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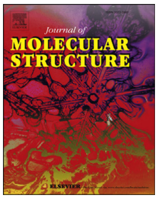

# Matrix-isolation infrared spectrum of acenaphthene in the lowest electronically excited triplet ($T_1$) state

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Since acenaphthene isolated in an Ar matrix at 15 K emits green-yellow phosphorescence for ~10 s after stopping UV-light irradiation, its transient IR spectrum is expected to be measured with an FTIR spectrometer during UV irradiation. The transient spectrum observed is found to be consistent with the simulated spectrum of acenaphthene in the lowest electronically excited triplet ($T_1$) state calculated at the B3LYP/6–31++G(d,p) level. The spectral pattern obtained using the B3LYP functional, which is the most popular DFT hybrid functional, reproduces the observed spectrum more satisfactorily than that obtained using the recently proposed M06-2x functional, although the optimized geometrical parameters in the both calculations are not so different from each other. The IR-band assignments of the $T_1$ state and the structural changes from the $S_0$ state to the $T_1$ state are discussed based on the results of B3LYP calculation.

## 1. Introduction

In order to confirm the accuracy of quantum chemical calculation methods, estimated vibrational frequencies are frequently compared with experimental ones [1,2]. However, in the case of the lowest electronically excited triplet ($T_1$) states, it is not easy to measure vibrational IR spectra because the direct transition between the $T_1$ state and the ground ($S_0$) state is optically inhibited. Thus vibrational spectra of the $T_1$ state are usually measured in solution by time resolved IR or Raman spectroscopy [3–7], but their bandwidths are so broaden due to their short lifetime and solvent effects that no bands except for intense bands are difficult to be detected.

The lifetime of the $T_1$ states is known to be prolonged under low-temperature condition [8]; for example, electron para-magnetic resonance (EPR) and phosphorescence spectra of various aromatic molecules are usually measured in solvent frozen at 77 K. The lifetime of phosphorescence for some aromatic molecules is relatively long at low temperature, implying that IR spectra of the sample in cryogenic materials are measurable using a conventional IR spectrometer and a continuous radiation source to excite the sample electronically [9–19]. A typical example is naphthalene, the IR spectrum in the $T_1$ state of which was first reported by Clarke et al., in 1973 [9]. They dispersed the deuterated naphthalene-$d_8$ sample in nujol at 80 K and succeeded in detecting an intense band at 535 cm$^{-1}$ in the $T_1$ state. The IR spectra of naphthalene in the $T_1$ state are also reported by other research groups [10–12], but the reports on the IR spectra of other aromatic molecules in the $T_1$ state are few. Guillory et al. reported the IR spectra of acridine, phenadine, and anthracene in the $T_1$ state by low-temperature matrix-isolation IR spectroscopy [13–15]. We also measured the IR spectra of dicyanobenzenes [16], tetracyanobenzene, tetracyanopyridine [17] and dicyanonaphthalenes in the $T_1$ state [18] and claimed that the spectra in the $T_1$ state are satisfactorily reproduced by the calculation at the B3LYP/6–31++G(d,p) level, which is the most popular hybrid functional of density functional theory (DFT) as well as the spectra in the ground ($S_0$) state.

In the present study, we report the fine IR spectrum of acenaphthene in the $T_1$ state. No IR spectrum of acenaphthene in the $T_1$ state has been reported except for only one intense transient band at 688 cm$^{-1}$ measured in rigid glass at 77 K [19]. We observe at least 15 significant transient IR bands and assign them by comparison with the theoretical values obtained using the B3LYP hybrid functional [20,21] and the recently proposed M06-2x functional [22]. We discuss which functional is better to reproduce the IR spectra in the $T_1$ state.

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## 2. Experimental and calculation methods

A small amount of acenaphthene (Tokyo Chemical Industry Co., Ltd.) placed in a glass sample holder located on the pathway of a deposition system was evaporated at room temperature. The evaporated sample gas was mixed with excess pure argon gas (Nippon Sanso, 99.9999% purity) in the holder, and deposited on a CsI plate cooled by a closed-cycle helium refrigerator (CTI Cryogenics, Model M − 22) to about 15 K.

IR spectra were measured with an FTIR spectrometer (JEOL, JIR-7000). The IR beam of the spectrometer was introduced into the matrix sample through a KBr window and detected with an MCT placed on the opposite side of a vacuum chamber. The spectral resolution was 0.5 cm$^{-1}$, the number of accumulations was 100, and the measurement time was about 7.5 min. A superhigh-pressure Hg lamp (USHIO, 500 W) was used as a radiation source to increase the population of the $T_1$ state through a short-wavelength cutoff filter (ASAHI spectra) and a water filter (10 cm path). See Refs. [16–18] for other experimental detail.

Theoretical energies, optimized geometries, and predicted IR spectra were obtained by the DFT calculations using B3LYP, M06-2x and M06-HF hybrid functional with a basis set of 6–31++G(d,p) on Gaussian 09 W program package [23].

## 3. Results and discussion

### 3.1. Photoinduced transient IR spectrum of acenaphthene in an Ar matrix

As described in Introduction, the $T_1$ states of aromatic molecules such as acenaphthene are mainly investigated by EPR and phosphorescence spectroscopies [24–26]. For example, the phosphorescence lifetime of acenaphthene was reported to be 2.64 s at 77 K [24]. Its lifetime expected to be prolonged under Ar matrix condition at ~15 K. After shutting UV ($\lambda \geq 275$ nm) radiation in the photolysis of acenaphthene isolated in an Ar matrix, the matrix sample emitted bright green-yellow light for more than 10 s, as expected, implying that the population of acenaphthene in the $T_1$ state increases during UV light irradiation enough for us to measure the IR spectrum.

Fig. 1a shows the spectral change measured during UV irradiation. The increasing bands are due to photoinduced transient species or photoproducts, while the decreasing bands are consistent with the bands of the reactant, acenaphthene, shown in Fig. 1c. Banisaukas et al. investigated photochemistry of acenaphthene isolated in a low-temperature matrix and reported that singly dehydrogenated acenaphthene radical and doubly dehydrogenated acenaphthylene were yielded when the sample was exposed to UV radiation coming from a medium-pressure Hg lamp [27]. In order to distinguish the bands of the transient species from the photoproduct bands, a spectrum of the photoproducts was measured after UV irradiation for 7.5 min, which is shown in Fig. 1b. The increasing bands of photoproducts are assignable to acenaphthylene or singly dehydrogenated acenaphthene radical. Besides the reported bands, some transient bands appear in Fig. 1a. They are distinguishable from the bands of the photoproducts by comparison of the both spectra shown in Fig. 1a and b. For example, the intense band at 684 cm$^{-1}$ appearing in Fig. 1a disappears in Fig. 1b, meaning that this band is due to the UV-induced transient species. The 684 cm$^{-1}$ band is consistent with the reported band at 688 cm$^{-1}$ of acenaphthene in the $T_1$ state measured in rigid glass at 77 K [19]. Note that the absorbance of the transient species and the reactant bands appearing in Fig. 1a are almost negligible in Fig. 1b, meaning that acenaphthene in the $S_0$ state restitutes from the photoinduced transient species after stopping UV irradiation. The population of acenaphthene in the transient state during the UV irradiation is estimated to be roughly 10%, calculated from the absorbance decrease of the 783 cm$^{-1}$ band of acenaphthene in the $S_0$ state.

In order to find other weak transient bands, the spectral region between 800 and 1700 cm$^{-1}$ is expanded in Fig. 2. Except for the photoproducts bands assigned to acenaphthylene or singly dehydrogenated acenaphthene radical, at least 15 weak bands of

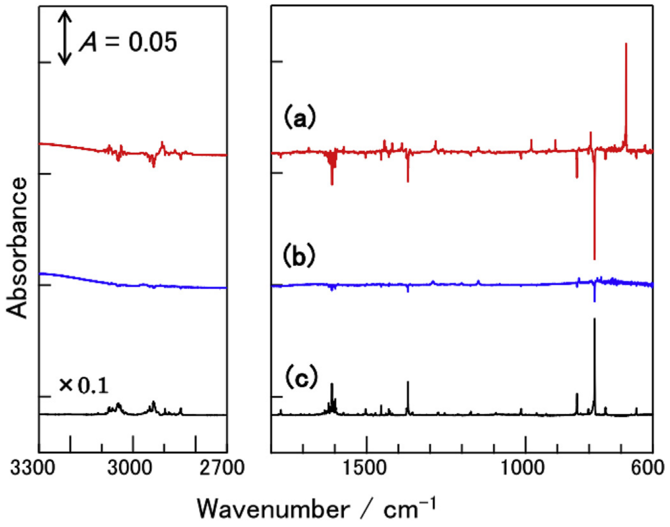

**Fig. 1.** Matrix-isolation IR spectra of transient species measured during UV irradiation (a), photoproducts measured after UV irradiation for 7.5 min (b), and acenaphthene measured before UV irradiation (c). Absorbance of (c) is divided by 10.

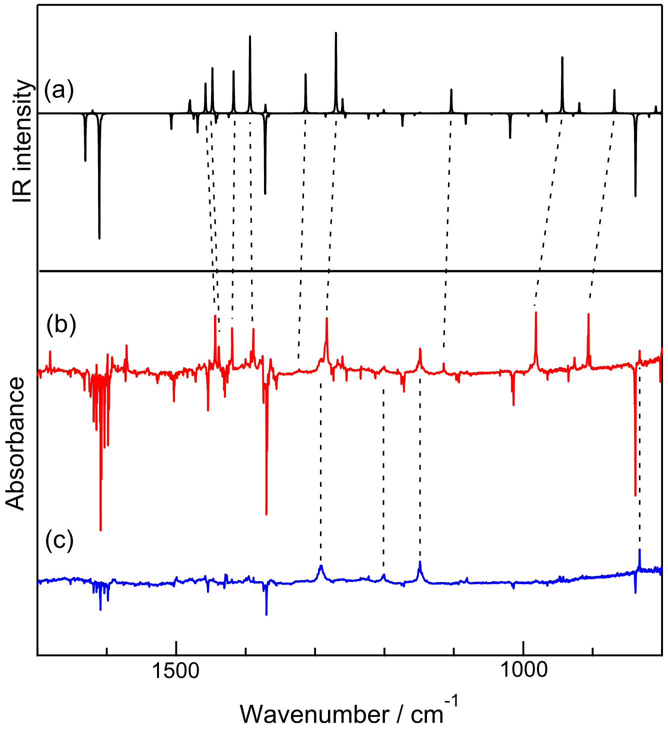

**Fig. 2.** Expanded IR spectra in the region between 1700 and 800 cm$^{-1}$. A simulated spectrum of acenaphthene in the $T_1$ (upside) and $S_0$ (downside) states obtained at the B3LYP/6–31++G(d,p) level, where a scaling factor of 0.98 is used (a), and matrix-isolation IR spectra of transient species measured during UV irradiation (b), and photoproducts measured after UV irradiation for 7.5 min (c).

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