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Internal rotation of methyl group in 2- and 1-methylanthracene studied by electronic spectroscopy and DFT calculations

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Abstract

The S_1–S_0 fluorescence excitation and dispersed fluorescence spectra of 2- and 1-methylanthracene are measured in a supersonic free jet expansion. The barrier heights to internal rotation in the S_0 and S_1 states of 2-methylanthracene are determined to be 69 and 335 cm^{-1}, respectively, by using a one-dimensional free-rotor model. A prominent 0–0 transition has been observed in the fluorescence excitation spectrum of 1-methylanthracene, but no methyl rotational bands have been detected in both the excitation and dispersed fluorescence spectra. The potential energy curves of the methyl rotation are obtained for 2- and 1-methylanthracene with density functional theory (DFT) calculations and time-dependent (TD)-DFT calculations at the B3LYP/6-31 + G(d,p) level. The barrier heights and the phase of the potential energy curve are very different between 2- and 1-methylanthracene and substantially depend on the electronic state. These differences are consistently explained by a $\pi^*-\sigma^*$ hyperconjugation effect introduced by Nakai and Kawai [Chem. Phys. Lett. 307 (1999) 272].

Keywords: Methyl rotation; Methylanthracene; Electronic spectrum; Supersonic free jet; Density functional theory calculation; Fluorescence; Hyperconjugation

1. Introduction

The internal rotation of the methyl group in the S_0 and S_1 states and ground-state cation (D_0) of many aromatic molecules has been extensively studied by measuring the electronic spectra and pulsed-filed zero-kinetic energy (PFI-ZEKE) photoelectron spectra in a supersonic molecular beam [1–13]. These studies reveal that the internal rotational potential is very sensitive to the substituted position of the methyl group and the electronic state. The analysis of the internal rotational potentials has provided insight into non-covalent interaction and the intramolecular vibrational energy redistribution. It is crucial to determine the methyl rotational potentials to discuss the non-covalent interaction between the methyl group and the aromatic ring. The origin of the rotational barrier to internal rotation in the methyl-substituted aromatic molecules has been theoretically investigated. The barrier heights are correlated with the difference in the bond order of the C–C bond and with that in the charge [14,15]. Such a theory is useful for analyzing the methyl rotational potentials of the S_0 and D_0 states, but inapplicable to the change

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in the barrier upon $S_1 \leftarrow S_0$ excitation [16]. Nakai and coworkers [16–20] introduced a new model, which is based on a $\pi^*-\sigma^*$ hyperconjugation (HC) effect between the π^* orbital of the carbon atom and the σ^* orbital of the hydrogen atoms of the methyl group. This model has been successfully used to explain the stability of the lowest unoccupied molecular orbitals (LUMOs) and the highest occupied molecular orbitals (HOMOs) of several molecules such as substituted toluenes [17,19,20] and 1- and 2-methylnaphthalene [18].

In this work, we focus on the difference in the internal rotation of the methyl group in 2-methylanthracene (2MA) and 1-methylanthracene (1MA). The methyl rotation in 2MA was investigated by measuring the laser fluorescence excitation (LIF) spectrum [21]. The barrier to internal rotation was obtained for the S_1 state. However, the barrier for the S_0 state was predicted by calculating the Franck–Condon factors for the S_1–S_0 transition, while the rotational levels in the S_0 state were not determined. To our best of knowledge, there has been no report on the electronic spectrum of 1MA. In 1MA the distance between a hydrogen atom of the methyl group and the nearest CH hydrogen atom(s) is much shorter than that in 2MA. The steric repulsion may significantly influence the shape of the potential energy surface. The S_1–S_0 electronic spectra of the two molecules have been measured in a supersonic free jet expansion to investigate the effect of the non-covalent interaction on the methyl rotational potential energy surface. The stable geometries and potential energy curves of methyl rotation for the S_0 and S_1 states have been calculated with density functional theory (DFT) and time-dependent (TD)-DFT calculations, respectively. The shape of the internal rotational potential curve remarkably depends on the substituted position of the methyl group in the anthracene ring. The origin of the variations of the barrier heights and the phase of the potential upon electronic excitation has been discussed.

2. Experiment

2MA and 1MA were purchased from Wako Pure Chemical Ind. Ltd., and were used without further purification. The experimental apparatus for the measurement of the LIF and dispersed fluorescence (DF) spectra was essentially the same as that reported previously [22,23]. Briefly, 2MA or 1MA was vaporized by heating the solid sample in a nozzle housing to 100–120 °C. Gas mixture of the vaporized molecules and helium was expanded into a vacuum chamber with a pulsed nozzle (General Valve Series 9, 0.5 mm orifice diameter). The backing pressure was 200–300 kPa. An excimer laser pumped dye laser system (Lumonics EX-600 and HD-300) excited the molecules seeded in the helium gas. LIF spectra were measured by monitoring total fluorescence with a photomultiplier tube (Hamamatsu 1P28A). DF spectra were measured with a monochromator equipped with a photomultiplier tube (Hamamatsu R955). The electric current from the photomultiplier tubes was fed into a digital oscilloscope (LeCroy 9310A) and processed by a PC.

3. Results

3.1. LIF and DF spectra

Fig. 1(a) and (b) display the $S_1 \leftarrow S_0$ ($\pi\pi^*$) LIF spectra of 2MA and 1MA around the electronic origin region. The S_1–S_0 origin of 2MA is observed at 27389 cm^{-1}. Several methyl rotational bands are assigned in the figure. The procedure for assigning the rotational levels is described in Section 3.2. The LIF spectrum of 2MA is essentially the same as that reported previously [21]. A strong band is observed at 27463 cm^{-1} in the LIF spectrum of 1MA. This band

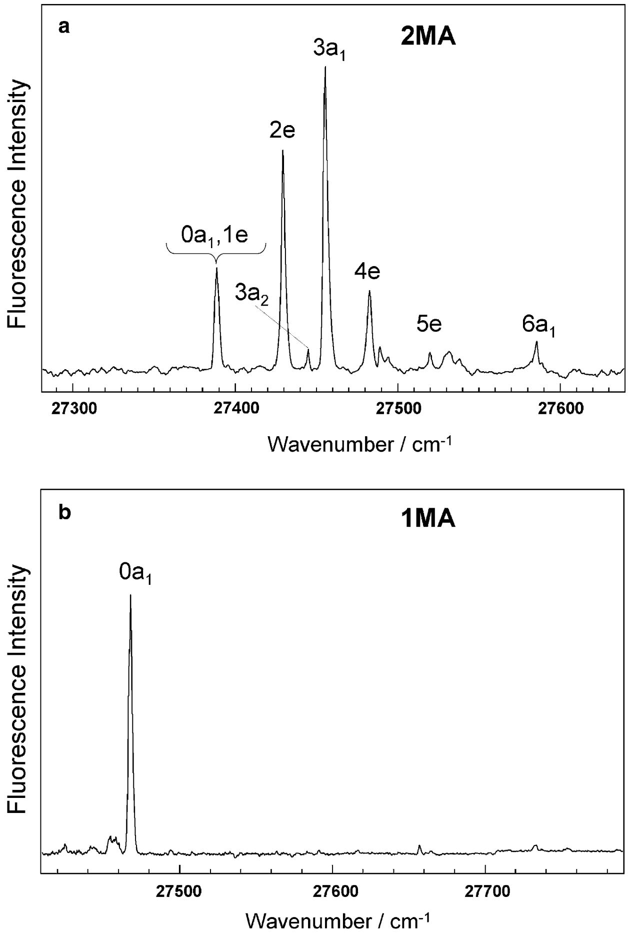

Fig. 1. LIF spectra of jet-cooled (a) 2MA and (b) 1MA. The assignments for the rotational levels of 2MA are indicated in the figure.