Resonant two-photon ionization (R2PI) time-of-flight mass spectroscopy is used to record $S_0 \rightarrow S_1$ spectra of the neutral complexes $C_6 H_6-H_2 O$, $C_6 H_6-HDO$, $C_6 H_6-D_2 O$, $C_6 H_6-(H_2 O)_2$, and $C_6 H_6-(D_2 O)_2$. In $C_6 H_6-H_2 O$, the lack of an $S_0 \rightarrow S_1$ origin transition and the presence of a splitting at $6^1$ (which is absent in $C_6 H_6-HDO$) provide vibronic level evidence that the water molecule is on the sixfold axis undergoing internal rotation about that axis. Rotational band contour analysis of the $6^1$ transitions of the isotopomers confirms this picture and also determines a ground state center-of-mass separation between $C_6 H_6$ and $D_2 O$ of $3.32 \pm 0.07 \text{ Å}$, very close to that predicted by $ab initio$ calculations. R2PI scans of the van der Waals structure in the isotopic series $C_6 H_6-H_2 O$, $C_6 H_6-HDO$, and $C_6 H_6-D_2 O$ provide tentative assignments for three of the six van der Waals modes in the complex. In $C_6 H_6-(H_2 O)_2$, rotational band contour analysis of the origin transition provides a best-fit structure in which the two water molecules reside on the same side of the benzene ring at a $H_2 O-H_2 O$ separation close to that in the free water dimer. Qualitatively, the structure of the $1:2$ cluster is thus one which maximizes the strength of the water–water hydrogen bond at the expense of a somewhat poorer interaction of the second water molecule with the benzene ring in an off-axis geometry. Several intriguing features of the structure are suggested by our analysis, but are near the limit of our ability to distinguish from band contour fitting. Among these features are (i) the on-axis water molecule is pulled slightly in toward the ring from that in the $1:1$ complex; (ii) the water dimer prefers an orientation bisecting a $C-C$ bond in the benzene ring; (iii) the water–water separation is $\sim 0.2 \text{ Å}$ less than that in the free water dimer; and (iv) the water dimer axis is tilted by about $10^\circ$ relative to the plane of the benzene ring. Finally, the van der Waals structure in $C_6 H_6-(H_2 O)_2$ and $C_6 H_6-(D_2 O)_2$ suggests the possibility of large amplitude motion in these complexes as well. We postulate that this motion involves a hindered rotation of the on-axis water molecule.

**I. INTRODUCTION**

The hydrophobic interaction between non-polar hydrocarbons and water is one of the most important forces in nature.\(^1,2\) It gives rise to the immiscibility of the bulk liquids,\(^5\) plays a major role in the conformations of proteins,\(^3\) and is central to the formation of micelles and biological membranes.\(^4\) Despite this importance, a molecular-scale description of the hydrophobic effect lacks a strong experimental underpinning, and models upon which much of our present understanding are based rely on theory alone for their support.\(^5-16\) At the basis of all such theories must be accurate, experimentally determined two-body (and ultimately many-body) intermolecular potentials. Such potentials have been determined in only a very few cases. For example, in the case of water–X interactions, the intermolecular potential is known with spectroscopic accuracy only for the case that X is Ar.\(^17(a),(b)\) or CO.\(^17(c)\)

Aromatic hydrocarbon–$H_2 O$ interactions present a special challenge to experiment and theory due to the presence of the conjugated $\pi$ system.\(^12\) $C_6 H_6$, the prototypical aromatic, is essentially immiscible in water. Yet, while the in-plane interactions of water with benzene could be readily termed hydrophobic, the polarizable $\pi$ electron density should lead to hydrophilic out-of-plane interactions. Since many of the common constituents of globular proteins (e.g., phenylalanine, tryptophan, and tyrosine) possess aromatic sidechains,\(^18\) the interactions with water play a significant role in the tertiary structure taken up by the proteins.\(^19\) The primary interaction of the aqueous solvent with these phenyl rings is thought to be via hydrogen bonding with the aromatic $\pi$ cloud, a contention which recent x-ray diffraction studies have confirmed.\(^20\)

Benzene's role as the prototypical aromatic molecule beckons detailed fundamental studies of its intermolecular interactions with water. It is not surprising, then, that significant experimental\(^21-25\) and theoretical\(^12,15,26-30\) effort has been directed at studies of benzene/water solutions and their microscopic progenitors, the gas phase clusters. In an earlier report,\(^28\) we provided vibronic level arguments constraining the geometry of the $C_6 H_6-H_2 O$ complex and presented a broad-brush overview of spectra taken of the higher clusters with two to five water molecules. Here we present a detailed account of our investigations which extend our initial report in several significant ways. Our focus in this paper will be on the $C_6 H_6-H_2 O$ and $C_6 H_6-(H_2 O)_2$ complexes, while a second paper will take up larger clusters containing up to eight water molecules. In the case of $C_6 H_6-H_2 O$, we present and analyze rotational band contours of the isotopic series

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C₆H₆–H₂O, C₆H₆–HDO, and C₆H₆–D₂O. These provide the C₆H₆/H₂O intermolecular separation and confirm that the water molecule is internally rotating about the sixfold axis of C₆H₆. The van der Waals structure of the isotopomers provides tentative assignments of three of the six van der Waals modes in the excited state. In C₆H₆–(H₂O)₃, the rotational band contour is analyzed to provide the center-of-mass positions of the three molecules, indicating that the water molecules hydrogen bond to one another on the same side of the benzene ring. The structure provides some insight to the effects of the benzene molecule on the hydrogen bonding in the water dimer itself.

II. EXPERIMENT

A schematic diagram of the molecular beam time-of-flight mass spectrometer used in the present studies is shown in Fig. 1. C₆H₆–(H₂O)₃ clusters are formed by expansion of a mixture containing C₆H₆ and H₂O in helium from a pulsed valve (General Valve) of 0.8 mm diameter operating at 20–40 Hz. The first chamber is pumped by an unbaffled 10 in. diffusion pump, while the second chamber incorporates a 6 in. diffusion pump with a baffle cooled by a closed-cycle refrigeration unit. The pulsed valve is mounted on an xyz translation stage for alignment of the valve relative to the skimmer (2 mm diam opening). Initial alignment is achieved by maximization of the pressure reading in an on-axis ion gauge located on the far side of the second chamber. Typical operating pressures in the first and second chambers are 8×10⁻³ and 2×10⁻⁶ Torr, respectively. The first chamber can be isolated from the second chamber when desired by a small, custom-made, sliding gate valve attached to a linear translation stage (not shown).

The clusters formed are resonantly ionized by the unfocused output of an excimer-pumped dye laser (Lambda LPX 120/TL3002E) doubled in a beta barium borate (BBO) crystal. Typical per pulse energies of ~0.03–1.0 mJ/pulse are used. The ions formed are accelerated to ~2800 eV in a two-stage ion source of Wiley–McLaren design and focused by an einzel lens. Ions are detected either with a 25 mm diam. chevron microchannel plate (MCP) detector at the end of the linear time-of-flight (TOF) region or after reflection in a retarding field by a 40 mm MCP detector located 76 cm below the reflectron. Typical mass resolutions (m/Δm) at mass 100 are 350 in the linear configuration and 600 in the reflectron mode. Both these figures are limited significantly by the laser pulse duration (15 ns). Nonetheless, the additional resolution of the reflectron is important in experiments on isotopomers where complete rejection of ions at adjacent masses is required. Under identical operating conditions, signal sizes are typically a factor of 2–3 times less in the reflectron than in the linear modes.

TOF mass spectra are recorded on a fast digital oscilloscope (LeCroy 9400). R2PI scans involve integrating the ion signal in 30–50 ns time windows about the arrival time(s) of the masses of interest using either a 12 channel separately gateable analog-to-digital converter, or the digital oscilloscope.

Rotational band contour scans are recorded by angle tuning an intracavity etalon under computer control. In these scans, it was particularly important to use low laser powers (<0.05 mJ/pulse) in order to avoid saturation broadening. This resulted in etalon scans being recorded with signal levels of about one ion per laser shot. Laser resolution in these scans after doubling is ~0.08 cm⁻¹ full width at half-maximum (FWHM).

C₆H₆ and distilled water were used at commercially available purities. Concentrations of the liquids are controlled by metering flows of helium over the room temperature liquid using needle valves and mixing these flows with the main flow of helium to achieve concentrations in the range 0.4%–0.7% for C₆H₆ and 0.01%–0.4% for H₂O at a total pressure of 2–4 bar.

III. RESULTS

A. Survey R2PI scans and assignments

In these studies, extensive use is made of vibronic level arguments to constrain the geometries of the clusters. To set the stage for such arguments, a brief review of the S₀→S₁ spectroscopy of C₆H₆ is provided here. The free C₆H₆ molecule has an electric dipole forbidden S₀→S₁ transition which is vibronically induced in first order by vibrations of e₂g symmetry. Thus while the S₀→S₁ origin transition is not observed in C₆H₆, S₀→S₁ (ν₃ being an e₂g in-plane ring deformation) is a prominent transition, as are members of the 6₁₀ progression (ν₁ being an a₁g ring breathing mode). Simple symmetry considerations show that, upon complexation, the H₂O molecule(s) can induce an origin transition in benzene if they break its sixfold symmetry to lower than threefold symmetric. The ratio of intensity at the origin to that at 6₁₀ is
thus a crude measure of the degree of this symmetry break-
ing in the complex.

Figures 2(a) and 2(b) present one-color R2PI scans of
the regions just to the blue of the origin and 61 transitions of
C6H6 monitoring the [C6H6-H2O] + mass in the TOF
mass spectrum. The assignment of the transitions to a given
cluster size is complicated by the efficient fragmentation
these π hydrogen-bonded complexes undergo following
photoionization.32-34 Since the details of our assignment
have been presented elsewhere,34 we present only a sum-
mary of the assignment and its experimental basis here.

The transition 50 cm⁻¹ blue shifted from C6H6 61 is
assigned to the 1:1 complex. No corresponding transition is
observed at the origin, with an upper bound on its intensity
of 0.1% that at 61. Transitions to other totally symmetric
vibrations (e.g., 10) are also not observed. The 50 cm⁻¹
band is favored over those assigned to the 1:2 complex at low
water concentrations in the expansion. The 1:1 complex un-
dergoes fragmentation following one-color R2PI with an ef-
ciciency of about 80% (extrapolated to the zero laser power
limit), indicating a π hydrogen-bonding interaction of the
H2O molecule with the ring.32 The rotational band contour
analysis which follows confirms the transition’s assignment
to the 1:1 complex.

All transitions at the origin and the closely spaced set of
transitions beginning 75 cm⁻¹ blue of C6H6 61 are assigned
to the C6H6-(H2O)2 complex (i.e., 1:2) fragmenting into
the [C6H6-H2O] + channel (i.e., 1:1) with 98% efficiency
following photoionization.32,33 Careful scans monitoring
the 1:2 mass channel confirm this assignment, as does the
analysis of the origin band’s rotational contour (see Sec.
III C). The intensity of the origin transition is 14% of that
observed at 61, indicating a strong breaking of the sixfold
symmetry of benzene by the pair of water molecules.

The twofold symmetry of the water molecule precludes
any rigid geometry for the 1:1 complex which retains three-
fold or higher symmetry. Thus, the lack of an induced S0 → S1
origin in C6H6-H2O requires that the water molecule un-
dergo large-amplitude motion in such a way that on a vibra-
tionally averaged basis, the complex retains the sixfold sym-
metry of the benzene ring. We conclude that the H2O
molecule must be on or near the sixfold axis of C6H6 under-
going internal rotation about the sixfold axis.

Figure 3 presents further evidence of internal rotation in
C6H6-H2O. There the rotational band contours of the 61
transitions of C6H6-H2O, C6H5-HDO, and C6H5-D2O are
shown. The comparison of Fig. 3(a) with Fig. 3(b)
shows that, while the C6H5-H2O 61 transition is a doublet,
the C6H5-HDO transition is a singlet. Both the lack of split-
ting in the C6H5-HDO contour and the lack of an origin
transition in either C6H5-H2O or C6H5-HDO argue
against the H2O molecule inducing a splitting by breaking
the degeneracy of the νs vibration. Instead, the splitting
arises from transitions from internal rotor levels of different
nuclear spin symmetry (i.e., ortho- and para-H2O) which
are interconverted inefficiently by collisions in the expan-
sion.17,35 The reduced symmetry of HDO allows intercon-

FIG. 2. (a) Origin and (b) 61 R2PI scans monitoring the [C6H6-H2O] +
mass channel. The frequency scale is relative to the corresponding transi-
tions of C6H6.

FIG. 3. R2PI etalon scans (±0.08 cm⁻¹ resolution) of the 61 transitions of
(a) C6H6-H2O; (b) C6H5-HDO; and (c) C6H5-D2O.
version of the corresponding levels in the $\text{C}_8\text{H}_8$–HDO complex, resulting in a single $6^0$ transition in that case. A more thorough discussion of these points is left until the molecular symmetry analysis is presented.

With benefit of hindsight, the internal rotation of the H$_2$O molecule in the $\text{C}_8\text{H}_6$–H$_2$O complex is a physically reasonable result. The large internal rotation constant of H$_2$O (20 cm$^{-1}$ from Linse’s calculations) indicates that a sixfold barrier to internal rotation of several hundred wave numbers would be necessary to quench the internal rotation of the H$_2$O molecule. This would necessitate H$_2$O sensitively distinguishing between orientations along or bisecting adjacent carbon atoms on the ring, which seems unlikely. Furthermore, the infrared studies of $\text{C}_8\text{H}_6$–H$_2$O in a matrix also indicated the presence of large amplitude motion in the complex, as does Linse’s computed potential energy surface for H$_2$O moving in the field of a $\text{C}_8\text{H}_6$ molecule.

Already at the vibronic level much of the important structural data on the complex is determined; namely, that the H$_2$O molecule is on the sixfold axis of $\text{C}_8\text{H}_6$ and is undergoing internal rotation about this axis. Given the partially resolved rotational band contours of Fig. 3, the band contour fitting is approached with two goals in mind. First, we wish to test whether the rotational band contours are consistent with the vibronic level analysis of the complexes. Second, we seek to determine the most important remaining structural feature of the complex; namely, the separation between the $\text{C}_8\text{H}_6$ and H$_2$O centers of mass.

### B. $\text{C}_8\text{H}_6$–H$\text{O}$, $\text{C}_8\text{H}_6$–HDO, and $\text{C}_8\text{H}_6$–D$_2$O

#### 1. The $G_{24}$ molecular symmetry group

The nonrigidity of the $\text{C}_8\text{H}_6$–H$\text{O}$ complex (by virtue of the free or nearly free internal rotation of the H$_2$O molecule) and the observed splitting in our spectra demands the use of permutation–inversion groups in analyzing the spectra. Figure 4(a) presents the reference configuration we have chosen for the $\text{C}_8\text{H}_6$–H$\text{O}$ complex. Feasible permutation operations in this case are those which rotate the benzene and H$_2$O tops with respect to one another about the axis joining their centers of mass (the $z$ axis). We consider as nonfeasible the rotation of the benzene ring about one of its own $C_2$ axes while holding H$_2$O fixed since this requires the breaking and reforming of the van der Waals bond. With this operational definition of feasibility, there are 24 allowed permutation–inversion operations for the $\text{C}_8\text{H}_6$–H$_2$O/D$_2$O system, designating the group as $G_{24}$.

To our knowledge, neither the class structure nor the character table of this group have been reported previously. As a result, we have carried out such an analysis using the methods outlined in Bunker. The results are presented in Table I.

Inspection of the $G_{24}$ character table shows it to be isomorphic with $D_{4h}$. Note that the $\{78\}$ operation which exchanges protons (deuterons) on the H$_2$O (D$_2$O) molecule plays the role that the inversion operation does in $D_{6h}$. To avoid confusion between the $D_{6h}$ point group designations appropriate to the free benzene molecule and the $G_{24}$ molecular symmetry group designations of $\text{C}_8\text{H}_6$–H$_2$O, we have used $+/-$ designations for the symmetry with respect to the $\{78\}$ operation rather than the $g/u$ designations of $D_{6h}$.

The molecular symmetry group appropriate to $\text{C}_8\text{H}_6$–HDO is $G_{12}$, in which all operations involving $\{78\}$ are removed. The $G_{12}$ character table is isomorphic with $C_{3v}$ and the reduction of symmetry designations from $G_{24}$ to $G_{12}$ can be made trivially by dropping the $+/-$ superscript.

#### 2. Nuclear spin statistical weights

The intensities of transitions in the rotational band contour are determined in part by the ground state nuclear spin statistical weights. The Pauli exclusion principle places constraints on the allowed symmetries of the total internal wave functions of the complex $\Gamma_{\text{int}}$ as indicated in Table II. The symmetries of the ground state rotation–torsion levels are then determined by

$$\Gamma_{\text{int}} = \Gamma_{\text{nuc}} \times \Gamma_{\text{tor}} \times \Gamma_{\text{rot}}$$

The nuclear spin symmetries of the $\text{C}_8\text{H}_6$–H$_2$O isotopomers
are readily determined (Table II). For symmetry considerations, the torsional motion can be treated as a completely free internal rotation of the H$_2$O molecule about the $z$ axis. Then $\psi_{rot} \propto e^{i\theta}$, where $\psi$ is the internal rotor angle defined in Fig. 4 and $m$ is the internal rotation quantum number. The dependence of the angle $\rho$ on the symmetry operations is included in the $G_24$ character table (Table I) and the resulting symmetries of the torsional wave functions are listed in Table II.

Due to the free internal rotation of the H$_2$O molecule in our model, the ground state rotational wave functions of C,H$_2$-H$_2$O are those of a symmetric top $|J K \rangle$. The symmetries of these levels and the resulting nuclear spin statistical weights of the rotation–torsion levels are given in Table III, where we have included rotation–torsion coupling in the $m = \pm 1$ levels.  

### 3. Nuclear spin symmetry and cooling in the supersonic expansion

There are a total of 12 different symmetry types for the nuclear spin states in C,H$_2$-H$_2$O/D$_2$O. Of these eight are allowed by the Pauli principle. Many examples are now known in which little population transfer occurs between states of different nuclear spin symmetry in the collisional cooling of the expansion. This spin selectivity in the cooling is readily seen in C,H$_2$ itself, where Beck et al. observed rovibronic transition intensities in $6_1^1$ characterized by a rotational temperature of 0.5 K, but with a nuclear spin “temperature” which was essentially room temperature. Levels of a given nuclear spin symmetry thus effectively have different zero point energies determined by the lowest energy state of that nuclear spin symmetry.

In C,H$_2$-H$_2$O(D$_2$O), the $m = 0$ ground state rotational levels are of antisymmetric (symmetric) nuclear spin symmetry with respect to the exchange of water’s protons (deuterons), while $m = \pm 1$ levels are symmetric (antisymmetric). Thus, cooling from $m = \pm 1$ to $m = 0$ is inhibited in C,H$_2$-H$_2$O/D$_2$O. The observed consequence is that in C,H$_2$-H$_2$O/D$_2$O, $Am = 0$ transitions will occur originating from both $m = 0$ and $m = \pm 1$. If either the average orientation or internal rotor barrier varies slightly upon electron excitation, these two transitions will be split, resulting in the observed doubling in the C,H$_2$-H$_2$O spectrum of Fig. 3. We assign the blue-shifted (red-shifted) peak to the $m = 0$ ($m = \pm 1$) transition. This assignment is borne out by scans taken with different nozzle backing pressures which show that the red-shifted peak ($m = 1$) decreases slightly in intensity relative to the blue-shifted peak ($m = 0$) at higher backing pressures.

Based on nuclear spin statistics alone, transitions from the $m = \pm 1$ levels in C,H$_2$-H$_2$O should be approximately three times the intensity of the corresponding transitions from $m = 0$ (Table III). We observe an $m = \pm 1/ m = 0$ intensity ratio of about 1.5, indicating some enhancement in the population of $m = 0$ C,H$_2$-H$_2$O complexes in the expansion. The most likely explanation for the low $m = \pm 1$ population is that small differences in the binding energy of C,H$_2$-H$_2$O($m = \pm 1$) complexes relative to $m = 0$ com-

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**Table I: The $G_{24}$ molecular symmetry group.**

<table>
<thead>
<tr>
<th>$E$</th>
<th>$R_1^0$</th>
<th>$R_2^0$</th>
<th>$R_3^0$</th>
<th>$R_4^0$</th>
<th>$R_5^0$</th>
<th>$R_6^0$</th>
<th>$R_7^0$</th>
<th>$R_8^0$</th>
<th>$R_9^0$</th>
<th>$R_{10}^0$</th>
<th>$R_{11}^0$</th>
<th>$R_{12}^0$</th>
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<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
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<td>(1)</td>
<td>(1)</td>
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</tr>
</tbody>
</table>

**Table II: The equivalent rotation of the molecule fixed (A, B, C) axes through $\pi$ radians about $z$ axis.**

<table>
<thead>
<tr>
<th>$E$</th>
<th>$R_1^0$</th>
<th>$R_2^0$</th>
<th>$R_3^0$</th>
<th>$R_4^0$</th>
<th>$R_5^0$</th>
<th>$R_6^0$</th>
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<th>$R_{10}^0$</th>
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</tr>
</tbody>
</table>
plexes lead to preferential formation of $C_6H_6-H_2O(m=0)$ in binary displacement reactions of the type\textsuperscript{15,39}

$$C_6H_6-H_2O(m = \pm 1) + H_2O(l,\omega)$$

$\rightarrow C_6H_6-H_2O(m = 0) + H_2O(l,\omega)$

in the expansion. In $C_6H_6-D_2O$, the $m = \pm 1$ contribution is only weakly observed in the spectrum, largely because the $m = \pm 1/m = 0$ intensity ratio is six times less in $C_6H_6-D_2O$ than it is in $C_6H_6-H_2O$ (Table II). In $C_6H_6-HDO$, no nuclear spin symmetry restrictions are placed on the cooling of $m = \pm 1$ to $m = 0$, effectively removing the transitions due to $m = \pm 1$ levels from the spectrum so that only a low-intensity shoulder remains.

In $C_6H_6-H_2O$, the presence of the doublet complicates and congests the rotational band contour and hinders its fitting significantly. However, the $C_6H_6-D_2O$ contour exhibits considerable structure and only minor interference from $m = \pm 1$, suggesting that our primary efforts in band contour fitting be focused on the $C_6H_6-D_2O$ contour.

4. Rotational band contour analysis

a. $C_6H_6-D_2O$. The rotational band contours of Fig. 3 are $e_i$ transitions of the isotopomers. By virtue of the degeneracy of $v_6$ (which is not broken by a freely internally rotating $D_2O$), the excited state levels populated possess vibrational angular momentum. As a result, our analysis must take into account three sources of angular momentum about the top axis due to vibration ($\xi$), internal rotation ($m$), and overall rotation ($k$). In the free internal rotor limit, the energy level expression is simply

$$E_{jkm} = BJ(J + 1) + (A_j - B)k^2 + (A_j + A_i)m^2 - 2A_i mk - 2\xi k A_j + 2\xi m A_j,$$

where the last three terms couple the three types of angular momenta.\textsuperscript{37} In the expression, $A_j$ is the benzene frame rotational constant about the $a$ axis (the $z$ axis), $A_i$ is the top rotational constant (which is essentially that of the internally rotating $D_2O$ molecule), and $\xi$ is the effective Coriolis coupling parameter for $6^1$. We further assume that (i) the transition moment of the $e_i$ transition remains in the plane of the benzene ring as it is in the free benzene molecule; (ii) the $D_2O$ and $C_6H_6$ molecules are not deformed upon complexation; (iii) $C_6H_6$ undergoes the same change in geometry upon electronic excitation as it does in the free molecule; and (iv) the nuclear spin temperature within a given $m$ internal rotor level is $T_{spin} = 300$ K. We apply selection rules appropriate to a perpendicular transition of a symmetric top with a free internal rotor $\Delta J = 0$, $\pm 1$; $\Delta K = 0$, $\pm 1$; $\Delta m = 0$. Since in the $C_6H_6-D_2O$ spectrum the $m = \pm 1$ contour appears only weakly, much of our fitting has been done using only the $m = 0$ contour with the $m = \pm 1$ contour playing a role only in the final stages of fitting. For the $m = 0$ contour

<table>
<thead>
<tr>
<th>Rotational wave function</th>
<th>$\Gamma_{rot}$</th>
<th>$H_2O$</th>
<th>$D_2O$</th>
<th>$HDO$</th>
<th>Positive</th>
<th>Negative</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k = 0$, $J$ even</td>
<td>$A_i^+$</td>
<td>10</td>
<td>60</td>
<td>60</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>$k = 0$, $J$ odd</td>
<td>$A_i^+$</td>
<td>10</td>
<td>60</td>
<td>60</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>$k = 6q + 1$</td>
<td>$E_i^+$</td>
<td>22</td>
<td>132</td>
<td>132</td>
<td>60</td>
<td>54</td>
</tr>
<tr>
<td>$k = 6q + 2$</td>
<td>$E_i^+$</td>
<td>18</td>
<td>108</td>
<td>108</td>
<td>66</td>
<td>84</td>
</tr>
<tr>
<td>$k = 6q + 3$</td>
<td>$B_i^+ + B_i^+$</td>
<td>28</td>
<td>168</td>
<td>168</td>
<td>54</td>
<td>54</td>
</tr>
<tr>
<td>$k = 6q + 6$</td>
<td>$A_i^+ + A_i^+$</td>
<td>20</td>
<td>120</td>
<td>120</td>
<td>66</td>
<td>66</td>
</tr>
</tbody>
</table>

*a* These levels occur in degenerate pairs based on the sign of $k + m$; positive $= |+k, +m| \pm |k, -m|$; negative $= |+k, -m| \pm |k, +m|$.

*b* In $C_6H_6-HDO$, the $G_{10}$ symmetry designations are obtained by removing the (+) superscript.
within this model, the only adjustable parameters are $B'$, $B''$, $\xi$, and $T_{\text{rot}}$, and the spectrum is that of a perpendicular transition of a rigid symmetric top.

Figure 5 presents our best fit of the C$_6$H$_6$-D$_2$O spectrum within this model. Note the high quality of the fit both in terms of positions and in its reproduction of the intensity alternations present in the experimental contour. The best fit parameters are given in Table IV. Not unexpectedly, $\xi$ is, within our error bars, the same as that for the $6_i$ transition of free benzene. All essential features are reproduced admirably with only the $m = 0$ contour. In the best fit presented in the figure, we have included a small contribution from the $m = \pm 1$ contour which gives a better fit to the red tail in the experimental contour for $\Delta A_I = -2.2$ cm$^{-1}$.

This fit lends considerable support to our vibronic level arguments for a C$_6$H$_6$-D$_2$O geometry in which D$_2$O is on the sixfold axis, freely internally rotating about that axis. It also provides us with a measure of the separation of masses of C$_6$H$_6$ and D$_2$O in the ground and first excited singlet states, yielding a ground state intermolecular separation of $3.32 \pm 0.07$ Å and excited state separation of $3.23 \pm 0.04$ Å.

b. C$_6$H$_6$-HDO. The reduction in symmetry in going from D$_2$O to HDO has one major consequence in the present context—it allows cooling from $m = \pm 1$ to $m = 0$ internal rotor levels in the complex. We noted earlier that even on a qualitative level, the rotational band contour of the $6_i$ transition of C$_6$H$_6$-HDO confirms our model of an internally rotating water molecule by virtue of its being a single band (from $m = 0$) rather than the doublet observed for the $6_i$ contour of C$_6$H$_6$-H,O. It is nevertheless puzzling that the shape of the contour is so different from that in C$_6$H$_6$-H$_2$O and C$_6$H$_6$-D$_2$O in having a strong Q branch present. In fact, the $m = 0$ rotational band contours of C$_6$H$_6$-D$_2$O and C$_6$H$_6$-HDO would be expected to be nearly identical to one another.

Given the sparsity of structure in the spectrum, we can only hope to address qualitatively the source of the difference in rotational band contours. Within our model, the only adjustable parameter which is capable of qualitatively changing the shape of the rotational band contour in a physi-

![Figure 5](image1.png)

![Figure 6](image2.png)

**TABLE IV. Summary of the best-fit parameters in the rotational band contour analysis.**

<table>
<thead>
<tr>
<th></th>
<th>$A'$</th>
<th>$A''$</th>
<th>$B'$</th>
<th>$B''$</th>
<th>$C'$</th>
<th>$C''$</th>
<th>$\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$H$_6$-D$_2$O</td>
<td>0.0906</td>
<td>0.0948</td>
<td>0.0652</td>
<td>0.0636</td>
<td>...b</td>
<td>...b</td>
<td>-0.56</td>
</tr>
<tr>
<td>C$_6$H$_6$-HDO</td>
<td>0.0906</td>
<td>0.0948</td>
<td>0.0676</td>
<td>0.0635</td>
<td>...b</td>
<td>...b</td>
<td>-0.05</td>
</tr>
<tr>
<td>C$_6$H$_6$-(H$_2$O)$_2$</td>
<td>0.0762</td>
<td>0.0784</td>
<td>0.0511</td>
<td>0.0520</td>
<td>0.0461c</td>
<td>0.0467c</td>
<td>...d</td>
</tr>
</tbody>
</table>

*Coriolis coupling constant in the $6_i$ bands of the 1:1 complex. See the text for details.
*The 1:1 complex is fit as a perpendicular transition of a symmetric top.
*The 1:2 complex is fit as a rigid asymmetric top.
*The rotational contour of the 1:2 complex was taken at the origin which lacks vibrational angular momentum.
c. $C_6H_6-H_2O$. The rotational band contour of $C_6H_6-H_2O$ is complicated by the overlapping bands present in the spectrum. The overall contour is dominated by what is likely the $m = \pm 1$ contour in the red portion of the contour. Unfortunately, unlike the $m = 0$ contour which is independent of the magnitude of the barrier to internal rotation, the $m = \pm 1$ band contour is sensitive to this barrier through the internal rotation/overall rotation coupling term. In Fig. 7, we present $m = 0$ and $m = \pm 1$ band contours for $C_6H_6-H_2O$ at the best-fit geometry of $C_6H_6-D_2O$ in the limit of completely free internal rotation for the $H_2O$ molecule. The spacing of the structure that is present in the experimental spectrum is qualitatively consistent with the calculated contours. However, we are unable to fit the overall contour to the same level of satisfaction as in $C_6H_6-D_2O$. To our consolation, in the high resolution $S_1$ contour of $C_6H_6-N_2$, where internal rotation is also present, $\sim 30\%$ of the observed lines were unassigned and suggested to be due to the $m = \pm 1$ contour in that complex.

Part of the reason for this less than satisfactory fit appears to be our assumption of completely free internal rotation. As the barrier to internal rotation is raised, the splitting and appearance of the two bandheads in the $m = \pm 1$ contour changes significantly. In addition, it is possible that the observed band contour is actually a composite of three rather than two bands. In fact, the calculations of Linse predict a near degeneracy of the $m = \pm 1$ level with the intermolecular bending mode in the plane of the water molecule. This level is of $a_{\pi}$ symmetry and thus cannot cool to the $m = 0$ level, just as the $m = \pm 1$ level cannot. By contrast, in $C_6H_6-D_2O$, the $m = \pm 1$ state has dropped well below the bending mode so that no such interference should exist.

We have in fact obtained a satisfactory fit to the $C_6H_6-H_2O$ transition by including contributions from all three bands, but cannot claim uniqueness given the large number of adjustable parameters such a fit allows. As with $C_6H_6-HDO$, higher resolution spectra are needed before a full account of the observed rotational band contour in $C_6H_6-H_2O$ can be given.

5. van der Waals structure in $C_6H_6-H_2O$, $C_6H_6-HDO$, and $C_6H_6-D_2O$.

In recording spectra of the van der Waals structure of the complexes, we are motivated by the insight such spectra can give to the form of the potential energy surface governing the interactions of $C_6H_6$ and $H_2O$. Six intermolecular modes are formed upon complexation of $H_2O$ to $C_6H_6$. Due to the internal rotation of the $H_2O$ molecule about the $z$ axis, the descriptions and symmetries of the intermolecular modes are best defined in terms of an axis system which rotates with the water molecule [Fig. 4(b)] rather than one which is fixed on benzene [Fig. 4(a)] as is done in our reference configuration. We define this axis system so that the $z$ and $x'$ axes coincide, the $x'$ axis is placed in the plane of the water molecule along $H_2$, and the $y'$ axis is perpendicular to this plane. Three of the intermolecular modes will be correlated asymptotically with translations of the water molecule: (i) a stretch along the $z$ ($z'$) axis $s_z$; (ii) a bending mode in the plane of the water molecule along $x'$, $b_{op}$; and (iii) a bending mode out of the plane of the water molecule along $y'$, $b_{op}$. The other three modes are correlated with rotations of water: (iv) internal rotation about $z$; (v) torsion of the water molecule in its plane about the $y'$ axis, $\phi_{op}$, and (vi) torsion of the water molecule "out of plane" about the $x'$ axis, $\phi_{op}$. These modes are illustrated in Fig. 4(c) and their symmetries in $G_{3v}$ and $G_{12}$ are collected in Table V.

The facile formation of the 1:2 complex, coupled with its extremely efficient fragmentation into the 1:1 channel f...
TABLE V. Symmetry and assigned frequencies of the van der Waals modes in \( \text{C}_6\text{H}_6-\text{H}_2\text{O} \), \( \text{C}_6\text{H}_6-\text{HDO} \), and \( \text{C}_6\text{H}_6-\text{D}_2\text{O} \).

<table>
<thead>
<tr>
<th>Symmetry Assignment (cm(^{-1}))</th>
<th>( \text{H}_2\text{O} )</th>
<th>( \text{HDO} )</th>
<th>( \text{D}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_\sigma )</td>
<td>( a_1^* )</td>
<td>43</td>
<td>43</td>
</tr>
<tr>
<td>( \phi_\rho )</td>
<td>( a_1^* )</td>
<td>94</td>
<td>77</td>
</tr>
<tr>
<td>( s_z )</td>
<td>( a_1^* )</td>
<td>60</td>
<td>61</td>
</tr>
<tr>
<td>( b_\pi )</td>
<td>( a_2^* )</td>
<td>\ldots</td>
<td>\ldots</td>
</tr>
<tr>
<td>( \phi_\phi )</td>
<td>( a_2^* )</td>
<td>\ldots</td>
<td>\ldots</td>
</tr>
<tr>
<td>( \phi_\delta )</td>
<td>Internal rotation*</td>
<td>\ldots</td>
<td>\ldots</td>
</tr>
</tbody>
</table>

* The symmetries of the internal rotor levels are given in Table II.

The absolute frequencies of the \( \epsilon \) transitions of \( \text{C}_6\text{H}_6-\text{H}_2\text{O} \), \( \text{C}_6\text{H}_6-\text{HDO} \), and \( \text{C}_6\text{H}_6-\text{D}_2\text{O} \) are 38 658, 38 665, and 38 659 cm\(^{-1}\), respectively.

In approaching an assignment of these features, several comments should be made. First, we are guided in our assignments by the \textit{ab initio} calculations of the ground state \( \text{C}_6\text{H}_6-\text{H}_2\text{O} \), \( \text{HDO} \), and \( \text{D}_2\text{O} \) intermolecular modes by Linse.\(^{26}\) Since the R2PI spectra determine excited state frequencies, the comparison can be only semiquantitative; nevertheless, the small intensity of the van der Waals transitions suggests only modest changes in the vibrational frequencies upon electronic excitation. Second, isotopic substitution will produce only slight changes in the stretching and bending mode frequencies (which involve motion of the water molecule as a whole), while the frequencies of the torsional modes will be quite sensitive to isotopic substitution. Third, Table V indicates, the reduced symmetry of the \( \text{C}_6\text{H}_6-\text{HDO} \) complex results in the \( b_\sigma \) and \( \phi_\rho \) fundamentals becoming allowed (\( a_1 \) in \( G_{13} \)), even though they are forbidden in \( \text{C}_6\text{H}_6-\text{H}_2\text{O} \) and \( \text{C}_6\text{H}_6-\text{D}_2\text{O} \) (\( a_1^* \) in \( G_{12} \)). Fourth, Linse's calculations\(^{26}\) predict that significant state mixing between the intermolecular modes will be more the rule than the exception. This is suggested already in a cursory inspection of the spectra which reveals little in the way of harmonic progressions which can aid the assignment. Such mixing can significantly change intensities and positions from their uncoupled values and can render the assignment of the transition in terms of uncoupled normal modes approximate at best.\(^{42}\) We thus present here a consistent set of assignments which must await future calculations and/or dispersed fluorescence data as further tests of their reliability.

Of the six van der Waals modes present in the complex, only the stretching mode fundamental (\( s_z \)) will be allowed in \( \text{C}_6\text{H}_6-\text{H}_2\text{O} / \text{D}_2\text{O} \). Even overtones and totally symmetric combination bands of the bends and torsions may also be present. In \( \text{C}_6\text{H}_6-\text{HDO} \), the in-plane bend and torsion will also have allowed fundamentals (Table V). Only two bands of significant intensity appear in the spectra of all three isotopomers with little change in frequency; namely, those 60 and 86 cm\(^{-1}\) blue of their respective \( \epsilon \) transitions. One of these is almost certainly the stretch \( s_z \), while the other is likely an

![Diagram](https://via.placeholder.com/150)

**FIG. 8. R2PI scans taken under conditions in which the van der Waals structure built on \( \epsilon \) transition is observed clearly in the 1:1 mass channel.**

(a) \( \text{C}_6\text{H}_6-\text{H}_2\text{O} \); (b) \( \text{C}_6\text{H}_6-\text{HDO} \); and (c) \( \text{C}_6\text{H}_6-\text{D}_2\text{O} \). The frequency scale given is relative to the \( \epsilon \) transition of the complex at 38 658, 38 665, and 38 659 cm\(^{-1}\), respectively. The water concentration for each scan was kept at 0.01%-0.02% to minimize interference from the 1:2 complex fragmenting into the 1:1 mass channel as noted in the figure. The feature at 170 cm\(^{-1}\) in the \( \text{C}_6\text{H}_6-\text{HDO} \) scan is not due to \( \text{C}_6\text{H}_6-\text{HDO} \). See the text for a discussion of the proposed assignments.

TABLE VI. Observed van der Waals transitions built on the \( \epsilon \) transitions of \( \text{C}_6\text{H}_6-\text{H}_2\text{O} \), \( \text{C}_6\text{H}_6-\text{HDO} \), and \( \text{C}_6\text{H}_6-\text{D}_2\text{O} \).

<table>
<thead>
<tr>
<th>( \text{H}_2\text{O} )</th>
<th>( \text{HDO} )</th>
<th>( \text{D}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative frequency* (cm(^{-1}))</td>
<td>Relative intensity</td>
<td>Relative frequency* (cm(^{-1}))</td>
</tr>
<tr>
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<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>0.22</td>
<td>43</td>
</tr>
<tr>
<td>86</td>
<td>0.18</td>
<td>61</td>
</tr>
<tr>
<td>110</td>
<td>0.12</td>
<td>77</td>
</tr>
<tr>
<td>141</td>
<td>0.18</td>
<td>86</td>
</tr>
<tr>
<td>124</td>
<td>0.25</td>
<td>124</td>
</tr>
</tbody>
</table>

* The absolute frequencies of the \( \epsilon \) transitions of \( \text{C}_6\text{H}_6-\text{H}_2\text{O} \), \( \text{C}_6\text{H}_6-\text{HDO} \), and \( \text{C}_6\text{H}_6-\text{D}_2\text{O} \) are 38 658, 38 665, and 38 659 cm\(^{-1}\), respectively.
even overtone of one of the bends which would also show little sensitivity to isotopic substitution. Since reasonable arguments can be given for either band being the symmetric stretch, we use the $C_6H_6-HDO$ spectrum of Fig. 8(b) to guide our choice. Two new transitions at 43 and 77 cm$^{-1}$ are observed in the $C_6H_6-HDO$ spectrum with good intensity. Their absence in the $G_{14}$ isotopomers suggests an assignment of the features as the in-plane bend and torsion fundamentals which become allowed in $C_6H_6-HDO$. Linse's$^{26}$ calculations in the ground state place the in-plane bend and torsion at 20 and 50 cm$^{-1}$, respectively. As a result, we tentatively assign the 43 cm$^{-1}$ peak as $b_{\nu_0}$ and the 77 cm$^{-1}$ transition as $b_{\nu_0}$. Then the 86 cm$^{-1}$ transition in the three isotopomers is assigned as $b_{\nu_0}$, relegating the stretch fundamental to the transition at 60 cm$^{-1}$.

Finally, we tentatively assign the peaks at 141, 124, and 113 cm$^{-1}$ in $C_6H_6-H_2O/HDO/D_2O$ as the totally symmetric $b_{\nu_{1}}$, $b_{\nu_{2}}$, $b_{\nu_{3}}$ combination band. Based on the assignments of $b_{\nu_{1}}$ and $b_{\nu_{2}}$ in $C_6H_6-HDO$, the combination band is predicted at 120 cm$^{-1}$. Corrections of $\delta_{\nu_{0}}$ for changes in the reduced mass of the torsion accompanying isotopic substitution predict the combination bands to lie at 137, 120, and 109 cm$^{-1}$ in the isotopic series, close to that observed.

C. $C_6H_6-(H_2O)_2$ and $C_6H_6-(D_2O)_2$

We indicated earlier that, unlike the single water molecule in $C_6H_6-H_2O$, the pair of water molecules in $C_6H_6-(H_2O)_2$ induce an origin intensity which is about 14% that at $6_0^1$. One may conclude on this basis that the water molecules bind to benzene in such a way as to reduce the symmetry of the benzene $\pi$ cloud to lower than threefold symmetric.

By the same token, the degeneracy of the $6_0^1$ transition is observed (Fig. 2) to be split by 5.4 cm$^{-1}$ in $C_6H_6-(H_2O)_2$. The case of $C_6H_5D$ (whose $6_0^1$ transition is split by 3.2 cm$^{-1}$ even though its origin transition is not observed$^{43}$) suggests that mass effects, rather than electronic effects are of primary importance in determining the $6_0^1$ splitting. In $C_6H_6-(H_2O)_2$, the observed $6_0^1$ splitting thus suggests that the water molecules are aligned preferentially along a given axis of the benzene ring, so that more mass is effectively moved when the benzene ring deforms along one axis than along the other. Both these vibronic level arguments are consistent only with a distinctly asymmetric structure for $C_6H_6-(H_2O)_2$, even on a vibrationally averaged basis.

1. Rotational band contour analysis

Figure 9 (a) shows the rotational band contour of the origin transition in $C_6H_6-(H_2O)_2$. Unlike the $C_6H_6-H_2O$ contour, the spectrum shows no evidence of tunneling splittings at our resolution, though such may be present at higher resolution. As a result, we have carried out a rotational band contour analysis of this transition treating the $C_6H_6-(H_2O)_2$ complex as a rigid asymmetric top. We have been guided in our fitting by Monte Carlo searches for the lowest energy structures for $C_6H_6-(H_2O)_2$ using the semiempirical intermolecular potential of Severance and Jorgenson.$^{14}$ Figure 9(b) presents our best-fit contour which reproduces nicely both the positions and intensities of the partially resolved structure in the experimental contour.

The strong $Q$ branch observed in the contour is characteristic of a mixed contour containing components of the transition moment along both $A$ and $B$ axes of the cluster. Roughly speaking, the $A$ axis of the complex follows the line joining the benzene center of mass to the water dimer center of mass. If the direction of the transition moment remains in the plane of the benzene ring in $C_6H_6-(H_2O)_2$, moving the water molecules off the sixfold axis increases the percent $A$ character in the contour, thereby increasing the $Q$-branch intensity as observed.

The rotational constants obtained from the fit are summarized in Table IV. At the present experimental resolution, the rotational band contour is sensitive only to the positions of the centers of mass of the two water molecules and not to the position of their hydrogen atoms. The water center-of-mass positions are shown in Fig. 10, together with pictures of two possible structures in which the hydrogen atoms have been placed in chemically intuitive positions.

Several features of the structure of $C_6H_6-(H_2O)_2$ deserve highlighting.

(a) The best-fit structure places the water molecules on the same side of the benzene ring at a water–water separation of 2.75 ± 0.1 Å. This distance is close to, but slightly less than that in the free water dimer (2.98 Å).

(b) As indicated in Fig. 10(b), the band contour is best fit by a structure in which the on-axis water molecule is pulled in by ~0.3 Å from that in the $C_6H_6-H_2O$ complex.

(c) The water dimer intermolecular axis is tilted down slightly (by about 10°) toward the benzene ring from a geometry parallel to the benzene ring.

(d) The mixed $A/B$ character of the band contour iden-
FIG. 10. (a) Best fit center-of-mass positions of the water molecule(s) in the \( \text{C}_6\text{H}_6-\text{H}_2\text{O} \) and \( \text{C}_6\text{H}_6-(\text{H}_2\text{O})_2 \) complexes. The center-of-mass separation distances between the subunits are benzene-water\#1 = 2.97 Å, \( \theta_1 = 97^\circ \); benzene-water\#2 = 3.39 Å, \( \theta_2 = 46^\circ \); water\#1-water\#2 = 2.75 Å. Errors in distances are \( \pm 0.10 \) Å, in angles \( \pm 2^\circ \). Two plausible geometries are given at the top of the figure since the hydrogen positions are completely undetermined at our resolution. The complex may be able to tunnel between these structures. See the text for further discussion.

The major conclusion of our fitting is obvious—the strong hydrogen bonding between the two water molecules results in a geometry for the \( \text{C}_6\text{H}_6-(\text{H}_2\text{O})_2 \) cluster in which both molecules reside on the same side of the ring in a slightly modified water dimer geometry. In some sense, the cluster has taken the first step along the way toward immiscibility.
TABLE VII. Observed van der Waals transitions built on the $X_e$ - $S_e$ origins of C$_6$H$_6$-(H$_2$O)$_2$ and C$_6$H$_6$-(D$_2$O)$_2$.

<table>
<thead>
<tr>
<th>Relative frequency$^*$ (cm$^{-1}$)</th>
<th>Relative intensity</th>
<th>Relative frequency$^*$ (cm$^{-1}$)</th>
<th>Relative intensity</th>
</tr>
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</tr>
<tr>
<td>36</td>
<td>0.12</td>
<td>70</td>
<td>0.27</td>
</tr>
</tbody>
</table>

$^*$The absolute frequencies of the $C_6$ transitions of C$_6$H$_6$-(H$_2$O)$_2$ and C$_6$H$_6$-(D$_2$O)$_2$ are 38 167 and 38 166 cm$^{-1}$, respectively.

The analogous scans of clusters containing HDO were not recorded due to interference caused by the fragmentation of several isotopomers (e.g., C$_6$H$_6$-(HDO)$_2$, C$_6$H$_6$-(HDO)(H$_2$O), and C$_6$H$_6$-(HDO)D$_2$O) into the possible 1:1 mass channels. The frequencies and intensities of the main features in the C$_6$H$_6$-(H$_2$O)$_2$ and C$_6$H$_6$-(D$_2$O)$_2$ spectra are summarized in Table VII. Given the limited data set and the large number (12) of intermolecular modes in the cluster, definitive assignments will need to await dispersed fluorescence or stimulated emission pumping experiments and/or calculations of the intermolecular frequencies in C$_6$H$_6$-(H$_2$O)$_2$.

Nevertheless, a few comments can be made. First, of the 12 intermolecular modes of the cluster, we can roughly categorize six as being associated with motion within the water dimer, three with translation of the water dimer relative to benzene (two bends and a stretch), and the other three with torsional modes of a water dimer subunit relative to benzene. The sparse set of observed transitions are due to the small number (12) of intermolecular modes in the cluster, definitive assignments will need to await dispersed fluorescence or stimulated emission pumping experiments and/or calculations of the intermolecular frequencies in C$_6$H$_6$-(H$_2$O)$_2$.

Lower frequency bands show large frequency changes upon isotopic substitution, indicating that significant H/D motion is involved. The most intriguing of these is the satellite band of only 5.4 cm$^{-1}$ built on both the origin and 16 cm$^{-1}$ transitions in C$_6$H$_6$-(H$_2$O)$_2$. Given the comparatively light masses of the water molecules, it seems highly unlikely that this transition is a fundamental of a vibration. A corresponding band is not readily observed in C$_6$H$_6$-(D$_2$O)$_2$. However, a careful look at the origin in C$_6$H$_6$-(D$_2$O)$_2$ suggests that the 5.4 cm$^{-1}$ splitting in C$_6$H$_6$-(H$_2$O)$_2$ has been reduced so that the origin band is actually a composite of two transitions in C$_6$H$_6$-(D$_2$O)$_2$. This anomalous frequency change suggests a tunneling splitting as its source. Given the 3:1 ratio in C$_6$H$_6$-(H$_2$O)$_2$, it seems likely that the two bands reflect a hindered internal rotation of one of the water molecules. Then, in a manner analogous to the C$_6$H$_6$-H$_2$O complex, cooling would be prohibited between the two lowest internal rotor levels in the ground state, giving rise to a splitting in transitions to the corresponding levels in the excited state due to a change in the barrier to internal rotation. One might suspect that the on-axis H$_2$O molecule could most easily undergo this motion since this motion does not involve breaking and reforming the water-water hydrogen bond as the hindered rotation of the other water molecule would. Once again, fully rotationally resolved spectra of the bands of interest are needed to confirm or deny these arguments.

IV. DISCUSSION AND CONCLUSION

Table VIII collects the various theoretical predictions for the global and local minima in the C$_6$H$_6$-H$_2$O intermolecular potential energy surface. All calculations agree that the lowest energy structure for the complex places the water molecule on the sixfold axis in a $\pi$ hydrogen-bonded configuration. A structure which places the water molecule in the plane of the benzene ring has at most about 60% as strong binding.$^{28}$ The $ab$ initio calculations$^{26-29}$ predict a benzene--H$_2$O center-of-mass separation in the range 3.21-3.33 Å, while semiempirical calculations are ~0.2 Å smaller.$^{14,23}$ Calculated binding energies for the complex are in the range of 3.0-4.0 kcal/mol. In terms of the more subtle features of the water orientation relative to benzene, all but one calculation predict that the water molecule lies in a plane perpendicular to the benzene plane. However, there is more variation in the predicted orientation of water within this plane, i.e., whether water is $\pi$ hydrogen bonded to benzene via one or two hydrogen atoms. The semiempirical potential of Severance and Jorgenson$^{14}$ favor a single hydrogen atom down, while others show large-amplitude bending motion in which both hydrogens sample the benzene ring equally already at the zero point level.$^{23,26-29}$

The major results of our work are in substantial agreement with the calculational results, especially the $ab$ initio calculations. The experimental structure places the water molecule's center of mass on or very near the sixfold axis. The center-of-mass separation is 3.32 ± 0.07 Å, very much in keeping with the calculations. At the present resolution, we cannot determine the vibrationally averaged orientation
of the water molecule relative to benzene. Nevertheless, the
doubling in the $C_6H_6-H_2O$ spectrum, its disappearance in
the spectrum of $C_6H_6-D_2O$, and the calculated fit to the
band positions and intensities using the $G_{24}$ nuclear spin sta-
tistics provide strong arguments that the exchange of hydro-
gen on water is feasible, independent of the precise orienta-
tion of the water molecule. As pointed out earlier, this is not
surprising given the large internal rotation constant of $H_2O$
which would require a very large $V_6$ barrier to quench inter-

cal rotation in the complex.

There are several obvious features of the intermolecular
interactions which have not been addressed adequately by
this study. Among these are an experimental determination
of the ground state intermolecular vibrations (which would
allow direct comparison with Linse's calculations),
more accurate measures of the binding energy of the complex,
and fully rotationally resolved scans in both the ground and ex-
cited states. We are presently pursuing experiments aimed at
the first two deficiencies.

The present study has also provided the major features
of the structure of the 1:2 complex. This structure is best
described as a water dimer in which one of the water mole-
cules is hydrogen bonded to benzene's $\pi$ cloud. Both the
rotational band contour and vibronic level arguments are
consistent with a vibrationally averaged structure in which
internal rotation about the sixfold axis of benzene is no long-
er feasible. The direction of the transition moment points to
a preference of the off-axis water molecule for a position
which bisects a C-C bond in the ring. There are also several
features of the structure which are near the limit of our reso-
lution and which by that fact deserve closer attention both
experimentally and computationally. Most notable among
these are the benzene–water intermolecular separation
which is reduced relative to $C_6H_6-H_2O$, the water–water
separation which is reduced relative to $(H_2O)_2$, and the
tilting of the water dimer axis relative to the benzene plane.
On the experimental front it will be important (i) to deter-
mine ground state frequencies and assignments of the inter-
molecular modes; (ii) to record and analyze high resolution
scans capable of resolving tunneling splittings in the com-
plex, and (iii) to determine accurate $C_6H_6-H_2O$ and
$H_2O-H_2O$ binding energies in the cluster.

From the computational viewpoint, the Monte Carlo
simulations using the intermolecular potential of Severance
and Jorgenson has already proven successful in reproduc-
ing the gross features of the $C_6H_6-(H_2O)_2$ structure. How-
ever, to the author's knowledge, there are no ab initio calcu-
lations on benzene–$(H_2O)_2$. Ab initio predictions of the
geometry of $C_6H_6-(H_2O)_2$ and its vibration–libration
structure would be highly desirable.

ACKNOWLEDGMENTS

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carrying out Monte Carlo simulations on the 1:2 cluster.
Acknowledgment is also made to the Donors of the Petrole-

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**TABLE VIII. Geometry and binding energy of benzene–$H_2O$. A comparison of our experimental data with theoretical predictions for the 1:1 complex.**

<table>
<thead>
<tr>
<th>Source</th>
<th>$\phi_{in}$ (degree)</th>
<th>$\phi_{op}$ (degree)</th>
<th>$R_{cm}$ (Å)</th>
<th>$E_{bind}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0</td>
<td>0</td>
<td>3.21</td>
<td>3.04</td>
</tr>
<tr>
<td>b</td>
<td>0</td>
<td>$\sim$5</td>
<td>3.21</td>
<td>3.15</td>
</tr>
<tr>
<td>c</td>
<td>0</td>
<td>0</td>
<td>3.28</td>
<td>1.90</td>
</tr>
<tr>
<td>d</td>
<td>0</td>
<td>0</td>
<td>3.28</td>
<td>3.01</td>
</tr>
<tr>
<td>e</td>
<td>0</td>
<td>52</td>
<td>3.33</td>
<td>3.81</td>
</tr>
<tr>
<td>f</td>
<td>0</td>
<td>$\sim$60</td>
<td>3.1</td>
<td>1.44</td>
</tr>
</tbody>
</table>

This work: H bonding

$3.32 \pm 0.07$  1.63$<D_6^2<2.78$

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*a* Reference 28.
*b* Reference 26.
*c* Reference 29 (a).
*d* Reference 27.
*e* Reference 14.
*f* Reference 23.

Water molecule coplanar with the benzene ring with the water oxygen atom pointing towards the benzene
hydrogen atom.

The precise minimum-energy orientation is not determinable at the present experimental resolution. Indirect
measures are used to surmise that the $H_2O$ molecule is hydrogen bonded to benzene's $\pi$ cloud (see the text).

The $R_{cm}$ is given for $C_6H_6-D_2O$.

Bounds on the binding energy are determined from dispersed fluorescence spectra. Note that these are $D_6$
rather than the $D_6$ values of the calculations. Details will be published elsewhere.

The in-plane torsional angle is defined so that $0'$ corresponds to the $C_2$ axis of $H_2O$ aligning along the $C_6$
axis of benzene with the water hydrogens pointing down. See Fig. 4(b).

The out-of-plane torsional angle is defined so that $0'$ corresponds to the plane of the water molecule lying
perpendicular to the plane of the benzene ring. See Fig. 4(b).
um Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Grant No. CHE-9108376) for their support of this research.


