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Rotamers of *m*-cresol cation studied by mass-analyzed threshold ionization spectroscopy

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Abstract

We have applied two-color resonant two-photon mass-analyzed threshold ionization technique to record the vibrational spectra of the selected rotamers of *m*-cresol. The adiabatic ionization energies of *cis* and *trans m*-cresol are determined to be 66,933 ± 5 and 67,084 ± 5 cm^{-1}, respectively. Frequencies of the in-plane ring vibrations 6a, 1, and 9b are measured to be 528, 720, 1167 cm^{-1} for the *cis* and 520, 698, and 1153 cm^{-1} for the *trans m*-cresol cation. This indicates that different orientation of the OH group with respect to the CH_3 group slightly influences these ring vibrations.

Keywords: Cresol; Rotamer; Cation spectra; Multiphoton ionization; Threshold ionization

1. Introduction

Cresol has OH and CH_3 groups which may act as active sites for many chemical reactions. *m*-Cresol has attracted attention for many spectroscopic studies [1–6] because it has *cis* and *trans* rotamers arising from the relative orientation of the OH group with respect to the CH_3 group. This molecule has been investigated by excitation and dispersed laser-induced fluorescence [1,2], resonance-enhanced multiphoton ionization [3,4], hole-burning [5], threshold resonant two-photon ionization [3], autoionization-detected infrared [6] spectroscopy. These results confirm the coexistence of two rotamers by identifying different origins of the lowest electronic transition and ionization energies (IEs). In addition, the CH_3 torsion and OH stretching vibration of the *cis* and *trans* rotamers in the neutral ground S_0, electronically excited S_1, and cationic ground D_0 states have been well characterized [1–3,6]. However, previous researchers did not attempt to investigate the vibrations mainly involving the aromatic ring of the rotamers in the S_1 and D_0 states.

To probe the ionic properties of the selected rotamers, one needs to use high-resolution spectroscopic methods because the band origins and the IEs of these isomers only differ by a few tens to a few hundreds of wavenumbers [2]. Both zero-kinetic energy (ZEKE) photoelectron and mass-analyzed threshold ionization (MATI) spectroscopy with a resonant excitation scheme can give precise IE and cation spectra of the selected rotamers [7,8]. However, the latter technique has an additional advantage since it provides mass information. In this paper, we report the vibrationally resolved MATI spectra of the selected *cis* and *trans* rotamers of *m*-cresol. In addition, we have performed ab initio and density functional theory (DFT) calculations to provide possible interpretation for our experimental findings.

2. Experimental and computational methods

The experiments were performed with a time-of-flight mass spectrometer described elsewhere [9]. The *m*-cresol (Sigma, 99% purity) sample was heated to about 80 °C to acquire sufficient vapor pressure. The vapors were seeded into 2–3 bar of helium and expanded into the vacuum through a pulsed valve with a 0.15 mm diameter orifice. The two-color resonant two-photon excitation process was initiated by utilizing two independent tunable UV laser systems controlled by a delay/pulse generator (Stanford Research Systems DG535). The first (excitation) tunable dye laser (Lambda-Physik, Scanmate UV with BBO-I crystal; Coumarin 540A dye) was pumped by a pulsed frequency-tripled Nd:YAG laser (Quanta-Ray GCR-3, 355 nm). The UV laser output was focused and directed perpendicu-

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larly into the molecular beam. The second (ionization) tunable UV laser (Lambda-Physik, Scanmate UV with BBO-III crystal; DCM dye) was pumped by another frequency-doubled Nd:YAG laser (Quanta-Ray LAB-150, 532 nm). A Fizeau-type wavemeter (New Focus 7711) was used to calibrate the wavelengths of both lasers. 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, about 0.16 μs after the occurrence of the laser pulses, a pulsed (spoiling) electric field of −2.0 V/cm was switched on to reject the prompt ions. About 11.6 μs later, a second pulsed electric field of 120 V/cm was applied to field-ionize the Rydberg neutrals. These threshold ions were then accelerated and passed a field-free region before being detected by a dual-stacked microchannel plate particle detector.

All ab initio and DFT calculation were performed by using the GAUSSIAN 03 program package [10]. The computations give information about the molecular structures, total energies, and vibrational frequencies of *cis* and *trans* *m*-cresol in the S_0, S_1, and D_0 states. The IEs were obtained as the difference in the zero-point energy levels (ZPLs) of the cation and the corresponding neutral in the ground state. Since the frequency calculation are on the basis of the harmonic oscillator model, the obtained frequencies are scaled by an appropriate value to correct approximately for the combined errors stemming from basis set incompleteness, neglect of electron correction, and vibrational anharmoncity. The calculated vibrational frequencies and scaling factors are listed in the tables for comparison with the measured values.

3. Results and discussion

3.1. Vibronic spectra

We have applied both one-color (1C) and two-color (2C) R2PI techniques to record the vibronic spectra of *m*-cresol. The latter approach was done by scanning the excitation laser in the range of 35,900–37,000 cm^{-1} while fixing the ionization laser at 31,250 cm^{-1}. Thus, the 2C-R2PI process has a less excess energy than the 1C-R2PI scheme by a few thousand wavenumbers. It follows that some vibronic bands in the 2C-R2PI spectrum are more prominent, as seen in Fig. 1. The bands at 35,982 and 36,098 cm^{-1} are assigned to the origins of the $S_1 \leftarrow S_0$ electronic transitions of the *cis* and *trans* rotamers, as reported previously [3]. To confirm this assignment, we have performed ab initio and DFT methods [11,12] to predict the electronic excitation energy.

The ZPLs in the S_0 and S_1 states were calculated by using the Hartree-Fock (HF) and configuration interaction singles (CIS) calculations with the 6-311G** basis set, respectively. The $S_1 \leftarrow S_0$ electronic transition energies (E_1's) of *cis* and *trans* *m*-cresol are estimated to be 46,339 and 46,468 cm^{-1}, respectively. With the same basis set, the time-dependent Becke three-parameter functional with the PW91 correlation functional (TD-B3PW91) method gives 39,228 and 39,319 cm^{-1} for these two isomeric species. Although these calculations overestimate the E_1, both predict that the *trans* has a slightly higher E_1 than the *cis* rotamer. Thus, the calculated results are in consistency with the experimental finding.

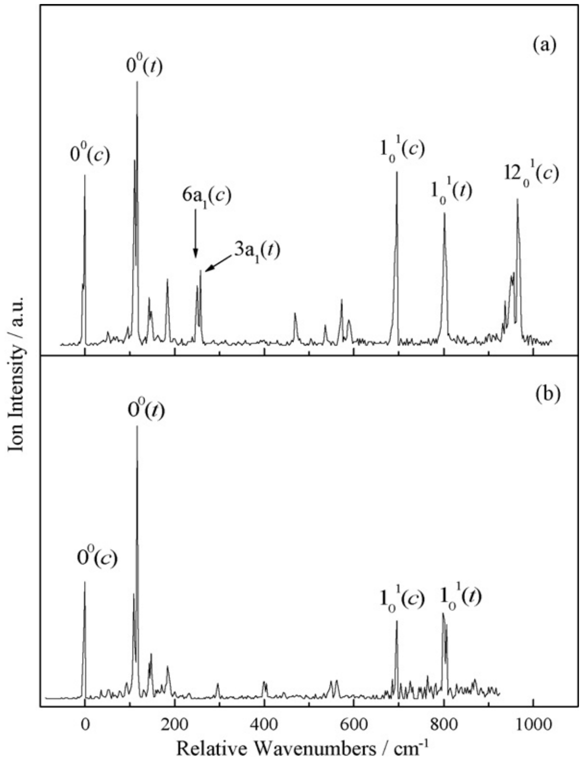

Fig. 1. Vibronic spectra of *m*-cresol recorded by the (a) 2C-R2PI and (b) 1C-R2PI methods. The 2C-R2PI spectrum was obtained by scanning the excitation laser while fixing the ionization laser at 31,250 cm^{-1}. The transition origins of the *cis* (*c*) and *trans* (*t*) rotamers appear at 35,982 and 36,098 cm^{-1}, respectively.

Mizuno et al. [3] studied the CH_3 torsion and did not report the ring vibrations of *m*-cresol. Here, we accomplish the spectral assignment for the ring vibrations by comparing these experimental data with those for the S_0 state [13] and those from our CIS calculations for the S_1 state. All of the major vibronic bands in Fig. 1 and their possible assignments are listed in Table 1. The pronounced bands corresponding to the $6a_0^1$ and 1_0^1 transitions appear at 469 and 696 cm^{-1} for the *cis* and at 457 and 686 cm^{-1} for the *trans* rotamer of *m*-cresol. This result indicates that different orientation of the OH with respect to the CH_3 group slightly influences the frequencies of these two in-plane ring vibrations.

3.2. Cation spectra

We have performed the 2C-R2PI and MATI experiments to record the cation spectra of *m*-cresol. It is noted that this 2C-R2PI procedure is different from that for recording the vibronic spectrum stated in the previous section. The present 2C-R2PI spectra were recorded by scanning the ionization laser while fixing the frequency of the excitation laser via the respective $S_1 0^0$ levels of the *cis* and *trans* rotamers. Namely, the excitation laser is used to select the desired rotamer for the successive ionization, as that described in our previous publication [9]. Analyses on the rising steps in the photoionization efficiency curves of the 2C-R2PI spectra (not shown) give the respective IEs of these two rotamers to be 66,925 and 67,083 cm^{-1}, with an uncertainty of