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Rotamers of *p* isopropylphenol studied by hole-burning resonantly enhanced multiphoton ionization and mass analyzed threshold ionization spectroscopy

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ABSTRACT

The resonance enhanced multiphoton ionization (REMPI), ultraviolet-ultraviolet (UV-UV) hole burning and mass analyzed threshold ionization (MATI) spectroscopy have been applied to investigate the vibrational features of *p* isopropylphenol in its first electronically excited state S_1 and cationic ground state D_0. Two stable conformational structures of *p* isopropylphenol are distinctly found in the supersonic molecular beam and identified as the *cis* and *trans* rotamers through REMPI and UV-UV hole burning spectroscopy. The electronic excitation energies of $S_1 \leftarrow S_0$ transition of two rotamers are determined to be 35,578 and 35,593 cm^{-1}, and the adiabatic ionization energies are 65,331 and 65,350 cm^{-1}, respectively. The MATI spectra recorded via different intermediate levels of S_1 state indicate the similarity in the molecular geometry between the S_1 state and the D_0 state for each rotamer of *p* isopropylphenol. Geometrical optimizations of *p* isopropylphenol have also been performed using the density functional theory (DFT) for S_0 and D_0 states, and time-dependent density functional theory (TDDFT) for S_1 state. The simulated spectra for $S_1 \leftarrow S_0$ and $D_0 \leftarrow S_1$ transitions of two rotamers are able to reproduce qualitatively the experimental spectral profile, which help us to assign the vibronic modes. Most of the observed vibrations of two rotamers in the S_1 and D_0 states are related to the in-plane ring deformation and some active modes involving isopropyl group.

1. Introduction

The spectroscopy of the phenol and substituted phenols in the gas phase is popular topic of theoretical and experimental studies with the aim to understand their photochemical and photophysical properties, such as the photodissociation dynamics [1–4], and noncovalent interactions [5,6]. Furthermore, these investigations can also provide valuable information on the many chemical and biological processes because phenol is the chromophore site in several biologically active molecules including the amino acid tyrosine and the estrogenic hormones [7–9]. The vibronic spectra and geometrical structures of some *para*-alkyl phenols in the first electronically excited S_1 and cationic ground D_0 states have been the topic of several experimental and theoretical studies. For these molecules, alkyl is an electron-donor group that introduces the electronic charge in the π orbital of the aromatic ring by the hyperconjugation, resulting in a change of the electron density distribution of the molecule [3]. The resonance enhanced multiphoton ionization (REMPI), laser induced fluorescence (LIF) excitation, dispersed fluorescence, autoionization-detected infrared (ADIR), and mass analyzed threshold ionization (MATI) spectroscopy have been applied to study *p* methylphenol, *p* ethylphenol, and *p* *n* propylphenol [6,10–15]. Several *p* methylphenol water cluster [14,16], *p* methylphenol NH_3 H_2O complex [17–19], *p* methylphenol *p* aminophenol heterodimer [20], and *p* ethylphenol Ar cluster [21] have also been studied for exploring the intermolecular interaction. In contrast, the detailed spectral information of *p* isopropylphenol in the S_1 and D_0 states is still limited.

Several studies of the physical and chemical properties of *p* isopropylphenol have been carried out over the past several decades. Szostak et al. reported the infrared, Raman and UV–Vis spectra of *p* isopropylphenol in the solid and solution in order to understand the nonlinear optical property of the crystal [22]. Wojcik and Holband explored the structural changes and intermolecular interactions of crystalline *p* isopropylphenol at several temperatures by Raman scattering, inelastic neutron scattering, and X-ray diffraction experiments [23]. The LIF spectrum of *p* isopropylphenol in the gas phase was reported by Song and Hayes, and only a few of vibrational bands in the S_1 state were assigned [11]. They suspected that there may be two stable rotamers for *p* isopropylphenol due to a doublet origin structure found in the LIF spectra. With the theoretical calculations at the MP2/6-31G (d,p) level, Jones's group predicted two stable rotamer structures of

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p isopropylphenol in its ground electronic state S_0 [24], here we named them as *trans* and *cis* rotamers depending on the orientation of the isopropyl group with respect to the hydrogen group, as shown in Fig. 1. However, the molecular crystal structure from X-ray diffraction shows that there is only one *trans* rotamer of *p* isopropylphenol at room temperature [25]. The UV-UV hole burning spectroscopy with a supersonic jet-cooled expansion is one of the most powerful tools for the study on rotamer in the gas phase, which can easily determinate the variety of rotamers and distinguish the vibronic transitions in the REMPI spectrum from each rotamer [26–30]. In this paper we report the one-color resonance enhanced two-photon ionization (R2PI) and UV-UV hole burning spectra of *p* isopropylphenol to identify the rotamers and distinguish their vibronic transitions in the first excited state S_1. The adiabatic ionization energy and cationic vibronic features were obtained by MATI [31] spectroscopy, which is based on the same principle as ZEKE [32,33] except for the difference that the ZEKE detects electrons and the MATI detects ions. The REMPI and MATI spectra were simulated by Frank-Condon approach to help to assign the observed bands in S_1 and D_0 states.

2. Experimental and Computational Details

2.1. Experimental Method

The experimental apparatus employed in this paper was a supersonic molecular beam time-of-flight spectrometer combined with two tunable dye lasers [34]. *p* isopropylphenol was purchased from MACKLIN (98% purity) and used without further purification. The sample was heated to approximately 100 °C to obtain a sufficient vapor pressure. In order to generate the supersonic molecular beam, the sample vapors were seeded in 2 bar of argon and expanded into the vacuum chamber through a pulsed valve (Parker valve) with a nozzle orifice of 0.5 mm in diameter, which operated at a repetition rate of 10 Hz with the pulse duration of 210 μs. A 1 mm diameter skimmer located at about 20 mm downstream from the nozzle orifice was applied to collimate the molecular beam. During the experiments, the expansion and ionization regions were maintained at a pressure of about 1.1×10^{-4} and 1.6×10^{-6} Pa, respectively.

The one-color R2PI spectrum of *p* isopropylphenol was recorded by scanning the tunable UV excitation laser in the 274–282 nm, which was generated by a frequency-doubled dye laser (Sirah CBR-D-24 with BBO crystal, Coumarin 540A dye) pumped by a third harmonic of a Nd: YAG laser (Quanta-Ray INDI-40-10: 355 nm). In order to confirm the variety of the rotamers and investigate the spectral features in the R2PI spectrum, we measured the UV-UV hole-burning spectra of *p* isopropylphenol using a second frequency-doubled dye laser (Sirah PrecisionScan-D with BBO crystal, Coumarin 540A dye) as a hole-burning laser, which is pumped by a third harmonic of a Nd: YAG laser (Quantel Q-smart 850: 355 nm). The wavelength of probe laser (excitation laser) was fixed to a resonant transition of a rotamer, while the hole-burning laser was scanned with a time advance of 150 ns. When the hole-burning laser was resonant with the rotamer selected by the probe laser, it caused a decrease in the R2PI signals of the probe laser. Thus, by monitoring the signal of the probe laser, the hole-burning spectrum involving vibronic bands of a single specific rotamer can be obtained [26,35]. Both counter-propagating UV lasers were operated at 10 Hz and perpendicularly intersected with the molecular beam. The absolute wavelengths of both lasers were calibrated with a wavelength meter (HighFinesse WS-7).

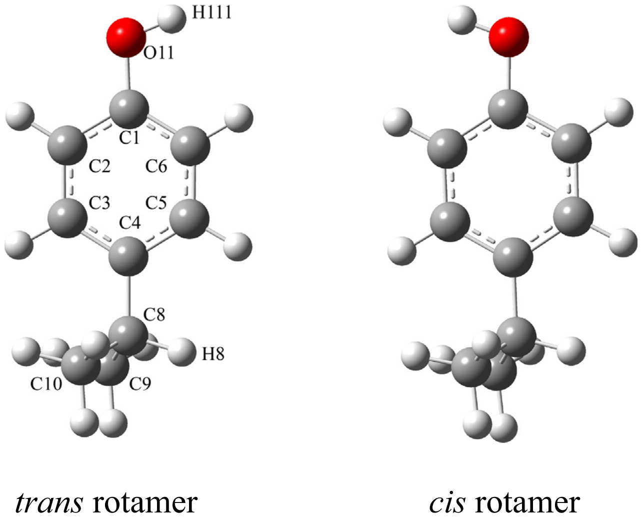

Fig. 1. Molecular structures of *trans* and *cis* rotamers of *p* isopropylphenol.

In the two-color MATI experiments, the pump laser was fixed to a specific vibronic transition of $S_1 \leftarrow S_0$, while the probe laser was scanned to populate excited molecule to long-lived high *n* Rydberg states. About 200 ns after lasers, a weak pulse electric field of −1.3 V/cm was applied to move the prompt ions towards the opposite direction to the detector. The Rydberg molecules kept moving and then were ionized and accelerated by two pulse electric fields of 140 V/cm and 570 V/cm. The threshold ions passed a 48 mm field-free region and were detected by a dual-stack microchannel plate (MCP) detector. A multichannel scaler (MCS, Stanford Research Systems, SR430) interfaced to a computer was used to collect and analyze the ion signal from the detector. Each mass spectrum was accumulated for 300 laser shots.

2.2. Computational Method

In order to investigate the vibrational features in the R2PI, hole-burning and MATI spectra of *p* isopropylphenol, we used the Gaussian 09 program package [36] to optimize the molecular structures and calculate the harmonic vibrational frequencies for all the involved electronic states of *p* isopropylphenol. 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 performed with the aug-cc-pVDZ basis set. The first electronically excited state (S_1) was calculated using the time dependent density functional theory (TDDFT) with the B3LYP functional. Since the vibrational frequency calculations were based on the harmonic oscillator model, the calculated frequencies were scaled by a factor to approximately correct for the deviations arising from the neglect of anharmonic effects, the incomplete treatment of electron correlation and the use of a finite basis set [37,38]. All calculated frequencies and scaling factors were listed in Tables 2–4 together with the experimental results. On the basis of the above calculations, the vibrationally resolved electronic spectra of *p* isopropylphenol for $S_1 \leftarrow S_0$ and $D_0 \leftarrow S_1$ transitions were simulated using the Gaussian 09 program under the Franck-Condon approximation [36].

3. Results

3.1. Molecular Structure of p isopropylphenol

The different initial geometries of *p* isopropylphenol in S_0 state have been optimized without any constraint at the B3LYP/aug-cc-pVDZ level. Two stable structures were obtained as shown in Fig. 1, which is consistent with the previous results at the MP2/6-31G(d,p) level [24]. The C_8—H_8 bond and hydroxyl group lie in the plane of aromatic ring, and two methyl groups of the isopropyl group are located on both sides of the plane of the aromatic ring. The optimized geometrical parameters for the S_0 state of *p* isopropylphenol together with the experimental data [25] obtained from the crystallographic X-ray diffraction are listed in Table 1. For the S_0 state of *trans* rotamer, the theoretical bond lengths and bond angles are in good agreement with the experimental values