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Research paper

Photoinduced reversible isomerization of 9*H*-fluorene into 1*H*-fluorene by means of hydrogen-atom migration and the lowest electronically excited triplet state studied by matrix-isolation FTIR spectroscopy



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HIGHLIGHTS

- 9H-Fluorene isomerizes to 1H-fluorene by photoinduced hydrogen-atom migration.
- The backward isomerization occurs upon longer-wavelength light irradiation.
- The experimental IR spectrum of 9H-fluorene in the T₁ state was obtained.

ARTICLE INFO

Keywords: Fluorene Photoinduced hydrogen-atom migration Matrix-isolation infrared spectrum Electronically excited T₁ state

ABSTRACT

Photoinduced reversible intramolecular hydrogen-atom migration between 9*H*-fluorene and 1*H*-fluorene isolated in an Ar matrix is found by FTIR spectroscopy with an aid of DFT calculation. The forward isomerization from 9*H*-fluorene to 1*H*-fluorene occurs upon UV irradiation ($\lambda \ge 295$ nm), while the backward isomerization occurs upon $\lambda \ge 320$ nm light irradiation. The less stable isomer, 1*H*-fluorene, is identified by comparison of the measured IR spectrum with the corresponding simulated spectral pattern obtained at the B3LYP/6-31 + +G(d,p) level. In addition, an IR spectrum of 9*H*-fluorene in the T₁ state is measured during UV irradiation ($\lambda \ge 275$ nm).

1. Introduction

The photoreaction mechanism of polycyclic aromatic hydrocarbons (PAHs) is an important research subject in general chemistry. Since most of the PAHs were recognized as notorious pollutants and/or precursors, their photochemistry has been actively investigated in environmental chemistry [1-3]. In addition, since the PAHs are included in a lot of organic molecules as a basic framework, the reactivity of PAHs has been studied in fundamental organic and physical chemistries for long time [4]. Various experimental and theoretical researches have been in progress and published. However, the photochemistry of 9Hfluorene is not elucidated clearly, although this molecule is not only one of the typical PAHs but also frequently used for basic materials to yield organic electroluminescence elements, dyes and pesticides. In 2002, vacuum UV photolysis of 9H-fluorene isolated in an Ar matrix has been studied by Szczepanski et al. from the point of view in interstellar chemistry [5,6], where a neutral ring-opening species, a radical species due to dehydrogenation from position 9 of 9H-fluorene, and its radical cation have been spectroscopically detected and confirmed by densityfunctional-theory (DFT) calculations. In the present study, the spectroscopic detection and characterization of species produced in the photolysis of 9*H*-fluorene in an Ar matrix are initially performed, and the isomerization from 9*H*-fluorene to the less stable isomer, 1*H*fluorene shown in Fig. 1, due to intramolecular hydrogen-atom migration upon UV irradiation is found.

Reports on the photolysis of 9*H*-fluorene are few so far, but the electronically excited states of 9*H*-fluorene are sometimes investigated by several spectroscopies and theories [7–12] because 9*H*-fluorene and its derivatives have interesting π -electron conjugation and are used as basic materials to yield organic electroluminescence elements [13–15]. The π -electron conjugation between the two benzene rings is comparable with that in biphenyl structure [16–19]. Especially, the lowest electronically excited triplet (T₁) state is investigated in detail [16,17]; Buntinx and Poizat reported time-resolved resonance Raman spectra of the T₁ state of 9*H*-fluorene and its radical cation [16], and Matsunuma et al. reported time-resolved resonance CARS spectrum in the T₁ state of 9*H*-fluorene and its deuterated species [17]. Although the lifetime of the T₁ state is known to be relatively long, ca. 5 s [20], no IR spectrum

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has been reported except for only three bands of a sample in polyethylene matrix at 77 K [20]. We have established a technique to measure IR spectra of transient species existing only during irradiation and reported IR spectra of some aromatic molecules in the T_1 states so far [21–26]. In the present study, the IR spectrum of 9*H*-fluorene in the T_1 state is also reported, providing complementary information against the Raman spectra reported previously.

2. Experimental and calculation methods

A small amount of 9*H*-fluorene (Tokyo Chemical Industry Co., Ltd.) was placed in a glass sample holder located on the pathway of a deposition system and evaporated at room temperature. The evaporated sample gas was mixed with much excess Ar 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 ca. 15 K.

IR spectra were measured with an FTIR spectrometer (JEOL, JIR-7000) equipped with an MCT detector. The spectral resolution was 0.5 cm^{-1} , and the number of accumulations was 100. A superhigh-pressure Hg lamp (USHIO, 500 W) was used as a radiation source to induce photoreaction through short-wavelength cutoff filters (ASAHI spectra) and a water filter (10 cm path). See Refs. [21–26] for other experimental detail.

Theoretical energies, optimized geometries, electronic transition energies, and predicted IR spectra were obtained by the DFT and timedependent DFT calculations using B3LYP hybrid functional with a basis set of 6-31 + + G(d,p) on the Gaussian 09 W program package [27].



3. Results and discussion

3.1. Intramolecular hydrogen-atom migration from position 9 to position 1

The matrix-isolated sample of 9H-fluorene was prepared by slow deposition on the CsI plate for 120 min, and the IR spectrum of 9Hfluorene was measured, which is essentially same as the previous reports [7,10]. Spectral change of 9H-fluorene in an Ar matrix was observed when the matrix sample was exposed to the light of $\lambda \ge 295$ nm, but not 320 nm, which is consistent with the reported S_1 - S_0 transition energy of 9H-fluorene [28,29]. Fig. 2(a) shows a difference spectrum between spectra measured before and after UV irradiation, $\lambda \ge 295$ nm. for 60 min. Roughly 10% of 9H-fluorene was changed to photoproducts when the spectrum changed no longer. In order to classify the photoproduct bands into a few groups, a matrix sample irradiated by $\lambda \ge 275$ nm light for 70 min was continuously exposed to various wavelength lights. It is noted that the bands of the reactant of 9H-fluorene increase upon $\lambda \ge 320$ nm irradiation (Fig. 2(b)), which decrease in Fig. 2(a); for example, see the most intense 740 cm^{-1} band. On the other hand, most of the bands increasing in Fig. 2(a) decrease in Fig. 2(b); for example, see the doublet bands at 752 and 754 cm^{-1} , implying that a reversible transformation occurs between 9H-fluorene and its isomer in the course of the irradiations. By comparison of the measured spectrum with simulated spectral patterns of some candidates for the isomer, 1H-fluorene is found to be the most suitable isomer of 9H-fluorene, as shown in Fig. 2(c); theoretical IR spectra of other fluorene isomers are shown in Fig. S1 in Supporting information. Judging from the absorbance of the both fluorene, roughly 30% of 9Hfluorene changes to 1*H*-fluorene upon $\lambda \ge 275$ nm, and about 25% of yielded 1*H*-fluorene reconverts to 9*H*-fluorene upon $\lambda \ge 320$ nm, suggesting that photochemical equilibrium between the both isomers depends on irradiation wavelength. The observed and calculated wavenumbers of 1H-fluorene are summarized in Table 1 with their vibrational assignments. The characterized vibration modes of 1Hfluorene appear at 752/754 cm⁻¹ doublet, 818 cm⁻¹, 1418 cm⁻¹ and $1453/1457 \text{ cm}^{-1}$ doublet, which are assigned to theoretical values of 754 cm⁻¹ (C-H out-of-plane bending), 823 cm⁻¹ (C9-H out-of-plane bending), 1413 cm^{-1} (CH₂ scissoring) and 1453 cm^{-1} (aromatic-ring stretching), respectively. No vibrational spectrum of 1H-fluorene has been reported so far, to our knowledge. Two bands at 834 and

Fig. 2. Difference IR spectra between spectra measured before and after the first irradiation $(\lambda \ge 295 \text{ nm for } 60 \text{ min})$ (a), measured before and after the second irradiation $(\lambda \ge 325 \text{ nm for } 90 \text{ min})$ continuously after $\lambda \ge 275 \text{ nm for } 70 \text{ min}$ irradiation (b), and the simulated IR spectrum composed of 9*H*-fluorene (positive bands) and 1*H*-fluorene (negative bands) calculated at the B3LYP/6-31 + +G(d,p) level (c). The bands marked with "+" are due to unknown products.

Table 1

Observed and calculated wavenumbers (in cm⁻¹) of 1*H*-fluorene in the region between 600 and 3100 cm⁻¹.

Obsd.		Calcd. ^a		Sym.	Assignment ^b
$\widetilde{\nu}/\mathrm{cm}^{-1}$	Abs.	$\widetilde{\nu}/\mathrm{cm}^{-1}$	IR Int./km mol ⁻¹		
630	37.6	624	11.8	A'	β (ring)
652	60.2	660	36.0	A"	γ(C2,3,4-H), CH ₂ rock.
707	12.7	711	8.2	A"	γ(C2,3,4-H)
747	36.2	748	37.8	A"	γ(C5,6,7,8-H)
752/754	90.5	754	30.8	A"	γ(C5,6,7,8-H)
815	23.1	812	7.8	A'	v(C4a-C9a)
818	35.3	823	18.3	A"	γ(C9-H)
866	8.1	870	5.6	A"	γ(C9-H),γ(C5,6,7,8-H)
931	13.1	917	7.0	A'	ν (C1-C2)
1008	21.3				Combination?
1012	21.7	1010	8.8	A'	ν (C3-C4)
1020	26.7	1022	4.7	A'	ν (C3-C4)
1133	7.7	1134	1.5	A'	β(С9-Н)
1153/1155	21.3	1154	6.6	A'	β(H-C6-C7-H)
1189	16.7	1191	11.6	A'	ν(C4b-C8a-C9)
1202	23.1	1203	10.3	A'	ν(C8a-C9), β(C5-H)
1276/1278	14.0	1280	1.9	A'	v(C2-C1-C9a-C4a)
1343	67.0	1354	19.1	A'	ν(C4a-C9a), ν(C4b-C8a)
1352	20.4				Combination?
1364	14.0	1372	5.8	A'	v(C4a-C9a),v(C8a-
					C9),v(C6-C7)
1398/1403	21.7	1402	2.6	A'	β(H-C2-C3-H)
1418	11.8	1413	14.2	A'	CH ₂ scissor.
1453/1457	100.0	1453	72.4	A'	ν (aromatic ring)
1466	26.2	1468	4.0	A'	β(H-C6-C7-H)
1562/1564	19.5	1572	25.4	A'	v(C9-C9a),v(C6-C7)
1568	76.5	1584	9.9	A'	ν(C2-C3-C4-C4a)
1587	19.5	1599	16.0	A'	ν(C4b-C8a),ν(C6-
					C7),v(C9-C9a)
1609	35.3	1616	14.7	A'	ν (aromatic ring)
2843	2.3	2877	20.3	A'	$\nu_{sym}(CH_2)$
2852	9.0	2889	6.1	A"	$\nu_{\rm asym}(\rm CH_2)$
3007	2.5	3045	5.5	A'	ν(C-H)
		3056	18.9	A'	ν(C2-H),ν(C4-H)
3048	38.9	3062	29.8	A'	v(C5,6,7,8-H)
3054	24.9	3070	35.9	A'	ν(C2,3,4-H)
3057	19.0	3075	32.0	A'	ν(C5,6,7,8-H)
		3084	13.4	A'	ν(C9-H)

^a Obtained at the B3LYP/6-31 + + G(d,p) level. The calculated wavenumbers are adjusted by scaling factors of 0.98 below $2000 \,\mathrm{cm^{-1}}$ and 0.96 above $2000 \,\mathrm{cm^{-1}}$. Calculated wavenumbers with IR intensity less than 5.5 are omitted. All calculation results are provided in supporting information.

 b Dominantly vibrational modes are shown in. Symbols of $\gamma,~\beta$ and ν represent out-of-plane bending, in-plane bending and stretching modes, respectively. Numbering of atom is defined in Fig. 3.

884 cm⁻¹ marked with "+" in Fig. 2 are due to unknown products, not assigned to 1*H*-fluorene.

The optimized structure of 1*H*-fluorene is shown in Fig. 3: the symmetry of 1*H*-fluorene is changed to C_s symmetry from C_{2y} symmetry of 9H-fluorene. The hydrogen-atom migration largely affects not only the right six-membered ring, which is changed from a benzene ring to a 1,3-cyclohexadiene ring with CH₂ group, but also the central fivemembered ring; the bond lengths of C9-C9a and C8a-C9 are shortened to 1.362 and 1.465 Å, respectively, from 1.516 Å of the corresponding bond of 9*H*-fluorene. It may be assumed that the delocalized π -electron system of 1*H*-fluorene expands on the right six-membered ring and the left benzene ring through the C9a-C9-C8a fragment, leading to the conclusion that the lowest electronic transition energy of 1H-fluorene is lower than that of 9H-fluorene [30]. Actually, the first, the second, and the third electronic transitions of 1H-fluorene are estimated by the time-dependent DFT calculation to be 452 nm (its estimated oscillator strength f = 0.049), 361 nm (f = 0.266) and 284 nm (f = 0.061), respectively, while the corresponding values of 9H-fluorene are 276 nm (f = 0.162), 266 nm (f = 0.287) and 257 nm (f = 0.007), implying that



Fig. 3. Numbering of carbon atoms and optimized structure of 1*H*-fluorene. Blue, red and black-colored lines have single, double bond and aromatic characters, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

1*H*-fluorene absorbs longer-wavelength light than 9*H*-fluorene. This expectation is consistent with the experimental results that the backward isomerization from 1*H*-fluorene to 9*H*-fluorene occurs by $\lambda \ge 320$ nm irradiation (Fig. 2(b)) and the forward isomerization from 9*H*-fluorene to 1*H*-fluorene occurs by $\lambda \ge 295$ nm irradiation (Fig. 2(a)).

9H-fluorene is more stable than 1H-fluorene by ca. 117 kJ mol⁻¹, and the barrier height from 9H-fluorene to 1H-fluorene is estimated to be ca. 271 kJ mol^{-1} in the electronic ground state at the B3LYP/6-31 + +G(d,p) level with zero-point energy correction. The barrier height inhibits thermal isomerization between the two isomers in low-temperature Ar matrices. Another possible isomer is 3H-fluorene, the relative energy of which is estimated to be ca. 104 kJ mol⁻¹ against 9Hfluorene, meaning that 3H-fluorene is more stable than 1H-fluorene. However, no IR bands assigned to 3H-fluorene were detected in the present experiment. We assume that the hydrogen-atom migration to produce 3H-fluorene is difficult, because hydrogen-atom migration easily occurs between next nearest carbon atoms from C1 to C9 by photo-induced dissociation-association (PIDA) mechanism as described below. Relative energies of other possible isomers, 2H- and 4Hfluorene, are estimated to be 174 and 188 kJ mol⁻¹, respectively, which are much higher than that of 9H-fluorene (see Table S5 in Supporting information).

The reversible isomerization between 9*H*-fluorene and1*H*-fluorene is interesting because intramolecular hydrogen-atom migration occurs between two carbon atoms. This is exceptionally rare case, to our knowledge, beside the 2,4-shift at cyclohexadiene-1-thione produced from thiophenol [31], to our knowledge, although photoinduced reversible intramolecular hydrogen-atom migration between a carbon atom and a hetero atom such as O or N or between hetero atoms is well-known and investigated by matrix-isolation spectroscopy with quantum chemical calculations; for example, hydroxypyridines (2(1*H*)-pyridones) [32,33], cytosines [34,35], acetylacetones [36,37] and indole [38].

The irradiation energies for the forward and the backward reactions are ca. 405 kJ mol^{-1} (295 nm) and 375 kJ mol⁻¹ (320 nm), respectively, which are sufficiently higher than the estimated dissociation energies for the C9-H bond of 9*H*-fluorene and the C1-H bond of 1*H*-



Fig. 4. Matrix-isolation IR spectrum of 9*H*-fluorene, (a), and IR difference spectra of 9*H*-fluorene in an Ar matrix: UV pump ($\lambda \ge 275$ nm) source on minus source off, (b), where IR bands of transient species and photoproducts increase while those of 9*H*-fluorene in the S₀ state decreases; and after UV excitation for 7.5 min minus before, (c), where IR bands of photoproducts and 9*H*-fluorene in the S₀ state increase and decrease, respectively.

Fig. 5. An expanded difference IR spectrum of Fig. 4b, (a), compared with theoretical spectrum of 9*H*-fluorene in the T₁ state (positive bands) and S₀ state (negative bands), (b), and theoretical spectrum of 1*H*-fluorene in the T₁ state, (c), obtained at the B3LYP/6-31 + +G(d,p) level. The bands marked with asterisk "*" are assigned to 1*H*-fluorene as a photoproduct.

fluorene, ca. 326 kJ mol^{-1} (367 nm) and 210 kJ mol^{-1} (570 nm), respectively, at the B3LYP/6–31 + + G(d,p) level. Szczepanski et al. studied the vacuum UV photolysis of 9H-fluorene in an Ar matrix at 12 K and identified the dehydrogenated fluorene radical and its radical cation, and neutral ring-opening species as photoproducts, but 1Hfluorene was not recognized at all [5]. On the other hand, no infrared bands of dehydrogenated fluorene radical, which is expected to be an intermediate, were observed in the present study. This discrepancy may be explained by difference on the irradiation photon energy. In their previous experiment [5], the dissociated hydrogen atom freely migrates from a matrix cage by excess energy of vacuum UV light to form H₂ molecules, and the counterpart radicals can be kept in the matrix cage. In the present experiment, the dissociated hydrogen atom is kept in a matrix cage to recombine with the counterpart radical immediately, because the difference between irradiation energy and dissociation energy is too small to go out of the matrix cage.

This reversible tautomerization between 9*H*- and 1*H*-fluorene could be explained by PIDA mechanism proposed for photoinduced tautomerization reactions in the cryogenic matrix [39]. The intermediate fluorene radical yielded by dissociation of hydrogen atom upon light irradiation has a reactive carbon atom. Since Mulliken spin density distributions of C1, C3 and C9 are calculated to be 0.20, 0.10 and 0.66, respectively, at the B3LYP/6-31 + + G(d,p) level, it is expected that the hydrogen atom dissociated from C9 (or C1) is immediately recombined to C9 or close C1, while the hydrogen-atom migration from C1 to C3 across C2 is more difficult.

3.2. IR spectrum of transient species photoproduced from 9H-fluorene

By analogy with the previously reported molecules [21–26], the T_1 lifetime of 9*H*-fluorene is expected to be prolonged in an Ar matrix at ca. 15 K. Actually, blue phosphorescence was observed for ca. 20 s after stopping UV light for excitation. Fig. 4 shows a transient spectrum which is spectrum measured "during" UV excitation ($\lambda \ge 275$ nm) minus before and a difference spectrum between spectra measured before and "after" the light irradiation. The bands increasing in the both difference spectra (Fig. 4(b) and (c)) are due to stable photoproducts, and the bands increasing only during the light excitation (Fig. 4(b) but not 4(c)) are due to transient species produced from 9*H*-fluorene, which are expected to be assigned to 9*H*-fluorene in the T_1 state. To confirm the expectation, theoretical spectrum of the T_1 state is predicted at the B3LYP/6-31 + + G(d,p) level, which is known to be the most popular

Table 2

Observed and calculated wavenumbers (in cm⁻¹) of 9*H*-fluorene in the T₁ state in the region between 590 and 3100 cm⁻¹.

Obsd.			Calcd. ^b		Sym.	Assignment ^c
$\widetilde{\nu}/\mathrm{cm}^{-1}$	Abs.	$\widetilde{\nu}/cm^{-1}$ a	$\widetilde{\nu}/\mathrm{cm}^{-1}$	IR Int./ km mol ⁻¹		
592	41.3	593	595	30.1	B_1	γ(C2,4,5,7-H)
681	100	680	679	103.2	B_1	γ(C(all)-H)
768	11.5		756	7.1	B_1	γ(C(all)-H)
769	9.3		760	4.5	B_2	β(aromatic ring)
853	10.4		858	10.7	B_1	γ(C1-H), γ(C8-H), CH ₂ rock.
910	11.5		896	3.8	B_2	ν(C1-C2-C3),ν(C6-C7- C8)
944	4.5		956	3.5	B_1	CH ₂ rock.
977	6.3		970	9.3	B_2	β(C1,4,5,8-H)
1045	3.0		1042	4.9	A_1	ν(C2-C3), ν(C6-C7)
1078	3.0		1077	2.2	A_1	β(C2-H), β(7-H)
1220	3.3		1219	3.5	A_1	β(C(1,4,5,8)-H)
1314	13.8		1313	11.5	A_1	ν(C1-C2-C3), ν(C6-C7-
						C8), β(C2-H), β(C7-H)
1338	7.1		1323	1.5	B_2	ν (aromatic ring),
						β(C2-H), β(C7-H)
1415	33.5		1411	8.2	B_2	β(H-C3-C4-H)
1424	15.2		1441	3.6	A_1	CH ₂ scissor.
1486	4.1	1476	1471	3.3	B_2	ν(C3-C4), ν(C5-C6)
1531	5.2		1532	18.2	B_2	ν(C1-C9a), ν(8-C8a)
1687	2.6					Combination
1718	7.4					Combination
1740	2.2					Combination
1854	5.9					Combination
2827	4.5					Combination
2832	2.6		2896	31.4	A_1	$\nu_{\rm sym}(\rm CH_2)$
2907	13.8		2918	9.1	B_1	$\nu_{asym}(CH_2)$
			3049	7.6		
			3050	16.2		
			3053	5.4		
3046	7.1		3054	19.1	A ₁	ν(C1,3,4,5,6,8-H)
3066	8.2		3075	23.1	A_1	v(C2,4,5,7-H)
3075	5.6		3082	42.8	B_2	ν(C2,7-H)

Chemical Physics Letters 714 (2019) 160-165



Bond length in Å					
	$S_0 \rightarrow T_1$				
C1-C2	: 1.401→ 1.433				
C2-C3	$: 1.401 \rightarrow 1.424$				
C3-C4	$: 1.398 \rightarrow 1.374$				
C4-C4a	$: 1.398 \rightarrow 1.454$				
C4a-C9a	$: 1.411 \rightarrow 1.469$				
C9a-C1	: 1.392→ 1.365				
C9-C9a	$: 1.516 \rightarrow 1.520$				
C4a-C4b	$: 1.470 \rightarrow 1.381$				

Fig. 6. Numbering of carbon atoms and optimized structure of 9*H*-fluorene in the T_1 state. Blue and red lines represent longer and shorter bonds than the corresponding values in the S_0 state, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

^a Measured in polyethylene matrix at 77 K [20].

 $^{\rm b}$ Obtained at the B3LYP/6-31 + +G(d,p) level. The calculated wavenumbers are adjusted by scaling factors of 0.98 below 2000 cm $^{-1}$ and 0.96 above 2000 cm $^{-1}$. Calculated wavenumbers withIR intensity less than 3.0 are omitted. All calculation results are in supporting information.

 c Dominantly vibrational modes are shown in. Symbols of $\gamma,~\beta$ and ν represent out-of-plane bending, in-plane bending and stretching modes, respectively. Numbering of atom is defined in Fig. 6.

DFT functional [26], and compared with the transient spectrum in the region between 580 and 1780 cm⁻¹ in Fig. 5. It is found that the simulated spectrum satisfactorily reproduces the observed one. One may concern the existence of 1*H*-fluorene in the T₁ state. However, the predicted spectrum, Fig. 5(c), poorly reproduces the experimental one, Fig. 5(a). After UV ($\lambda \ge 275$ nm) irradiation to yield 1*H*-fluorene as much as possible, we tried to detect bands due to any transient species of 1*H*-fluorene during light irradiation, but no transient bands were obtained.

We have observed at least 25 bands of species in the T_1 state besides the three bands at 593, 680 and 1476 cm⁻¹ reported by Krumschmidt and Kryschi [20]. The observed and calculated wavenumbers are summarized in Table 2 with their vibrational assignments, where the theoretical wavenumbers are adjusted by scaling factors of 0.98 below 2000 cm⁻¹ and 0.96 above 2000 cm⁻¹. They are consistent within 17 cm⁻¹ in the IR region below 1600 cm⁻¹ each other, although the relative absorbance of the bands at 944, 1424, 2832 and 2907 cm⁻¹, which are assigned to the characteristic CH₂ rocking (956 cm⁻¹), CH₂ scissoring (1441 cm⁻¹), CH₂ symmetric stretching (2896 cm⁻¹) and CH₂ asymmetric stretching (2918 cm⁻¹) modes, respectively, is not reproduced by the theory. Some bands appearing in the region between 1600 and 1900 cm⁻¹ could be assigned to overtones or combination modes relating to the intense 592 and 681 cm⁻¹ bands.

The optimized structure of 9*H*-fluorene in the T_1 state is shown in Fig. 6, which keeps C_{2v} symmetry even in the T_1 state like the S_0 state. As mentioned in the previous reports [16,17], the structural change in the T_1 state is similar to biphenyl, where the two benzene rings changes to quasi quinoid rings. The lengthening and shortening bonds are colored by blue and red lines, respectively, in Fig. 6. The bond lengths of C1-C2 (1.433 Å), C2-C3 (1.424 Å) and C4-C4a (1.454 Å) in the T_1 state are longer than the corresponding values in the S_0 state, 1.401, 1.401 and 1.398 Å, respectively. On the other hand, the bond lengths of C3-C4 (1.374 Å), C1-C9a (1.365 Å) and C4a-C4b (1.381 Å) in the T_1 state are shorter than 1.398, 1.392 and 1.470 Å in the S_0 state, respectively. Other optimized geometrical parameters are summarized in supporting information.

4. Summary

Photoreaction of 9*H*-fluorene isolated in an Ar matrix was investigated by FTIR spectroscopy with an aid of the DFT calculation. Photoinduced isomerization from 9*H*-fluorene, which is the most stable fluorene isomer, to 1*H*-fluorene, which is the third stable isomer, upon UV irradiation ($\lambda \geq 295$ nm) was found. The backward isomerization also occurred upon $\lambda \geq 320$ nm light irradiation, suggesting that the both tautomers isomerize in photochemical equilibrium. The vibrational assignments for 1*H*-fluoreneare performed for the first time, to our knowledge. The time-dependent DFT calculation showed that 1*H*-fluorene absorbs longer-wavelength light than 9*H*-fluorene, which was consistent with our experimental results.

An IR spectrum of 9H-fluorene in the lowest electronically excited

triplet (T₁) state was measured during UV irradiation, which was confirmed by the comparison between the observed spectrum and calculated spectral pattern obtained at the B3LYP/6-31 + +G(d,p) level. It was found that the C-C bond length in the center five-membered ring is shorter in the T₁ state than in the S₀ state, implying that π -conjugation expands between the five-membered ring and benzene rings.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cplett.2018.11.011.

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