ray PRO-190-10/Lambda-Physik, Scanmate UV with BBO-III crystal; R610 and R640 dyes). The generated visible radiation is frequency doubled to produce UV radiation. The ionization UV laser (Lambda-Physik, Scanmate UV with BBO-III crystal; DCM and LDS698 dyes) is pumped by a frequency-doubled Nd-YAG laser (Quanta-Ray LAB-150). The wavelengths of both lasers are calibrated by using a laser wavelength meter (Coherent, WaveMaster).

In the MATI experiments, both the prompt ions and the Rydberg neutrals are formed simultaneously in the laser-molecular beam interaction zone. A pulsed electric field of −1 V/cm in this region is switched on about 18 ns after the occurrence of the laser pulses to guide the prompt ions towards the opposite direction of the flight tube. In this way, the prompt ions are not detected by the particle detector. Because the Rydberg neutrals are not affected by the electric field, they keep moving with molecular beam velocity of about 1500 m/s to enter the field-ionization region. About 11.8 μs later, a second pulsed electric field of 200 V/cm is applied to field-ionize the Rydberg neutrals. These generated threshold ions are then accelerated and pass through a field-free region before being detected by dual-stacked microchannel plate detector.

2.2. Computational method

We performed the quantum chemical calculations by using the GAUSSIAN 09 program package [28]. The restricted, time-dependent, and unrestricted Becke three-parameter functional with the PW91 functional (B3PW91) calculations with the 6-311++G(d,p) basis set predict various molecular properties of 4C3FA in the ground S_0, electronically excited S_1, and cationic ground D_0 states, respectively. The calculations give a spin multiplicity $<S^2>$ of about 0.75 for the cation. The predicted IE is 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

Due to the natural abundance of chlorine isotope, the TOF mass spectrum of 4C3FA shows two peaks resulting from the ^{35}Cl and ^{37}Cl isotopologues, as those reported previously [9]. Because the obtained vibronic and cation spectra of the two isotopologues are nearly identical, only those of ^{35}Cl-4C3FA are shown in this Letter. Figure 1 shows the vibronic spectrum of 4C3FA, recorded by using the one-color resonant two-photon ionization (1C-R2PI) technique. The band origin of the $S_1 \leftarrow S_0$ electronic transition (E_1) appears at 33 242 ± 2 cm^{-1}. The time-dependent (TD) B3PW91 and Becke three-parameter functional with the Lee–Yang–Parr functional (B3LYP), calculations with the 6-311++G(d,p) basis set predict the E_1 of 4C3FA to be 33 837 and 33 340 cm^{-1}, corresponding to overestimations by about 1.8% and 0.3%, respectively.

Table 1 lists the vibronic bands of 4C3FA observed in Figure 1. The spectral assignment has been made by comparing the present data with those of aniline [23,24], 4-chloroaniline [25], 3-fluoroaniline [26], 3,4-difluoroaniline [6], 3-chloro-4-fluoroaniline [9], and the predicted values from the TD-B3PW91/6-311++G(d,p) calculations. The numbering system for the normal vibrations of benzene derivatives follows that used by Varsanyi [1] and is based on Wilson's notations [29]. The strongest band at 755 cm^{-1} is assigned to transition $I^2{}_0$, which is related to the out-of-plane NH_2 wagging (or called inversion) motion. The corresponding transitions $I^2{}_0$ for aniline, 4-chloroaniline, 3-fluoroaniline, 3,4-difluoroaniline, and 3-chloro-4-fluoroaniline have been observed with frequencies of 760, 723, 753, 756, 756 cm^{-1}, respectively [6,9,23–26]. The pronounced bands at 306, 357, 633, 711, and 906 cm^{-1} result from vibronic transitions $9a^1{}_0$, $6b^1{}_0$, $6a^1{}_0$, $1^1{}_0$, and $7b^1{}_0$ of 4C3FA, respectively. Modes 6a, 6b, and 1 designate in-plane ring deformation, whereas 9a and 7b are substitutent-sensitive ring–NH_2 bending and ring–F and ring–NH_2 stretching vibrations, as described in Table 1. These normal vibrations can be viewed by following the GAUSSVIEW procedure of the GAUSSIAN 09 program [28]. It is noted that vibronic transitions $9a^1{}_0$, $6b^1{}_0$, $6a^1{}_0$, and $1^1{}_0$ of 3-chloro-4-fluoroaniline are found to be 210, 379, 443, and 629 cm^{-1}, respectively [9]. The weak band at 144 cm^{-1} (labelled $X^1{}_0$) in Figure 1 is likely related to the out-of-plane motion of 4C3FA. Similar observations have been reported for 2,4-difluoroaniline [7], 3,4-difluoroaniline [6], and 3-chloro-4-fluoroaniline [9] at 87, 138, and 92 cm^{-1}, respectively. Another weak band at 222 cm^{-1} is assigned to transition $15^1{}_0$, which is related to in-plane ring–Cl and ring–F bending vibration of 4C3FA. The corresponding transition appear at 306 cm^{-1} for 3-chloro-4-fluoroaniline [9]. These data show that the frequency difference of each mode of these multiple substituted benzenes and their relevant isomers depends on the nature, location, and vibrational pattern of the substituents.

3.2. Cation spectra

Because spectroscopic data are not available in the literature, we have performed both photoionization efficiency (PIE) and MATI experiments to investigate the ionic properties of 4C3FA. The PIE experiment detects total ion current and often yields strong intensity [15]. It allows us to locate the ionization limit in a convenient way. Analysis of the abruptly rising step in the PIE curve (not shown) indicates that the IE of 4C3FA is 63 868 cm^{-1} with

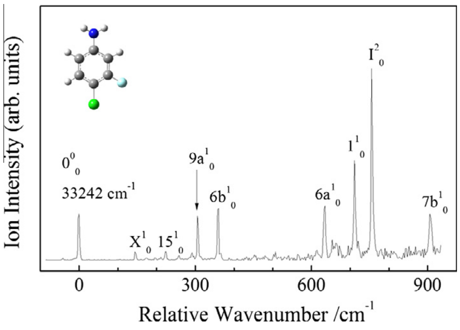

Figure 1. Vibronic spectrum of 4C3FA, recorded by using the 1C-R2PI technique.

Table 1
Observed bands (in cm^{-1}) in the vibronic spectrum of 4C3FA and possible assignments.[a]

Exp.	Cal.	Assignment and approximate description [b]
144		$X^1{}_0$, γ(CN), γ(CCl),
222	218	$15^1{}_0$, β(CCl), β(CF)
306	350	$9a^1{}_0$, β(CN)
357	443	$6b^1{}_0$, β(CCC)
633	597	$6a^1{}_0$, β(CCC)
711	723	$1^1{}_0$, β(CCC)
755		$I^2{}_0$, γNH(wag)
906	939	$7b^1{}_0$, ν(CF), ν(CN)

[a] The experimental values are shifts from 33 242 cm^{-1}, whereas the calculated ones (not scaled) are obtained from the TD-B3PW91/6-311++G(d,p) calculations.

[b] β, In-plane bending; γ, out-of-plane bending; ν, stretching.