

Laser-Induced Fluorescence Excitation Spectrum and CF_3 Torsional Potential Energy Function of 7-Amino-4-(trifluoromethyl)coumarin in Its S_1 Electronic Excited State

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Received February 21, 1996

The laser-induced fluorescence excitation spectrum of 7-amino-4-(trifluoromethyl)coumarin in a supersonic jet has been recorded in the 340-352 nm region. The electronic band origin was observed at 28622.8 cm^{-1} . Vibrational assignments for the three fundamental low-frequency modes and eight combination bands have been made for the S_1 electronic excited state. The out-of-plane vibrations of this molecule have been characterized from the low-frequency assignments of the spectrum. The periodic potential energy function for the CF_3 torsion, which satisfactorily fits the observed data, were also determined to be $V(\phi) = 95 \times (1 - \cos 3\phi) - 32 \times (1 - \cos 6\phi)$ where ϕ is the torsional angle. The relatively low torsional barrier of 99 cm^{-1} in S_1 state could be explained by the small steric interactions between the functional groups attached to a bicyclic ring.

Introduction

The laser-induced fluorescence (LIF) spectroscopy together with a supersonic jet cooling system has provided very useful means to study the conformational dynamics of ring compounds in their electronic excited states. The free-jet expansion technique allowed for much simpler spectroscopic analysis since the supersonic expansion cooling eliminated a great number of the hot bands. In recent years, the out-of-plane vibrations of various ring compounds have been successfully analyzed using this jet-cooled LIF technique. For example, a number of papers about the vibrational potential energy functions in their electronic excited states for the ring-twisting and ring-bending vibrations of benzene-fused rings,¹ the C=O wagging vibrations of carbonyl containing rings,² and the CF_3 torsions of aminobenzotrifluorides³ have been reported. In the present paper, we have investigated 7-amino-4-(trifluoromethyl)coumarin (7-ATC) which includes all the three out-of-plane vibrational modes (ring-bending, carbonyl wagging, and CF_3 torsion) in order to better understand the out-of-plane conformational dynamics in its electronic excited state.

7-ATC is one of the well-known laser dyes which can be used for tunable high power lasers. This compound has 60 vibrational modes. Among these vibrational modes, the low-frequency out-of-plane vibrational modes are of special interest because they determine the equilibrium conformation of the ring compound. In this work, we have recorded the jet-cooled LIF spectrum of 7-ATC and used these data to assign the low-frequency vibrational frequencies in its S_1 electronic excited state. In addition, we have determined the periodic potential energy function for the CF_3 torsional mode of this molecule. The results have allowed us to understand the out-of-plane conformational structure of 7-ATC as well as to determine the CF_3 torsional barrier in its S_1 state.

Experimental

The supersonic free jet apparatus consists of a vacuum chamber, a pulsed valve, and a pumping system. The chamber is basically an 8" o.d. stainless steel 6-way cross. It is pumped with 6" diffusion pump (Varian VHS-6), which is equipped with a liquid N_2 cold trap and backed with a rotary with a pumping speed of 600 l/min. The pressure of the chamber is below 2.0×10^{-5} torr during operation of the valve. The pulsed valve made by slight modification of a fuel injector of automobiles is appended to the top flange of the chamber and the jet directs down into the diffusion pump. Two-side arms with 3-4 irises and threaded tubes inside are attached to the chamber to block the room light and the scattered laser light. On the port perpendicular to the directions of the jet and side-arms, a view port for a photomultiplier tube (PMT) is placed to detect fluorescence.

Solid 7-amino-4-(trifluoromethyl)coumarin placed inside the pulsed valve maintained at $130 \text{ }^\circ\text{C}$ sublimates into the He carrier gas. The mixture was expanded through a nozzle with a 0.5 mm diameter. The stagnation pressure was kept at 600 torr for most of the experiment but sometimes decreased down to 300 torr or increased to 2.0 atm to find out the hot band transitions. The output beam from a pulsed dye laser (Lambda Physik SCANmate 2E) pumped with the second harmonic output of a Q-switched Nd:YAG laser (Spectra Physics GCR-150) was frequency-doubled in a KDP crystal. The ultraviolet (UV) output was separated from the fundamental and crossed the supersonic jet at 15 mm from the nozzle. The laser pulse and nozzle opening were synchronized with a home-made delay pulse generator. Fluorescence from the excited molecules was collected with a 2" diameter quartz lens, filtered with a color filter and an aperture, and then detected with a PMT (Hamamatsu H1161). The PMT signal was integrated with a gated integrator (SRS 250), digitized, and stored with the laser wavelength in a personal computer. Fluorescence excitation spectrum of 7-ATC was recorded from 340 to 352 nm, which corresponds to the fre-

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quency region where the $S_1 \leftarrow S_0$ transitions take place. The energy of the excitation pulse was kept $< 500 \mu\text{J}$ and the laser beam was unfocused to avoid saturation of transitions. The optogalvanic spectrum of a Ne hollow cathode lamp provided a frequency calibration for the dye laser with an accuracy of $\pm 0.3 \text{ cm}^{-1}$. The 7-Amino-4-(trifluoromethyl)coumarin sample was purchased from Exciton, Inc., and used without further purification.

Vibrational Assignments

7-ATC is expected to be a non-planar structure in its S_1 state and belongs to C_1 symmetry. Figure 1 shows the low-frequency LIF spectrum of 7-ATC which has been recorded in the 340-352 nm region. The electronic band origin was observed at 28622.8 cm^{-1} . Table 1 shows our vibrational assignments for the LIF spectrum of 7-ATC.

An intense series of bands at 35.3, 89.3, 142.7, and 183.3 cm^{-1} was assigned to the CF_3 torsion. The band progression is very similar to that of aminobenzotrifluorides³ and these four transitions have been used to determine the CF_3 torsional potential energy function of 7-ATC. The next lowest frequency band series at 57.3, 106.5, and 142.7 cm^{-1} was assigned to the ring-bending vibration. This assignment is consistent with the frequencies of corresponding vibrations of cyclic ketones.² An approximate barrier height of $170 \pm 50 \text{ cm}^{-1}$ was calculated from these three transitions, even though we could not determine the accurate ring-bending potential energy function. A couple of intense bands at 283.5 and 288.6 cm^{-1} were assigned to the $0 \rightarrow 2$ and $0 \rightarrow 3$ carbonyl wagging transitions based on the the LIF spectra for the recently reported cyclic ketones.² Unfortunately, the further progression, which is necessary for the determination of carbonyl wagging potential, was not found in higher frequency region. The disappearance of fluorescence over 450 cm^{-1} might be caused by the twisted intramolecular charge transfer conversion to the ground state. Nonetheless, the small split of 5.1 cm^{-1} between 58_0^2 and 58_0^3 bands indicates a relatively low potential barrier for the carbonyl wagging vibration. The low potential barriers for both ring-bending and carbonyl wagging vibrations in their electronic excited states could be explained

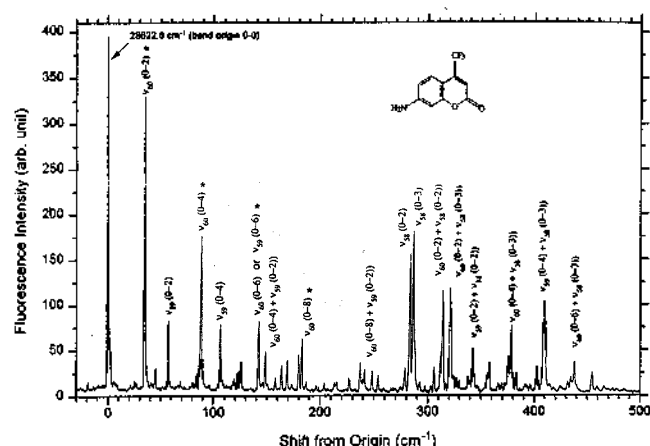


Figure 1. Jet-cooled laser-induced fluorescence excitation spectrum of 7-Amino-4-(trifluoromethyl)coumarin. Each progression for the CF_3 torsion is marked with an *.

ned by the fact that the conjugation effects between the carbonyl group and ring π bonds maintains the carbonyl oxygen and the six-membered ring in the plane of the benzene ring. Eight combination bands were also observed and these confirmed our vibrational assignments for the LIF spectrum of 7-ATC.

Potential Energy Function for CF_3 Torsion

The wave equation for the internal rotation can be expressed by

$$-B \frac{d^2 \psi}{d\phi^2} + V\psi = E\psi \quad (1)$$

where B is the internal rotational constant and ϕ is the phase angle. Laane *et al.*⁵ developed a computer program to calculate the eigenvalues for the periodic potential function

$$V = \frac{1}{2} \sum_{n=1}^6 V_n (1 - \cos n\phi) \quad (2)$$

where V_n is an n -fold barrier. We used this program to calculate the energy levels and eigenfunctions for the CF_3 torsion of 7-ATC. In this case, the torsional potential is supposed to be the following form by the symmetry.

$$V(\phi) = \frac{1}{2} V_3 (1 - \cos 3\phi) + \frac{1}{2} V_6 (1 - \cos 6\phi) \quad (3)$$

The potential barrier is determined by both V_3 and V_6 values. Gordon *et al.*³ determined the CF_3 torsional potentials of 2-aminobenzotrifluoride in the S_0 (barrier = 450 cm^{-1}) and S_1 states (barrier = 240 cm^{-1}) using their LIF spectra and the program mentioned above. For this molecule, the rotational

Table 1. Observed S_1 transition frequencies (cm^{-1}) and assignments from the fluorescence excitation spectrum of 7-Amino-4-(trifluoromethyl)coumarin

ν (cm^{-1})	Displacement from origin (0_0^0)		Assignment ^a
28622.8	0.0	0_0^0	band origin
28658.1	35.3	60_0^2	CF_3 torsion(0-2)
28682.1	57.3	59_0^2	ring-bend(0-2)
28714.2	89.4	60_0^4	CF_3 torsion(0-4)
28731.3	106.5	59_0^4	ring-bend(0-4)
28767.5	142.7	60_0^6 or 59_0^6	CF_3 torsion(0-6) or ring-bend(0-6)
28773.5	148.7	60_0^4 59_0^2	torsion(0-4) + bend(0-2)
28808.1	183.3	60_0^8	CF_3 torsion(0-8)
28873.0	241.3	60_0^8 59_0^2	torsion(0-8) + bend(0-2)
28908.3	283.5	58_0^2	C=O wag(0-2)
28913.4	288.6	58_0^3	C=O wag(0-3)
28941.4	313.6	60_0^2 58_0^2	torsion(0-2) + wag(0-2)
28949.0	321.2	60_0^2 58_0^3	torsion(0-2) + wag(0-3)
28970.4	342.6	59_0^2 58_0^2	bend(0-2) + wag(0-2)
29006.3	378.5	60_0^4 58_0^3	bend(0-4) + wag(0-3)
29036.6	408.8	59_0^4 58_0^2	bend(0-4) + wag(0-3)
29066.4	438.6	60_0^6 58_0^3	torsion(0-6) + wag(0-3)

^aAssignment notation $[v_x]_y^z$ indicates a $x \rightarrow y$ transition for v_x .

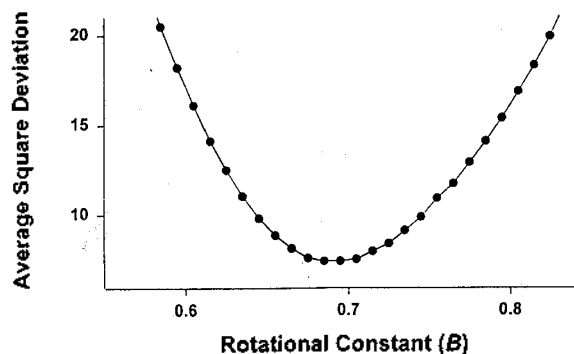


Figure 2. Average square deviation, $(\text{observed}-\text{calculated})^2$, in the calculation of transition frequencies as a function of rotational constant.

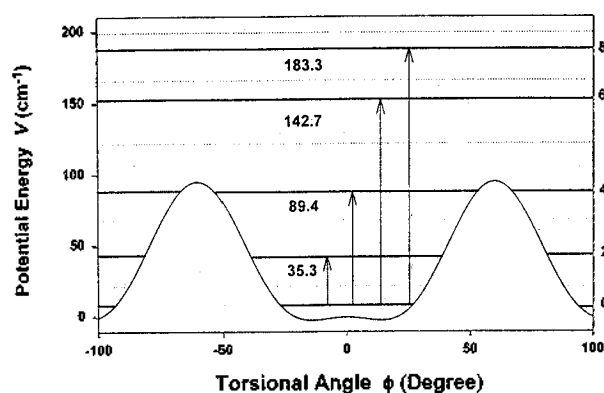


Figure 3. The CF_3 torsional potential energy function for 7-Amino-4-(trifluoromethyl)coumarin in its S_1 state.

constant for the CF_3 torsion, attached to a benzene ring, was assumed to be constant ($B=0.286 \text{ cm}^{-1}$) because this compound does not include any large-amplitude vibrational ring mode. In the case of 7-ATC, however, a significant contribution to the rotational constant may be made by the out-of-plane vibration because the large amplitude of vibration changes the reduced mass of this molecule by changing the center of mass point during the vibration. The variations of rotational constants with ring-puckering vibrations were previously reported for cyclobutanone and methylene-cyclobutane.⁶ In order to get a reasonable rotational constant of 7-ATC, we utilized a routine in the program which allowed us to fix the potential barrier to a particular value and then optimize the rotational constant to obtain the best frequency fit. Figure 2 shows the average square deviation as a function of rotational constant. The best fit of CF_3 torsional potential to the observed values was obtained when $B=0.69 \text{ cm}^{-1}$, $V_3=190 \text{ cm}^{-1}$, and $V_6=64 \text{ cm}^{-1}$. Figure 3 shows the periodic potential energy function and the vibrational transitions for the CF_3 torsion of 7-ATC in S_1 state. The low torsional energy barrier of 99 cm^{-1} in this figure may be due to the less steric interaction compared with the relative high barrier (240 cm^{-1}) of 2-aminobenzotrifluoride.² Table 2 compares the observed data with the frequencies calculated for this potential function and they show very good agreement. Only even transitions were observed in the LIF spectrum because the torsional mode is non-totally symmetric. The selection rule for this vibrational mode was reported by Gordon *et al.*²

Table 2. Observed and Calculated Energy Spacings (cm^{-1}) for the CF_3 Torsional Vibration of 7-Amino-4-(trifluoromethyl)coumarin in the S_1 state

	Observed	Calculated ^a	Δ^b
0→2	35.3	37.7	-2.4
0→4	89.4	89.6	-0.2
0→6	142.7	142.4	0.3
0→8	183.3	183.1	0.2

^a rotational constant $B=0.69 \text{ cm}^{-1}$; $V(\phi)=95 \times (1-\cos 3\phi)-32 \times (1-\cos 6\phi)$. ^b observed-calculated

Conclusions

The LIF spectrum of 7-ATC did a good job to characterize the low-frequency out-of-plane vibrations in the S_1 electronic state. Both ring-bending and carbonyl wagging vibrations showed relatively low potential barriers due to the conjugation effects between the carbonyl group and ring π bonds. We also determined the CF_3 torsional potential energy surface up to about 180 cm^{-1} from the four intense series of bands in the low-frequency region. The low CF_3 torsional barrier (99 cm^{-1}) could be explained by the less steric interactions between the functional groups attached to a bicyclic ring. However, the vibrational study in its S_0 electronic ground state, using dispersive fluorescence or far-infrared techniques, needs to be done to get a more detailed information about the conformational dynamics of 7-ATC in both S_0 and S_1 states.

Acknowledgment. This work was supported by the 1995-1996 Basic Science Research Institute Program (Project No. BSRI-95-3432) by the Ministry of Education of Korea.

References

- (a) Gordon, R. D.; Hollas, J. M. *J. Chem. Phys.* **1993**, *99*, 3380. (b) Hassan, K. H.; Hollas, J. M. *Chem. J. Mol. Spectrosc.* **1991**, *147*, 100. (c) Shin, Y.-D.; Saigusa, H.; Zgierski, M. Z.; Zerbetto, F.; Lim, E. C. *J. Chem. Phys.* **1991**, *94*, 3511. (d) Zgierski, M. Z.; Zerbetto, F.; Shin, Y.-D.; Lim, E. C. *J. Chem. Phys.* **1992**, *96*, 7229.
- (a) Cheatham, C. M.; Laane, J. *J. Chem. Phys.* **1991**, *94*, 7743. (b) Zhang, J.; Chiang, W. Y.; Laane, J. *J. Chem. Phys.* **1993**, *98*, 6129. (c) Zhang, J.; Chiang, W. Y.; Laane, J. *J. Chem. Phys.* **1994**, *100*, 3455.
- (a) Gordon, R. D.; Hollas, J. M.; Ribeiro-Claro, P. J. A.; Teixeira-Dias, J. J. C. *Chem. Phys. Lett.* **1991**, *182*, 649. (b) Gordon, R. D.; Hollas, J. M.; Ribeiro-Claro, P. J. A.; Teixeira-Dias, J. J. C. *Chem. Phys. Lett.* **1991**, *183*, 377. (c) Gordon, R. D.; Hollas, J. M.; Ribeiro-Claro, P. J. A.; Teixeira-Dias, J. J. C. *Chem. Phys. Lett.* **1993**, *211*, 392.
- Guchhait, N.; Chakraborty, T.; Majumdar, D.; Chowdhury, M. *J. Phys. Chem.* **1994**, *98*, 9227.
- Lewis, J. D.; Malloy, T. B. Jr.; Chao, T. H.; Laane, J. *J. Mol. Struct.* **1972**, *12*, 427.
- (a) Scharpen, L. H.; Laurie, V. W. *J. Chem. Phys.* **1968**, *49*, 221. (b) Scharpen, L. H.; Laurie, V. W. *J. Chem. Phys.* **1968**, *49*, 3041.