# HIGH-RESOLUTION FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY OF METHYL- AND DIMETHYLNAPTHALENES

ELIJAH G. SCHNITZLER, BRANDI L. M. ZENCHYZEN, AND WOLFGANG JÄGER Department of Chemistry, University of Alberta, Edmonton, Alberta, T6G 2G2, Canada; wolfgang.jaeger@ualberta.ca Received 2015 February 1; accepted 2015 March 30; published 2015 May 28

# ABSTRACT

High-resolution pure rotational spectra of four alkylnaphthalenes were measured in the range of 6-15 GHz using a molecular-beam Fourier-transform microwave spectrometer. Both *a*- and *b*-type transitions were observed for 1-methylnaphthalene (1-MN), 1,2-dimethylnaphthalene (1,2-DMN), and 1,3-dimethylnaphthalene (1,3-DMN); only *a*-type transitions were observed for 2-methylnaphthalene (2-MN). Geometry optimization and vibrational analysis calculations at the B3LYP/6-311++G(d,p) level of theory aided in the assignments of the spectra and the characterization of the structures. Differences between the experimental and predicted rotational constants are small, and they can be attributed in part to low-lying out-of-plane vibrations, which distort the alkylnaphthalenes out of their equilibrium geometries. Splittings of rotational lines due to methyl internal rotation were observed in the spectra of 2-MN, 1,2-DMN, and 1,3-DMN, and allowed for the determination of the barriers to methyl internal rotation, which are compared to values from density functional theory calculations. All four species are moderately polar, so they are candidate species for detection by radio astronomy, by targeting the transition frequencies reported here.

Key words: astrochemistry - ISM: molecules - molecular data

Supporting material: machine-readable tables

# 1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are abundant in regions of our solar system, such as the atmosphere of Titan (López-Puertas et al. 2013), and they may be ubiquitous throughout the interstellar medium (ISM; Siebenmorgen et al. 2014). PAHs are likely carriers of several spectral features of the ISM (Van der Zwet & Allamandola 1985; Vijh et al. 2004), including the unidentified infrared bands (UIRs) between 3 and 20  $\mu$ m, the range of stretching and bending vibrations of aromatic hydrocarbons (Tielens 2008; Kwok & Zhang 2013). Although the presence of PAHs can explain the UIRs, no specific PAHs have been identified since vibrational bands are broad and not unique to individual molecules; in contrast, pure rotational transitions are unambiguous, making high-resolution microwave spectroscopy a candidate method for the identification of specific PAHs in the ISM.

The rotational spectra of several small PAHs, including azulene, acenaphthene, acenaphthylene, and fluorine (Thorwirth et al. 2007), have previously been measured. The rotational spectrum of corannulene, a symmetrical PAH with a large dipole moment, due to its bowl-shaped structure, has also been observed (Lovas et al. 2005). However, many symmetrical, planar PAHs are nonpolar. Substitution in PAHs often results in non-zero dipole moments; for example, polycyclic aromatic nitrogen hetero-cycles (PANHs) have higher dipole moments than their parent PAHs, and the rotational spectra of several PANHs have been measured (McNaughton et al. 2008). Alkyl substitution for hydrogen can also lead to non-zero dipole moments. Furthermore, laboratory-generated carbon nanoparticles containing alkyl-substituted naphthalenes have been shown to have infrared emission features consistent with dust in the ISM (Duley & Hu 2012), so alkylnaphthalenes are candidate species for identification in the ISM. Although rotationally resolved electronic spectra for 1-methylnapthalene, 2-methylnaphthalene (Tan et al. 1991b), and 2.3dimethylnaphthalene (Tan et al. 1991a) have been reported in the past, no pure rotational spectra have previously been measured for alkylnaphthalenes.

In an effort to aid in the identification of specific PAHs in the ISM, we measured the rotational spectra of 1-methylnaphthalene (1-MN), 2-methylnaphthalene (2-MN), 1,2-dimethylnaphthalene (1,2-DMN), and 1,3-dimethylnaphthalene (1,3-DMN) in the range of 6–15 GHz using a molecular-beam Fourier-transform microwave (MB-FTMW) spectrometer. Assignments and structural characterizations were aided by density functional theory calculations. Barriers to internal rotation were derived and compared to results of relaxed and rigid scans of the potential energy surface using density functional theory.

#### 2. METHODS

## 2.1. Experimental

Reagent grade 1-MN (Aldrich, 95%), 2-MN (General Intermediates), 1,2-DMN (Aldrich, 95%), and 1,3-DMN (Aldrich, 96%) were used without purification. The alkyl-naphthalenes have very low vapor pressures at room temperature, so it was necessary to heat each sample to approximately 473 K in a stainless steel container. The nozzle and the tubing connecting it to the sample container were also heated to prevent condensation of the alkylnaphthalenes. Ne (Praxair) was used as backing gas at 1–2 atm.

Rotational spectra of each sample were measured in the range of 6–15 GHz using a cavity-based molecular-beam FTMW spectrometer, which has been described in detail previously (Xu & Jäger 1997; Xu et al. 2005). In short, the gaseous sample is first injected into an evacuated resonator, through a pulsed nozzle. As the molecules enter the resonator, they undergo supersonic expansion and are rapidly cooled (rotationally) to 1–2 K by collisions with the backing gas. The resonator consists of two aluminum mirrors, whose separation

is adjusted to match the frequency of a given rotational transition. A pulse of near-resonant microwave radiation is then used to excite the molecules, which in turn emit radiation at the transition frequency that is detected in the time domain, analog-to-digital converted, and then Fourier transformed to yield the frequency spectrum. This process is repeated for signal averaging until a reasonable signal-to-noise ratio is achieved. In the case of small molecular dipole moment components, a 0.5 W solid-state amplifier was used to increase the power of the excitation pulses.

# 2.2. Computational

Geometry optimization and vibrational analysis calculations were carried out using the Gaussian09 ab initio package (Frisch et al. 2009) at the B3LYP/6-311++G(d,p) level of theory. B3LYP calculations have been shown to accurately predict rotational constants for other species (McNaughton et al. 2008; Schnitzler & Jäger 2014). Initial structures were generated and optimized using molecular mechanics in Avogadro (Hanwell et al. 2012) before being input into Gaussian; output structures and vibrational normal modes were visualized in Avogadro as well. No imaginary frequencies were calculated for the stationary points, so the optimized structures are indeed minima on the potential energy surface. Rotational constants and centrifugal distortion constants were predicted (using keywords "Freq = VibRot" and "Output = Pickett"), and transition frequencies were calculated in PGOPHER (Western 2010), using the ab initio rotational constants. The barriers to methyl internal rotation were determined by varying the dihedral angle between the aromatic plane and a certain hydrogen atom of the methyl substituent, calculating the energy at each point-with or without optimization of all the other internal coordinates (using keywords "Opt = ModRedundant" and "Scan," respectively).

The experimental transition frequencies were assigned and fitted using PGOPHER, which employs a semi-rigid rotor model, and XIAM (Hartwig & Dreizler 1996), which employs the combined axis method to treat the methyl group internal rotation. In both programs, Watson's *A* reduction Hamiltonian in its  $I^{\rm r}$  representation (Watson 1967) was employed. The experimental rotational constants obtained from the final fits in either PGOPHER or XIAM were compared to the calculated rotational constants, to evaluate the quality of the ab initio calculations.

### 3. RESULTS AND DISCUSSION

### 3.1. Spectra

In general, our searches for rotational transitions were guided by theoretical rotational constants and dipole moments (see Table 1), calculated at the B3LYP/6-311++G(d,p) level of theory. The calculations gave one minimum energy structure for each alkylnaphthalene (see Figure 1). For 1-MN and 2-MN, transitions were easily located using previously reported rotational constants, which were determined from the rotationally resolved electronic spectra of the species (Tan et al. 1991b). For 1,2- and 1,3-DMN, automated frequency scans (consisting of 0.2 MHz frequency steps) were used to search for targeted a- and b-type transitions within 100 MHz intervals, centered at the predicted frequencies. For both species, the first three transition frequencies observed were assigned and used in preliminary fits to locate additional

 Table 1

 Spectroscopic Constants and Dipole Moments Calculated Using Density

 Functional Theory at the B3LYP/6-311++G(d,p) Level

Constant	1-MN	2-MN	1,2-DMN	1,3-DMN
A (MHz)	1895.95	2810.86	1872.13	1572.52
B (MHz)	1125.13	821.83	778.24	815.88
C (MHz)	709.20	638.42	553.49	540.77
$\Delta_J (\text{kHz})$	0.0175	0.00805	0.00683	0.00734
$\Delta_{JK}$ (kHz)	0.0449	0.187	0.0507	0.0404
$\Delta_{K}$ (kHz)	0.0127	0.0143	0.0124	0.0192
$\delta_J (kHz)$	0.00638	0.00203	0.00204	0.00238
$\delta_K (\text{kHz})$	0.0324	0.0226	0.0176	0.0192
$\Delta A/A^{\mathbf{a}}$ (%)	0.07	0.23	0.07	-0.05
$\Delta B/B~(\%)$	-0.10	-0.12	-0.11	-0.10
$\Delta C/C~(\%)$	-0.07	-0.07	-0.10	-0.11
Ave <sup>b</sup> (%)	0.08	0.14	0.09	0.09
$\kappa^{c}$	-0.30	-0.83	-0.66	-0.47
$\mu_a$ (D)	0.15	0.51	0.64	0.49
$\mu_b$ (D)	0.34	0.03	0.36	0.30
$\mu_c$ (D)	0.00	0.00	0.00	0.00

#### Notes.

<sup>a</sup> Relative difference between calculated and experimental values; for example,  $((A_{exp}-A_{calc})/A_{exp})100\%$ .

<sup>b</sup> Average magnitude of relative differences.

<sup>c</sup> Ray's asymmetry parameter,  $\kappa = (2B - A - C)/(A - C)$ .



Figure 1. Minimum energy structures of (1) 1-MN, (2) 2-MN, (3) 1,2-DMN, and (4) 1,3-DMN calculated at the B3LYP/6-311++G(d,p) level of theory and oriented with respect to their *a* and *b* principal inertial axes.

transitions whose frequencies were subsequently used in the final fits.

Representative transitions illustrate the features of the spectra. Each observed transition is split into a Doppler doublet as a result of the molecular beam being parallel to the microwave propagation direction. For 1-MN (see Figure 2), no splittings attributable to methyl internal rotation were observed, and its spectrum was fitted using the PGOPHER program (Western 2010). When all distortion constants are optimized in the fit, the uncertainties are very large; with a value of  $0.03 \pm 0.03$  kHz,  $\Delta_K$  is the most problematic. Rather than



**Figure 2.** Representative *a*-type transition  $(6_{1,6}-5_{1,5})$  of 1-MN, measured using an excitation pulse length of 1  $\mu$ s and 250 averaging cycles.

fixing  $\Delta_K$  at zero, we fixed it at the value predicted from harmonic vibrational frequency calculations, 0.0449 kHz, at the B3LYP/6-311++G(d,p) level of theory; in the fits for the other alkylnaphthalenes, as well,  $\Delta_K$  was fixed at the respective calculated values (see Table 1).

For 2-MN (see Figure 3) and 1,3-DMN (see Figure 4), methyl internal rotation splittings were observed, so two pairs of Doppler components, corresponding to the A and E symmetry components, were detected for each transition. The XIAM program (Hartwig & Dreizler 1996) was used to fit all of the spectra that exhibit splitting of rotational lines due to methyl internal rotation. For 1,2-DMN (see Figure 5), additional splittings due to internal rotation of both methyl substituents occurred, resulting in five fine structure components with symmetry labels AA, AE, EA, EE, and EE'. For most transitions, the EE and EE' components overlapped, so only four lines were observed. For some transitions, only two lines were observed, because of additional overlapping components. For example, the EA, EE, and EE' components of the  $7_{2.6}-6_{2.5}$  transition are so close in frequency that they appear as one Doppler pair; however, in the fit, the experimental frequency is 13 kHz too low and 10 kHz too high for the outer components, EE and EE', respectively. As a result, the standard deviation of the 1,2-DMN fit is higher than those of the other alkylnaphthalenes. In this fit, the distortion constants  $\Delta_{JK}$  and  $\delta_{K}$ , in addition to  $\Delta_{K}$ , were fixed at their calculated values.

The final fits gave rotational, centrifugal distortion (see Table 2), and internal rotation constants (see Table 3). In all, we observed 48 transitions for 1-MN (see Table 4), 39 transitions (including 78 methyl internal rotation components) for 2-MN (see Table 5), 37 transitions (including 70 components) for 1,3-DMN (see Table 6), and 35 transitions (including 147 components) for 1,2-DMN (see Table 7). Both *a*- and *b*-type transitions were observed for 1-MN, 1,3-DMN, and 1,2-DMN; however, only *a*-type transitions were observed for 2-MN. The rotational transition line strengths, *S*, were calculated using the experimental rotational and centrifugal distortion constants and are included in Tables 4–7.

### 3.2. Structures

Optimized geometries of the alkylnaphthalenes are illustrated in Figure 1. The point group of each molecule is  $C_s$ , and one hydrogen atom from each methyl substituent in a given molecule is eclipsed by the plane of symmetry. In 1,2- and 1,3-DMN, the two in-plane hydrogen atoms of the methyl groups were found to be oriented in the same clockwise direction with respect to the *c* principal inertial axis, even when calculations were repeated with the hydrogen atoms initially oriented in



**Figure 3.** Representative *a*-type transition  $(11_{1,11}-10_{1,10})$  of 2-MN, measured using an excitation pulse length of 0.15  $\mu$ s and 1000 averaging cycles.



Figure 4. Representative *a*-type transition  $(9_{1,9}-8_{1,8})$  of 1,3-DMN, measured using an excitation pulse length of 0.15  $\mu$ s and 300 averaging cycles.



**Figure 5.** Representative *a*-type transition  $(8_{1,7}-7_{1,6})$  of 1,2-DMN, collected at two different excitation frequencies using an excitation pulse length of 1  $\mu$ s and number 500 averaging cycles.

opposite directions. All of the alkylnaphthalenes have negative values of the asymmetry parameter  $\kappa$ , calculated as (2B - A - C)/(A - C), so they are prolate asymmetric tops (see Table 2).

Based on the calculated dipole moments (see Table 1), the molecules are moderately polar, so they are candidate species for detection in the ISM using radio astronomy in the microwave region. For each molecule, the component of the dipole moment along the c principal axis is zero because of the  $C_s$  symmetry. This is consistent with the absence of *c*-type transitions in the measured spectra. 1-MN is the only molecule in which the strongest component of the calculated dipole moment is along the *b* principal axis; the calculated value of 0.34 D is similar to that of acenaphthylene, 0.31 D (Thorwirth et al. 2007). In the other molecules, the strongest components of the dipole moments are along their a principal axes; 1,2-DMN is the most polar molecule, because the two methyl substituents occur at neighboring positions. In 2-MN, the dipole moment component along the b principal axis is so small that we were not able to detect *b*-type transitions in its experimental spectrum. The calculated dipole moment components are consistent with the optimal lengths of the excitation

Table 2						
Experimental	Spectroscopic	Constants				

Constant	1-MN	2-MN <sup>a</sup>	1,2-DMN <sup>a</sup>	1,3-DMN <sup>a</sup>
A (MHz)	1894.6564(1) <sup>b</sup>	2804.519(4)	1870.779(1)	1573.2606(4)
B (MHz)	1126.2936(2)	822.8100(2)	779.1260(4)	816.7064(1)
C (MHz)	709.68277(7)	638.8528(1)	554.0210(2)	541.37179(4)
$\Delta_J$ (kHz)	0.016(2)	0.0084(7)	0.008(1)	0.0066(8)
$\Delta_{JK}$ (kHz)	0.018(7)	0.016(5)	0.0124 <sup>c</sup>	0.021(6)
$\Delta_K$ (kHz)	0.0449 <sup>c</sup>	0.187 <sup>c</sup>	0.0507 <sup>c</sup>	0.0404 <sup>c</sup>
$\delta_J$ (kHz)	0.0055(8)	0.0022(4)	0.003(1)	0.0021(4)
$\delta_K$ (kHz)	0.034(7)	0.02(3)	0.0176 <sup>c</sup>	0.012(5)
$\kappa^{d}$	-0.30	-0.83	-0.66	-0.47
N <sup>e</sup>	48	39	35	37
$N_T^{f}$	48	78	147	70
$\sigma^{g}$ (kHz)	1.1	1.8	8.0	0.7

#### Notes.

<sup>a</sup> Internal rotation constants also determined from the fit, as shown in Table 3.

<sup>b</sup> Standard deviation in the last decimal place before the parentheses.

<sup>c</sup> Constant fixed at ab initio value, because it could not be well determined.

<sup>d</sup> Ray's asymmetry parameter,  $\kappa = (2B - A - C)/(A - C)$ .

<sup>e</sup> Number of rotational transitions included in the fit.

<sup>f</sup> Total number of transitions, including methyl internal rotation symmetry components.

<sup>g</sup> rms deviation of residuals.

 Table 3

 Experimental Internal Rotation Parameters

Constant	2-MN	1,2-I	DMN	1,3-DMN
Position	2	1	2	3
$V_3^{a}$ (kJ mol <sup>-1</sup> )	2.717(5)	3.672(3)	5.239(9)	2.896(2)
$\delta^{b}$ (°)	19.9	80.0	6.6	22.4
$F_0^{\rm c}$ (GHz)	159.70	161.23	160.31	160.51
$F_{12}^{d}$ (MHz)	•••	4	17	

#### Notes.

<sup>a</sup> Height of the three-fold barrier to rotation of the methyl top.

<sup>b</sup> Angle between the methyl top axis and the *a* principal inertial axis. Another parameter,  $\epsilon$ , is the angle between the *a* principal axis and the projection of the methyl top axis onto the *bc* plane;  $\epsilon$  was zero for all alkylnaphthalenes, since the axes of the methyl rotors are in the *ab* plane.

<sup>c</sup> Internal rotation constant; analogous to the *A*, *B*, and *C* rotational constants, it is related to the inverse of the moment of inertia of the methyl top about its axis.

<sup>d</sup> Top-top interaction constant.

Table 4	
Measured Transition Frequencies of 1-methylnaphthalen	ıe

J'	$K_a$	$K_c$	<i>J</i> "	$K_a$ "	$K_c$ "	Frequency (MHz)	Residual (MHz)	S
5	1	5	4	0	4	7869.7251	0.0010	4.094
4	2	2	3	2	1	8128.0811	-0.0012	3.060
5	1	4	4	2	3	8230.1119	0.0007	2.005
5	2	4	4	2	3	8895.5740	0.0014	4.123
4	2	3	3	1	2	9019.0185	-0.0008	2.007
6	0	6	5	1	5	9198.3039	0.0019	5.096
6	1	6	5	1	5	9210.2517	-0.0027	5.715
6	0	6	5	0	5	9233.4406	-0.0025	5.720
6	1	6	5	0	5	9245.3947	-0.0009	5.104
5	1	4	4	1	3	9417.1262	-0.0016	4.471

(This table is available in its entirety in machine-readable form.)

pulses for the respective transitions and we conclude that they may be relied upon to identify intense candidate transitions for astronomical searches. The dipole moments can, in principle, be measured using Stark spectroscopy, but those measurements are anticipated to be difficult because of the high J quantum numbers of the accessible transitions.

The quality of the ab initio calculations was evaluated by comparing the experimental and predicted rotational constants. Agreement is very good for all of the alkylnaphthalenes (see Table 1), leading to very good agreement between the predicted and experimental spectra. (For instance, the  $6_{0,6-}$   $5_{0,5}$  transition of 1-MN is predicted to occur 6 MHz lower than it is observed, a difference of only -0.06%.) Similarly, theoretical rotational constants of small PANHs, calculated at the same level of theory, were previously found to be within 0.25% of experimental values (McNaughton et al. 2008). Based on these low average discrepancies, B3LYP is an excellent method for predicting the rotational constants of PAHs.

The differences between experimental and calculated rotational constants can be attributed to shortcomings in the ab initio calculations and effects of zero-point vibrational motions and centrifugal distortion. For planar molecules, it has been shown that zero-point out-of-plane vibrational motions can contribute significantly to negative values for the inertial defect  $\Delta = I_c - I_b - I_a$  (Oka 1995). The inertial defect is zero for a rigid planar molecule. Values for  $\Delta$  of the methylnaphtalenes studied in this work are given in Table 8 and reflect primarily the contributions of the out-of-plane hydrogen atoms of the methyl groups. We can approximate the contribution to the inertial defect from out-of-plane vibrational motions by subtracting the equilibrium contribution from the out-of-plane hydrogen atoms to yield a "methyl top-corrected inertial defect,"  $\Delta^{\text{corr}} = \Delta - 2\sum m_{\text{H}} C_{\text{H}}^2$  (see Table 8). Here,  $m_{\text{H}}$  is the hydrogen atom mass in amu,  $c_{\rm H}$  is the *c*-coordinate of the hydrogen atom from the ab initio calculations, and the sum is over the out-of-plane hydrogen atoms. The doubly substituted

 Table 5

 Measured Transition Frequencies of 2-methylnaphthalene

J'	$K_a$	$K_c$ '	<i>J</i> "	$K_a$ "	$K_c$ "	State	Frequency (MHz)	Residual (MHz)	S
5	1	5	4	1	4	А	6800.1010	0.0011	4.793
5	1	5	4	1	4	E	6800.8682	0.0008	4.791
5	0	5	4	0	4	E	7078.5153	0.0016	4.950
5	0	5	4	0	4	А	7078.8459	0.0005	4.951
5	2	4	4	2	3	А	7281.2551	0.0003	4.197
5	2	4	4	2	3	E	7314.9415	-0.0022	4.024
5	3	3	4	3	2	А	7345.2851	0.0008	3.201
5	3	2	4	3	1	E	7350.1874	-0.0014	3.202
5	3	3	4	3	2	E	7350.8029	-0.0012	3.198
5	3	2	4	3	1	А	7355.8616	0.0003	3.201

(This table is available in its entirety in machine-readable form.)

 Table 6

 Measured Transition Frequencies of 1,3-dimethylnaphthalene

J'	$K_a$	$K_c$	<i>J</i> "	$K_a$ "	$K_c$ "	State	Frequency (MHz)	Residual (MHz)	S
7	2	6	6	2	5	А	9058.4357	-0.0004	6.294
7	2	6	6	2	5	Е	9058.4733	-0.0018	6.292
8	0	8	7	1	7	Е	9187.5324	0.0003	6.972
8	0	8	7	1	7	А	9187.6482	-0.0002	6.970
8	1	8	7	1	7	Е	9192.7723	0.0007	7.752
8	1	8	7	1	7	А	9192.9065	-0.0007	7.754
8	0	8	7	0	7	Е	9200.8758	0.0005	7.753
8	0	8	7	0	7	А	9201.037	0.0000	7.756
8	1	8	7	0	7	Е	9206.1154	0.0006	6.975
8	1	8	7	0	7	А	9206.2947	-0.0011	6.973

(This table is available in its entirety in machine-readable form.)

 Table 7

 Measured Transition Frequencies of 1,2-dimethylnaphthalene

J	$K_a$	$K_c$ '	<i>J</i> "	$K_a$ "	$K_c$ "	State	Frequency (MHz)	Residual (MHz)	S
7	1	7	6	1	6	EE	8270.7574	0.0049	6.799
7	1	7	6	1	6	EE'	8270.7574	0.0057	6.799
7	1	7	6	1	6	EA	8270.7691	0.0086	6.799
7	1	7	6	1	6	AE	8270.8293	-0.0060	6.798
7	1	7	6	1	6	AA	8270.8412	-0.0025	6.798
7	0	7	6	0	6	EE	8340.6600	-0.0014	6.816
7	0	7	6	0	6	EE'	8340.6600	-0.0015	6.816
7	0	7	6	0	6	EA	8340.6837	0.0049	6.816
7	0	7	6	0	6	AE	8340.6999	-0.0075	6.816
7	0	7	6	0	6	AA	8340.7251	0.0003	6.816

(This table is available in its entirety in machine-readable form.)

 Table 8

 Low-lying Out-of-plane Vibrations Calculated Using B3LYP/6-311++G(d,p)

Constant	1-MN	2-MN	1,2-DMN	1,3-DMN
$\nu_1  (\text{cm}^{-1})$	132	96	99	94
$\nu_2 ({\rm cm}^{-1})$	166	124	122	118
$\nu_3 ({\rm cm}^{-1})$	183	180	145	152
$\nu_4  ({\rm cm}^{-1})$	247	280	222	172
$\nu_5 ({\rm cm}^{-1})$			300	217
$\nu_{6} (cm^{-1})$				295
$\Delta^{\mathbf{a}}$ (amu Å <sup>2</sup> )	-3.329	-3.340	-6.590	-6.516
$\Delta^{\text{corrb}}$ (amu Å <sup>2</sup> )	-0.200	-0.214	-0.336	-0.261

#### Notes.

<sup>a</sup> Inertial defect,  $\Delta = I_c - I_b - I_a$ .

<sup>b</sup> "Methyl top-corrected inertial defect," calculated as described in the text.

molecules have the most significant "methyl top-corrected inertial defects," because they have more low-lying out-ofplane vibrational modes with frequencies below 400 cm<sup>-1</sup> (see Table 8) than the singly substituted molecules. Planar PANHs exhibit the same trend; their inertial defects (like the "methyl top-corrected inertial defects" in our study) have been shown to increase with the number of low-lying out-of-plane modes (McNaughton et al. 2007).

# 3.3. Barriers to Internal Rotation

The experimentally derived internal rotation parameters are given in Table 3. The parameters of the lone methyl substituent of 1-MN could not be determined, because no splitting was observed in the spectrum. This observation is indicative of a

 Table 9

 Barriers to Internal Rotation Calculated Using B3LYP/6-311++G(d,p)

Species	Position	$V_{3,\mathrm{rigid}}~(\mathrm{kJ}~\mathrm{mol}^{-1})$	V <sub>3,relaxed</sub> (kJ mol <sup>-1</sup> )
1-MN	1	10.53	8.03
2-MN	2	2.70	2.57
1,2-DMN	1	6.91	2.70
1,2-DMN	2	8.38	4.41
1,3-DMN	1	10.45	7.98
1,3-DMN	3	2.78	2.68

high barrier to internal rotation, consistent with an earlier experimental study; the barrier has been determined to be  $9.7 \text{ kJ mol}^{-1}$ , based on the rotationally resolved electronic spectrum (Tan et al. 1991b). In contrast, the methyl substituent of 2-MN causes splitting in the rotational spectrum, and the barrier was determined to be much lower,  $2.717 \text{ kJ mol}^{-1}$ , in close agreement with the previously measured value of  $2.8 \text{ kJ mol}^{-1}$  (Tan et al. 1991b).

1,2-DMN is an interesting prototype of molecules that have two methyl substituents at adjacent carbon atoms of an aromatic ring, analogous to 3,4-dimethylbenzaldehyde, which has previously been studied in detail (Tudorie et al. 2013). The methyl substituents at both the 1 and 2 positions of 1,2-DMN cause splittings in the rotational spectrum, and the barriers were determined to be 3.670 and 5.238 kJ mol<sup>-1</sup>, respectively. No previous measurements have been reported; however, we can compare to calculated values. In general, barriers to internal rotation can be determined using ab initio calculations by stepping a single internal coordinate (in this case, a dihedral angle) and either fixing all of the others or allowing them to simultaneously relax. The barriers to rotation of the methyl substituents at the 1 and 2 positions were calculated to be 2.70 and  $4.41 \text{ kJ mol}^{-1}$  (see Table 9), respectively, when all the internal coordinates, besides the stepped dihedral angle, were allowed to relax at each value of the dihedral angle. Though these values are lower than those determined experimentally, their relative magnitude is similar. Interestingly, the barrier to rotation of the methyl substituent at position 1 is lower in 1,2-DMN than in 1-MN and 1,3-DMN, although the rotor is expected to experience a much greater steric hindrance in 1,2-DMN. Our calculations indicate that steric hindrance indeed increases the energy of the transition state of 1,2-DMN, compared to that of its isomer 1,3-DMN, but it increases the energy of the minimum to an even greater extent (see Figure 6); as a result, the energy difference between the minimum and the transition state is smaller. This observation is consistent with earlier calculations (Kassaee et al. 2007), and it can be attributed to the environment around the methyl group becoming more isotropic. The barrier to internal rotation is greater for the methyl substituent at position 2 than 1 because in the equilibrium geometry the in-plane hydrogen atom of the methyl group at position 1 is oriented toward the methyl group at position 2. When all of the internal coordinates, besides the stepped dihedral angle, were fixed, the barriers to rotation of both methyl substituents were calculated to be much higher; for example, the barrier height at position 1 is  $6.91 \text{ kJ mol}^{-1}$  (see Figure 7). Furthermore, using the rigid approach, we find that the three barrier heights calculated through a 360° rotation of the methyl substituent at position 1 differ slightly (see Figure 7) because the group is not perfectly tetrahedral in the equilibrium geometry.



**Figure 6.** Potential energy of 1,3- and 1,2-DMN as a function of the dihedral angle between the aromatic plane and the initially in-plane hydrogen atom of the methyl substituent at position 1.



**Figure 7.** Potential energy of 1,2-DMN at fixed values of the dihedral angle between the aromatic plane and the initially in-plane hydrogen atom of the methyl substituent at position 1, with ("relaxed") and without ("rigid") optimization of all the other internal coordinates.

These features constitute a strong argument against using single point energy calculations to predict barriers to rotation—and tunneling motions, in general (Schnitzler & Jäger 2014).

Only one methyl substituent in 1,3-DMN causes splitting in the spectrum. Based on the angle,  $\delta$ , between the methyl top axis and the *a* principal axis, 22°5, the rotor at position 3 is responsible for the splitting. This assignment is consistent with theory, since the calculated barrier to rotation of the methyl substituent at position 1, 7.98 kJ mol<sup>-1</sup>, is too high to expect this group to cause any splitting. The experimental height of the barrier to rotation of the methyl substituent at position 3 is 2.896 kJ mol<sup>-1</sup>; since the methyl substituents are not as crowded as in 1,2-DMN, this value is in good agreement with the values predicted using both the relaxed and rigid approaches to barrier calculations, 2.68 and 2.78 kJ mol<sup>-1</sup>, respectively.

# 4. CONCLUSIONS

The pure rotational spectra of four alkylnaphthalenes were measured in the range of 6–15 GHz. Density functional theory calculations gave accurately predicted rotational constants, which aided in the assignments of the spectra. Methyl topcorrected inertial defects were found to be greater for 1,2- and 1,3-DMN than the singly methyl-substituted species, because the doubly methyl-substituted species have a greater number of low-lying out-of-plane vibrational modes. Barriers to internal rotation were derived, and they are consistent with relaxed barrier calculations. In particular, the spectroscopic fits confirm that the barrier for rotation of the methyl group at position 1 decreases with increased crowding, an unintuitive result of the environment becoming more isotropic. Finally, the four alkylnaphthalenes are moderately polar, so they are candidate THE ASTROPHYSICAL JOURNAL, 805:141 (7pp), 2015 June 1

species for the detection by radio astronomy. Since the reported transitions are in the range of the Green Bank Telescope and the Arecibo Observatory, for example, they could facilitate further searches for specific PAHs in the ISM. Furthermore, extrapolation based on these low-*J* transitions could guide future laboratory measurements of transitions in the millimeter/ sub-millimeter range of the Atacama Large Millimeter Array and other observatories.

We thank Javix Thomas and Yunjie Xu for discussions regarding methyl internal rotation. Computing resources were provided by Westgrid and Compute/Calcul Canada. E.G.S. thanks the Natural Sciences and Engineering Research Council (NSERC) of Canada for a Postgraduate Scholarship and the University of Alberta for a President's Doctoral Prize of Distinction. B.L.M.Z. gratefully acknowledges a Dr. R. Norman and Magda Kemeny Jones Summer Studentship. This research was funded by NSERC.

### REFERENCES

- Duley, W. W., & Hu, A. 2012, ApJ, 761, 115
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., et al. 2009, Gaussian09, Revision B.01 (Wallingford, CT: Gaussian Inc.)
- Hanwell, M. D., Curtis, D. E., Lonie, D. C., et al. 2012, J. Cheminform., 4, 17

- Hartwig, H., & Dreizler, H. 1996, ZNatA, 51A, 923
- Kassaee, M. H., Keffer, D. J., & Steele, W. V. 2007, J. Chem. Eng. Data, 52, 1843
- Kwok, S., & Zhang, Y. 2013, ApJ, 771, 5
- López-Puertas, M., Dinelli, B. M., Adriani, A., et al. 2013, ApJ, 770, 132
- Lovas, F. J., McMahon, R. J., Grabow, J.-U., et al. 2005, JAChS, 127, 4345
- McNaughton, D., Godfrey, P. D., Brown, R. D., & Thorwirth, S. 2007, PCCP, 9, 591
- McNaughton, D., Godfrey, P. D., Brown, R. D., Thorwirth, S., & Grabow, J.-U. 2008, ApJ, 678, 309
- Oka, T. 1995, JMoSt, 352/353, 225 Schnitzler, E. G., & Jäger, W. 2014, PCCP, 16, 2305
- Siebenmorgen, R., Voshchinnikov, N. V., & Bagnulo, S. 2014, A&A, 561, A82
- Tan, X.-Q., Clouthier, D. J., Judge, R. H., et al. 1991a, JChPh, 95, 7862
- Tan, X.-Q., Majewski, W. A., Plusquellic, D. F., & Pratt, D. W. 1991b, JChPh, 94, 7721
- Tielens, A. G. G. M. 2008, ARA&A, 46, 289
- Thorwirth, S., Theulé, P., Gottlieb, C. A., McCarthy, M. C., & Thaddeus, P. 2007, ApJ, 662, 1309
- Tudorie, M., Kleiner, I., Jahn, M., et al. 2013, JPCA, 117, 13636
- Van der Zwet, G. P., & Allamandola, L. J. 1985, A&A, 146, 76
- Vijh, U. P., Witt, A. N., & Gordon, K. D. 2004, ApJL, 606, L65
- Watson, J. K. G. 1967, JChPh, 46, 1935
- Western, C. M. 2010, PGOPHER, A Program for Simulating Rotational Structure, Univ. Bristol, http://pgopher.chm.bris.ac.uk
- Xu, Y., & Jäger, W. 1997, JChPh, 106, 7968
- Xu, Y., van Wijngaarden, J., & Jäger, W. 2005, IRPC, 24, 301