Rotational Spectroscopy of PAHs:
Acenaphthene, Acenaphthylene and Fluorene

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Abstract. Pure rotational spectra of three polycyclic aromatic hydrocarbons – acenaphthene,
acenaphthylene and fluorene – have been obtained by Fourier transform microwave spectroscopy
of a molecular beam and subsequently by millimeter wave absorption spectroscopy for acenaph-
thene and fluorene. The data presented here will be useful for deep radio astronomical searches
for PAHs employing large radio telescopes.

Keywords. astrochemistry, molecular data, ISM: molecules

Polycyclic aromatic hydrocarbons (PAHs) have been studied extensively in the labora-
tory over the last 20 years (see Salama (1999) and Tielens & Peeters (2004) for reviews)
owing to their astronomical significance as possible carriers of the unidentified infrared
bands (UIRs, e.g. Allamandola et al. 1989). These studies have been performed almost ex-
clusively in the uv-, optical-, and infrared regions of the electromagnetic spectrum. Very
little is known, however, about the rotational spectra of small and polar PAHs, since mi-
crowave studies have been reported so far only for azulene (C_{10}H_{8}, Huber et al. (2005)
and references therein) and corannulene (C_{20}H_{10}, Lovas et al. 2005).

In the present study, we have investigated the rotational spectra of selected small PAHs
(see Fig. 1) employing Fourier transform microwave (FTM) spectroscopy (Balle & Flygare
with a heated nozzle recently developed for studies of low volatile compounds (Thorwirth
et al. 2005). Initial searches were guided by rotational constants obtained from quantum

Figure 1. Molecular structures of acenaphthene (C_{12}H_{10}, 1), acenaphthylene (C_{12}H_{8}, 2) and
fluorene (C_{13}H_{10}, 3).

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chemical calculations performed at the B3LYP/cc-pVTZ level of theory (see Table 1) using the program package Gaussian03 (Frisch et al. 2003). All three molecules exhibit \( \beta \)-type rotational spectra and are calculated to be moderately polar, with dipole moments of order 0.3 to 0.9 D. Rotational transitions were found readily for all three molecules and based on improved predictions several tens of lines could be measured for each one. Rotational constants obtained from least-squares analyses of the experimental data are shown in Table 1. As can be seen, the calculated equilibrium values and experimentally obtained ground state rotational constants agree very well, to within 1%. Subsequently, selected rotational transitions of acenaphthene and fluorene could also be measured by standard millimeter wave absorption spectroscopy at 90 GHz.

The present investigation highlights the potential of FTM spectroscopy for the characterization of polar PAHs, including the nitrogen variants (PANHs; e.g., see the contribution by D. Hudgins, these proceedings).

A detailed account on the present study will be given elsewhere.

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