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Methyl torsional potentials of rotational isomers of *m*-methylanisole studied by spectral hole-burning spectroscopy

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Received 17 February 2003; revised 18 February 2003; accepted 18 April 2003

Abstract

Laser-induced fluorescence (LIF) excitation spectra of *m*-methylanisole in a supersonic jet were measured. Two series of progressions were observed in the spectrum, originating at 36048 and 36115 cm^{-1}, which were successfully assigned to the transitions to the methyl internal rotational vibronic levels of the two isomers, i.e. *cis* and *trans* isomers, with the aid of hole-burning spectrum measurements and quantum-chemical calculations. The progression for the *trans* isomer was observed up to the $6a_1$ band, while only the $3a_1$ band in addition to the $0a_1$ and 1e bands was observed for the *cis* isomer. This finding can be explained by the conformational change upon the electronic excitation; the 60° rotation of the methyl torsional angle takes place for the *trans* isomer but not for the *cis* isomer.
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Keywords: m-Methylanisole; Rotational isomerism; Methyl torsional potential; Laser-induced fluorescence spectroscopy; Hole-burning spectroscopy

1. Introduction

Large amplitude vibrations have fascinated many researchers because of their unique characteristics of low frequencies and large anharmonicity; they are considered to play important roles in dynamics of the excited molecules. The internal rotation of the methyl groups on the aromatic rings, which is one of the large amplitude vibrations, has been extensively investigated since the spectroscopic study of fluorotoluenes in their electronically excited states was carried out by Okuyama et al. [1].

In this paper, the internal rotation of the methyl group on the aromatic ring of *m*-methylanisole (abbreviated as *m*-MA, hereafter) is discussed. There exist rotational isomers, namely, *cis* and *trans*

isomers, for m-MA, which are due to the orientation of the methoxy (-OCH$_3$) group with respect to the methyl group. LIF (laser-induced fluorescence) and REMPI (resonance-enhanced multi-photon ioniz-ation) spectra of m-MA around their origin bands show congested spectral features even under super-sonic jet conditions because the bands due to the isomers are observed in a same spectral region. The spectrum of each isomer in this region consists of a progression attributable to the methyl internal rotation. Assigning the bands observed in the region is quite difficult. The spectral hole-burning technique is a powerful tool to selectively distinguish transitions due to a specific species in a specific vibrational state among others. The first application of the hole-burning spectroscopy to toluene derivatives was carried out by Lipert and Colson [2]. Recently, the hole-burning spectroscopy has been applied to observe methyl internal rotations of m-tolunitrile complexes with a rare gas or a small molecule such as H$_2$O or N$_2$O [3,4].

Here, vibronic transitions due to the methyl internal rotation for each isomer were observed selectively by the hole-burning spectroscopy. Tran-sitions from a single vibrational state are observed in a hole-burning spectrum; vibronic transitions from the ground vibrational and low-lying vibrationally excited torsional states are observed in different hole-burning spectra. The dependence of relative intensities of the bands observed in the LIF excitation spectrum on the stagnation pressure was measured. Reasonable assignments of transitions could be achieved on the basis of these measurements.

The isomers were found to be different in the change of the internal-rotational potential upon the electronic excitation. The difference is also discussed in detail.

2. Experimental

The experimental apparatus used for the spectral measurements has been described in detail elsewhere [3]. Briefly, the second-harmonic outputs of a dye laser pumped by a XeCl excimer laser (Lumonics, HE-420-SM-B and Lambda Physik, FL3002; $100 \sim 500$ μJ/pulse, line width(0.2 cm^{-1}) was used for the measurements of LIF excitation spectra and for

the probe source in the hole-burning measurements, while the second harmonic of another dye laser pumped by a Nd:YAG laser (Quantel, YG571C and TDL-50; ~ 1 mJ/pulse, line width $0.2 \sim 0.5$ cm^{-1}) was used for the pump source in the hole-burning measurements. Delay between the pump and probe pulses was set to 1 μs in the hole-burning measure-ments. Wavelengths of the laser outputs were calibrated with a see-through hollow cathode lamp (Hamamatsu, GALVATRON L2783).

Vaporized m-MA (Tokyo Kasei, reagent grade; used without further purification) was diluted by helium or neon and was expanded into a vacuum chamber through a pulsed valve with an orifice diameter of 0.8 mm. Stagnation pressure of 1-3 atm was employed.

3. Results and discussion

Fig. 1 shows a LIF excitation spectrum of m-MA diluted in neon. Bands due to the cis and $trans$ isomers of m-MA are expected in the spectrum. Two intense bands at 36048 and 36115 cm^{-1} have been found to be the origin bands for the two isomers, since vibronic bands presumably due to the ring vibrational modes are observed commonly at about 520, 680 and 960 cm^{-1} from each of the origin bands. Assignments of the origin bands to the isomers and of the congested bands observed at the low-frequency region to torsional vibronic transitions are discussed below.

Similar to anisole, torsional vibronic transitions in relation to the methoxy group are too weak to be observed; progressions observed in the low-frequency region should be due to torsional motion of the methyl group on the phenyl ring. The conventional notation [5] is used to denote the levels of internal rotation of the methyl group such as 0a$_1$, 1e, 2e, 3a$_1$, 3a$_2$, 4e and so on, using a combination of the rotational quantum number in a one-dimensional free rotor and the symmetry species.

3.1. Assignment of cis and trans isomers

Optimized geometries for the cis and $trans$ isomers of m-MA in their S$_0$ states together with their relative energies calculated with HF/6-31G** are shown, respectively, in Fig. 2(a) and 2(b). The energies are
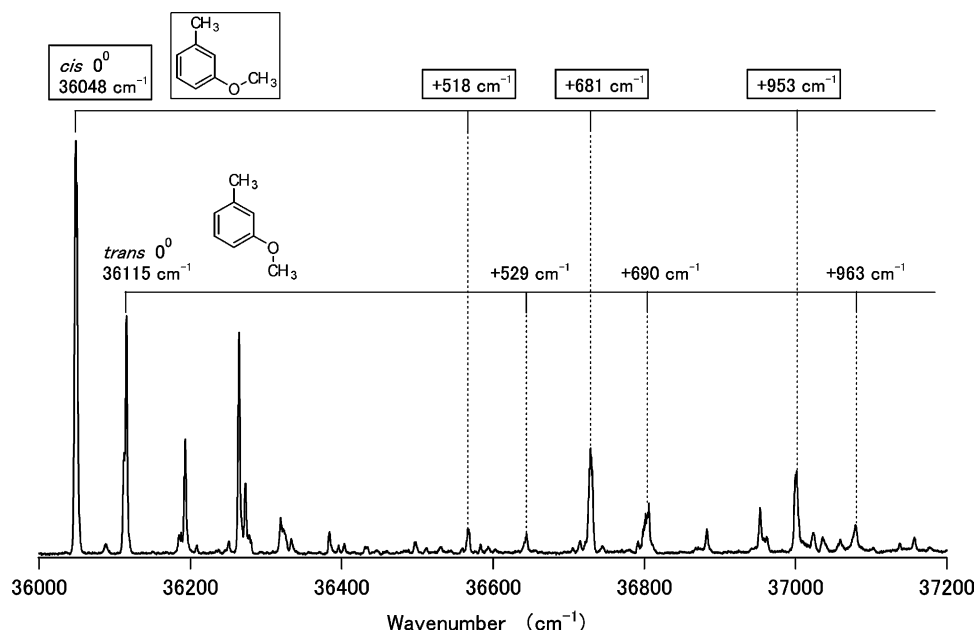
Fig. 1. LIF excitation spectrum of jet-cooled *m*-MA diluted by neon. Two vibronic series are observed.

compared at their zero-point vibrational levels. The energy of the *cis* isomer was found to be higher by 50 cm⁻¹ than that of the *trans* isomer. This result can be understood in relation to steric hindrance between methyl and methoxy groups. The *cis* isomer is less stable because of the possible larger steric hindrance, although the difference of stabilities for the isomers is small because the steric hindrance between the substituents in meta positions is not so large.

In order to assign two intense bands at 36048 and 36115 cm⁻¹ in the LIF excitation spectrum to the *cis* and *trans* isomers, stagnation pressure dependence of the LIF excitation spectrum was investigated. The LIF excitation spectra of *m*-MA diluted in neon measured with the stagnation pressures of (a) 3 and (b) 1 atm are shown in Fig. 3, where spectra only around the origin bands are shown in an expanded horizontal scale. The vertical scales of the spectra are normalized at the intensity of the band at 36115 cm⁻¹. The relative intensity of the band at 36048 cm⁻¹ decreased by increasing the stagnation pressure, suggesting that the band is due to the less stable *cis* isomer; higher stagnation pressure causes the lower temperature of the jet and the decrease of the population of the less stable *cis* isomer. Therefore, the bands at 36048 and

36115 cm⁻¹ were assigned to the origins of the *cis* and *trans* isomers, respectively.

The *cis* isomer was calculated to be less stable by 50 cm⁻¹ than the *trans* isomer, as shown in Fig. 2. On the other hand, the origin band of the *cis* isomer was observed at the frequency lower by 67 cm⁻¹ than that of the *trans* isomer. These findings mean that the energy of the *cis* isomer in the S_1 state is lower than that of the *trans* isomer. This conclusion is supported by the results of CIS/6-31G** calculations shown in Figs. 2(c) and 2(d), where optimized geometries obtained for the *cis* and *trans* isomers in the S_1 state together with their relative energies are shown; the *cis* isomer was calculated to be more stable by 81 cm⁻¹ than the *trans* isomer. Here again, the energies are compared at the zero-point vibrational levels. In the S_1 state, the stabilities of the isomers are presumably determined not by the steric hindrance but by other factor such as the charge distribution in the molecules.

Since the *trans* isomer is more stable than the *cis* isomer in the S_0 state, larger population is expected for the former in the supersonic jet. Nevertheless, the intensity of the origin band for the *trans* isomer was smaller than that for the *cis* isomer. The cause of this observation is discussed later.
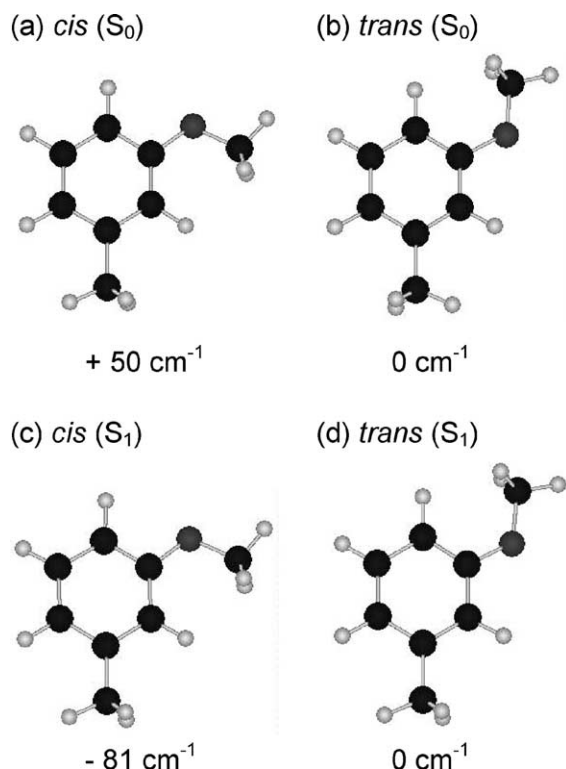
(a) *cis* (S_0)

+ 50 cm^{-1}

(b) *trans* (S_0)

0 cm^{-1}

(c) *cis* (S_1)

− 81 cm^{-1}

(d) *trans* (S_1)

0 cm^{-1}

Fig. 2. Geometries of *m*-MA in the S_0 state optimized by HF/6-31G** [(a) *cis* and (b) *trans* isomers] and in the S_1 state optimized by CIS/6-31G** [(c) *cis* and (d) *trans* isomers].
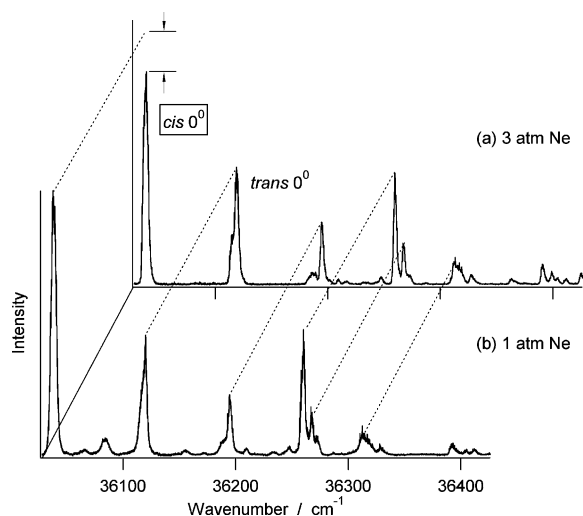

Fig. 3. LIF excitation spectra of jet-cooled *m*-MA measured with different stagnation pressures of (a) 3 atm and (b) 1 atm.

3.2. Assignments of low-frequency vibronic bands

Intensities of all the main bands observed in the LIF excitation spectra in Fig. 3 except for the band at 36048 cm^{-1} showed a similar stagnation pressure dependence, suggesting that most of the observed bands are due to the *trans* isomer. In order to elucidate this point, hole-burning spectra were measured by probing the origin bands at 36048 and 36115 cm^{-1}. Both origin bands consist of two peaks as fine structures, which corresponds to the $0a_1-0a_1$ and $1e-1e$ transitions. In the hole-burning measurements, each of the peaks were probed so that the transitions of a specific species, i.e. the *cis* and *trans* isomers, in a specific torsional level, i.e. $0a_1$ and $1e$ levels, are selectively observed.

Results of the hole-burning measurements are shown in Fig. 4, where four hole-burning spectra (a)–(d) and a LIF excitation spectrum (e) are shown. Hole-burning spectra (a)–(d) were measured, respectively, by probing bands marked with a–d in the LIF excitation spectrum.

Fig. 4(a) and 4(b) are the hole-burning spectra measured by probing the $0a_1-0a_1$ and $1e-1e$ transitions of the *cis* isomer, respectively. In the spectrum in Fig. 4(a), a dip assignable to the $3a_1-0a_1$ transition was observed in addition to the dip corresponding to the $0a_1-0a_1$ transition. On the other hand, no dip in relation to the methyl internal rotation was observed in Fig. 4(b) except for the dip corresponding to the $1e-1e$ transition. Dips marked with asterisks cannot be assigned to the transitions to the internal-rotational vibronic levels because they were observed both in Figs. 4(a) and 4(b); transitions to the $2e$ and $4e$ states from the $0a_1$ state are forbidden by symmetry. Bands due to the $2e-1e$ and $4e-1e$ transitions, which are observed in the LIF excitation spectra of many meta-substituted toluene derivatives [1,3,6–10], were not observed for the *cis* isomer of *m*-MA. Vibronic transitions due to the methyl internal rotation for the *cis* isomer were found to be very weak.

Figs. 4(c) and 4(d) are the hole-burning spectra measured by probing the $0a_1-0a_1$ and $2e-1e$ transitions of the *trans* isomer, respectively. In contrast to the spectrum for the *cis* isomer, many dips due to the methyl internal rotation were observed. In the spectrum in Fig. 4(c), dips assignable to
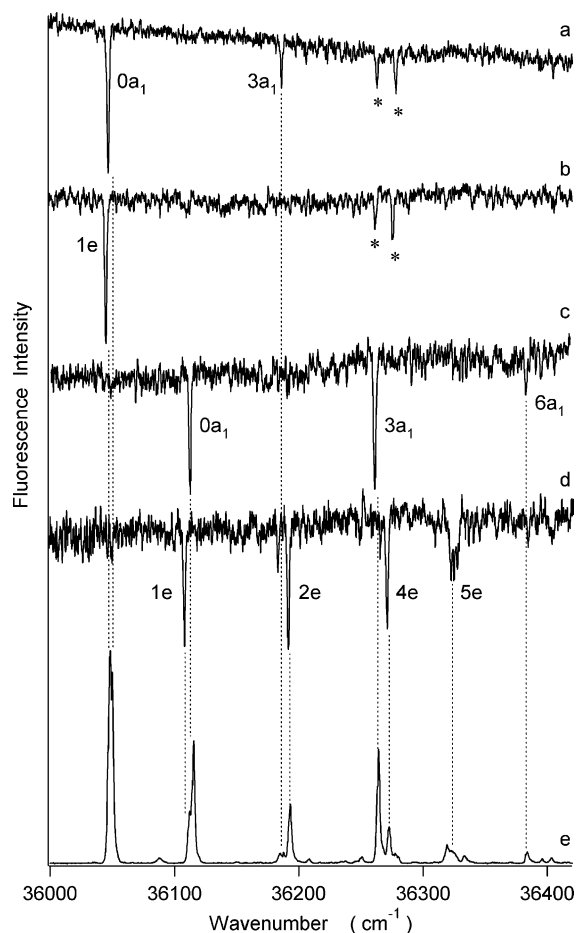
Fig. 4. Hole-burning spectra of jet-cooled *m*-MA in helium (stagnation pressure: 2.5 atm) measured by probing (a) the $0a_1–0a_1$ band of the *cis* isomer, (b) the $1e–1e$ band of the *cis* isomer, (c) the $0a_1–0a_1$ band of the *trans* isomer, and (d) the $2e–1e$ band of the *trans* isomer. (e) LIF excitation spectrum of jet-cooled *m*-MA in helium. Bands marked with a-d correspond to the probing bands in the hole-burning measurements, respectively.

the $3a_1–0a_1$ and $6a_1–0a_1$ transitions were observed in addition to the dip corresponding to the $0a_1–0a_1$ transition, while dips assignable to the transitions to $2e$, $4e$, and $5e$ vibronic states from $1e$ were observed in the spectrum in Fig. 4(d).

The present assignments of the bands observed in the LIF excitations spectrum, which do not agree with those of Breen et al. [11], seem more reliable because the assignments of bands to the *cis* and *trans* isomers and the symmetries of the observed vibronic states

were clarified by the hole-burning measurements in the present study.

Vibronic bands due to the methyl internal rotation up to the $6a_1$ level were observed for the *trans* isomer, while only the $0a_1–0a_1$, $1e–1e$ and $3a_1–0a_1$ transitions were observed for the *cis* isomer. The difference can be understood by considering the optimized conformations of methyl group shown in Fig. 2. In the *trans* isomer, equilibrium torsional angle of the methyl group was found to rotate by 60 degrees upon the electronic excitation, resulting in large values of Franck–Condon factors and a long progression due to internal rotation. In contrast, equilibrium torsional angles were found to be same for the S_0 and S_1 states of the *cis* isomer; small change in the geometry results in the concentration of Franck–Condon factors to the $0a_1–0a_1$ and $1e–1e$ transitions. Bands due to the $0a_1–0a_1$ and $1e–1e$ transitions for the *cis* isomer are more intense than those for the *trans* isomer, while other vibronic bands due to the internal rotation for the former are not distinct.

The reason for the non-rotation of the equilibrium torsional angle upon the electronic excitation in the *cis* isomer is ascribed to steric hindrance between the two methyl groups, i.e. methyl groups on the phenyl ring and in the methoxy group, and the phenyl hydrogen between them. In the *trans* isomer, only steric hindrance between the phenyl methyl group and the neighbouring hydrogen atom should be considered. The methyl group can change equilibrium torsional angle according presumably to the change of the charge distribution in the molecule; the neighbouring hydrogen atom can escape from the methyl group by changing in-plane bonding angle. On the other hand, the phenyl hydrogen atom between two methyl groups in the *cis* isomer cannot change in-plane bonding angle because it suffers steric hindrance from both methyl groups; no room for the methyl group to rotate in the space where two methyl groups and the phenyl hydrogen are tightly packed even when the electronic structure of the molecule changes. The hydrogen atoms in the methyl groups, which are on the plane of the phenyl ring, should point to outside of the tightly packed space.

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