

ROTATIONAL SPECTRA OF SMALL PAHS: ACENAPHTHENE, ACENAPHTHYLENE, AZULENE, AND FLUORENE

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ABSTRACT

Pure rotational spectra of four small polycyclic aromatic hydrocarbons have been observed by Fourier transform microwave spectroscopy of a molecular beam in the frequency range from 7 to 37 GHz. Initial searches for acenaphthene ($C_{12}H_{10}$), acenaphthylene ($C_{12}H_8$), and fluorene ($C_{13}H_{10}$) were guided by quantum chemical calculations performed at the B3LYP/cc-pVTZ level of theory. All three molecules exhibit *b*-type rotational spectra and are calculated to be moderately polar, with dipole moments of 0.3–0.9 D. Close agreement (to better than 1%) between the calculated equilibrium and experimentally derived ground-state rotational constants is achieved. Selected transitions of acenaphthene and fluorene have also been measured in the 3 mm region by conventional free-space absorption spectroscopy, as have transitions of the previously studied azulene ($C_{10}H_8$). The data presented here facilitate deep radio astronomical searches with large radio telescopes.

Subject headings: astrochemistry — ISM: molecules — molecular data

Online material: machine-readable tables

1. INTRODUCTION

The mid-infrared spectra from 3 to 20 μm of many astronomical objects are dominated by emission features usually referred to as the unidentified infrared bands (UIRs). Owing to reasonable agreement between some of the UIRs and their vibrational spectra, polycyclic aromatic hydrocarbons (PAHs) are widely believed to be responsible molecular carriers (e.g., Leger & Puget 1984; Allamandola et al. 1985). The problem with this PAH hypothesis is, however, that no individual PAH has been identified in space to date to yield conclusive evidence, despite all observational and laboratory investments (Peeters et al. 2004b; Salama 1999; Oomens et al. 2003; Tielens & Peeters 2004). Here, high-resolution microwave spectroscopy might play a crucial role in future astronomical investigations.

While PAHs are generally nonpolar or only weakly polar molecules, some have sufficiently large dipole moments for rotational spectroscopy, but only a few have been studied. The rotational spectrum of azulene ($C_{10}H_8$), a structural isomer of nonpolar naphthalene, has been observed in the microwave range (Tobler et al. 1965; Huber et al. 2005). Very recently, Lovas et al. (2005) reported the Fourier transform microwave spectrum of corannulene ($C_{20}H_{10}$), a nonplanar, bowl-shaped PAH. The combination of a fairly large dipole moment (2.1 D) and high molecular rigidity, causing all *K*-components of a given rotational transition to collapse to a single line, leads to a comparably strong rotational spectrum and makes this molecule a plausible target for astronomical searches with large radio telescopes.

In the following, a combined theoretical and experimental rotational spectroscopic investigation of selected simple PAHs C_nH_m with $n \leq 13$ is presented (Fig. 1). The rotational spectra of acenaphthene ($C_{12}H_{10}$; molecule 1 in Fig. 1), acenaphthylene

($C_{12}H_8$; molecule 2), and fluorene ($C_{13}H_{10}$; molecule 3) have been obtained for the first time employing Fourier transform microwave (FTM) spectroscopy. Centimeter-wave transitions of azulene (molecule 4) were also measured, complementing the data reported previously by Huber et al. (2005 and references therein). Selected transitions of acenaphthene, fluorene, and azulene have also been observed at a wavelength of 3 mm, employing free-space millimeter-wave absorption spectroscopy.

2. EXPERIMENT AND QUANTUM CHEMICAL CALCULATIONS

The FTM spectrometer used in the present investigation operates between 5 and 43 GHz and has been described in detail elsewhere (McCarthy et al. 1997, 2000). All samples were purchased commercially (Sigma-Aldrich) and used without further purification (Acenaphthene 99%, Acenaphthylene 75%, Fluorene 98%, and Azulene 99%). Since they are all solids at room temperature, experiments were carried out using a heated nozzle recently developed for measurements of compounds of low volatility (Thorwirth et al. 2005). The nozzle was operated at temperatures from 100°C to 130°C, with neon as the buffer gas.

In the millimeter-wave region, selected transitions of azulene, acenaphthene, and fluorene were measured in a free-space glass cell (1.5 m long and 7 cm in diameter) with a spectrometer described elsewhere (Gottlieb et al. 2003). Measurements of azulene were done at room temperature, those of acenaphthene and fluorene at room temperature and slightly above (to 50°C). The effect of heating was found to be small.

Initial searches for rotational transitions were based on quantum chemical calculations of rotational constants and dipole moments performed with the standard program package GAUSSIAN03 (Frisch et al. 2003) using the density functional theory (DFT) variant B3LYP (Becke 1993) and the correlation-consistent polarized valence basis set cc-pVTZ (Dunning 1989).

3. RESULTS

Fitting of experimental data was done with the SPFIT program (Pickett 1991), a Watson Hamiltonian in the *A* reduction, and either the *I'* (azulene, fluorene) or *III'* (acenaphthene,

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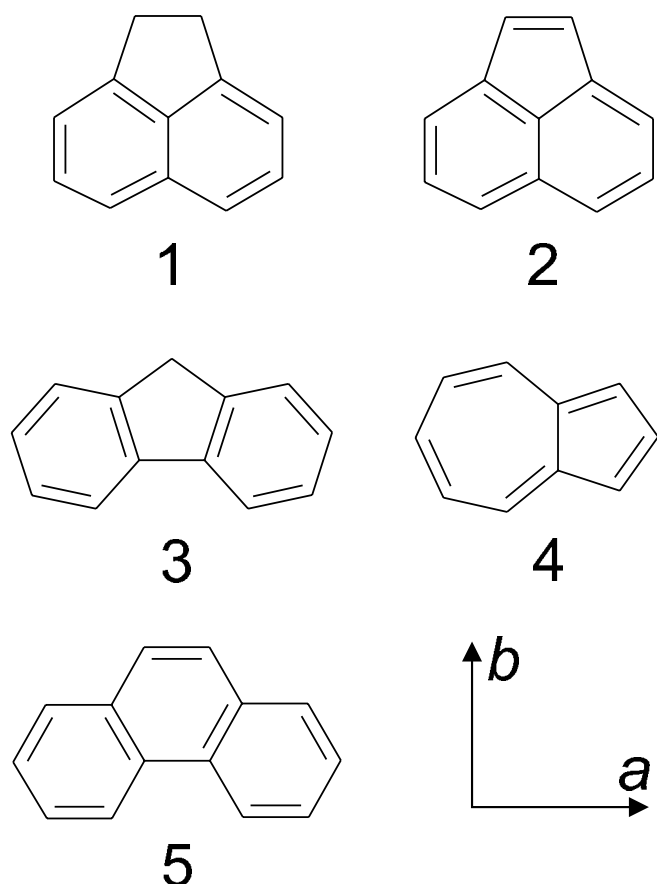


FIG. 1.— PAHs investigated here: acenaphthene (“1”), acenaphthylene (“2”), fluorene (“3”), azulene (“4”), and phenanthrene (“5”). All molecules are of C_{2v} symmetry. Except for azulene, whose dipole moment is oriented along the a -axis, all other molecules exhibit b -type rotational spectra.

acenaphthylene) reduction. The estimated experimental uncertainties (1σ) are 2–5 kHz in the microwave band and 20–40 kHz in the millimeter-wave band.

3.1. Azulene

Azulene (Fig. 1, molecule 4) is a somewhat prolate asymmetric top⁵ ($\kappa = -0.61$) with an a -type rotational spectrum. In the present study, azulene was used as a test molecule to check the feasibility of observing rotational spectra of PAHs. Transitions were found already at moderate temperatures of the heated nozzle of about 80°C based on predictions from the parameter set given in Huber et al. (2005). Forty one centimeter-wave lines were then newly measured at a temperature of 100°C between 5.8 and 23 GHz, with angular momentum quantum numbers $3 \leq J \leq 12$ and $0 \leq K_a \leq 6$. Based on predictions from the resulting improved set of molecular parameters, rotational transitions were also measured in the millimeter-wave band. A sample spectrum of azulene at 91.9 GHz is shown in Figure 2. Table 1 gives 45 lines, measured from 91.4 to 94.9 GHz (paired transitions counted once) in the millimeter-wave range, together with the new centimeter-wave data. The derived rotational constants obtained from a fit to the centimeter-wave data and from a global fit to all available data are shown in Table 2. As can be seen, the

⁵ Ray’s parameter is a measure to quantify the symmetric character of asymmetric top molecules and is defined as $\kappa = (2B - A - C)/(A - C)$. The limiting values of $\kappa = -1$ and $+1$ correspond to prolate and oblate symmetric top rotors, respectively.

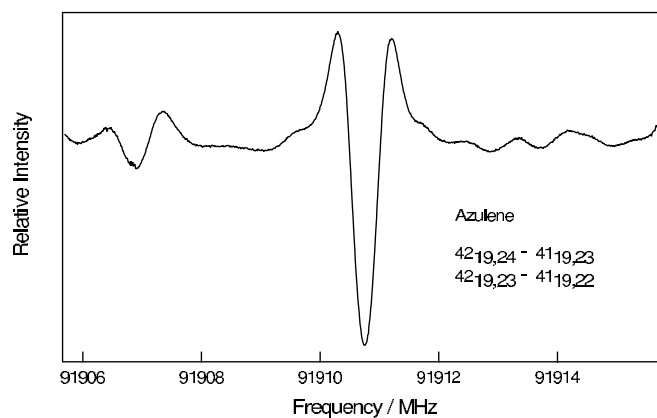


FIG. 2.— Sample spectrum of azulene at 91.9 GHz.

calculated equilibrium rotational constants are slightly larger, but well within 1% of the experimental ground-state rotational constants.

3.2. Acenaphthene

Acenaphthene (Fig. 1, molecule 1) is a somewhat oblate asymmetric top molecule ($\kappa_{\text{qcc}} = +0.4$) with a dipole moment of 0.90 D along the b -axis. Based on the rotational constants from the B3LYP/cc-pVTZ calculation (Table 4) a search for the $6_{0,6} - 5_{1,5}/6_{1,6} - 5_{0,5}$ doublet at 8.5 GHz was performed at a temperature of the heated nozzle of 105°C. This doublet was chosen because of the small but well-resolved predicted splitting of the lines (~ 140 kHz), yielding an easily recognized signature. The doublet was found to be located about 40 MHz lower in frequency than predicted (Fig. 3). In addition to the $J = 6-5$ doublet, the initial survey scan also showed two more lines that, because of both intensity and separation, were assigned to the $3_{3,0} - 2_{2,1}$ and $5_{1,4} - 4_{2,3}$ transitions at 8385 and 8417 MHz, respectively.

The better rotational constants which resulted from these assignments then allowed many more transitions to be found. In all, 144 transitions were measured in the centimeter-wave from 7.0 to 33.4 GHz, at quantum numbers $2 \leq J \leq 16$ and $0 \leq K_c \leq 16$ (Table 3), which yielded the full set of quartic centrifugal distortion constants. The corresponding fit is shown in Table 4, column (3). Based on this experimental parameter set, transitions of acenaphthene were also found in the millimeter-wave region between 92 and 96 GHz, and another 45 lines were then measured

TABLE 1
EXPERIMENTAL ROTATIONAL TRANSITION FREQUENCIES OF AZULENE

J'	K'_a	K'_c	J''	K''_a	K''_c	Frequency (MHz)	$o-c$ (MHz)	$\Delta\nu$ (MHz)
3	1	3	2	1	2	5764.5899	-0.0007	0.002
3	0	3	2	0	2	6139.8457	0.0002	0.002
3	1	2	2	1	1	6910.6951	0.0003	0.002
6	1	5	6	1	6	7588.9097	0.0008	0.002
4	1	4	3	1	3	7627.2339	-0.0003	0.002
9	1	9	8	1	8	16536.5967	-0.0014	0.002
9	0	9	8	0	8	16557.3955	-0.0009	0.002
8	6	3	7	6	2	17239.8496	0.0005	0.002
8	6	2	7	6	1	17240.0703	0.0003	0.002
8	5	4	7	5	3	17306.9571	0.0013	0.002
8	5	3	7	5	2	17315.4483	0.0017	0.002

NOTE.— Table 1 is published in its entirety in the electronic edition of the *Astrophysical Journal*. A portion is shown here for guidance regarding its form and content.

TABLE 2
 SPECTROSCOPIC CONSTANTS OF AZULENE

Constant	B3LYP/cc-pVTZ (MHz)	Experimental ^a (MHz)	Experimental ^b (MHz)
A	2867.9	2841.95182(22)	2841.95225(18)
B	1260.7	1254.843143(49)	1254.843096(23)
C	875.8	870.712741(44)	870.712786(20)
$\Delta_J \times 10^6$		22.55(23)	22.528(22)
$\Delta_{JK} \times 10^6$		37.0(14)	35.45(14)
$\Delta_K \times 10^3$		0.1974(60)	0.1893(31)
$\delta_J \times 10^6$		7.477(60)	7.5273(80)
$\delta_K \times 10^6$		74.7(12)	67.59(52)
$\Phi_{JK} \times 10^{12}$			-23.7(25)
Δ^c (amu \AA^2).....		-0.151	-0.151
Weighted rms ^d		0.74	0.71

^a Centimeter-wave data only.

^b Centimeter-wave and millimeter-wave data.

^c Inertial defect, $\Delta = I_c - I_b - I_a$.

^d This measure is dimensionless.

(Table 3; asymmetry doublets counted once). A global fit taking all data into consideration is shown in Table 4, column (4); there is considerable improvement over the fit derived from the centimeter-wave data alone.

3.3. Acenaphthylene

The molecular structures of acenaphthylene and acenaphthene are very similar, differing only in the central double bond in the five-membered ring that replaces the single bond in the latter molecule (Fig. 1). Like acenaphthene, acenaphthylene is calculated at the B3LYP/cc-pVTZ level of theory to be a somewhat oblate asymmetric top ($\kappa = +0.3$). The b -type dipole moment is calculated to be smaller, about one-third that of acenaphthene, or 0.31 D. Owing to the structural similarity, the theoretical rotational constants of acenaphthylene were empirically corrected for vibration-rotation interaction (Table 5), employing correction factors derived from a comparison between the theoretical and experimental rotational constants of acenaphthene (Table 4). This yielded improved frequency predictions, and the $6_{0,6}-5_{1,5}/6_{1,6}-5_{0,5}$ pair of transitions was readily found at a temperature of 100°C. For acenaphthylene, a total of 50 transitions with $3 \leq J \leq 15$ and $0 \leq K_c \leq 15$ in the frequency range from 7.4 to 26.7 GHz were observed (paired transitions counted only once; see Table 6). The experimentally determined molecular parameters are collected in Table 5. Four out of five quartic centrifugal distortion constants (Δ_J , Δ_{JK} , Δ_K , and δ_J) were needed to reproduce the experimental data to within the estimated uncertainties. In addition, Table 5 gives the result of an alternative fit, in which δ_K

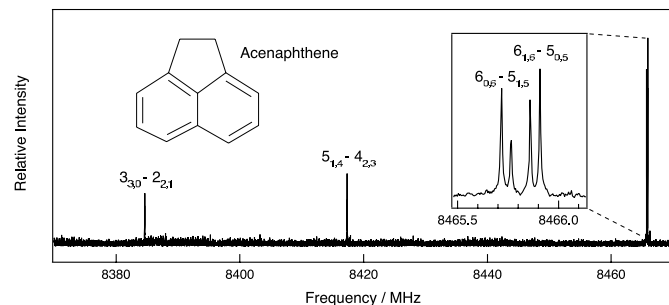


FIG. 3.—Rotational spectrum of acenaphthene at 8.4 GHz. The Doppler doubling of each line is clearly apparent in the insert on the right-hand side.

 TABLE 3
 SELECTED EXPERIMENTAL ROTATIONAL TRANSITION FREQUENCIES
 OF ACENAPHTHENE

J'	K'_a	K'_c	J''	K''_a	K''_c	Frequency (MHz)	$o-c$ (MHz)	$\Delta\nu$ (MHz)
4	1	3	3	2	2	6994.5354	0.0004	0.002
5	0	5	4	1	4	7161.2532	0.0007	0.002
5	1	5	4	0	4	7162.4805	0.0003	0.002
4	2	3	3	1	2	7297.9449	-0.0027	0.003
3	3	1	2	2	0	7788.5647	0.0008	0.002
3	3	0	2	2	1	8384.6040	0.0022	0.005
5	1	4	4	2	3	8417.3565	-0.0012	0.002
6	0	6	5	1	5	8465.7402	-0.0002	0.002
6	1	6	5	0	5	8465.8838	-0.0005	0.002
5	2	4	4	1	3	8483.6455	-0.0022	0.002

NOTE.—Table 3 is published in its entirety in the electronic edition of the *Astrophysical Journal*. A portion is shown here for guidance regarding its form and content.

has been adopted from acenaphthene (Table 4) and was kept fixed (see also § 4).

3.4. Fluorene

Fluorene (Fig. 1, molecule 3) is a prolate asymmetric top molecule ($\kappa_{\text{qcc}} = -0.86$) with a calculated b -type dipole moment of 0.53 D. Based on predictions from the ab initio rotational constants (Table 7) a search for the $3_{3,1}-2_{2,0}/3_{3,0}-2_{2,1}$ pair of transitions was carried out at 11.5 GHz at a temperature of the heated nozzle of 125°C. The lines were found to be located at 11,403 and 11,410 MHz, respectively (see Fig. 4). Shortly thereafter, another confirming pair of transitions was found, the $4_{4,1}-3_{3,0}/4_{4,0}-3_{3,1}$ doublet at 15,759 MHz. In total, 82 lines from 8.3 to 37.5 GHz with $2 \leq J \leq 18$ and $0 \leq K_a \leq 9$ were measured (Table 8; paired transitions only counted once). From a fit to these centimeter-wave data (Table 7, col. [3]) transitions were predicted at a wavelength of 3 mm.

A sample spectrum of fluorene showing the paired $97_{2,95}-96_{3,94}/97_{3,95}-96_{2,94}$ transitions at 92.2 GHz is shown in Figure 5. Some 20 lines of fluorene were measured at 3 mm and added to the centimeter-wave data to perform a global fit. In the final fit, some lines with residuals $o - c$ larger than 3σ were omitted. The

 TABLE 4
 SPECTROSCOPIC CONSTANTS OF ACENAPHTHENE

Constant (1)	B3LYP/cc-pVTZ (MHz) (2)	Experimental ^a (MHz) (3)	Experimental ^b (MHz) (4)
A	1416.5	1410.278969(61)	1410.278918(26)
B	1200.6	1193.865928(72)	1193.865936(36)
C	655.0	652.052760(42)	652.052803(17)
$\Delta_J \times 10^6$		30.10(28)	30.01(10)
$\Delta_{JK} \times 10^6$		-48.6(10)	-48.29(52)
$\Delta_K \times 10^6$		21.24(83)	21.23(42)
$\delta_J \times 10^6$		-3.33(13)	-3.234(46)
$\delta_K \times 10^6$		4.3(20)	4.51(91)
Δ^c (amu \AA^2).....		-6.608	-6.609
μ_b (D).....	0.90		
Weighted rms ^d		0.50	0.51

^a Centimeter-wave data only.

^b Combined fit of centimeter- and millimeter-wave data.

^c Inertial defect, $\Delta = I_c - I_b - I_a$.

^d This measure is dimensionless.

TABLE 5
 SPECTROSCOPIC CONSTANTS OF ACENAPHTHYLENE

Constant (1)	B3LYP/cc-pVTZ (MHz) (2)	Scaled Constants ^a (MHz) (3)	Experimental ^b (MHz) (4)	Experimental ^c (MHz) (5)
<i>A</i>	1520.7	1514.0	1511.82609(12)	1511.82605(12)
<i>B</i>	1228.2	1221.3	1220.63105(29)	1220.63108(29)
<i>C</i>	679.4	676.3	675.529854(65)	675.529851(65)
$\Delta_J \times 10^6$			31.4(26)	31.4(26)
$\Delta_{JK} \times 10^6$			-49.2(68)	-50.9(68)
$\Delta_K \times 10^6$			20.8(44)	22.5(44)
$\delta_J \times 10^6$			-5.4(14)	-5.4(14)
$\delta_K \times 10^6$			0.0	4.5
Δ^d (amu Å ²)			-0.192	-0.192
μ_b (D)	0.31			
Weighted rms ^e			0.35	0.34

^a From acenaphthene; see text.

^b δ_K kept fixed at zero in the analysis.

^c δ_K constrained to value from acenaphthene (Table 4).

^d Inertial defect, $\Delta = I_c - I_b - I_a$.

^e This measure is dimensionless.

corresponding molecular parameters are given in column (4) of Table 7. As for acenaphthene (Fig. 1, molecule 1), no sextic centrifugal distortion terms were needed, but the improvement in the quartic terms (Table 7, col. [3] vs. [4]) is clearly apparent. It should be noted that a structurally very closely related compound, carbazole (C₁₂H₉N), has been investigated by FTM spectroscopy in the gas phase before (Suenram et al. 1988), where the central methylene group in fluorene is replaced by NH. As expected, the rotational constants of both molecules are similar.

3.5. Phenanthrene

Phenanthrene consists of three fused benzene rings (Fig. 1, molecule 5) and is the largest system investigated here theoretically (14 carbon atoms). It is calculated (B3LYP/cc-pVTZ) to be a prolate asymmetric top molecule ($A = 1627.1$ MHz, $B = 554.3$ MHz, and $C = 413.424$ MHz, $\kappa_{\text{qcc}} = -0.8$) with the dipole moment oriented along the main inertial *b*-axis. However, the dipole moment is calculated here to be very small, of order 0.03 D, and hence, the rotational spectrum is extremely weak. As

a consequence, phenanthrene is not a good candidate for radio astronomical searches and no attempt was made to record rotational transitions.

4. DISCUSSION

The PAHs azulene, acenaphthene, acenaphthylene, and fluorene have been characterized by Fourier transform microwave and free-space millimeter-wave absorption spectroscopy, the latter three for the first time. The initial spectroscopic search was guided by DFT calculations at the B3LYP/cc-pVTZ level of theory and the experimental (ground-state) rotational constants are found to be very close to the theoretical (equilibrium) constants. A corresponding calculation for azulene (Table 2), for which the rotational constants had already been known prior to the present work, finds that the experimental ground-state rotational constants are somewhat smaller than the calculated equilibrium values and agree to each other within 1%. As can be seen from Tables 4, 5, and 7, this

 TABLE 6
 SELECTED EXPERIMENTAL ROTATIONAL TRANSITION FREQUENCIES
 OF ACENAPHTHYLENE

<i>J'</i>	<i>K'_a</i>	<i>K'_c</i>	<i>J''</i>	<i>K''_a</i>	<i>K''_c</i>	Frequency (MHz)	<i>o-c</i> (MHz)	$\Delta\nu$ (MHz)
5	0	5	4	1	4	7429.4251	-0.0004	0.002
5	1	5	4	0	4	7432.8877	-0.0002	0.002
6	0	6	5	1	5	8781.6787	0.0000	0.002
6	1	6	5	0	5	8782.1948	0.0002	0.002
6	1	5	5	2	4	10122.8550	-0.0001	0.002
7	0	7	6	1	6	10132.8218	-0.0002	0.002
7	1	7	6	0	6	10132.8936	-0.0007	0.002
6	2	5	5	1	4	10153.7192	0.0006	0.002
5	3	3	4	2	2	10803.7618	0.0023	0.003
6	2	4	5	3	3	11248.6905	0.0012	0.002

NOTE.—Table 6 is published in its entirety in the electronic edition of the *Astrophysical Journal*. A portion is shown here for guidance regarding its form and content.

 TABLE 7
 SPECTROSCOPIC CONSTANTS OF FLUORENE

Constant (1)	B3LYP/cc-pVTZ (MHz) (2)	Experimental ^a (MHz) (3)	Experimental ^b (MHz) (4)
<i>A</i>	2195.1	2176.210160(70)	2176.210153(70)
<i>B</i>	588.2	586.65338(12)	586.653414(70)
<i>C</i>	465.2	463.568993(63)	463.569028(20)
$\Delta_J \times 10^6$		4.61(33)	4.73(18)
$\Delta_{JK} \times 10^6$		-4.4(14)	-4.68(84)
$\Delta_K \times 10^6$		98.4(14)	98.4(11)
$\delta_J \times 10^6$		1.26(16)	1.243(88)
$\delta_K \times 10^6$		15.7(90)	17.5(31)
Δ^c (amu Å ²)		-3.498	-3.498
μ_b (D)	0.53		
Weighted rms ^d		0.38	0.66

^a Centimeter-wave data only.

^b Centimeter- and millimeter-wave data.

^c Inertial defect, $\Delta = I_c - I_b - I_a$.

^d This measure is dimensionless.

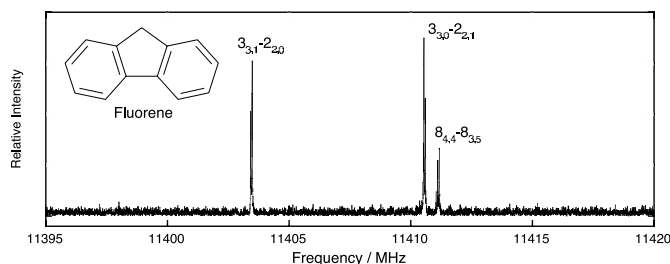


FIG. 4.—Rotational spectrum of fluorene at 11.4 GHz. In addition to the $3_{3,1}-2_{2,0}/3_{3,0}-2_{2,1}$ pair of transitions, the $8_{4,4}-8_{3,5}$ Q -branch ($\Delta J = 0$) transition is detected.

finding holds also for acenaphthene, acenaphthylene, and fluorene, respectively. An experimental value for the dipole moment had also only been obtained so far for azulene, $\mu_a = 0.8821(24)$ D (Huber et al. 2005). The corresponding B3LYP/cc-pVTZ value calculated here is 1.0 D, which is larger than the experimental value by 14%. A comparison B3LYP/cc-pVTZ versus experiment for several selected carbon-chain molecules has revealed agreement to within 10% (Thorwirth et al. 2004). Hence, the values obtained here theoretically for acenaphthene (0.90 D), acenaphthylene (0.31 D), and fluorene (0.53 D) are probably fairly good.

The full sets of quartic centrifugal distortion (CD) terms could be determined from the present data for acenaphthene and fluorene; for azulene, additionally, one sextic constant could be determined from the fit. For acenaphthylene, no millimeter-wave lines could be assigned with confidence. The purity of the sample purchased was 75% and as specified by the vendor (Sigma-Aldrich) some 20% of the 25% impurities were acenaphthene. While this gives a ratio of acenaphthylene/acenaphthene in the sample of ~ 4 , the ratio of the dipole moments squared is only 0.1. Consequently, assuming similar abundances of the two compounds in the gas phase, one expects the weak and dense millimeter-wave rotational spectrum of the “impurity” acenaphthene to be stronger by approximately a factor of 2.5, making detection and assignment of the millimeter-wave spectrum of acenaphthylene difficult. Owing to the lack of sufficient experimental data, only four out of five quartic centrifugal distortion constants could be determined in the case of acenaphthylene. Inspection of the CD terms of acenaphthene and acenaphthylene reveals that the values are very similar, which is hardly surprising given the close structural

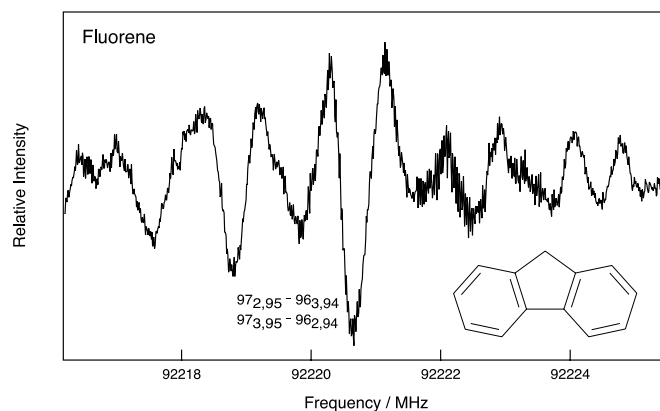


FIG. 5.—Sample spectrum of fluorene at 92 GHz. The central absorption feature is due to two collapsed rotational transitions, $97_{2,95}-96_{3,94}$ and $97_{3,95}-96_{2,94}$. The weaker transitions are thought to be vibrational satellites, i.e., pure rotational transitions from fluorene in vibrationally excited states.

similarity of the two molecules. Therefore, an alternative fit has been performed for acenaphthylene keeping δ_K fixed at the value previously determined for acenaphthene (Table 5, col. [5]). This approach is found to have little impact on the released distortion constants that change only within their uncertainties, but should enable a more reliable extrapolation of transition frequencies into the millimeter-wave regime.

It may be noted here briefly that spin statistics owing to the presence of pairs of equivalent hydrogen atoms are only of minor importance in the present work. For azulene with six hydrogen atoms in three equivalent pairs, the ortho : para spin-statistical weight ratio is 9 : 7, not entirely negligible in the rotational spectra. For four equivalent hydrogen pairs, as in acenaphthylene, the ortho : para ratio is 15 : 17 and can be taken as unity.

For a rigid planar molecule in its equilibrium configuration, the zero-point inertial defect $\Delta = I_c - I_b - I_a$ is zero, and for a nonplanar molecule it is negative. Because of zero-point vibration, however, inertial defects are often small and positive for many planar molecules (Gordy & Cook 1984). There are planar molecules, however, that show negative inertial defects, because they possess energetically low-lying out-of-plane (OOP) vibrational modes (e.g., Oka 1995). These considerations apply to two of the molecules investigated here, azulene and acenaphthylene, both of which show substantial negative inertial defects of $\Delta = -0.15$ and -0.19 amu \AA^2 , respectively. For azulene, the three lowest vibrational modes are OOP modes, two of which have vibrational frequencies below 200 cm^{-1} (see, e.g., Kozłowski et al. [1995] for a comparison of theoretical values at different levels of theory and experimental values). The situation for acenaphthylene is found to be rather similar; a calculation at the B3LYP/6-31G* level of theory indicates that the four lowest modes are OOP vibrations. In addition to the two b_1 modes given in Banisaukas et al. (2003) at 163 and 227 cm^{-1} , there are two vibrational modes of a_2 symmetry at 209 and 367 cm^{-1} (B3LYP/6-31G*; scaling factor 0.97). The contribution of the OOP (methylene) hydrogen atoms to the inertial defect in case of fluorene (one pair) and acenaphthene (two pairs) manifests itself in the much more pronounced negative inertial defect values of -3.5 and -6.6 amu \AA^2 , respectively.

The energetically low-lying vibrational modes of fluorene and acenaphthene are also the cause of the congested spectra observed in the millimeter-wave region (e.g., Fig. 5). At room temperature many vibrational states are significantly populated, each with its own rotational spectrum. No attempt has been made here

TABLE 8

SELECTED EXPERIMENTAL ROTATIONAL TRANSITION FREQUENCIES OF FLUORENE

J'	K'_a	K'_c	J''	K''_a	K''_c	Frequency (MHz)	$o-c$ (MHz)	$\Delta\nu$ (MHz)
8	1	8	7	0	7	8340.8286	-0.0013	0.002
9	0	9	8	1	8	8469.5835	-0.0014	0.002
9	1	9	8	0	8	9142.3521	-0.0001	0.002
10	0	10	9	1	9	9499.6836	-0.0002	0.002
5	2	4	4	1	3	9587.2783	-0.0016	0.003
10	1	10	9	0	9	9970.5103	0.0010	0.002
11	0	11	10	1	10	10501.2818	-0.0001	0.002
11	1	11	10	0	10	10823.5806	0.0009	0.002
7	2	6	6	1	5	11021.2842	-0.0021	0.002
3	3	1	2	2	0	11403.4639	0.0002	0.002
3	3	0	2	2	1	11410.5791	0.0004	0.002
8	4	4	8	3	5	11411.1514	0.0007	0.002

NOTE.—Table 8 is published in its entirety in the electronic edition of the *Astrophysical Journal*. A portion is shown here for guidance regarding its form and content.

to assign any of these vibrational satellites to a particular vibrational mode. In contrast, as can be seen from the survey spectra in Figures 3 and 4, the microwave regions look comparably clean, which may be attributed to efficient vibrational cooling taking place during adiabatic expansion of the molecular beam.

It has been shown recently that besides pure hydrocarbon PAHs, deuterated (PADs) and nitrogen-bearing variants (PANHs) may also be present in space (Peeters et al. 2004a; Hudgins et al. 2005). The PANHs are especially interesting spectroscopically, because they should exhibit strong rotational spectra, owing to the polarity of as much as several debye, introduced by the inclusion of nitrogen in the carbon skeleton of the molecule (e.g., Mattioda et al. 2003; Hudgins et al. 2005). While the microwave spectra of simple aromatic systems incorporating nitrogen such as pyridine (C_5H_5N ; Ye et al. 2005 and references therein), pyrimidine ($C_4H_4N_2$; Kisiel et al. 1999 and references therein), and quinoline/isoquinoline (C_9H_7N ; Kisiel et al. 2003) have been studied by microwave/millimeter-wave spectroscopy, only very little is known about larger systems. A millimeter-wave study of phenanthridine

($C_{13}H_9N$), a monoaza variant of phenanthrene, has very recently been reported by McNaughton et al. (2007).

With the data here, astronomical searches for acenaphthene, acenaphthylene, and fluorene are now possible with large radio telescopes. The transition frequencies have been determined to a few parts in 10^7 , corresponding to $\approx 150 \text{ m s}^{-1}$ and better in equivalent radial velocity up to wavelengths of 3 mm. Based on these data, reliable transition frequencies can be calculated from the centimeter- into the millimeter-wave regime to probe both the cold and warm molecular objects.

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