

## Supersonic Free Jet and *Ab initio* Studies of Electronic-Vibrational Structures of Fluorene

Bong Hyun Boo,<sup>\*,\*\*†</sup> Young Sik Choi<sup>†</sup>, Taek-Soo Kim<sup>†</sup>, Sung Kwon Kang<sup>\*\*</sup>, and Jae Ryong Kim<sup>\*\*</sup>

Chemistry Departments of <sup>\*\*</sup>Chungnam National University, Taejeon 305-764, Korea, and

<sup>†</sup>Inha University, Incheon 402-751, Korea, and

<sup>\*</sup>Center for Molecular Science, 373-1 Kusung-dong Yusung-gu, Taejeon 305-701, Korea

Received January 4, 1995

Laser-induced fluorescence (LIF) excitation spectra were measured for fluorene (FR) cooled in pulsed supersonic expansions of He in the range 283.7-296.7 nm. *Ab initio* studies of FR have also been carried out for determining the electronic and vibrational structures by using the standard 3-21G basis sets. In the LIF excitation spectra of FR, highly resolved vibronic bands are observed having the band origin of 33,791 cm<sup>-1</sup>. The vibrational bands above the electronic origin were assigned on the basis of the well-characterized electronic vibrational bands reported previously and of normal modes of vibrations derived by our HF/3-21G calculations.

### Introduction

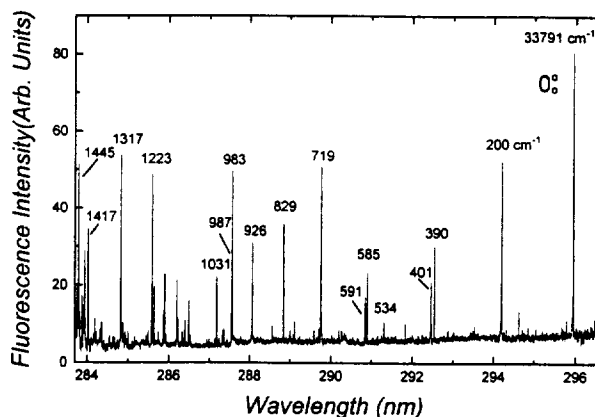
Highly resolved electronic-vibrational spectroscopy of large "isolated" molecules cooled adiabatically in seeded supersonic free jets or molecular beams provided information regarding excited state structures and dynamics.<sup>1</sup> To gain information about the excited state energetics, previous low-temperature spectroscopic studies in the solid phase have revealed the significant inhomogeneous broadening of the spectral features. It is interesting and quite useful to study isolated molecules generated by the pulsed supersonic expansion technique.

Here we report the fluorescence excitation spectroscopic studies of FR cooled in pulsed supersonic expansions of He in the ranges 283.7-296.7 nm and the *ab initio* studies of the electronic-vibrational structures and their energetics of the molecule. Since the FR molecule is well known to fluoresce efficiently upon excitation of S<sub>0</sub> to S<sub>1</sub>, the excited state dynamics of FR and its derivatives have numerously been studied by fluorescence excitation spectroscopy.<sup>2-7</sup> The fluorescence excitation spectroscopic studies of FR molecules in supersonic expansions were performed previously to gain information on the dimer-excimer transformation of FR<sup>2</sup> and the spectral behaviors of FR-Ar<sub>n</sub> van der Waals complexes.<sup>5</sup> Only the band origin and symmetries of the vibrational mode of the molecule are elucidated in those papers.<sup>2,5</sup> Also the electronic vibrational spectral ranges examined before were limited to narrow ranges of 286-298 nm<sup>2</sup> and 289-299 nm.<sup>5</sup>

We have reinvestigated the fluorescence excitation spectroscopy of the "isolated" bare molecules generated from supersonic expansions in the relatively wide range 283.7-296.7 nm. On the basis of the symmetry assignments of the electronic vibrational modes of the crystal spectra<sup>8</sup> and of our *ab initio* studies, we could assign the vibrational modes in the excited S<sub>1</sub> state.

Our high resolution spectroscopic and *ab initio* studies shed light on the ground and excited state energetics and structures.

### Experimental



**Figure 1.** Fluorescence excitation spectrum of fluorene in helium at  $T_0=100^\circ\text{C}$ , where  $T_0$  is the temperature of the fluorene sample in the nozzle.

A Newport pulsed nozzle whose slit is 0.5 mm was used for measuring the fluorescence excitation spectra. Pressures of about  $10^{-4}$  torr were achieved at stagnation pressures of about 1.0 atm of He. A gaseous mixture of He seeded with FR heated in the nozzle chamber to  $100^\circ\text{C}$  was expanded through the nozzle. A Lambda Physik EMG MSC 104 + FL 3002 excimer-pumped dye laser (R6G) was used as an excitation source. The spectral resolution of the laser beam after doubling is  $0.4\text{ cm}^{-1}$ . The laser pulse was synchronized with the electronic pulse to drive the nozzle. The laser beam crossed the supersonic free jet 15 mm downstream from the nozzle. The total fluorescence collected through a lens was detected with a Hamamatsu H 3177 photomultiplier.

Standard *ab initio* calculations on the vibrational modes and their energetics were carried out with a Gaussian 92 Package and Crayc 90-YMP at SERI. The Hartree-Fock calculations were performed by using the 3-21G basis sets.<sup>9,10</sup>

### Results and Discussion

The fluorescence excitation spectrum of the jet-cooled FR

molecule seeded in He is shown in Figure 1. As seen in Figure 1, internal cooling of the vibrational degrees of freedom is effectively accomplished at a He pressure of 1.0 atm. Highly resolved electronic and vibrational bands were observed with reasonable intensities.

As seen in Figure 1, the lowest energy spectral features of the isolated bare FR molecules cooled adiabatically was observed at 33,791 cm<sup>-1</sup> with dominating intensity. The spectral feature is assigned to the electronic origin of the lowest spin-allowed S<sub>0</sub>→S<sub>1</sub> transition. Our quantum mechanical calculation indicates that the electronic transition is assigned to a <sup>1</sup>A<sub>1</sub>→<sup>1</sup>B<sub>2</sub> transition in the C<sub>2v</sub> symmetry, with the electronic transition dipole moment being polarized along the long-axis (y-axis). This theoretical interpretation on the electric polarization of the transition dipole is quite consistent with the previous assignment.<sup>5</sup>

The value of 33,791 cm<sup>-1</sup> is quite close to the reported values<sup>2,5</sup> of 33,777 and 33,784 cm<sup>-1</sup> of the adiabatically cooled FR molecules generated from the supersonic expansions, and to a value of 33,783 cm<sup>-1</sup> for the 0<sub>0</sub><sup>0</sup> band determined from a resonant two photon ionization of FR in supersonic jets.<sup>11,12</sup>

The FR molecule involves 63 fundamentals having the various symmetries of 22A<sub>1</sub>+10A<sub>2</sub>+11B<sub>1</sub>+20B<sub>2</sub>. The electronic vibrational assignments can not be obtained only from our fluorescence excitation spectrum. The assignments of the main bands above the 0<sub>0</sub><sup>0</sup> are based on our *ab initio* calculations and the well-characterized electronic and vibrational modes of FR determined from the absorption and fluorescence spectra which were measured at 15 K of a FR molecular crystal and the molecules in an *n*-heptane matrix.<sup>8</sup> The vibrational intervals shown in Figure 1 corresponding to the fundamentals are close to those observed in the infrared and Raman spectra,<sup>13</sup> and excellently agree with the absorption and fluorescence spectra in *n*-heptane matrix at ~15 K.<sup>8</sup>

A quantum mechanical calculation using the HF/3-21G method is performed to assign the vibrational intervals above the 0<sub>0</sub><sup>0</sup> band. Our computed unscaled frequencies are larger by 13.8% than the experimental frequencies. It should be noted that mean absolute deviations of theoretical frequencies from the corresponding experimental frequencies are 12.8% for the HF/3-21G,<sup>10</sup> thus very often a scaling factor is uniformly applied to the computed vibrational frequencies.<sup>14-16</sup> A uniform scaling factor 0.89 is applied to our theoretical frequencies derived by the HF/3-21G method to achieve better agreement with the experimental frequencies. The corrected theoretical frequencies listed in Table 1 are in excellent agreement with the experimental spectrum.

It is also found in our laboratory that the similar scaling factor such as 0.87 is also an appropriate value applied to the other molecular system such as a cross conjugated polyene molecule.<sup>17</sup> The discrepancies between theoretical and experimental frequencies arise from the neglect of anharmonicity and the insufficiency of the theoretical methods.<sup>14</sup> The extent of the overestimation of the experimental anharmonic frequencies depends on the chosen 1-particle basis set and to which extent electron correlation effect is included. The inclusion of the electron correlation effects using 2nd order Moller-Plesset perturbation theory reduces the discrepancy to 5-6% at MP2/6-31G\* and MP2/6-311G\*\*.<sup>14</sup>

Most of the fundamentals identified in the supersonic jets

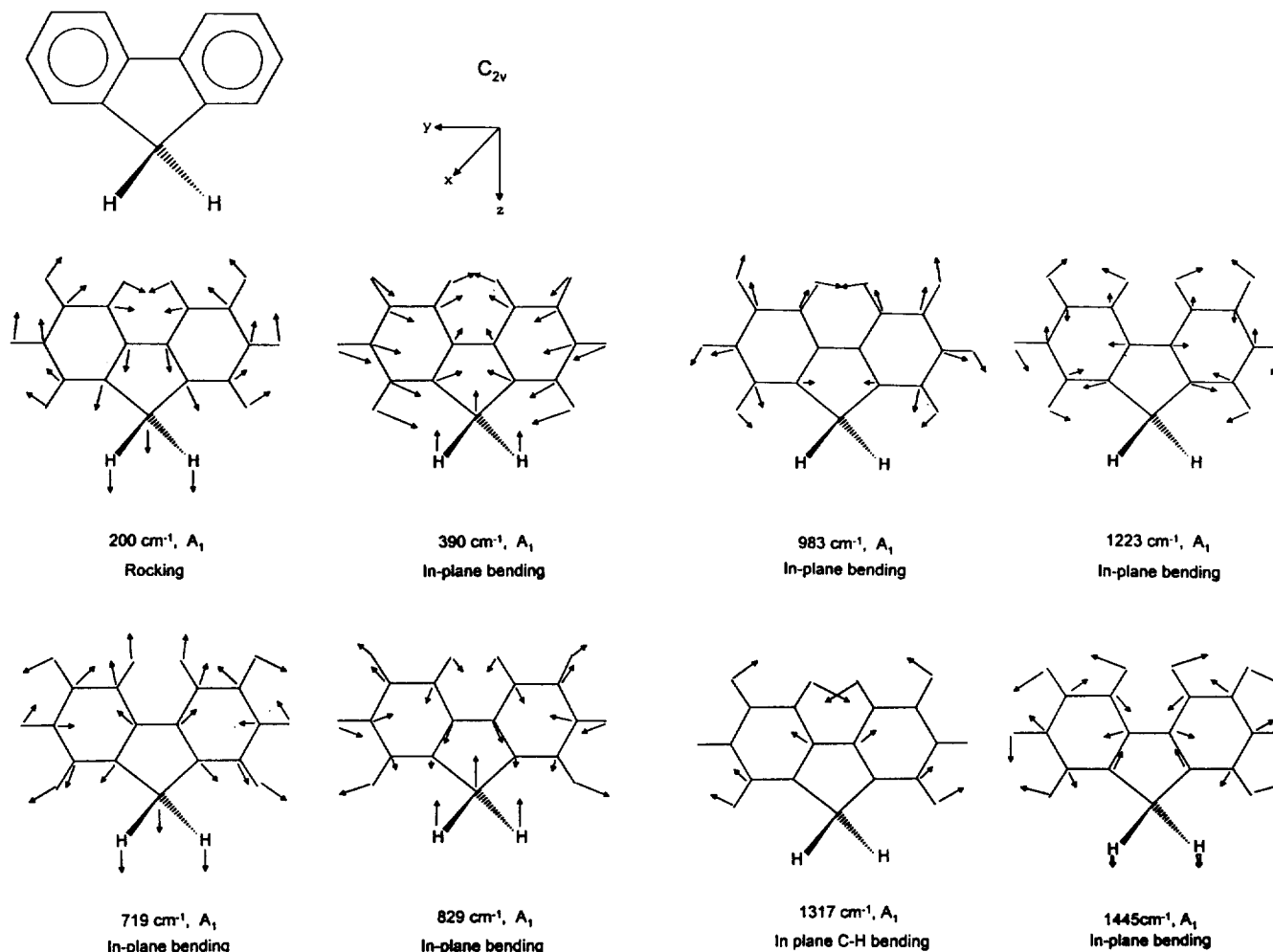
**Table 1.** Vibrational assignments of the S<sub>1</sub> state of the isolated cooled fluorene molecule. Electronic origin ν<sub>00</sub>=33,791 cm<sup>-1</sup>

| Δν=ν-ν <sub>00</sub><br>(cm <sup>-1</sup> ) | <i>Ab Initio</i><br>Calcd. | Rel. int. <sup>a</sup> | Assignment              |
|---------------------------------------------|----------------------------|------------------------|-------------------------|
| 0                                           |                            | vs                     | electronic origin       |
| 150                                         |                            | w                      |                         |
| 200                                         | 207                        | vs                     | a <sub>1</sub>          |
| 390                                         | 400                        | m                      | a <sub>1</sub>          |
| 401                                         |                            | m                      | 200×2+1                 |
| 534                                         |                            | w                      |                         |
| 585                                         |                            | m                      | b <sub>2</sub>          |
| 591                                         |                            | m                      | 200+390+1               |
| 608                                         |                            | vw                     | 200×3+8                 |
| 719                                         | 729                        | vs                     | a <sub>1</sub>          |
| 799                                         |                            | w                      |                         |
| 829                                         | 823                        | s                      | a <sub>1</sub>          |
| 861                                         |                            | w                      |                         |
| 907                                         |                            | vw                     |                         |
| 926                                         |                            | s                      | 200+719+7               |
| 983                                         | 996                        | vs                     | a <sub>1</sub>          |
| 987                                         |                            | m                      |                         |
| 1008                                        |                            | w                      |                         |
| 1031                                        |                            | m                      | 200+829+2               |
| 1110                                        |                            | m                      | 390+719+1               |
| 1147                                        |                            | m                      |                         |
| 1182                                        |                            | m                      | 200+983-1               |
| 1215                                        |                            | m                      |                         |
| 1223                                        | 1265                       | vs                     | a <sub>1</sub>          |
| 1317                                        | 1287                       | vs                     | a <sub>1</sub>          |
| 1374                                        |                            | w                      | 390+983+1               |
| 1417                                        |                            | s                      |                         |
| 1429                                        |                            | m                      | 200+1223+6              |
| 1445                                        | 1461                       | vs                     | 719×2+7, a <sub>1</sub> |
| 1517                                        |                            | m                      | 200+1317                |
| 1566                                        |                            | m                      |                         |

<sup>a</sup> Experimental intensities.

were assigned to A<sub>1</sub> symmetry. It is noted that the calculated fundamental vibrational frequencies having only the A<sub>1</sub> symmetries determined in the crystal spectra are listed in Table 1. Further assignments of the other vibrational frequencies listed in Table 1 necessitate more experimental and theoretical analyses of the spectrum of FR. Actually our calculation predicts only the vibrational frequencies in the electronically ground-state of the molecule. The good agreement between the calculated vibrational bands in the fundamental state, and the vibrational intervals above the 0-0 band in the electronically excited S<sub>1</sub> state indicates that the effective force constants and masses in the normal coordinates of FR in the excited S<sub>1</sub> state may be close to those in the electronically ground-state S<sub>0</sub>. It should be noted that the vibrational frequencies of the electronically ground-state are correctly determined by measuring dispersed fluorescence spectra rather than the excitation spectra. The fundamental vibrational modes with the a<sub>1</sub> symmetries are shown in Figure 2.

The electronic origins in FR in both crystal and the *n*-



**Figure 2.** Calculated vibrational modes with the  $a_1$  symmetries. The vibrational frequencies described in the figures are the experimental values corresponding to the theoretical frequencies.

heptane matrix, 33,039 and 33,174  $\text{cm}^{-1}$ ,<sup>8</sup> respectively are fairly lower in energy than those measured in the supersonic free jet systems. The red spectral shift arises from the dominating behaviors of dispersive interactions.<sup>18</sup> As seen in Table 1, we have observed various fundamental, overtone and combination bands. Such overtones and combination bands above the electronic band origin are also exhibited in the resonant multiphoton ionization spectra of FR.<sup>11,12</sup> These spectral features observed in the excited state are contrasted with those observed in the fundamental state. Such overtones and combination bands are not observed in the infrared<sup>13,19</sup> and Raman spectra of FR.<sup>13,19,20</sup>

Finally, we wish to estimate the vibrational frequencies in the  $^1B_2$  state by a higher level calculation and to measure the frequencies in the  $^1A_1$  state by dispersed fluorescence spectroscopy.

**Acknowledgment.** The present studies were supported in part by the Basic Science Research Institute Program, Ministry of Education, 1994-1995 Project No. BSRI-94-3432. BHB is grateful to Korea Atomic Energy Research Institute and Center for Molecular Science for partial financial support.

## References

1. Levy, D. H. *Ann. Rev. Phys. Chem.* **1980**, *31*, 197.
2. Saigusa, H.; Itoh, M. *J. Phys. Chem.* **1985**, *89*, 5486.
3. Chung, Y. B.; Jang, D.-J.; Kim, D.; Lee, M.; Kim, H. S.; Boo, B. H. *Chem. Phys. Lett.* **1991**, *176*, 453.
4. Lee, M.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1988**, *153*, 1.
5. Amirav, A.; Even, U.; Jortner, J. *J. Chem. Phys.* **1982**, *67*, 1.
6. Kim, Y. R.; Share, P.; Pereira, M.; Sarisky, M.; Hochstrasser, R. M. *J. Chem. Phys.* **1989**, *91*, 7557.
7. Labhart, H.; Pantke, E. R.; Seibold, K. *Helv. Chim. Acta* **1972**, *55*, 658.
8. Bree, A.; Zwarich, R. *J. Chem. Phys.* **1969**, *51*, 903.
9. Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.
10. Hehre, W. J.; Radom, L.; Schleyer, R. V. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.
11. Amirav, A.; Even, U.; Jortner, J. *J. Chem. Phys.* **1981**, *75*, 3151.

12. Leutwyler, S.; Even, U.; Jortner, J. *J. Chem. Phys.* **1983**, 79, 5769.
13. Bree, A.; Zwarich, R. *J. Chem. Phys.* **1969**, 51, 912.
14. Pacansky, J.; Koch, W.; Miller, M. D. *J. Am. Chem. Soc.* **1991**, 113, 317.
15. Pople, J. A.; Krishnan, R.; Schlegel, H. B.; DeFrees, D.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. F.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem. Symp.* **1981**, 15, 269.
16. Foresman, J. B. *Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian*; Gaussian: Pittsburgh, 1993.
17. Boo, B. H.; Seo, H. Y.; Kang, S. K.; Hong, D. S.; Nak, H.-K. to be submitted for publication.
18. Longuet-Higgins, H. C.; Pople, J. A. *J. Chem. Phys.* **1957**, 27, 192.
19. Infrared and Raman spectra of **FR** were also measured in our laboratory. The spectral assignments are under way.
20. Decker, C. *Chim. Acta* **1979**, 35A, 1303.

## Chiral Recognition Models for the Liquid Chromatographic Resolution of Enantiomers on (S)-Naproxen-Derived Chiral Stationary Phase Bearing Both $\pi$ -Acidic and -Basic Sites

Myung Ho Hyun\*, Jong Sung Jin, Myoung Seon Na, and Kyung Kyu Jyung†

*Department of Chemistry, Pusan National University, Pusan 609-735, Korea*

*†Department of Chemistry Education, Pusan National University, Pusan 609-735, Korea*

*Received January 11, 1995*

As an effort to elucidate the chiral recognition mechanisms exerted by the (S)-naproxen-derived CSP bearing both  $\pi$ -acidic and  $\pi$ -basic sites, a homologues series of  $\pi$ -basic N-acyl- $\alpha$ -(1-naphthyl)alkylamines and  $\pi$ -acidic N-(3,5-dinitrobenzoyl)- $\alpha$ -amino esters were prepared and resolved. Based on the chromatographic resolution trends of the homologues series of analytes on the (S)-naproxen-derived chiral stationary phase, we proposed chiral recognition mechanisms which demonstrate that the intercalation of the substituent in the analyte molecule between the strands of bonded phase does significantly influence the enantioselectivity for resolving N-acyl- $\alpha$ -(1-naphthyl)alkylamines but the intercalation process is not involved in resolving N-(3,5-dinitrobenzoyl)- $\alpha$ -amino esters.

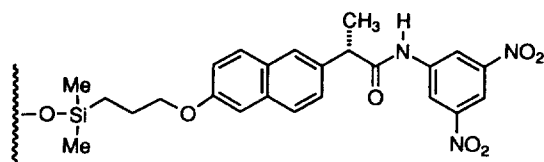
### Introduction

Liquid chromatographic resolution of enantiomers on chiral stationary phases (CSPs) has been known to be a very convenient and accurate technique in solving the problems related to stereochemistry including the determination of optical purity of chiral drugs.<sup>1</sup> Therefore, there have been significant efforts of developing new CSPs for the liquid chromatographic resolution of enantiomers. For example, various CSPs named Pirkle-type have been developed and successfully employed in determining the optical purity of chiral compounds.<sup>2</sup> Pirkle-type CSPs are known to resolve racemates by forming energetically different two transient diastereomeric  $\pi$ - $\pi$  complexes with two enantiomers.<sup>3</sup> In order to utilize the effective formation of  $\pi$ - $\pi$  complexes with two enantiomers, Pirkle-type CSPs have been usually designed to contain a  $\pi$ -acidic or  $\pi$ -basic aryl functional group and utilized in resolving  $\pi$ -basic or  $\pi$ -acidic racemates.<sup>4</sup> In relation to these, CSPs bearing both  $\pi$ -acidic and  $\pi$ -basic aryl functional group are quite interesting in that they can be used for resolving both  $\pi$ -basic and  $\pi$ -acidic racemates. However, up to date, a few CSPs containing both  $\pi$ -acidic and  $\pi$ -basic aryl functional groups have been reported.<sup>5</sup>

Recently, we reported the preparation of CSP **1** starting

from (S)-naproxen.<sup>6</sup> CSP **1** which actually contains both  $\pi$ -basic and  $\pi$ -acidic aryl functional group has been successfully applied for resolving either  $\pi$ -acidic or  $\pi$ -basic racemates. However, the chiral recognition mechanism expected to be exerted by CSP **1** for resolving  $\pi$ -acidic or  $\pi$ -basic racemates have not been systematically studied yet. In the previous study, we only presumed that the 6-alkoxy-2-naphthyl group of CSP **1** acts as a  $\pi$ -basic interaction site for resolving  $\pi$ -acidic racemates while the 3,5-dinitrophenyl group of the CSP plays a role as a  $\pi$ -acidic interaction site for resolving  $\pi$ -basic racemates.<sup>6</sup>

In this study, we wish to propose chiral recognition models which can be applied for explaining the resolution behaviors of  $\pi$ -basic N-acyl- $\alpha$ -arylalkylamines and  $\pi$ -acidic N-(3,5-dinitrobenzoyl)- $\alpha$ -amino esters based on the chiral recognition trends for resolving a homologous series of  $\pi$ -acidic and  $\pi$ -basic racemates on CSP **1**.



CSP **1**