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# The structure of phenol(H<sub>2</sub>O) obtained by microwave spectroscopy

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The microwave spectrum of phenol(H<sub>2</sub>O) has been recorded using a pulsed molecular beam Fourier transform microwave spectrometer. Twenty *a*-type transitions have been observed and assigned. All *a*-type transitions are doublets with splittings varying from 1.13 to 4.01 MHz. These splittings are interpreted to result from the internal rotation of the water molecule. The ground state of this torsional motion is split into two levels with different spin statistical weights. Both torsional levels are treated independently as asymmetric rotor states. The resulting rotational constants are  $A=4291.486$  MHz,  $B=1092.1484$  MHz, and  $C=873.7263$  MHz for the lower torsional level ( $\sigma=0$ ) and  $A=4281.748$  MHz,  $B=1092.32955$  MHz, and  $C=873.90681$  MHz for the upper level ( $\sigma=1$ ). A fit of the molecular structure is performed by optimizing the intermolecular OO distance and two angles, describing the H-bonding arrangement. The resulting *trans*-linear structure is in reasonable agreement with the *ab initio* calculations © 1996 American Institute of Physics.

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## I. INTRODUCTION

Hydrogen bonded clusters of phenol with water have been extensively investigated in supersonic jet experiments. Intramolecular and intermolecular vibrational frequencies have been obtained using different experimental methods and the results have been compared with theoretical *ab initio* studies.<sup>1-4</sup> Vibrational frequencies of the electronically excited ( $S_1$ ) state have been measured by one and two color resonance enhanced multiphoton ionization<sup>5,6</sup> (REMPI), hole burning spectroscopy,<sup>7,8</sup> and fluorescence excitation spectroscopy.<sup>9</sup> Frequencies of the electronic ground state ( $S_0$ ) have been measured using ionization dip spectroscopy (IDS),<sup>10,5</sup> dispersed fluorescence,<sup>11</sup> and ionization-loss stimulated Raman spectroscopy (ILSRS).<sup>12</sup> The fluorescence life times of several phenol/water clusters have been determined by Colson and Lipert, using pump-probe photoionization spectroscopy.<sup>13,14</sup>

Several *ab initio* calculations at the HF and MP2 level have been performed in order to determine the structure of the clusters.<sup>1-4</sup> Additionally, vibrational analyses have been carried out. Comparing the calculated vibrational frequencies with the experimental values, a reliable assignment of several low frequency intermolecular vibrations of phenol(H<sub>2</sub>O) was achieved.<sup>4</sup> These assignments qualitatively confirm the calculated molecular structure.

Since the development of a pulsed molecular beam microwave Fourier transform spectrometer (MB-MWFT) by Balle and Flygare,<sup>15</sup> microwave spectroscopy of van der Waals<sup>16,17</sup> and hydrogen bonded clusters<sup>18</sup> found growing interest. While for the phenol monomer a considerable amount of microwave investigations have been published, no microwave spectra of the phenol(H<sub>2</sub>O) cluster have been reported. For bare phenol the complete substitution structure and the dipole moments have been determined by microwave

spectroscopy.<sup>19,20</sup> This complete  $r_s$  structure has been used for our fit of the cluster geometry. Furthermore, the barrier to internal rotation of the phenolic-OH group has been studied both experimentally<sup>21</sup> and theoretically.<sup>22</sup> In this work the result of a microwave spectroscopic investigation of phenol(H<sub>2</sub>O) is reported. The geometry fit to the rotational transitions of phenol(H<sub>2</sub>O) can be compared with *ab initio* calculations carried out for the electronic ground state. In a following publication the investigation will be extended to the electronically excited state.<sup>23</sup>

## II. EXPERIMENT

All measurements were performed using the pulsed molecular beam (MB) Fourier transform microwave (FTMW) spectrometer<sup>24,25</sup> at the University of Kiel. Phenol was kept in a small stainless-steel container upstream of the nozzle and heated to approximately 40 °C. Helium, moistened by flowing dry helium over ice at a temperature of -5 °C, was passed over the phenol sample at a pressure of 100 kPa. In the search for phenol(H<sub>2</sub>O) lines, the spectrometer was operated in a low resolution scanning mode. Figure 1 (lower trace) shows a low resolution spectrum in the 172 MHz wide region from 11378 to 11550 MHz. The scan was taken recording spectra at discrete polarizing frequencies with a step width of 0.25 MHz. Under these conditions about 100 MHz could be scanned within 1 h. Microwave pulses with a duration of 2  $\mu$ s and an average power of 50  $\mu$ W were used. 1024 data points were sampled at an interval of 100 ns and subsequently Fourier transformed. The logarithmic amplitude of the highest peak within each 5 MHz spectral range was plotted over the polarizing frequency. For the high resolution spectra (upper trace in Fig. 1) 8096 data points were sampled and Fourier transformed. A line width [halfwidth at half maximum (HWHM)] of 2 kHz at 12 GHz could be

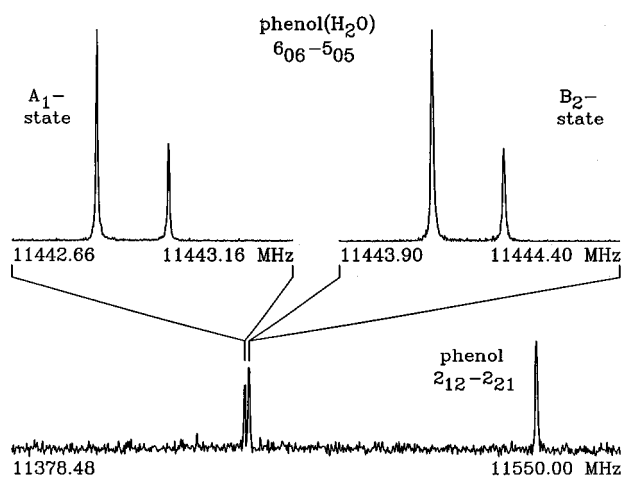


FIG. 1. 172 MHz broadband scan (lower trace) and high resolution spectrum (upper trace) of phenol and water in helium at a stagnation pressure of 100 kPa. Three lines can be recognized in the low resolution spectrum; a doublet consisting of a strong and weak transition of the  $6_{06} \rightarrow 5_{05}$  transition of phenol(H<sub>2</sub>O), and the low frequency component of the  $2_{12} \rightarrow 2_{21}$  internal rotation doublet of the phenol monomer.

achieved. The lines appear as Doppler doublets (upper trace in Fig. 1) according to the particle velocity in the beam, which is in the order of 1366 m/s for helium causing a Doppler splitting of approximately 91 kHz at 10 GHz. The asymmetry of the doublets is mainly due to instrumental effects and does not affect the accuracy of the frequency determination.

### III. RESULTS AND DISCUSSION

#### A. Analysis

Rotational constants, obtained from the *ab initio* calculations of Schütz *et al.*<sup>4</sup> were used to predict a microwave spectrum in the region from 5 to 26 GHz. From the resultant of the dipole moments of the monomers in the cluster a strong *a* type, weak *b* type, and, for symmetry reasons, no *c*-type spectrum is expected (cf. Fig. 2). After scanning several hundred MHz, we observed lines of phenol, of the water

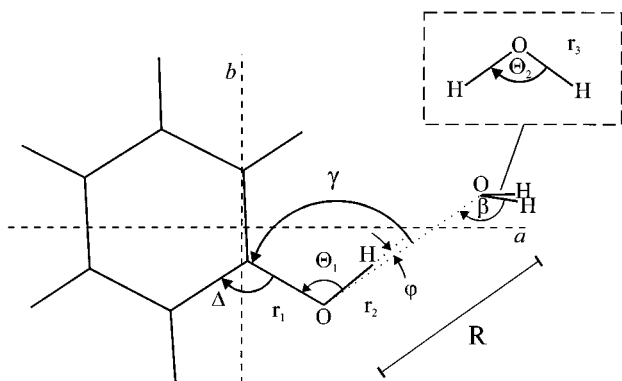


FIG. 2. Structural parameters of phenol(H<sub>2</sub>O). Additionally, the principal axes *a* and *b* are given. These axes lie in the plane of the phenol moiety.

dimer, some singlets of unknown origin, and a number of doublets with splittings varying from 1.13 to 4.01 MHz. The doublets are located close to the rotational transition frequencies of phenol(H<sub>2</sub>O) predicted from the *ab initio* data. An asymmetric rotor fit to the center frequencies of the doublets was used to obtain improved rotational constants, which, in turn, enabled us to make a better prediction and a refined fit. In this way further *a*-type lines could be measured. *b*- and *c*-type lines have not been found at all. No quantitative measurements of peak intensities can be carried out with our experimental setup, but it turns out that all doublets consist of a stronger high frequency component and a weaker low frequency component with the same intensity ratios for all doublets. Both states have been treated independently as asymmetric rotor states. The rotational constants and quartic centrifugal distortion constants for both states are determined by fitting the experimental data to a Hamiltonian described in Ref. 26. The observed frequencies are given in Table I, the results of the fit are compiled in Table II. The standard deviations of 1.7 and 0.7 kHz reflect the experimental uncertainty.

The most stable structure obtained from *ab initio* calculations contains a *trans*-linear hydrogen bonding arrangement with the H atoms of the water moiety above and below the aromatic plane.<sup>1-4</sup> The inertial defect calculated for this structure is  $-2.313 \text{ amu } \text{Å}^2$ . This value is close to the experimental inertial defects of  $-2.084$  and  $-2.396 \text{ amu } \text{Å}^2$  resulting from the two sets of rotational constants (cf., Table II). Although the  $\sigma=0$  state is less subject to vibrational averaging, its inertial defect points to a more planar structure than the  $\sigma=1$ . This may be due to a coupling of the torsional motion to an out of plane vibration of the water moiety.

To explain the doublet structure of the microwave signals an investigation of internal rotation in phenol(H<sub>2</sub>O) is required. Internal rotation leads to a splitting of the ground state torsional eigenvalues. A complete vibrational analysis of this cluster<sup>4</sup> shows a strong coupling of the in-plane bending vibration of the water molecule and the torsional motion about the OO axis. This complicated two-dimensional vibrational motion can be described more simply by the internal rotation of the H<sub>2</sub>O molecule about its C<sub>2</sub> axis measured by the angle  $\alpha$ . This motion interchanges the two equivalent H atoms of the water moiety. As this exchange does not affect the Euler angles, all rotational levels are of A symmetry. If inversion and permutation-inversion are taken into account, the rotational levels split into A<sub>1</sub> and A<sub>2</sub> symmetry, respectively. It can be shown that the torsional wave functions

$$|\nu, \sigma\rangle = \sum_{k=-\infty}^{\infty} A_k^{(\nu)} e^{i(2k+\sigma)\alpha}$$

transform like A<sub>1</sub> for  $\sigma=0$  and like B<sub>2</sub> for  $\sigma=1$  in the vibrational ground state. The spin functions transform like  $3A_1 + B_2$ . The exchange of one pair of H atoms demands for an antisymmetric total wave function (B<sub>1</sub> and B<sub>2</sub> symmetry). Since  $\Gamma_{\text{tot}} = \Gamma_{\text{tors}} \otimes \Gamma_{\text{rot}} \otimes \Gamma_{\text{ns}} \subset B_1, B_2$  it is obvious that transi-

TABLE I. Measured transitions of phenol(H<sub>2</sub>O) [*o*=observed; *c*=calculated;  $\Delta = \nu$  (strong transition) -  $\nu$  (weak transition)].

Upper level <i>J' K'_a K'_c</i>	Lower level <i>J'' K''_a K''_c</i>	Strong	<i>o-c</i> (kHz)	Weak	<i>o-c</i> (kHz)	$\Delta$ (MHz)
		transitions ( $\sigma=1$ ) (MHz)		transitions ( $\sigma=0$ ) (MHz)		
4 0 4	3 0 3	7758.0449	0.1	7756.9084	-0.2	1.1365
4 1 3	3 1 2	8278.9482	0.2	8277.5726	-0.5	1.3756
5 0 5	4 0 4	9621.8835	-0.2	9620.6580	-0.3	1.2255
5 2 4	4 2 3	9806.9896	-0.8	9805.2585	-0.2	1.7311
5 2 3	4 2 2	10 016.0061	0.4	10 013.6904	0.2	2.3157
6 1 6	5 1 5	11 064.2338	0.2			
6 0 6	5 0 5	11 444.1286	-0.5	11 442.8754	-0.4	1.2532
6 2 5	5 2 4	11 748.4982	0.3	11 746.4776	0.1	2.0206
6 3 4	5 3 3	11 847.8774	0.1	11 845.5952	0.1	2.2822
6 3 3	5 3 2	11 866.5106	-0.1	11 864.1171	-0.4	2.3935
6 1 5	5 1 4	12 355.9052	0.0	12 354.0515	0.1	1.8537
7 1 7	6 1 6	12 876.4834	0.2	12 874.2631	-0.2	2.2203
7 0 7	6 0 6	13 227.9347	-0.7	13 226.6548	-1.2	1.2799
7 2 5	6 2 4	14 213.4115	-0.1	14 209.8877	1.7	3.5238
8 0 8	7 0 7	14 981.8996	1.7	14 980.5316	3.7	1.3680
8 2 6	7 2 5	16 342.1580	0.0	16 338.1499	-1.1	4.0081
8 1 7	7 1 6	16 343.0087	-0.1	16 341.0108	0.0	1.9978
9 1 9	8 1 8	16 468.8552	-0.3			
9 0 9	8 0 8	16 717.1384	-0.6	16 715.5714	-1.7	1.5664
9 2 8	8 2 7	17 502.7896	0.0	17 500.0971	0.0	2.6925

tions originating from  $\sigma=0$  (*A*<sub>1</sub> symmetry) have a statistical weight of 1 while those originating from  $\sigma=1$  (*B*<sub>2</sub> symmetry) have a statistical weight of 3 (Fig. 3).

The experimental results support the assignment of the strong and weak transitions as originating from the *B* and *A* states, respectively. The splitting into *A* and *B* states in the electronic ground state leads to two sets of (effective) rotational constants. Thus, as observed in the microwave spectrum, each rotational transition is split into two lines due to the internal rotation of the H<sub>2</sub>O molecule as shown in Fig. 3. A perturbation theoretical treatment of the measured effec-

tive rotational constants allows in principle the determination of the potential barrier to internal rotation. This, however, demands knowledge of the energy differences between different torsional levels. These differences are unknown according to the selection rule  $\Delta\sigma=0$  which forbids transitions between *A* and *B* rotorsional levels. The high resolution UV data contain more information about the torsional splitting and therefore we performed a perturbation analysis of the torsion-rotation interaction in the following paper.<sup>23</sup>

TABLE II. Rotational and centrifugal distortion constants (representation *I'* and Watson's *A* reduction) of phenol(H<sub>2</sub>O). The least-squares fit includes all measured lines given in Table I. Single standard errors in parentheses in units of the least significant digit. The freedom coefficient is a measure of the fraction of a standard error by which parameter may be changed leaving the calculated data still within their standard deviation. For details see Refs. 29 and 30.

	Constants obtained from			
	strong transitions ( $\sigma=1$ )		weak transitions ( $\sigma=0$ )	
	Value	Freedom	Value	Freedom
<i>A</i> (MHz)	4281.748(22)	0.087	4291.486(70)	0.069
<i>B</i> (MHz)	1092.32955(36)	0.068	1092.1484(11)	0.060
<i>C</i> (MHz)	873.90681(35)	0.049	873.7263(11)	0.047
$\Delta_J$ (kHz)	0.42715(64)	0.151	0.4303(17)	0.162
$\Delta_{JK}$ (kHz)	-2.2509(65)	0.506	-2.406(17)	0.507
$\Delta_K$ (kHz)	18.6(200)	0.028	6.7(350)	0.024
$\delta_J$ (kHz)	0.11511(89)	0.110	0.1175(30)	0.100
$\delta_K$ (kHz)	1.28(20)	0.024	1.03(59)	0.022
Number of lines <i>N</i>	20		18	
Standard deviation (kHz)	0.7		1.7	
Inertial defect (amu Å <sup>2</sup> )	-2.396		-2.084	

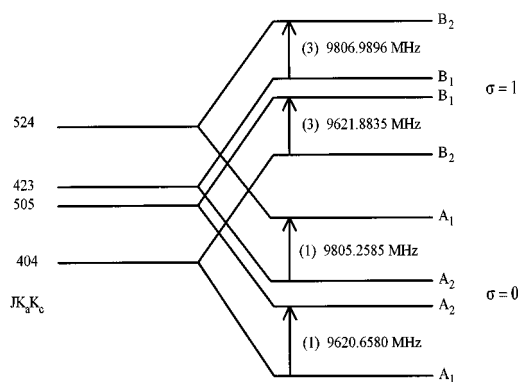


FIG. 3. Energy level scheme for the phenol(H<sub>2</sub>O) cluster. Shown are some observed transitions, their frequencies and statistical weights. For the sake of clarity the splitting of the torsional levels ( $\sigma=0,1$ ) is not drawn to scale.

## B. Molecular structure

The molecular structure of the phenol(H<sub>2</sub>O) cluster is calculated by a least-square fitting procedure. The two sets of experimental rotational constants belonging to the torsional states *A* and *B* are fitted separately to two sets of structural parameters, which can be taken as extreme values of the correct equilibrium structure parameters.<sup>27</sup>

The structures of the phenol and water monomers are taken from Larsen<sup>19</sup> and Benedict *et al.*<sup>28</sup> who carried out extensive microwave spectroscopic investigations. The bond lengths and angles of phenol and water (cf., Table III) remained unchanged in all fit procedures. The intermolecular OO distance (*R*) and the two “in-plane” angles  $\gamma$ ,  $\beta$  are optimized (cf., Fig. 2) in order to fit the experimental rotational constants. The parameter  $\beta$  is the angle between the plane of the water molecule and the OO distance, whereas  $\gamma$  (and  $\varphi$ ) describe the deviation from linearity of the hydrogen bond.

With regards to *ab initio* calculations, (cf., Table III) and the measured inertial defects, (cf., Table II) we assumed *C<sub>s</sub>* symmetry of the complex with the H atoms of the water moiety above and below the aromatic plane when performing the fit. The structural parameters are given in Table IV.

The small difference of the structural parameters obtained for the *A* and *B* states justifies the use of rotational constants which are not corrected for their perturbation by internal rotation.

The internuclear distance *R* and the angle  $\gamma$  turn out to be very sensitive to the fit, contrary to the angle  $\beta$  due to the small masses of the H atoms of H<sub>2</sub>O. Those angles  $\beta$  which describe a *trans*-linear, *cis*-linear, and linear-linear hydrogen bonding arrangement lead to a comparably good fit to the rotational constants. For different angles  $\beta$  the distance *R* and the angle  $\alpha$  vary from 2.866 to 2.888 Å and 113.5° to 116.2°, respectively. The structural parameters which result from the experimental rotational constants are very similar to those obtained from *ab initio* calculations. The interatomic OO distance calculated at the HF or MP2 level of theory is about 2.9 Å<sup>1-4</sup> if the basis sets include polarization functions (cf., Table III). This value is in close agreement with the experimental values of 2.888 and 2.880 Å. The angle  $\gamma$  calculated at the HF level using the 4-31G\*, 6-31G\*\*, and 6-311++G\*\* basis sets (114.58°, 114.92°, 115.11°) (Refs. 2 and 4) is similar to the experimental values of 113.47° and 113.72° (cf., Table IV).

Extensive *ab initio* calculations have been performed in order to obtain different local minimum energy structures of phenol(H<sub>2</sub>O),<sup>3</sup> but none of them turns out to be linear or *cis*-linear. In addition, the lack of *b*-type transitions in the phenol(H<sub>2</sub>O) MW spectrum points to a *trans*-linear arrangement of the H<sub>2</sub>O moiety, because in the case of a planar or *cis*-linear structure the dipole moment of the cluster should have a larger component in the direction of the *b* axis, cf. Fig. 3.

In the following paper,<sup>23</sup> the rotational constants of phenol(H<sub>2</sub>O) are analyzed in a different way to obtain the structural parameters. Only the position of the oxygen atom in the inertial system of the phenol monomer is required in this analysis but not the complete phenol structure with its inherent uncertainty. An O–O distance of 2.93 Å and an angle  $\gamma$  of 115.5° is obtained for the *S*<sub>0</sub> state when using this model, but it should be kept in mind that both methods strongly depend on the accuracy of the phenol structure given in Ref. 19.

TABLE III. Experimental structural parameters of phenol and H<sub>2</sub>O and calculated structural parameters of phenol(H<sub>2</sub>O) using different basis sets.

Structural parameters	Phenol (Ref. 19)	H <sub>2</sub> O (Ref. 28)	Phenol(H <sub>2</sub> O) cluster <sup>a</sup> (4-31G*) (Ref. 2)	Phenol(H <sub>2</sub> O) cluster (6-31G**) (Ref. 4)	Phenol(H <sub>2</sub> O) cluster (6-311++G**) (Ref. 4)
<i>r</i> <sub>1</sub> (Å)	1.3745		1.345	1.345	1.345
<i>r</i> <sub>2</sub> (Å)	0.9574		0.954	0.949	0.946
<i>R</i> (Å)			2.889	2.906	2.940
<i>r</i> <sub>3</sub> (Å)		0.957	0.949	0.944	0.942
$\Theta$ <sub>1</sub> (deg)	108.77		111.26	111.58	111.80
$\Delta$ (deg)	117.01		117.76	117.70	117.68
$\varphi$ (deg)			3.32	3.34	3.31
$\beta$ (deg)			138.38	135.79	147.66
$\Theta$ <sub>2</sub> (deg)		104.52	106.14	106.83	106.82

<sup>a</sup>See also, Ref. 3.

TABLE IV. Fitted structural parameters and rotational constants for the two torsional states (*A* and *B*).

	Torsional state <i>B</i> ( $\sigma=1$ )		Torsional state <i>A</i> ( $\sigma=0$ )	
	Structural parameters	Fit rotational constants	Structural parameters	Fit rotational constants
$R(\text{OO})$ (Å)	2.888		2.880	
$\beta$ (deg)	137.94		138.94	
$\gamma$ (deg)	113.47		113.72	
<i>A</i> (MHz)		4281.750		4291.476
<i>B</i> (MHz)		1092.386		1091.993
<i>C</i> (MHz)		873.814		873.967

#### IV. CONCLUSIONS

All fits of the experimental rotational constants to the phenol(H<sub>2</sub>O) structure using the known geometry of the phenol monomer in the cluster lead to nearly the same intermolecular O–O distance *R* and in-plane C–O–O angle  $\gamma$ . The calculated values of *R* and  $\gamma$  (about 2.86 Å and 114.8°) are in good agreement with the values obtained from *ab initio* calculations.

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