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# Competition between van der Waals and Hydrogen Bonding Interactions: Structure of the *trans*-1-Naphthol/$N_2$ Cluster

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The excitation energy in the multiphoton ionization spectrum of the *trans*-1-naphthol/$N_2$ cluster shows only a small red shift with respect to isolated naphthol, indicating a van der Waals $\pi$-bound structure rather than a hydrogen-bonded one. To confirm this interpretation, high-level electronic structure calculations were performed for several $\pi$- and hydrogen-bonded isomers of this cluster. The calculations were carried out at the second order Møller−Plesset (MP2) level of perturbation theory with the family of correlation consistent basis sets up to quintuple-$\zeta$ quality including corrections for the basis set superposition error and extrapolation to the MP2 complete basis set (CBS) limit. We report the optimal geometries, vibrational frequencies, and binding energies ($D_e$), also corrected for harmonic zero-point energies ($D_0$), for three energetically low-lying isomers. In all calculations the lowest energy structure was found to be an isomer with the $N_2$ molecule bound to the $\pi$-system of the naphthol ring carrying the OH group. In the CBS limit its dissociation energy was computed to be $D_0 = 2.67$ kcal/mol (934 $cm^{-1}$) as compared to $D_0 = 1.28$ kcal/mol (448 $cm^{-1}$) for the H-bound structure. The electronic structure calculations therefore confirm the assignment of the experimental electronic spectrum corresponding to a van der Waals $\pi$-bound structure. The energetic stabilization of the $\pi$-bound isomer with respect to the hydrogen-bonded one is rather unexpected when compared with previous findings in related systems, in particular phenol/$N_2$.

## Introduction

The structure of noncovalently bonded clusters still represents a challenge for both experiment and theory.[1−3] Ongoing research on this class of systems is mainly fueled by their importance as models for solvation and condensed-phase chemistry, but also by the role of noncovalent interactions in determining the structure of macromolecules, in particular biomolecules.[4] While numerous clusters solvated by rare gas atoms have been studied in great detail,[5−8] much less is known about clusters solvated by molecules such as nitrogen. Binding to the $\pi$-system of chromophores such as benzene,[9] halogenated benzenes,[10] *p*-difluorobenzene,[11] toluene,[12] and pyrimidine[13] has been previously investigated both experimentally and computationally.

Aromatic alcohols such as phenol or naphthol are a particularly interesting group of chromophores because they offer two different binding sites for ligands: the OH group and the $\pi$-system of the aromatic ring. While the proton acidity favors a H-bound structure, the polarizability of the aromatic ring can also result in $\pi$-bound structures. For phenol clusters a preference for H-bonded $N_2$ was found, as evident from the red shift of the $S_1 \leftarrow S_0$ transition and the observed red shift in the frequency of the O−H stretching vibration.[14−16] Subsequent rotationally resolved measurements confirmed this assumption[17] and resulted in good agreement between experimental data and ab initio calculations. On the other hand, clusters of less acidic chromophores offering two binding sites with nitrogen, such as aniline,[18] ethylaniline,[19] and aminophenol,[20] were shown to be van der Waals bound.

Since 1-naphthol and phenol have similar acidities, the H-bound structure was also expected to be more stable for the 1-naphthol cluster. Surprisingly, our earlier multiphoton ionization (MPI) experiments on various 1-naphthol clusters yielded only a small red shift of the $S_1 \leftarrow S_0$ transition for the cluster with one $N_2$ ligand and intermolecular vibrational wavenumbers that were more similar to the ones observed in $\pi$-bound clusters.[21] To our surprise, we found in accompanying RI-MP2 computations that two $\pi$-bound isomers were lower in energy than the H-bound isomer. However, the cc-pVTZ basis set employed in these earlier studies did not contain diffuse basis functions, which may be considered important for the proper description of van der Waals forces of noncovalently bound systems. In addition, no vibrational frequencies were computed; thus only the relative $D_e$ values were compared rather than including the effects of zero-point corrections ($D_0$).

In the present study we interpret the experimental data by comparing them with the results of highly accurate ab initio calculations employing basis sets with diffuse functions for a proper description of dispersion forces. We also report harmonic frequencies for all cluster structures to obtain binding energies corrected for zero point energy contributions, $D_0$. Several low-energy isomers of the *trans*-1-naphthol/$N_2$ cluster were investigated. Most previous studies of van der Waals bound clusters of aromatic molecules were carried out at the second order perturbation (MP2) level of theory and typically employed basis sets of double-$\zeta$ quality, which are hardly sufficient to quantitatively account for an accurate description of the absolute and relative energetics of structures with different bonding characteristics. Additionally, diffuse functions are necessary in order to obtain a better description of polarization effects.[22] In this study we carry out an extrapolation of the cluster binding energy,

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including corrections for basis set superposition error, to the MP2 complete basis set (CBS) limit for a comparably large complex. This includes the use of basis sets as large as quintuple $\zeta$. Previously, only small hydrogen-bonded complexes have been investigated at this level;[23−25] only recently the results for larger clusters of water with up to 20 molecules have been reported at this level of accuracy.[26−28]

## Computational Methods

Initially the geometries and ground electronic state dissociation energies $D_e$ (alternatively binding or stabilization energies $E$ are used, defined as $E = -D_e$) of several stable *trans*-1-naphthol/$N_2$ cluster structures were optimized at the Møller−Plesset second order perturbation theory within the valence electrons only (frozen core) approximation. The resolution of identity approximation RI-MP2 as implemented in the Turbomole program[29] was used for these initial calculations. This approximation uses an auxiliary basis set in computationally costly four-center integrals. The cc-pVTZ basis set and the RI auxiliary basis (also of the cc-pVTZ type) were used as supplied by the program.

Due to the flat nature of the potential energy surface describing these clusters, the SCF convergence for the energy was set to $10^{-9}$ hartree. For the optimization of the cluster structures we chose $10^{-8}$ hartree for the total energy convergence threshold and $10^{-5}$ hartree/bohr, respectively hartree/degree for the maximum norm of the Cartesian gradient as the convergence criterion.

The geometries of the three most stable isomers from these initial optimizations were subsequently refined during optimizations at the MP2 level of theory with the aug-cc-pVDZ and aug-cc-pVTZ basis sets.[30,31] During our earlier studies of small and medium size water clusters,[32] we have concluded that their geometries are converged at the MP2/aug-cc-pVTZ level of theory and, to converge the absolute binding energies, single-point calculations with larger basis sets (aug-cc-pVQZ and aug-cc-pV5Z) are required at the MP2/aug-cc-pVTZ optimized geometries. This strategy was followed in the present investigation. Vibrational frequencies for all three structures were computed at the MP2 level of theory with the aug-cc-pVDZ basis set. These calculations were carried out using the NWChem suite of codes[33] on phase 2 of the newly acquired massively parallel Hewlett-Packard supercomputer at the Molecular Science Computing Facility in the William R. Wiley Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory. The 11.4 teraflop supercomputer consists of 1900 1.5 GHz Intel Itanium 2 processors coupled together with Quadrics interconnect. The system has 7 terabytes of memory and over 1/2 petabyte of total disk storage, making it a uniquely balanced resource for computational chemistry. The largest single-point MP2 calculation was performed with the aug-cc-pV5Z basis set, which is comprised of the segmented contractions [6s5p4d3f2g1h] + (1s1p1d1f1g1h) for the carbon, nitrogen, and oxygen atoms and [5s4p3d2f1g] + (1s1p1d1f1g) for the hydrogen atoms, respectively, encompassing a total of 2291 contracted Gaussian basis functions. All calculations were performed under $C_1$ symmetry.

The cluster binding energies $E$ are computed as

$$\Delta E(n//n') = E_{AB}(n//n') - E_A(n//n') - E_B(n//n') \qquad (1)$$

where $E_{AB}(n//n')$ is the MP2 energy of the naphthol−$N_2$ complex with basis set $n$ ($n = 2, 3, 4, 5$ for the aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z sets, respectively) at the MP2 optimal geometry obtained with basis set $n'$ ($n' = 2, 3$), and $E_A(n//n')$ and $E_B(n//n')$ are the corresponding MP2 energies of the isolated fragments. In this notation the cluster binding energies $\Delta E(2//2)$, $\Delta E(3//3)$, $\Delta E(4//3)$, and $\Delta E(5//3)$ were computed.

The basis set superposition error (BSSE) correction was estimated via the function counterpoise (fCP) method[34] including the fragment relaxation terms[35] which arise from the change in the intramolecular geometry of each of the monomers in the cluster minimum. A total of four additional calculations (each monomer with the full cluster basis at the cluster and isolated geometries) are therefore required for each BSSE calculation. Note that the MP2 geometry optimization was performed on the BSSE-uncorrected potential energy surface.

The MP2/CBS (complete basis set) limit, $\Delta E_{CBS}$, was estimated for both the uncorrected and BSSE-corrected binding energies following an approach that is based on a least-mean-squares fitting of the binding energies $\Delta E$ with respect to the cardinal number of the basis set $n$ ($n = 2-5$) using the following equations:

(i) The first is a polynomial of inverse powers of 4 and 5 (4−5 polynomial):[36−38]

$$\Delta E = \Delta E_{CBS} + \gamma/(l_{max} + 1)^4 + \delta/(l_{max} + 1)^5 \qquad (2)$$

where $l_{max}$ is the value of the highest angular momentum function in the basis set.

(ii) The second is an exponential dependence[39−41] on the cardinal number of the basis set $n$ ($n = 2, 3, 4, 5$ for the sets of double through quintuple zeta quality, respectively):

$$\Delta E = \Delta E_{CBS} + a \exp(-\beta n) \qquad (3)$$

## Results

**Experiments.** The experimental details are described elsewhere.[21] In brief, [1 + 1] MPI spectra of 1-naphthol/$N_2$ clusters were recorded in a standard molecular beam apparatus equipped with a time-of-flight (TOF) mass spectrometer. The frequency-doubled output of a Nd:YAG laser pumped dye laser was employed for cluster excitation. The [1 + 1] REMPI spectrum of the 1-NpOH/($N_2$) clusters is depicted in the upper trace of Figure 1.

It is dominated by a single peak, assigned to the origin transition and red-shifted by about 14 cm$^{-1}$ relative to free *trans*-1-NpOH (bottom trace of Figure 1). In principle, 1-naphthol can exist in two different rotamers, with the OH group oriented in either the cis or trans position with respect to the aromatic ring, but from the analysis of the electronic spectrum of free 1-naphthol by Knee and co-workers[42,43] it is evident that neither the band origin nor the low-lying fundamentals of the cis isomer can be ionized in a [1 + 1] experiment. By comparing the cluster spectrum with that of free *trans*-1-NpOH, several intramolecular vibrations can be identified in the spectrum of the cluster, confirming that we indeed observe the region of the $S_1 \leftarrow S_0$ transition. A scan at better resolution, depicted in the lower trace of Figure 2, shows that the major peak, assigned to the origin, is accompanied by a low-frequency structure with several bands corresponding to a progression in either one or two intermolecular modes. In addition, a band around +56 cm$^{-1}$ is identified. To test whether all bands originate from the same isomer, spectral hole burning (SHB) spectra were recorded with the burn laser tuned to the most intense band in the REMPI spectrum (Figure 2, upper trace). All bands observed in the REMPI spectrum were indeed present in the SHB spectrum;

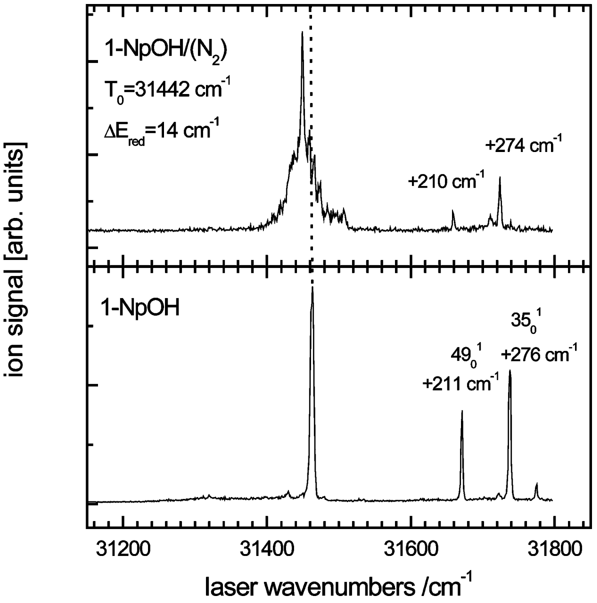

**Figure 1.** [1 + 1] REMPI spectrum of the 1-NpOH/($N_2$) cluster (upper trace). It is slightly red-shifted by 14 $cm^{-1}$ relative to the spectrum of free 1-naphthol (lower trace).

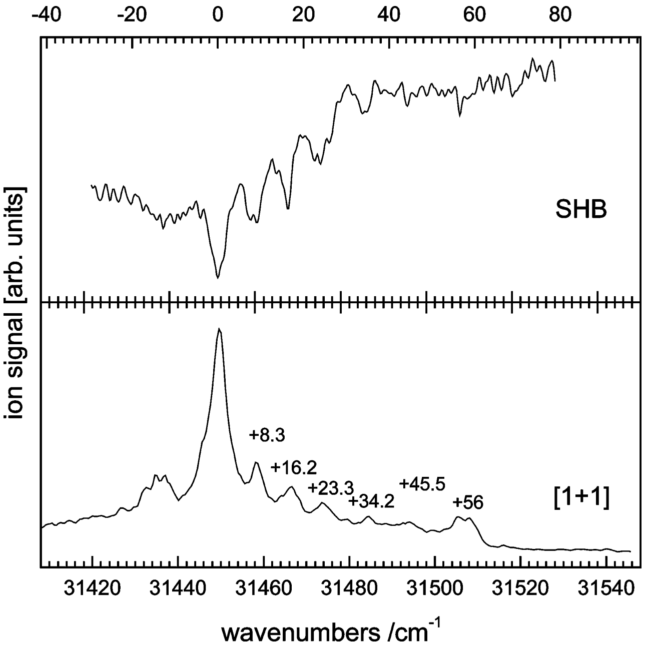

**Figure 2.** [1 + 1] REMPI (lower trace) and SHB (upper trace) spectra of the 1-NpOH/$N_2$ cluster in the energy region of the $S_1 \leftarrow S_0$ origin. In the SHB spectrum the signal laser was tuned to the origin transition of the cluster.

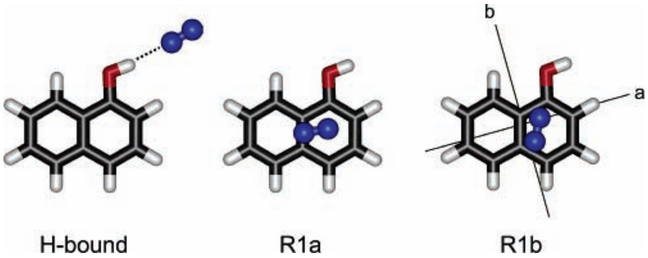

**Figure 3.** Geometries of the three lowest energy isomers of the *t*-1-NpOH/$N_2$ cluster considered in this study. The center-of-mass coordinate system of *t*-1-NpOH used to discuss the $\pi$-bound isomers is given for the **R1b** structure.

**TABLE 1: Geometric Parameters at the Minimum Energy Geometries of the $\pi$-Bound Isomers Obtained at the MP2/aug-cc-pVTZ Level of Theory**[a]

| | $N_2$ COM in *t*-1-NpOH COM coord system (Å) | | | angle (deg) between $N_2$ and | |
|---|---|---|---|---|---|
| isomer | *a* | *b* | *c* | *ab*-plane | *a*-axis |
| **R1b** | 0.560 | −0.414 | 3.086 | 3.8 | 62.5 |
| **R1a** | 0.408 | −0.330 | 3.106 | 5.0 | 7.8 |

[a] The position of the $N_2$ center of mass (COM) is given in the naphthol center-of-mass coordinate system. The position along the *c*-axis corresponds to the distance between $N_2$ and the aromatic ring.

**TABLE 2: Minimum Energy Geometry of the H-Bound Isomer at the MP2/aug-cc-pVDZ Level of Theory**

| | H−N distance (Å) | OHN angle (deg) | HNN angle (deg) |
|---|---|---|---|
| H-bound isomer | 2.24 | 172.7 | 176.4 |
| phenol/$N_2$[17] | 2.40 | 168.1 | 172.3 |

thus at first glance there seems to be no evidence for a second isomer. SHB experiments on some of the weaker bands were unsuccessful.

Surprisingly the red shift of the $S_1 \leftarrow S_0$ origin is much closer to the value observed for the 1-NpOH/Ar cluster ($\Delta E_{red} = 15$ $cm^{-1}$) and to nitrogen clusters of substituted benzenes than to the value observed in phenol/$N_2$. Although the red shift does not provide in itself evidence for any structure because it is a measure of the difference in binding energies between the ground state and the excited state, we would expect a significant increase in the binding energy upon excitation for a hydrogen-bound cluster, and thus a larger red shift. In addition, the vibrational intermolecular frequencies are considerably smaller than in phenol/$N_2$[14] and more similar to the frequencies observed in 1-NpOH/Ar.[21]

**Computations.** Figure 3 shows the three isomers of the cluster that are considered in the present investigation: one bound via a hydrogen bond to the naphthol OH group (left-hand side) and two bound by van der Waals interactions to the aromatic $\pi$-system. The two $\pi$-bound isomers differ by the orientation of the $N_2$ ligand relative to the ring. In one isomer (termed **R1a**) the nitrogen ligand lies almost perpendicular to the C−O bond; in the second one (termed **R1b**) the nitrogen molecule is oriented close to the short axis of the ring and has only a small angle relative to the C−O bond.

These two structures were identified as the two energetically most favorable $\pi$-bound structures in RI-MP2 calculations. The relevant intermolecular geometry parameters are summarized in Tables 1 ($\pi$-bound) and 2 (H-bound). Note that our earlier RI-MP2 results yielded similar geometric parameters. For the $\pi$-bound isomers we chose to report the position of the center of mass of the nitrogen molecule relative to the center-of-mass coordinate system of isolated *trans*-1-naphthol. The *a*- and *b*-axes of this coordinate system are drawn in the **R1b** structure on the right-hand side of the figure. The *c*-axis is oriented perpendicular to the naphthol plane. The distances between the ring and the $N_2$ are 3.086 and 3.106 Å, respectively, significantly less than the ones computed for the benzene/$N_2$ and toluene/$N_2$ complexes ($r_0 = 3.46$ and 3.48 Å, respectively).[12,44] However, due to the large anharmonicity of the potential, the experimentally measurable bond length $r_0$ might be longer by 20−30 pm. In both isomers the $N_2$ is tilted out of the aromatic plane by a small angle (3.8° and 5°, respectively).

For the H-bound isomer our MP2/aug-cc-pVTZ optimizations yielded a minimum energy structure that has $C_1$ symmetry. However, the MP2/aug-cc-pVTZ energy difference between this

**TABLE 3: MP2 Energies (in hartrees) of the Three Cluster Isomers and the Corresponding Fragments for the Different Basis Sets**[a]

| molecular system | aug-cc-pVDZ | aug-cc-pVTZ | aug-cc-pVQZ | aug-cc-pV5Z |
|---|---|---|---|---|
| $N_2$ | −109.280 650 3 | −109.364 799 9 | −109.393 666 1 | −109.404 028 9 |
| 1-*trans*-NpOH | −459.807 930 2 | −460.202 122 9 | −460.329 500 0 | −460.373 754 8 |
| H-bound isomer | −569.092 894 2 | −569.570 964 7 | −569.726 768 0 | −569.781 132 6 |
| $\pi$-bound isomer (**R1b**) | −569.096 325 4 | −569.573 206 7 | −569.728 686 9 | −569.783 008 8 |
| $\pi$-bound isomer (**R1a**) | −569.096 098 9 | −569.573 050 2 | −569.728 490 8 | −569.782 811 5 |

[a] The energies correspond to the optimized geometries with the aug-cc-pVDZ and aug-cc-pVTZ basis sets and to single point energy calculations with the aug-cc-pVQZ and aug-cc-pV5Z sets at the MP2/aug-cc-pVTZ optimal geometries for all molecular systems.

**TABLE 4: Dissociation Energies $D_e$ and $D_0$ (in Parentheses) in kcal/mol of the Three Cluster Isomers for the Different Basis Sets Used in This Study**[a]

| | | H-bound isomer | $\pi$-bound isomer (**R1a**) | $\pi$-bound isomer (**R1b**) |
|---|---|---|---|---|
| RI-MP2/cc-pVTZ | uncorrected | 2.35 | 3.08 | 3.23 |
| | BSSE-corrected | 1.76 | 2.08 | 2.22 |
| MP2/aug-cc-pVDZ | uncorrected | 2.707 (1.993) | 4.718 (4.249) | 4.860 (4.360) |
| | BSSE-corrected | 1.641 (0.932) | 2.384 (1.916) | 2.499 (1.999) |
| MP2/aug-cc-pVTZ | uncorrected | 2.536 (1.827) | 3.845 (3.374) | 3.943 (3.442) |
| | BSSE-corrected | 1.858 (1.149) | 2.817 (2.347) | 2.932 (2.430) |
| MP2/aug-cc-pVQZ | uncorrected | 2.257 (1.547) | 3.341 (2.873) | 3.464 (2.965) |
| | BSSE-corrected | 1.929 (1.221) | 2.942 (2.473) | 3.063 (2.562) |
| MP2/aug-cc-pV5Z | uncorrected | 2.101 (1.392) | 3.154 (2.685) | 3.279 (2.779) |
| | BSSE-corrected | | | 3.116 (2.630) |
| MP2/CBS (exponential) | uncorrected | | 2.65 (2.47) | 3.07 (2.57) |
| | BSSE-corrected | 1.96 (1.25) | 2.99 (2.52) | 3.13 (2.63) |
| MP2/CBS (polynomial) | uncorrected | 1.91 (1.20) | 2.81 (2.34) | 3.02 (2.52) |
| | BSSE-corrected | 1.99 (1.28) | 3.03 (2.56) | 3.17 (2.67) |

[a] Zero-point corrections were estimated from harmonic vibrational frequencies with the aug-cc-pVDZ basis set. In addition, the $D_e$ values obtained during earlier RI-MP2 calculations are also noted. The CBS estimates (see text) are also listed.

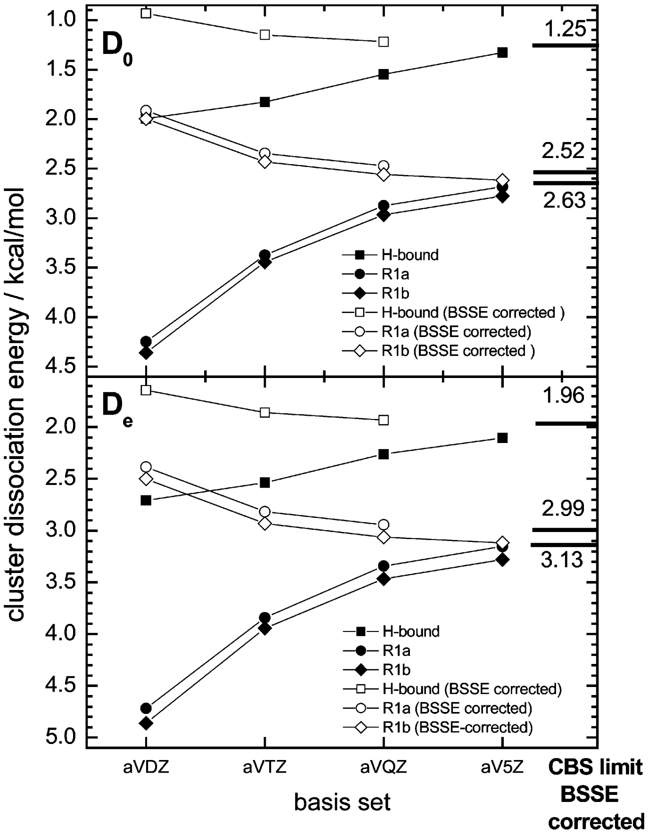

**Figure 4.** Variation of the cluster dissociation energies $D_e$ (lower panel) and $D_0$ (upper panel) with basis set for the three most stable cluster isomers of *t*-1-NpOH/$N_2$. The filled symbols correspond to the MP2 uncorrected energies; the open symbols correspond to BSSE-corrected ones. The $\pi$-bound isomer (**R1b**) is the most stable one with all basis sets employed in this study. The closeness of the energies to the CBS limit (exponential fit), indicated in the figure, shows that convergence has been practically achieved with the largest basis sets used.

minimum and the lowest energy structure optimized under $C_s$ symmetry is quite small (≈0.007 kcal/mol or 2.5 $cm^{-1}$); thus when zero point energy effects are considered, the cluster will be quasi-planar. As can be seen from Figure 3 and Table 2, the orientation of the nitrogen molecule with respect to the OH group deviates slightly (3.6°) from linearity. Overall, the geometry of the H-bound isomer is similar to the structure calculated for the phenol/$N_2$ cluster.[17,45]

The MP2 energies (in hartrees) for all three isomers and the individual fragments are summarized in Table 3 for the different basis sets used in this study. The dissociation energies $D_e$ and $D_0$ are listed in Table 4 and depicted graphically as filled symbols in Figure 4. Two observations are evident from the results with all basis sets used in this study: (i) both $\pi$-bound isomers are lower in energy than the H-bound isomer and (ii) the (**R1b**) isomer with the $N_2$ molecule oriented close to the short axis of the ring is the minimum energy structure. For example, the MP2/aug-cc-pV5Z results yield $D_0 = 2.779$ kcal/mol (972 $cm^{-1}$) for the (**R1b**) isomer compared to 1.392 kcal/mol (487 $cm^{-1}$) for the H-bound isomer. Inclusion of zero point energy corrections lowers the binding energy of the H-bound isomer slightly more than that of the $\pi$-bound isomer. Furthermore, the magnitude of the dissociation energies of all isomers tends to decrease upon increasing the size of the basis set. Since this effect is more pronounced for the $\pi$-bound isomers, the energy difference between them and the H-bound isomer becomes smaller. While the energy difference between the most stable (**R1b**) and the H-bound isomers is $\Delta D_0 = 2.367$ kcal/mol with the smallest aVDZ basis set, it reduces to $\Delta D_0 = 1.387$ kcal/mol with the largest aV5Z basis.

The strong basis set dependence of the isomer binding energies dictates the need to correct for the basis set superposition error (BSSE) to obtain an accurate description of binding in this noncovalently bound system. Therefore, we carried out the corresponding corrections for BSSE as well as complete basis set extrapolations using either a polynomial or an exponential fit (see previous section). The results are also summarized in Table 4 and represented as open symbols in Figure 4. The BSSE-corrected binding energies display a smaller relative variation with basis set than the uncorrected ones. For

**TABLE 5: Harmonic Wavenumbers of the Intermolecular Vibrational Modes (in cm$^{-1}$) of the Three Energetically Most Favorable Isomers**

| | H-bound isomer | $\pi$-bound isomer (**R1a**) | $\pi$-bound isomer (**R1b**) |
|---|---|---|---|
| $\nu_5''$ | 18.3 ($\beta_a$) | 26.9 ($\tau_{\|\|}$) | 36.5 ($\tau_{\|\|}$) |
| $\nu_4''$ | 19.6 ($\beta_b$) | 31.6 ($\beta_a$) | 31.4 ($\beta_a$) |
| $\nu_3''$ | 70.2 ($\gamma_{\text{in plane}}$) | 46.9 ($\beta_b$) | 48.6 ($\beta_b$) |
| $\nu_2'$ | 75.1 ($\sigma$) | 82.8 ($\tau_\perp$) | 92.7 ($\sigma$) |
| $\nu_1''$ | 82.0 ($\gamma_{\text{out of plane}}$) | 91.0 ($\sigma$) | 105.3 ($\tau_\perp$) |

instance, the difference $\Delta D_0$ between the most stable (**R1b**) and the less stable H-bound isomer is now 1.07 kcal/mol (aug-cc-pVDZ set) and 1.34 kcal/mol (aug-cc-pVQZ set). Furthermore, the dissociation energies in the CBS limit with and without BSSE corrections lie within 0.06 kcal/mol (20 cm$^{-1}$, CBS exponential fit) for the **R1b** isomer and 0.08 kcal/mol (28 cm$^{-1}$, CBS polynomial fit) for the H-bound isomer, an indication of the quality of the extrapolation process (should be close to zero since both uncorrected and BSSE-corrected binding energies should converge to the same value at the complete basis set limit). Finally, the dissociation energies obtained with the aV5Z basis are very close to the CBS limit, a fact that indicates that convergence to the complete basis set limit has been practically achieved with the largest of the basis sets used in this study. The small difference between the aV5Z calculation with and without BSSE correction and the CBS extrapolation confirms that the basis set is appropriate for computing dissociation energies in naphthol/nitrogen clusters.

It is also of interest to compare the results of the present work with the aVTZ basis with the ones of our earlier RI-MP2/cc-pVTZ computations. As evident from Table 4, the dissociation energies for the H-bound isomer are very similar with and without the additional diffuse functions. On the other hand, the BSSE-corrected binding energies of the $\pi$-bound isomers are underestimated by almost 1 kcal/mol (~350 cm$^{-1}$) when compared to the current CBS values. Thus augmenting the basis set by suitable diffuse functions considerably improves the description of the dispersion forces relevant in $\pi$-bound complexes.

The computed harmonic frequencies for the intermolecular vibrational modes of the three cluster isomers are given in Table 5, together with approximate assignments. The symbols $\beta$ and $\sigma$ denote bending and stretching vibrations, $\tau$ is the torsional motion of the $N_2$ parallel and perpendicular to the naphthol plane in the $\pi$-bound isomer, and $\gamma$ are the deformation modes in the H-bound isomer. The small frequencies for the bending motion of the $N_2$ in the H-bound structure reflect the flat nature of the potential along this coordinate. It is of course tempting to assign the experimentally observed bands to the calculated vibrations, but the computed ground-state frequencies cannot be compared directly to those obtained in MPI experiments, because the latter correspond to motion in the $S_1$ state.

## Discussion

The computational results presented here have considerable impact for the interpretation of the experimental spectra shown in Figure 1. The two lowest energy $\pi$-bound structures are calculated to have around twice the dissociation energy of the H-bound isomer, the **R1b** isomer being more stable by 1.39 kcal/mol (MP2/CBS-poly limit/BSSE-corrected). Therefore, the $\pi$-bound isomers are expected to be preferentially formed in a free jet. The current calculations therefore support our earlier tentative assignment of the electronic transition of the 1-NpOH/$N_2$ cluster at 31 442 cm$^{-1}$ to a $\pi$-bound isomer. However, the energy difference of the two lowest energy $\pi$-bound isomers is only 0.11 kcal/mol (38 cm$^{-1}$); thus both could be formed in almost equal amounts in a free jet expansion. We therefore can expect both isomers, which can be considered isomers of a hindered rotor, to contribute to the electronic spectrum. This assumption complicates the assignment of the vibrational structure. In principle, individual peaks can be assigned to one isomer by spectral hole burning (SHB). As discussed above, the SHB spectra (Figure 2) with the burn laser tuned to the most intense transition did not yield any evidence for the presence of a second isomer, but the two $\pi$-bound structures are so close in energy that similar electronic excitation energies $T_0$ can be expected. Their $S_1 \leftarrow S_0$ origins might overlap and cannot be easily separated.

The computed binding energy $D_0 = 2.63-2.67$ kcal/mol ($920-930$ cm$^{-1}$, CBS limit, BSSE corrected) for the (**R1b**) isomer is considerably larger than the corresponding one in related systems: Typically ground-state binding energies around 500 cm$^{-1}$ are found in clusters of aromatic molecules with nitrogen. For benzene/$N_2$, values of $D_e = 591$ cm$^{-1}$ and $D_0 = 520$ cm$^{-1}$ were computed[44] (MP2/6-31+G*) and 323 cm$^{-1}$ was measured;[46] for toluene/$N_2$, $D_0 = 474 \pm 37$ cm$^{-1}$ was measured[12] and $D_0 = 540$ cm$^{-1}$ computed by MP2. All these are roughly half the binding energy calculated for *t*-1-NpOH/$N_2$. The shorter $N_2$/ring distances in the van der Waals isomers of 1-NpOH/$N_2$ of 3.086 Å (**R1b** isomer) and 3.106 Å (**R1a** isomer) as compared to 3.48 Å in the toluene cluster reflect the stronger interaction suggested by the calculations. Similar binding energies around 500 cm$^{-1}$ were also found for $C_6H_5X$/$N_2$ clusters[10] with X = F, Cl, Br and for pyrimidine/$N_2$.[13] The calculated $D_0$ values in the CBS limit (exponential fit) of 448 and 420 cm$^{-1}$ (with and without BSSE correction, corresponding to 1.28 and 1.20 kcal/mol) for the H-bound isomer, on the other hand, are similar to the values of 430 cm$^{-1}$ (computed) and 445 cm$^{-1}$ (experimental) determined for the phenol cluster.[14,47] One reason for the comparably large binding energy in $\pi$-bound 1-naphthol/$N_2$ might be attributed to the larger quadrupole moment of the condensed ring system, yielding stronger quadrupole/quadrupole interactions when compared to substituted benzenes.

Although the observation of a $\pi$-bound van der Waals isomer is surprising in light of the results on phenol/$N_2$, it is not unprecedented in systems offering alternative binding sites. As shown by rotationally resolved electronic spectroscopy,[18] in aniline/nitrogen clusters the $N_2$ is van der Waals bound to the ring with an $N_2$ distance from the aromatic plane of 3.433 Å. The $N_2$ is oriented parallel to the axis containing the amino group, thus resembling the lowest energy **R1b** structure of 1-NpOH/$N_2$. Interestingly, a large increase in the barrier to internal rotation upon excitation to $S_1$ was found for aniline/$N_2$. Our initial RI-MP2 calculations yielded a barrier on the order of 50 cm$^{-1}$ between the two isomers of 1-NpOH/$N_2$. If we assume a barrier increase similar in magnitude in the excited state, no free rotation of the $N_2$ ligand about the ring can be expected to be visible in the MPI spectrum.

Relatively large binding energies were reported before for ethylaniline/$N_2$[19] ($D_0 = 630$ cm$^{-1}$) and *p*-aminophenol/$N_2$. The LIF and IR dip spectra of the latter were also interpreted on the basis of van der Waals bound structure.[20] For the most stable isomer a $D_e = 787$ cm$^{-1}$ value was estimated at the MP2/cc-pVDZ level. Thus relatively strong binding is found in clusters with the nitrogen ligand bound to the aromatic ring, but with an additional polar substituent being present. Schäfer et al.[11] suggested that an orientation parallel to the functional group indicates binding dominated by additional dipole/induced dipole interactions rather than quadrupole/quadrupole interactions only. The additional dipole/induced dipole and dipole/quadrupole interactions might also be responsible for the lower energy of the **R1b** isomer of 1-NpOH/$N_2$. Although these interactions are expected to be considerably smaller than the quadrupole/quadrupole interactions dominating the multipole expansion, they might very well account for the $\sim$50 $cm^{-1}$ difference in binding energy between the two van der Waals structures.

## Summary and Conclusion

High-level MP2 calculations were employed to obtain minimum energy structures and accurate absolute and relative binding energies for the three energetically most stable low-lying isomers of the *trans*-1-naphthol/$N_2$ cluster, in order to assign the electronic $S_1 \leftarrow S_0$ transition in the MPI spectrum. Augmenting the basis set by additional polarization functions was found to be necessary for an adequate description of the dispersion forces that govern the $\pi$-bound isomers. In the lowest energy structure the $N_2$ molecule is bound to the $\pi$-system of the naphthol ring carrying the OH group. It is oriented close to the short axis, with an angle of 62.5° to the $a$-axis of the naphthol moiety. The distance of the $N_2$ molecule from the ring plane amounts to 3.09 Å. With a large aug-cc-pV5Z basis set, a dissociation energy of $D_0 = 2.779$ kcal/mol (972 $cm^{-1}$) was computed for this structure compared to $D_0 = 1.392$ kcal/mol (487 $cm^{-1}$) for the H-bound structure. An extrapolation to the complete basis set limit, including correction of the basis set superposition error, yielded values of $D_0 = 2.63$ kcal/mol (920 $cm^{-1}$) and $D_0 = 2.63$ kcal/mol (465 $cm^{-1}$) for the lowest energy $\pi$-bound and the H-bound isomers, respectively. The binding energy is surprisingly large compared to other clusters with $N_2$, in particular phenol/$N_2$.

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