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Resonance-enhanced two-photon ionization spectroscopy and theoretical calculations of 3,5-difluoroanisole and its Ar-containing complex

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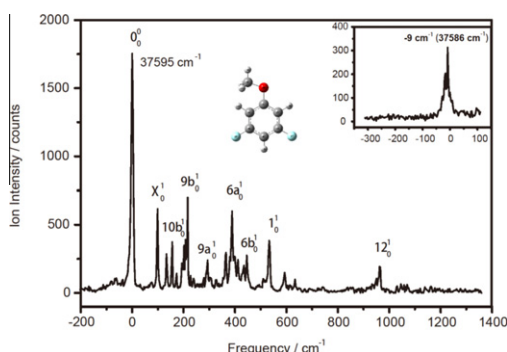
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HIGHLIGHTS

- ▶ Resonant two-photon ionization spectrum of 3,5-difluoroanisole was firstly obtained.
- ▶ The $S_1 \leftarrow S_0$ electronic transition energy and the ionization energy were determined.
- ▶ Formation of Ar complex gives a weak influence on the properties of 3,5-DFA moiety.
- ▶ The calculated results compared well with the experimental results.
- ▶ The dihalogen-substitution effect was discussed in detail.

GRAPHICAL ABSTRACT

1C-R2PI spectrum of 3,5-difluoroanisole. The inset shows the band origin of its complex with one Ar atom.



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ABSTRACT

The structure and vibrations of 3,5-difluoroanisole (3,5-DFA) in the first electronically excited (S_1) state were studied by mass-analyzed resonant two-photon ionization (R2PI) technique as well as the quantum chemical calculations. The *ab initio* and density functional theory (DFT) calculations reveal that only one structure is stable for each of the S_0 , S_1 , and D_0 states. In the one color R2PI spectrum, the band origin of the $S_1 \leftarrow S_0$ electronic transition (0_0^0 band) of 3,5-DFA is found to be $37,595 \pm 3 \text{ cm}^{-1}$. In the S_1 state, most of the bands observed are related to the in-plane ring deformation and out-of-plane bending vibrations. The adiabatic ionization energy (IE) of 3,5-DFA is determined to be $70,096 \pm 15 \text{ cm}^{-1}$ by the two color R2PI technique, in agreement with the values predicted by the DFT approaches. The dihalogen-substitution effects on the molecular structure, vibrational frequencies, and electronic transition and ionization energies were discussed in detail. The van der Waals complex of 3,5-DFA with argon (3,5-DFA...Ar) was also observed and studied. The 0_0^0 band of 3,5-DFA...Ar complex is red-shifted by about 9 cm^{-1} with respect to that of 3,5-DFA. Both the experimental data and the calculated results indicate that the formation of 3,5-DFA...Ar complex gives only a weak influence on the properties of 3,5-DFA moiety.

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Introduction

Investigations on molecular structures and conformations are essential for understanding the biochemical phenomena and processes [1,2]. To get a clear map about the functions of a large

complicated biological molecule, it is important to have a deep understanding of the molecular structures and other properties of its constituent units firstly. From this point of view, anisole [3–8], being a typical benzene derivative, and its halogen-substituted molecules [9–14], are attractive as models of biochemical systems and have been studied with various experimental methods. The information about the properties of these molecules in different electronic states is important to gain insights into their

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chemical reactivity and reaction processes [15], some of which may be related to the photodegradation of environmental pollutants [16]. Supersonic jet-cooled resonance enhanced multiphoton ionization (REMPI) in conjunction with time-of-flight mass spectrometry (TOF-MS) has been proved to be a powerful tool in investigating the photophysical and photochemical properties of polyatomic molecules and their complexes [17–20]. The well resolved REMPI spectra not only facilitate to unravel normal vibrations in the excited state but also can serve as unique fingerprints for molecular identification [21].

It is known that the substitution in the benzene derivatives will affect the extent of the π -electron interaction and hence the molecular geometry. Since the halogen-substituted anisole can serve as a typical system for studying the multi-substitution effect, the molecular properties of anisole and its mono-halogen-substituted derivatives in the ground S_0 and electronically excited S_1 states have been extensively investigated with many different spectroscopic techniques [7,13,14,22]. However, studies on dihalogen-substituted anisoles (as well as other aromatic compounds like phenols and anilines) are rare in the literature. Recently, Huang et al. reported a REMPI and MATI (mass-analyzed threshold ionization) spectroscopic study on 3,4-difluoroaniline (3,4-DFAN) [23]. Meanwhile, the REMPI spectroscopic investigation on 3-chloro-4-fluoroanisole (3C4FA) [24] has been recently conducted by our group. It seems that an additive rule associated with the energy shifts of transition and ionization energies may exist. Further study on similar compounds will help to give a comprehensive understanding on the multi-halogen substitution effect. 3,5-Difluoroanisole (3,5-DFA) has been studied by gas-phase electron diffraction and quantum chemical calculations [25], and it is found that only the conformer with C_s symmetry is stable in the ground state. However, detailed studies on the molecular properties of 3,5-DFA in the electronically excited state remain unexplored.

In this work, we reported the resonant two-photon ionization (R2PI) spectrum of 3,5-DFA. Detailed analysis yielded information about the $S_1 \leftarrow S_0$ transition and ionization energies, as well as the frequencies of the active vibrations in the excited S_1 state. The *ab initio* and density functional theory (DFT) calculations were performed to obtain the optimized molecular geometries and allow us to assign the observed spectral bands. The multi-substitution effects on the geometric structures, vibrational frequencies, and transition energies were discussed. Besides, the structure of 3,5-DFA...Ar van der Waals (vdW) complex observed in our experiment was also investigated.

Experimental and computational details

Experimental details

The experimental system, consisting of a time-of-flight mass spectrometer and a pulsed supersonic molecular beam source, has been described elsewhere [26,27]. Here, we only give a brief description.

The sample, 3,5-DFA (Alfa Aesar, 97% purity), was heated (ca. 350 K) and expanded supersonically in the flowing argon (ca. 3.5 atm) through a pulsed valve (General Valve, orifice diameter 0.25 mm). After being collimated by a skimmer (diameter 1 mm), the molecular beam entered the ionization chamber. The ionization of 3,5-DFA was generated 70 mm downstream from the nozzle orifice by the UV laser perpendicular to the molecular beam. The produced cations were accelerated by two DC electric fields of 200 and 3500 V/cm. After being focused by the einzel lens with a DC electric field of 850 V, the cations flew through a 1.0-meter-long field-free region and were detected by a dual-stacked micro-channel plate (MCP) detector. The ion signals, amplified by a

preamplifier (SR445A, Stanford Research System), were then collected and analyzed by a multi-channel scaler (MCS, Stanford Research System, SR430). The synchronization of the whole system was controlled by a pulse delay generator (DG535, Stanford Research System). Typical operational pressures in the source and ionization chambers were maintained at approximately 2.0×10^{-3} and 2.2×10^{-5} Pa, respectively. Tunable UV lasers were produced by two independent Nd:YAG pumped dye lasers (Sirah Dye Laser-CSTR) at a repetition rate of 10 Hz. Coumarin 500 and DCM dyes were used in our experiment.

The one-color resonant two-photon ionization (1C-R2PI) technique was employed to record the vibronic spectrum of 3,5-DFA in the S_1 state, while the two-color resonant two-photon ionization (2C-R2PI) technique was applied to obtain the ionization energy (IE) of 3,5-DFA by recording the photoionization efficiency (PIE) curve. The latter was achieved by fixing the frequency of first laser to the electronic origin of $S_1 \leftarrow S_0$ transition while scanning the second laser from several hundred wavenumbers below to a few hundred wavenumbers above the ionization threshold of the molecule. In the 1C-R2PI experiment, typical laser pulse energy was kept at less than 60 μ J to maximize the signal-to-noise ratio and to avoid saturation. In the 2C-R2PI experiment, however, energy of the first laser pulse (ca. 15 μ J) was attenuated by a factor of about 50 as compared with that of the second laser (ca. 800 μ J) to weaken the one-color two-photon ionization due to the first beam alone.

Computational details

The structure of 3,5-DFA with ring numbering is given in Fig. 1. Gaussian 09 W program package [28] was used to perform geometry optimization and harmonic vibrational frequency calculations for the three electronic states of 3,5-DFA, including the neutral ground state (S_0), the first excited state of the neutral (S_1), and the cationic ground state (D_0). HF, MP2, and DFT methods were employed for the calculations of 3,5-DFA in the S_0 and D_0 states. For the S_1 state, calculations were performed using CIS and CASSCF methods. All stationary points were characterized as an energy minimum by verifying that all the corresponding frequencies were real. In addition, relaxed potential energy scan curves in different states were obtained to illustrate the energy barriers for internal rotation around the C1–O bond. Unless otherwise specified, the basis set of 6-311 G** was used for the above calculations.

The vibrational frequencies in the S_1 state were calculated at both the CIS/6-311 G** and the 8-electron, 7-orbital CASSCF/6-31 G levels of theory. For the latter, which was denoted as CAS(8,7)/6-31 G, the active space consisted of six ring π -electron orbitals, and one oxygen lone pair having π symmetry with respect to the molecular plane [24,29]. The calculated vibrational frequencies quoted in this paper were scaled by a certain factor to approximately correct the combined errors stemming from the basis-set incompleteness and vibrational anharmonicity.

As for the 3,5-DFA...Ar vdW complex, the geometry was optimized with the MP2 method, which has for a long time been, and still is, one of the most frequently applied methods for calculations on noncovalent interactions [30]. The DFT method was not used since it generally fails to describe the dispersion energy [30,31], which is expected to play an important role in the 3,5-DFA...Ar complex.

Results

1C-R2PI spectra

The TOF mass spectra recorded at the laser wavelength of 266.0 nm are shown in Fig. 2. By carefully adjusting the pressure

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