

## THE RADIO SPECTRUM OF THE PHENYL RADICAL

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### ABSTRACT

The phenyl radical, C<sub>6</sub>H<sub>5</sub>, derived from benzene by removal of one hydrogen atom, was detected at centimeter wavelengths in a pulsed supersonic molecular beam and subsequently at millimeter wavelengths in a low-pressure direct current glow discharge. Fourteen rotational transitions between 9 and 40 GHz and over 50 transitions between 150 and 330 GHz, each split by spin doubling, have been measured for the normal isotopic species, and a comparable number have been measured for the fully deuterated species. The spectrum of both isotopic species at millimeter wavelengths is reproduced to an uncertainty of 0.5 km s<sup>-1</sup> or better with seven spectroscopic constants. Rotational constants predicted from high-level molecular structure calculations are in excellent agreement with the measurements. Phenyl is a prime candidate for astronomical detection, because it is the prototypical aromatic hydrocarbon radical and a possible progenitor of other aromatic species.

*Subject headings:* ISM: molecules — line: identification — molecular data — molecular processes — radio lines: ISM

Phenyl, the cyclic radical C<sub>6</sub>H<sub>5</sub> shown in Figure 1, is a crucial intermediate in combustion and soot formation (Glassman 1996 and references therein) and may also play an important role in the chemistry of the interstellar gas and circumstellar envelopes. It is believed that phenyl is the first aromatic radical formed along a reaction pathway that begins with ions and molecules containing two or three carbon atoms and leads to polycyclic aromatic molecules (Woods et al. 2002; Kaiser et al. 2000). Although well characterized by electron spin resonance and by UV, visible, Raman, and IR spectroscopy (Friderichsen et al. 2001 and references therein), the radio spectrum of phenyl until now has eluded detection; in the absence of accurate rest frequencies, no searches for phenyl to our knowledge have been undertaken in astronomical sources. Here we describe the detection of this fundamental radical in a discharge through benzene by both Fourier transform microwave (FTM) spectroscopy and millimeter-wave absorption spectroscopy, and give the spectroscopic data needed for an astronomical search throughout the radio band.

Phenyl is a planar asymmetric rotor with C<sub>2v</sub> symmetry, a <sup>2</sup>A<sub>1</sub> electronic ground state, and a calculated electric dipole moment of 0.9 D along its intermediate principal inertial axis *b* (see Fig. 1). Because of the near equality of its *A* and *B* rotational constants, phenyl falls close enough to the oblate symmetric top limit that its rotational spectrum is that of a symmetric top with slightly broken symmetry. Owing to the interaction of the unpaired electron with molecular rotation and with the magnetic moments of the five protons, the lower rotational transitions are split into many resolved hyperfine components, but the hyperfine structure (hfs) collapses with increasing frequency, yielding in the millimeter-wave band a fairly simple rotational spectrum with spin doubling that is well described by a small number of spectroscopic constants.

To detect phenyl, we first undertook a FTM search for the

fundamental 1<sub>1,1</sub> → 0<sub>0,0</sub> transition predicted to occur near 9.2 GHz (Tonokura et al. 2002; Vereecken et al. 2002), using experimental conditions that optimized the production of *o*-benzynes, the closely related C<sub>6</sub>H<sub>4</sub> ring (Brown, Godfrey, & Rodler 1986). Using benzene as a precursor gas, a series of closely spaced magnetic lines with approximately the right multiplicity were found within 1% of the literature predictions. Subsequent searches for other transitions yielded additional series of closely spaced magnetic lines of comparable intensity, the centroids of which could be predicted to a few MHz.

On the basis of the preliminary rotational constants derived from the FTM measurements, searches for the millimeter-wave lines of phenyl were then undertaken, again at conditions that optimized the production of *o*-benzynes. Much to our surprise, lines of *o*-benzynes and phenyl—detected in either case within 50 MHz of those predicted—were remarkably strong when observed with our free space millimeter-wave spectrometer (Aponi et al. 1999), as the spectrum in Figure 2 shows. Phenyl was produced in a low-pressure direct current discharge through a flowing mixture of benzene and argon. The flow rate of argon at standard pressure and temperature was 2 cm<sup>3</sup> minute<sup>-1</sup>, and the total pressure in the cell with the discharge on was about 4 mtorr. The strongest lines were observed with a fairly low discharge current of 75 mA and the walls of the cell cooled to 220 K. Under these conditions, lines of phenyl are about 5 times weaker than those of *o*-benzynes, but the mole fraction of the two species is comparable (1.4 × 10<sup>-4</sup>; i.e., a concentration of 3 × 10<sup>10</sup> cm<sup>-3</sup>), owing to the difference in dipole moments (a factor of 2.5) and the absence of spin doubling (a factor of 2) in *o*-benzynes. Phenyl is more than 1000 times more abundant than the linear C<sub>6</sub>H radical observed with the same spectrometer in a discharge through acetylene and argon at a lower temperature (120 K) and somewhat higher pressure (20 mtorr).

In all, 62 rotational lines, each split by spin doubling from the unpaired electron, were measured between 150 and 330 GHz for the normal isotopic species; a comparable number of lines (50) were measured for C<sub>6</sub>D<sub>5</sub> when fully deuterated benzene was used in place of benzene. When the transition frequencies were analyzed with Watson's *A*-reduced Hamiltonian, the millimeter-wave spectrum of phenyl was reproduced with seven spectroscopic constants (Table 1): three rotational constants, the three leading fourth-order centrifugal distortion constants (Δ<sub>*J*</sub>, Δ<sub>*J**K*</sub>, and

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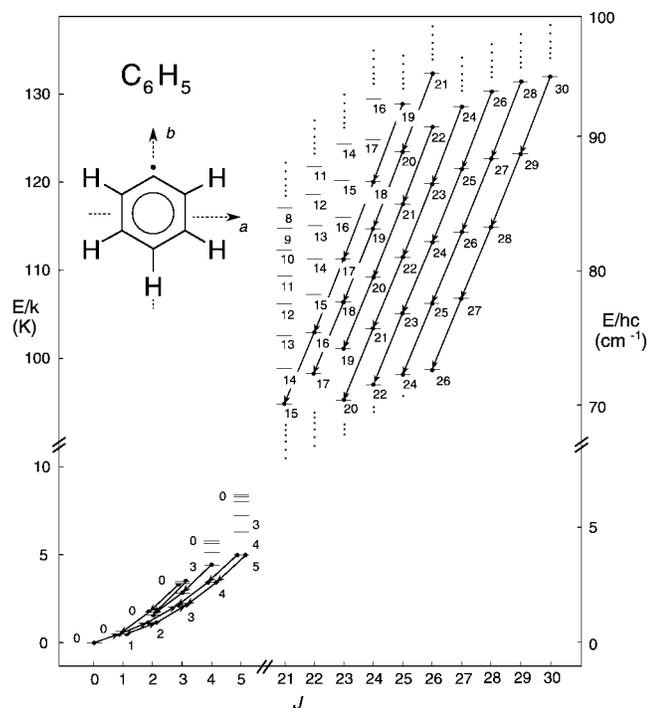


FIG. 1.—Geometrical structure of phenyl and part of its rotational energy level diagram showing all the transitions measured by FTM spectroscopy (*bottom left*) and about 25% of those measured by millimeter-wave spectroscopy. For simplicity, levels with the same rotational quantum number  $J$  are labeled only with  $K$ , the limiting oblate index. The small spin doubling of each level is not shown.

$\Delta_K$ ), and one component of the spin-rotation tensor ( $\epsilon_{cc}$ ). As can be seen in Table 1, all three centrifugal distortion constants are about 30% smaller than those of the well-studied *o*-benzynes, and the small positive inertial defect ( $\Delta = I_C - I_A - I_B$ ) is nearly identical to that of benzene, confirming that phenyl is planar. A more complete analysis of the data will be presented elsewhere.

Molecular structure calculations were performed in conjunction with the present work to determine a precise equilibrium structure of phenyl, as well as accurate harmonic and cubic force fields. The CCSD(T) method (Raghavachari et al. 1989) was used together with the cc-pVTZ basis set (Dunning 1989) in the geometry optimization; rigid rotor constants ( $B_J$ ) were based on the corresponding equilibrium structure. These were then corrected for centrifugal distortion (Gordy & Cook 1984) and vibrational effects (Mills 1972; using the anharmonic force field calculated at the self-consistent field SCF level) to yield the predicted rotational constants in Table 1. Full details of the calculations will be given elsewhere.

The identification of the molecule has been established beyond a reasonable doubt by the following tests: (1) the experimental rotational constants agree to within 0.1% with those predicted by high-level molecular structure (ab initio) theory, as Table 1 shows; (2) many lines of the fully deuterated isotopic species have been detected at exactly the predicted isotopic shifts (to within 0.07%); and (3) as expected for the paramagnetic doublet electronic ground state of phenyl, the assigned lines exhibit a pronounced Zeeman effect when a strong permanent magnet is brought near the molecular beam of our FTM spectrometer, and the lines in the millimeter-wave band are also modulated in a magnetic field of 50 G.

Many transitions of phenyl are accessible throughout the centimeter- and millimeter-wave bands. A prominent feature in the millimeter-wave band is the occurrence of an *R*-branch

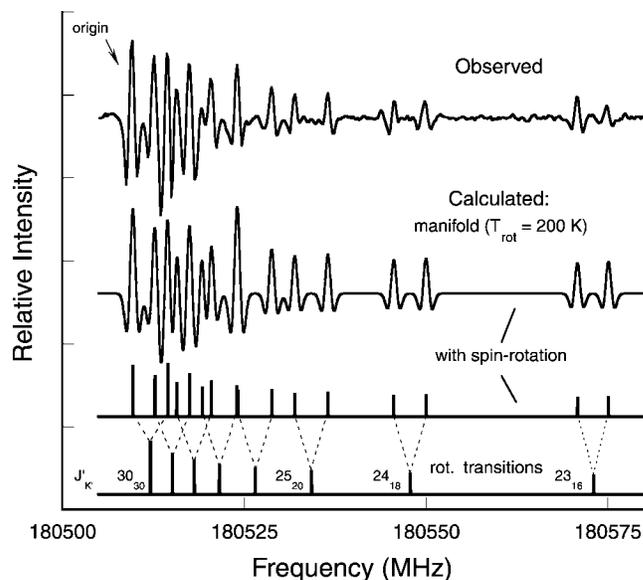


FIG. 2.—Typical laboratory lines of phenyl in the millimeter-wave band, showing  $K$ -structure and spin doubling. The calculated spectra were derived from the constants in Table 1. Rotational transitions in the *R*-branch series ( $\Delta J = +1$ ,  $\Delta K = +1$ ) are denoted with the upper-state label  $J'_K'$ , where  $K$  is the limiting oblate index. The experimental second-derivative line shapes result from the frequency modulation used to suppress  $1/f$  noise. The integration time is 15 s MHz<sup>-1</sup>, for a total of about 20 minutes.

series approximately every 6 GHz (i.e., twice the rotational constant  $C$ ). As shown in Figure 2, each series consists of four or five closely spaced rotational transitions of comparable intensity, which are further split by spin rotation into two components of nearly equal intensity. The hfs can be calculated approximately from the electron spin resonance data of Kasai et al. (1969); it collapses to less than 1 km s<sup>-1</sup> in the millimeter-wave band and can be neglected in a deep astronomical search. Listed in Table 2 are frequencies in the millimeter-wave band predicted with the spectroscopic constants in Table 1. An expanded version of Table 2 is available from the authors.

Two possible routes for the production of phenyl in space

TABLE 1  
SPECTROSCOPIC CONSTANTS OF C<sub>6</sub>H<sub>5</sub> AND C<sub>6</sub>D<sub>5</sub>

CONSTANT	C <sub>6</sub> H <sub>5</sub>		C <sub>6</sub> D <sub>5</sub>	
	This Work	Predicted <sup>a</sup>	This Work	Predicted <sup>a</sup>
$A$ .....	6279.8(3)	6282	5453.8(4)	5457
$B$ .....	5599.9(2)	5599	4640.8(3)	4642
$C$ .....	2959.4009(6)	2959	2506.8417(9)	2508
$10^3 \Delta_J$ .....	1.419(4)	1.89 <sup>b</sup>	0.878(5)	...
$10^3 \Delta_{JK}$ .....	-2.39(1)	-3.22 <sup>b</sup>	-1.46(1)	...
$10^3 \Delta_K$ .....	1.09(6)	1.46 <sup>b</sup>	0.654(8)	...
$\epsilon_{cc}^c$ .....	4.78(2)	...	4.22(2)	4.05 <sup>d</sup>
Inertial Defect (amu Å <sup>2</sup> )				
$\Delta$ .....	0.046(5)	0.043 <sup>e</sup>	0.035(10)	0.032 <sup>f</sup>

NOTE.—Constants (in units of MHz) derived for  $A$ -reduced Hamiltonian in the III' representation. Uncertainties (in parentheses) are 1  $\sigma$  in the units of the last significant digits. For both isotopic species, the rms of the fit was 0.16 MHz.

<sup>a</sup> Rotational constants with vibrational corrections from ab initio theory (see text).

<sup>b</sup> From *o*-benzynes (Robertson, Godfrey, & McNaughton 2003 and unpublished data).

<sup>c</sup> Assumed to be positive.

<sup>d</sup> Scaled from C<sub>6</sub>H<sub>5</sub> by the ratio of the  $C$  rotational constants.

<sup>e</sup> Inertial defect of benzene extrapolated from its partially deuterated isotopic species (Oldani et al. 1988).

<sup>f</sup> Average inertial defect of 1, 2- and 1, 3-benzene-*d*<sub>2</sub> (Oldani et al. 1988).

TABLE 2  
PREDICTED ROTATIONAL LINES OF PHENYL IN THE MILLIMETER-WAVE  
BAND

$J'_{K'} \rightarrow J_K$	$\nu^a$	$J'_{K'} \rightarrow J_K$	$\nu$	$J'_{K'} \rightarrow J_K$	$\nu$
12 <sub>12</sub> → 11 <sub>11</sub>	73983	11 <sub>10</sub> → 10 <sub>9</sub>	73988	10 <sub>8</sub> → 9 <sub>7</sub>	73998
	73988		73992		74002
13 <sub>13</sub> → 12 <sub>12</sub>	79902	12 <sub>11</sub> → 11 <sub>10</sub>	79906	11 <sub>9</sub> → 10 <sub>8</sub>	79914
	79907		79911		79919
14 <sub>14</sub> → 13 <sub>13</sub>	85821	13 <sub>12</sub> → 12 <sub>11</sub>	85824	12 <sub>10</sub> → 11 <sub>9</sub>	85831
	85825		85829		85836
15 <sub>15</sub> → 14 <sub>14</sub>	91739	14 <sub>13</sub> → 13 <sub>12</sub>	91743	13 <sub>11</sub> → 12 <sub>10</sub>	91749
	91744		91747		91753
16 <sub>16</sub> → 15 <sub>15</sub>	97657	15 <sub>14</sub> → 14 <sub>13</sub>	97661	14 <sub>12</sub> → 13 <sub>11</sub>	97667
	97662		97666		97671
17 <sub>17</sub> → 16 <sub>16</sub>	103576	16 <sub>15</sub> → 15 <sub>14</sub>	103579	15 <sub>13</sub> → 14 <sub>12</sub>	103584
	103581		103584		103589
18 <sub>18</sub> → 17 <sub>17</sub>	109494	17 <sub>16</sub> → 16 <sub>15</sub>	109498	16 <sub>14</sub> → 15 <sub>13</sub>	109502
	109499		109502		109507
19 <sub>19</sub> → 18 <sub>18</sub>	115412	18 <sub>17</sub> → 17 <sub>16</sub>	115416	17 <sub>15</sub> → 16 <sub>14</sub>	115420
	115417		115421		115425
21 <sub>21</sub> → 20 <sub>20</sub>	127249	20 <sub>19</sub> → 19 <sub>18</sub>	127252	19 <sub>17</sub> → 18 <sub>16</sub>	127256
	127254		127257		127261
22 <sub>22</sub> → 21 <sub>21</sub>	133167	21 <sub>20</sub> → 20 <sub>19</sub>	133170	20 <sub>18</sub> → 19 <sub>17</sub>	133174
	133172		133175		133179
23 <sub>23</sub> → 22 <sub>22</sub>	139085	22 <sub>21</sub> → 21 <sub>20</sub>	139088	21 <sub>19</sub> → 20 <sub>18</sub>	139092
	139090		139093		139097
24 <sub>24</sub> → 23 <sub>23</sub>	145003	23 <sub>22</sub> → 22 <sub>21</sub>	145006	22 <sub>20</sub> → 21 <sub>19</sub>	145010
	145008		145011		145015
25 <sub>25</sub> → 24 <sub>24</sub>	150921	24 <sub>23</sub> → 23 <sub>22</sub>	150924	23 <sub>21</sub> → 22 <sub>20</sub>	150928
	150926		150929		150932
26 <sub>26</sub> → 25 <sub>25</sub>	156839	25 <sub>24</sub> → 24 <sub>23</sub>	156842	24 <sub>22</sub> → 23 <sub>21</sub>	156845
	156844		156847		156850
27 <sub>27</sub> → 26 <sub>26</sub>	162757	26 <sub>25</sub> → 25 <sub>24</sub>	162760	25 <sub>23</sub> → 24 <sub>22</sub>	162763
	162762		162765		162768
28 <sub>28</sub> → 27 <sub>27</sub>	168675	27 <sub>26</sub> → 26 <sub>25</sub>	168678	26 <sub>24</sub> → 25 <sub>23</sub>	168681
	168679		168682		168685
29 <sub>29</sub> → 28 <sub>28</sub>	174592	28 <sub>27</sub> → 27 <sub>26</sub>	174595	27 <sub>25</sub> → 26 <sub>24</sub>	174598
	174597		174600		174603
36 <sub>36</sub> → 35 <sub>35</sub>	216013	35 <sub>34</sub> → 34 <sub>33</sub>	216016	34 <sub>32</sub> → 33 <sub>31</sub>	216019
	216018		216021		216024
37 <sub>37</sub> → 36 <sub>36</sub>	221930	36 <sub>35</sub> → 35 <sub>34</sub>	221933	35 <sub>33</sub> → 34 <sub>32</sub>	221936
	221935		221938		221941
38 <sub>38</sub> → 37 <sub>37</sub>	227847	37 <sub>36</sub> → 36 <sub>35</sub>	227850	36 <sub>34</sub> → 35 <sub>33</sub>	227853
	227852		227855		227857
39 <sub>39</sub> → 38 <sub>38</sub>	233764	38 <sub>37</sub> → 37 <sub>36</sub>	233767	37 <sub>35</sub> → 36 <sub>34</sub>	233769
	233769		233771		233774
40 <sub>40</sub> → 39 <sub>39</sub>	239680	39 <sub>38</sub> → 38 <sub>37</sub>	239683	38 <sub>36</sub> → 37 <sub>35</sub>	239686
	239685		239688		239691
41 <sub>41</sub> → 40 <sub>40</sub>	245597	40 <sub>39</sub> → 39 <sub>38</sub>	245600	39 <sub>37</sub> → 38 <sub>36</sub>	245602
	245602		245604		245607
42 <sub>42</sub> → 41 <sub>41</sub>	251513	41 <sub>40</sub> → 40 <sub>39</sub>	251516	40 <sub>38</sub> → 39 <sub>37</sub>	251519
	251518		251521		251523
43 <sub>43</sub> → 42 <sub>42</sub>	257430	42 <sub>41</sub> → 41 <sub>40</sub>	257432	41 <sub>39</sub> → 40 <sub>38</sub>	257435
	257434		257437		257440
44 <sub>44</sub> → 43 <sub>43</sub>	263346	43 <sub>42</sub> → 42 <sub>41</sub>	263348	42 <sub>40</sub> → 41 <sub>39</sub>	263351
	263350		263353		263356
45 <sub>45</sub> → 44 <sub>44</sub>	269262	44 <sub>43</sub> → 43 <sub>42</sub>	269265	43 <sub>41</sub> → 42 <sub>40</sub>	269267
	269266		269269		269272
46 <sub>46</sub> → 45 <sub>45</sub>	275178	45 <sub>44</sub> → 44 <sub>43</sub>	275180	44 <sub>42</sub> → 43 <sub>41</sub>	275183
	275182		275185		275188
47 <sub>47</sub> → 46 <sub>46</sub>	281093	46 <sub>45</sub> → 45 <sub>44</sub>	281096	45 <sub>43</sub> → 44 <sub>42</sub>	281098
	281098		281101		281103
48 <sub>48</sub> → 47 <sub>47</sub>	287009	47 <sub>46</sub> → 46 <sub>45</sub>	287012	46 <sub>44</sub> → 45 <sub>43</sub>	287014
	287014		287017		287019

NOTE.—Frequencies are in MHz. Owing to spin doubling, each rotational transition is split (by roughly 5 MHz) into two components of nearly equal intensity. Tabulated transitions are for the first three  $K$ -components in each  $R$ -branch series. Transitions between 116 and 125 and between 175 and 215 GHz are omitted owing to high atmospheric opacity.

<sup>a</sup> The lower frequency spin component is the origin of the  $R$ -branch series.

are (1) electron recombination with the  $C_6H_7^+$  ion for which a plausible mechanism has been proposed for regions with a high UV flux, such as the protoplanetary nebula CRL 618 (Woods et al. 2002), and (2) photodissociation of benzene in the UV

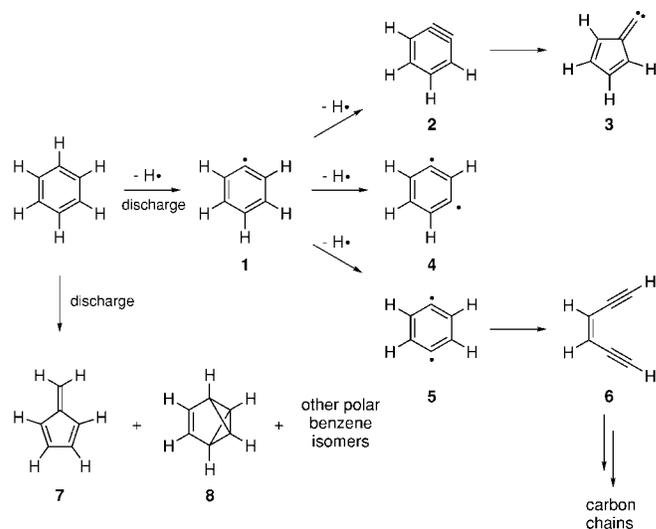


FIG. 3.—Fragmentation and isomerization pathways plausibly associated with a benzene discharge. Compounds **1**, **2**, **6**, **7**, and **8**, as well as various carbon chain and ring chains, have been detected by FTM spectroscopy. Detailed formation mechanisms are not implied.

(near 200 nm) for which phenyl is the primary photoproduct (Yokoyama et al. 1990). One also wonders whether mechanisms proposed for the production of aromatic hydrocarbons in carbon-rich stellar envelopes (Cherchneff, Barker, & Tielens 1992).

We have found no indication of phenyl in several published spectral line surveys of standard molecular galactic sources. Our limit for the column density of phenyl is 10 times higher than the column density observed for  $c\text{-C}_3\text{H}_2$  in Orion, IRC +10216, and Sgr B2 (Madden et al. 1989; Kawaguchi et al. 1995), in part owing to the fourfold smaller dipole moment of phenyl and its 13-fold larger rotational partition function. We have also examined published spectra of CRL 618. The envelope of fairly cold gas surrounding the central star is a rich source of polyatomic molecules (Bachiller et al. 1997), and benzene has been tentatively identified with the *Infrared Space Observatory* in the photon-dominated region (PDR) close to the star (Cernicharo et al. 2001). Our limit on phenyl in this source is comparable to the derived column density of benzene, but a deeper search there might yield a limit 5–10 times lower. The high apparent abundance of benzene in a region of high-UV flux suggests that sensitive searches for phenyl in other PDRs might prove successful. Limits on the column densities of phenyl are summarized in Table 3.

The present work demonstrates that the benzene discharge is a rich source of cyclic organic molecules of relevance to interstellar chemistry. In addition to phenyl (see Fig. 3, compound **1**), the reactive ring *o*-benzynes (**2**) has been detected in the present discharge, and the existence of the isomeric *p*-benzynes (**5**) may be plausibly inferred from the detection of its ring-opened isomer, the acyclic enediyne (**6**). Highly energetic polar isomers of  $C_6H_6$ , including fulvene (**7**) and benzvalene (**8**), which lie 1.3 and 3.1 eV, respectively, above benzene, are also readily detected. These polar isomers of aromatic compounds represent intriguing candidates for radioastronomical detection.

Beyond the parent hydrocarbon molecules described in the present study, laboratory measurements of other reactive rings and high-energy isomers may now be feasible. Analogs of the molecules shown in Figure 3 with polar substituents (CN, OH,

TABLE 3  
COLUMN DENSITY LIMITS ON PHENYL IN FOUR SOURCES

Source	Frequency (MHz)	$E/k$ (K)	$S$	$T_{\text{mb}}$ (mK)	$\Delta\nu$ (km s <sup>-1</sup> )	$T_{\text{rot}}$ (K)	$N_{\text{limit}}$ (10 <sup>14</sup> cm <sup>-2</sup> )
IRC +10216 .....	32,557	5	4.4	7 <sup>a</sup>	29	20	6
Sgr B2 .....	85,821	31	13.4	88 <sup>b</sup>	20	20	20
	97,657	41	15.4	84 <sup>b</sup>	20	20	20
Orion compact ridge .....	103,576	46	16.4	82 <sup>b</sup>	3.5	75	7
	227,847	216	37.4	650 <sup>c</sup>	3.5	75	50
Orion hot core .....	103,576	46	16.4	82 <sup>b</sup>	10	150	40
	227,847	216	37.4	650 <sup>c</sup>	10	150	200
CRL 618 .....	85,821	31	13.4	80 <sup>d</sup>	40	25	40

NOTE.— $E/k$  is the energy of the upper state of the transition,  $S$  is the asymmetric rotor line strength, and  $T_{\text{mb}}$  is the estimated  $3\sigma$  upper limit to the peak line intensity corrected for atmospheric absorption and beam efficiency. The upper limit to the column density  $N_{\text{limit}}$  was derived for an assumed line width  $\Delta\nu$  and rotational temperature  $T_{\text{rot}}$ , where the rotational partition function  $Z_{\text{rot}}$  is  $16.55(T_{\text{rot}})^{1.5}$ .

<sup>a</sup> Nobeyama 45 m telescope (Kawaguchi et al. 1995).

<sup>b</sup> Kitt Peak 11 m telescope (Turner 1989).

<sup>c</sup> Owens Valley 10 m telescope (Sutton et al. 1985).

<sup>d</sup> Goicoechea et al. 2001.

CO<sub>2</sub>H) or heteroatoms (N, O, P, S) in the ring will generally possess large dipole moments and are therefore good candidates for astronomical detection. In general, the strategies for inferring the existence of symmetrical molecules in space—introduction of a polar CN substituent, removal of H, addition of H<sup>+</sup>, detection of polar isovalent species, etc.—should work well for aromatic rings. Future spectroscopic studies of this type are likely to reveal important facets of the organic chemistry of interstellar clouds.

Lines of phenyl are so intense in the millimeter-wave band that it may be feasible to detect the <sup>13</sup>C isotopic species in natural abundance. Important structural information can be derived from the rotational constants of the four inequivalent <sup>13</sup>C species: specifically, the bond lengths and angles of all six carbon atoms in the ring. It also may be possible from the isotopic spectra to determine the Fermi contact hyperfine cou-

pling constant ( $b_F$ ) at different carbon atoms and thereby estimate the degree of localization of the unpaired electron in the ring. From electron spin resonance measurements of phenyl trapped in an inert matrix, it appears that  $b_F$  is very large at the carbon atom where the unpaired electron is formally localized in Figure 1. Such investigations are worth undertaking, because phenyl is a prototypical reactive ring whose geometric structure and chemical bonding are of considerable interest.

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