

# Investigations of OH–N- and NH–O-type hydrogen-bonded clusters by UV laser spectroscopy

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## Abstract

Resonant two-photon ionization spectra of OH–N hydrogen-bonded phenol–ammonia clusters  $\text{PhOH}(\text{NH}_3)_n$  up to  $n = 4$  were recorded via the  $(\text{NH}_3)_n\text{H}^+$  fragments of the proton transfer yield (PTY) spectroscopy. Under one-color conditions proton transfer already takes place for the 1:1 cluster. For the  $n = 2$  cluster the fragment spectrum is of much higher quality than the two-color ionization and the hole burning spectra. Resonant  $S_1$  spectra of the clusters with  $n > 2$  could be measured for the first time using PTY spectroscopy. Water clusters of benzotriazole have been investigated as NH–O hydrogen bond model. The monomer is interesting because its intramolecular proton transfer leads to the existence of two tautomers. While for the ground state an almost complete vibrational assignment is presented, the  $S_1$  spectra are much more difficult to interpret. By spectral hole burning it could be shown, that all bands in the excitation spectrum between the electronic origin at  $34917.8$  and  $0,0 + 1200 \text{ cm}^{-1}$  belong to the 2H tautomer. The  $n = 1, 2$  water clusters of this tautomer are blue-shifted by  $121.4$  and  $131.5 \text{ cm}^{-1}$  relative to the monomer. The clusters with one and two  $\text{H}_2\text{O}$  moieties both show two equivalent band systems, that can be traced back to a dominant vibration considerably affecting the spectra. © 1998 Elsevier Science B.V. All rights reserved.

## 1. Introduction

After numerous investigations concerning OH–O-type hydrogen bonded clusters we were interested in aggregates of other types. Hydrogen bonds containing nitrogen atoms in OH–N and NH–O bridges are important in chemistry and biology and we decided to concentrate on their investigation.

The simplest aromatic OH–N hydrogen-bonded cluster is phenol–ammonia, which has been investigated experimentally and theoretically by several

groups [1–10]. The intermolecular vibrational bands of the 1:1 cluster were identified by two-color R2PI spectroscopy and spectral hole burning (SHB) [6]. In this paper some totally symmetric modes and the  $2^+ \leftarrow 0^+$  transition arising from the hindered rotation of the  $\text{NH}_3$  moiety were assigned. For the  $\text{PhOH}(\text{NH}_3)_2$  cluster only a small part of the  $S_1$  spectrum has been published so far [2,6], whereas spectra of higher clusters ( $n \geq 3$ ) are broad and unstructured under one-color conditions. We present vibronic spectra up to  $\text{PhOH}(\text{NH}_3)_4$  using proton transfer yield (PTY) spectroscopy. As NH–O cluster representative we choose benzotriazole(BT)–water.

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Table 1

Observed and calculated frequencies ( $\text{cm}^{-1}$ ) of torsional transitions of the phenol–ammonia isotopomers

$S_1 \leftarrow S_0$ transition	PhOH(NH <sub>3</sub> )		PhOD(ND <sub>3</sub> )	
	observed	calculated	observed	calculated
0a <sub>1</sub> ← 0a <sub>1</sub>	0 (35714.0)	0.0	0 (35715.3)	0.0
1e ← 1e		−0.6		−0.3
2e ← 1e		31.4	26.9	26.5
3a <sub>1</sub> ← 0a <sub>1</sub>	64.5	64.8	45.9	44.6
4e ← 1e		99.2	59.8	59.2

Torsional constants of 6 and  $3 \text{ cm}^{-1}$  were used for the fit of the protonated and deuterated cluster, respectively, leading to  $V_3$  barriers of 43 ( $S_0$  state) and  $53 \text{ cm}^{-1}$  ( $S_1$ ). Absolute values for the electronic origins are given in parentheses.

There are many remaining questions concerning the monomer which is very interesting because of its tautomerism. The electronic origin of the  $S_1$  spectrum at  $34917.8 \text{ cm}^{-1}$  belongs to the 2H tautomer as shown by rotationally resolved LIF spectroscopy [11]. The vibronic spectrum in the region between 34900 and  $36200 \text{ cm}^{-1}$  had been taken by LIF spectroscopy [12] but is not assigned yet. Excitation spectra of BT–water clusters are not known until now. Low-resolution dispersed fluorescence (DF) spectra of BT were presented by Jalviste et al. [12] but there are no assignments of the  $S_0$  vibrations yet. In this paper the vibrational states of the electronic ground and excited states of BT are assigned and first interpretations of the BT(H<sub>2</sub>O)<sub>1,2</sub> spectra are given.

## 2. Experimental

The R2PI and SHB measurements were carried out with an apparatus described elsewhere [13,14]. The experimental setup for LIF and DF spectroscopy is described in Refs. [14,15]. A mixture of phenol, helium and NH<sub>3</sub> (5% in neon) at room temperature was expanded to produce small phenol–ammonia clusters. For benzotriazole, reservoir temperatures of 150–160°C were necessary to overcome the problem of small vapour pressure. At higher temperatures BT decomposes into aniline. Benzotriazole–water clusters were produced by coexpanding a mixture of H<sub>2</sub>O at  $-5^\circ\text{C}$ , helium and BT.

## 3. Results

### 3.1. Phenol–ammonia

In a previous publication [6] we reported theoretical and experimental results concerning the 1:1 cluster PhOH(NH<sub>3</sub>)<sub>1</sub>. Ab initio calculations at the 6-31G(d,p) level point to a C<sub>s</sub> symmetric molecule with a nearly linear OH–N hydrogen bond. The vibronic assignments are supported by the results of R2PI measurements of PhOD(ND<sub>3</sub>). Under the assumptions, that the barriers for hindered NH<sub>3</sub> rotation are the same for the protonated and the deuterated clusters in the same electronic state and that the torsional constants are nearly equal to the C rotational constants of NH<sub>3</sub> and ND<sub>3</sub>, respectively, some torsional bands (cf. Table 1) could be fitted using the method of Lewis et al. [16]. The  $V_3$  barriers for the hindered rotation of the ammonia moiety are calcu-

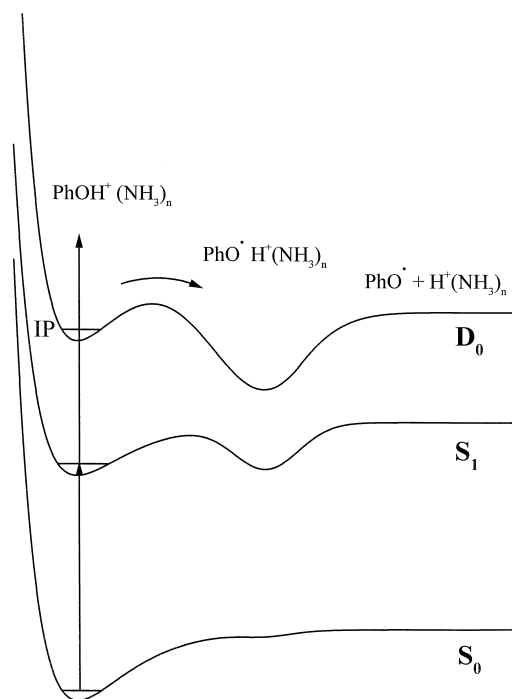


Fig. 1. Qualitative potential curves of the  $S_0$ ,  $S_1$  and  $D_0$  states of PhOH(NH<sub>3</sub>)<sub>n</sub> for  $n=1-4$ . The diagram exhibits the mechanism of proton transfer followed by dissociation. The proton affinities for (NH<sub>3</sub>)<sub>n</sub> clusters increase with  $n$  [17], thus lowering the PhO · H<sup>+</sup>(NH<sub>3</sub>)<sub>n</sub> minima in the  $S_0$ ,  $S_1$  and  $D_0$  states.

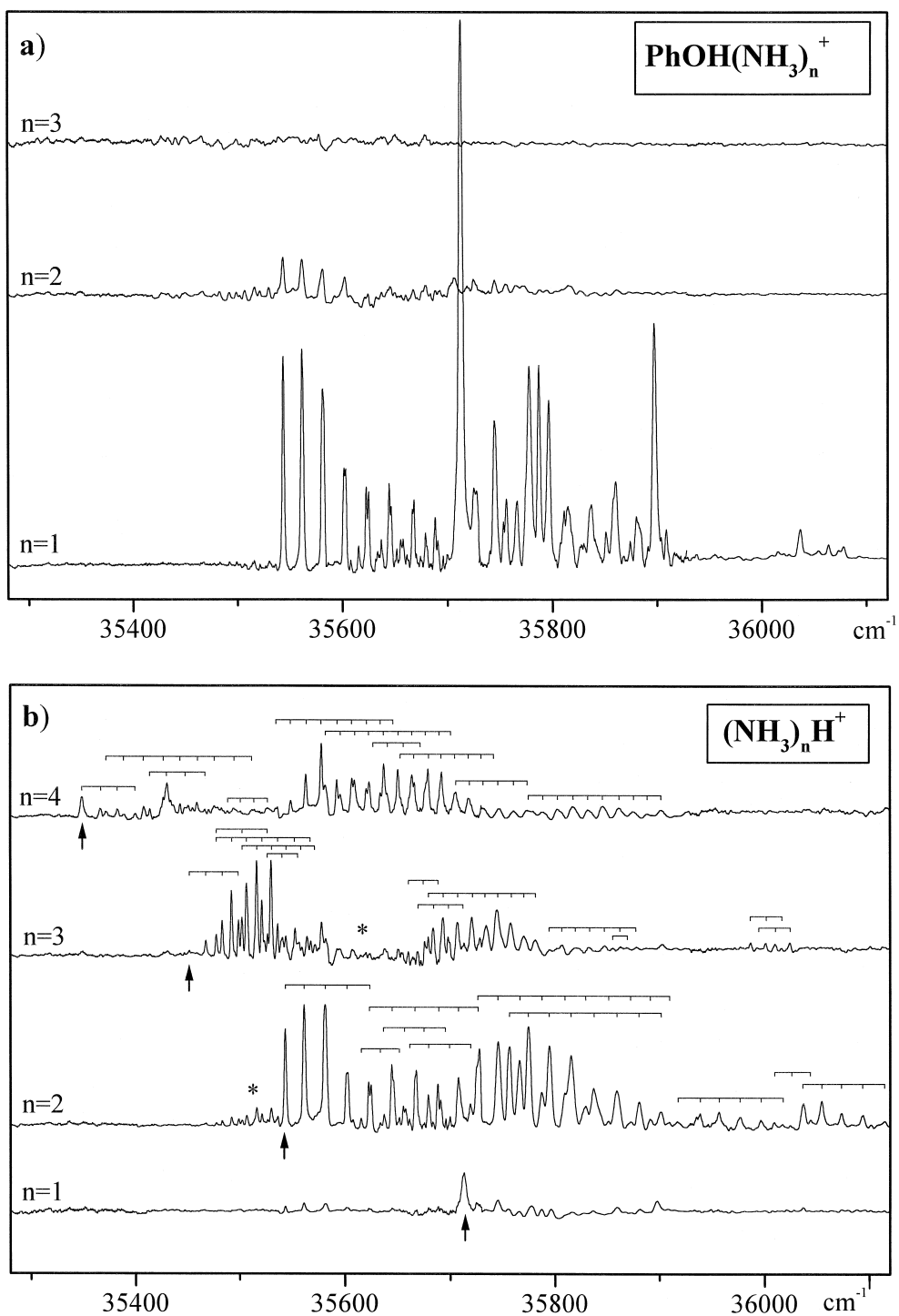


Fig. 2. R2PI spectra recorded on the mass channels of the clusters (a) and of the  $(\text{NH}_3)_n\text{H}^+$  fragments of the proton transfer products (b). The arrows in (b) mark the electronic origin of the respective cluster, cf. Table 2. The spectra in (a) and (b) show the unscaled intensities as obtained from a single scan.

Table 2  
Electronic origins, spectral shifts and excess energies in the  $D_0$  states of the  $\text{PhOH}(\text{NH}_3)_{1-4}$  clusters

Cluster	Electronic origin ( $\text{cm}^{-1}$ )	Spectral shift ( $\text{cm}^{-1}$ )	$D_0$ excess energy <sup>a</sup> ( $\text{cm}^{-1}$ )
$\text{PhOH}(\text{NH}_3)$	35714.0	-634.7	8100
$\text{PhOH}(\text{NH}_3)_2$	35544.3	-804.4	9100
$\text{PhOH}(\text{NH}_3)_3$	35452.3	-896.4	10300
$\text{PhOH}(\text{NH}_3)_4$	35349.5	-999.2	15100

The phenol monomer  $0_0^0$  is located at  $36348.7 \text{ cm}^{-1}$ .

<sup>a</sup>The ionization thresholds are taken from Ref. [2].

lated to 43 and  $53 \text{ cm}^{-1}$  for the  $S_0$  and  $S_1$  electronic state, respectively, using these approximations.

For the clusters  $\text{PhOH}(\text{NH}_3)_{2-4}$  high-quality R2PI spectra could be obtained even under one-color conditions by introducing a new technique. Instead of recording the spectra at the mass channels of the cluster ions  $\text{PhOH}(\text{NH}_3)_n^+$ , the signals of the corresponding fragments  $\text{H}(\text{NH}_3)_n^+$  are taken. The poten-

tial energy curves shown in Fig. 1 qualitatively explain these findings. After  $S_1 \leftarrow S_0$  excitation another photon can be absorbed to excite to an ionic state lying above the proton transfer barrier. The excess energy can lead to fragmentation by loss of either one or more  $\text{NH}_3$  moieties or by loss of a phenoxy radical. In the first case the cluster signals can be found on the mass channels of  $\text{PhOH}(\text{NH}_3)_{n \leq 2}^+$ . The spectra of the higher clusters are structureless (Fig. 2a). In the second case very little evaporation of  $\text{NH}_3$  is observed, so that the excess energy seems to be used almost quantitatively for the separation of fragment ion and phenoxy radical. In Fig. 2 cluster and fragment spectra are shown for comparison. Fig. 2b clearly shows that proton transfer already takes place in the 1:1 cluster for an excess energy of more than  $8000 \text{ cm}^{-1}$  in the ionic state. This is in contrast to the  $S_1$  state, where proton transfer is observed only for  $\text{PhOH}(\text{NH}_3)_n$  clusters with  $n \geq 5$  at an excess energy of around  $2000 \text{ cm}^{-1}$  [7].

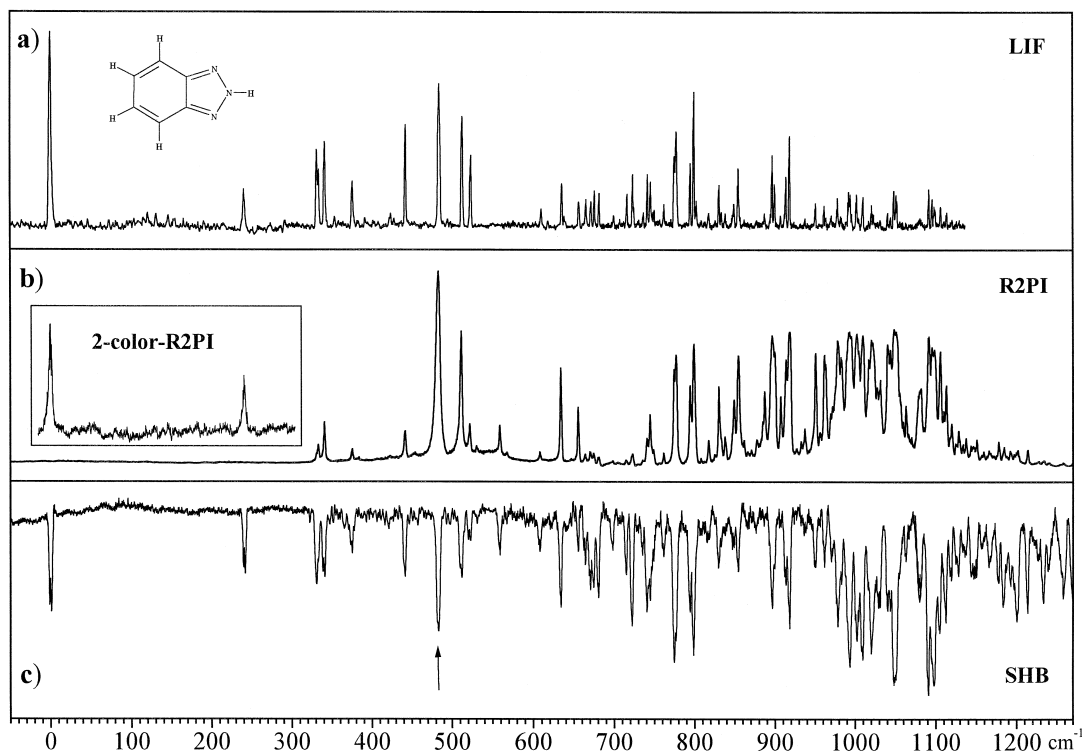


Fig. 3. LIF (a), R2PI (b) and SHB spectra (c) of 2H-BT. The picture shows the  $C_{2v}$  symmetric structure of the molecule. A two-color spectrum is given in the inset of (b). In the SHB spectrum the analysis band is marked by an arrow.

Table 3  
Relative frequencies, band types and some assignments of the excitation spectra of 2H-benzotriazole

Frequency <sup>a</sup> (cm <sup>-1</sup> )	Band type	Assignment
0	b	0,0
238.7	b	10a <sup>2</sup>
328.5	a	9b
330.7	b	10b <sup>2</sup>
338.2	b	
373.1	b	
439.2	a	
480.7	b	N <sub>inv.</sub> <sup>2</sup>
481.9	a	6b
509.5	b	6a
519.9	b	
631.9	a	
653.1	a	
661.8	b	10b <sup>4</sup>
672.5	a	
678.2	a	
696.3	a	
712.8	a	
719.7	a	
721	b	
738.1	a	
741.7	a	
746.7	b	1
758.5	b	
773.6	b	
791	a	
795.6	a	
798.2	b	
813.5	b	
826.7	a	
829.5	b	
844.8	b	
850.3	b	
892.6	a	
895.9	a	
903	b	
909.6	a	
914.1	a	
946.3	a	
957.3	a	
973.7	b	
987.4	b	
989.4	b	
997.4	b	
1005.5	a	
1016.5	a	
1035.8	a	
1038.9	a	
1043.5	a	
1045.7	a	
1086.7	a	

Table 3 (continued)

Frequency <sup>a</sup> (cm <sup>-1</sup> )	Band type	Assignment
1090.6	a	
1094.3	a	
1096.5	a	
1108.2	b	
1116.1	a	

<sup>a</sup> Values relative to the electronic origin at 34917.8 cm<sup>-1</sup>.

The fragment spectrum of the  $n = 2$  cluster is of much higher quality than the corresponding two-color R2PI and SHB spectra, while spectra of the clusters with  $n = 3$  and 4 could be observed for the first time using PTY spectroscopy. The electronic origins of the clusters are listed in Table 2 together with the spectral shifts and the approximate excess energies in the ionic states after one-color excitation.

In the cluster spectra with  $n > 1$  long progressions of one ( $n = 2, 3$ ) or two modes ( $n = 4$ ) can be observed in combination with most of the other vibrations. Furthermore the vibronic bands of the  $n = 2$  cluster are split into two components separated by  $\sim 2$  cm<sup>-1</sup>. By SHB spectroscopy we were able to show that these components are originating from different ground state levels, indicating the existence of a tunneling motion. Assuming a cyclic structure for PhOH(NH<sub>3</sub>)<sub>2</sub> this may be a ‘butterfly motion’ of the aromatic ring and the ONN moiety relative to each other, which tends to have a small barrier.

The similarity of the vibronic spectra and the regular spectral shifts point to similar structures for the clusters with  $n = 2-4$ . Ab initio calculations [10] show, that the geometries and the low-frequency vibrations should be comparable to those of the corresponding phenol–water clusters, which are cyclic [18]. Nevertheless, it should be mentioned, that for a cyclic structure of the  $n = 2$  cluster the electronic origin is expected to be blue shifted relative to the linear 1:1 cluster whereas a red shift is observed.

### 3.2. Benzotriazole monomer

Benzotriazole (BT) exists in two tautomeric forms, namely 1H- and 2H-BT. The relative stability of the two isomers has been investigated by several groups

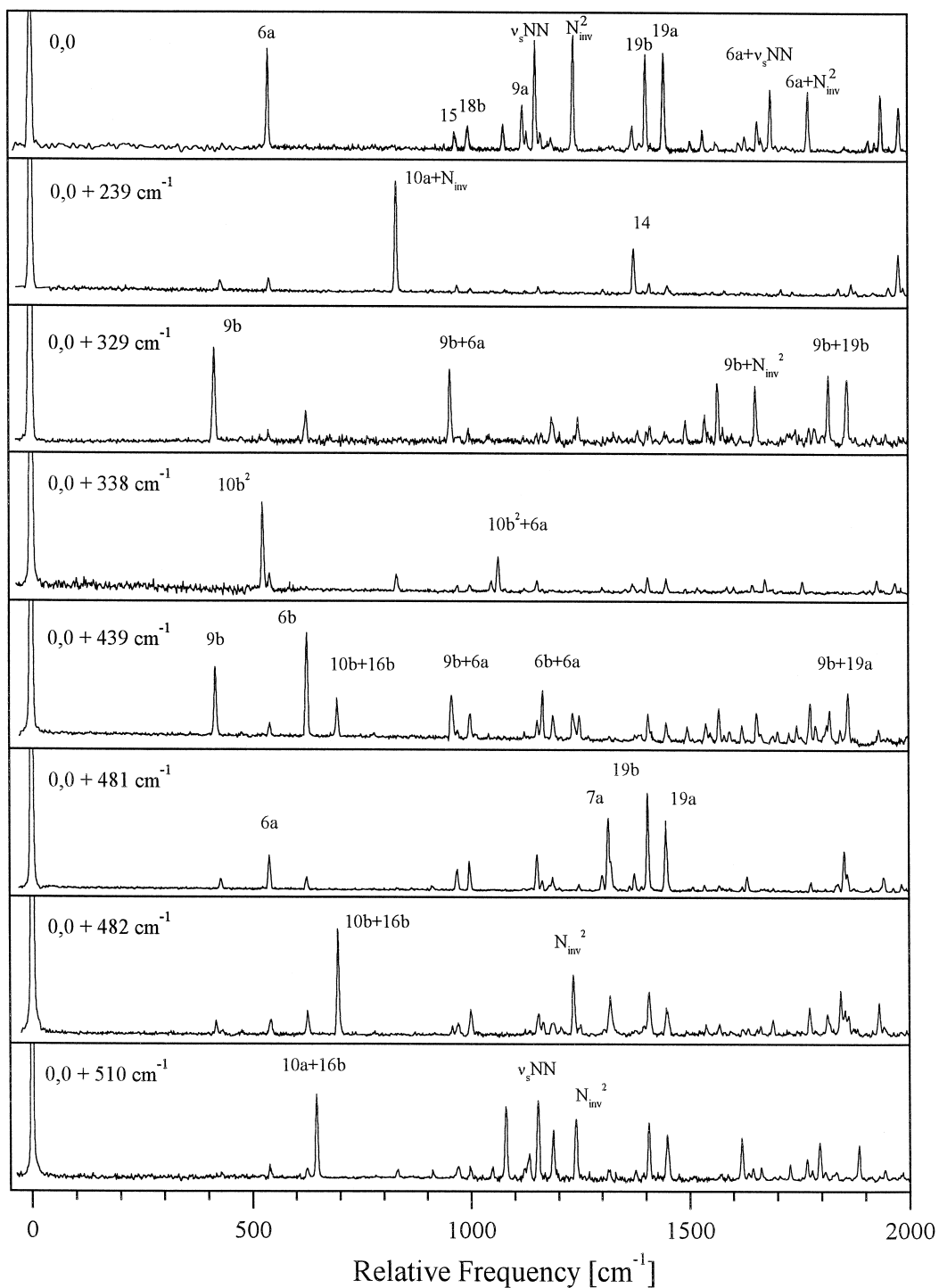


Fig. 4. DF spectra of 2H-BT recorded after excitation of several vibronic bands. The frequencies of these bands are given relative to the electronic origin at  $34917.8 \text{ cm}^{-1}$ .

Table 4

Assignments of  $S_0$  vibrational bands and comparison with calculated MP2/6-311G(d,p) frequencies for 2H-BT

Mode	Symmetry	Calculated	Observed <sup>a</sup>	Obs./calc.
10a	b <sub>1</sub>	216	430 <sup>b</sup>	1.00 <sup>c</sup>
10b	a <sub>2</sub>	253	526 <sup>b</sup>	1.03 <sup>c</sup>
16b	b <sub>1</sub>	408	833 (846) <sup>b</sup>	1.02 (1.04) <sup>c</sup>
9b	b <sub>2</sub>	415	417	1.00
4	a <sub>2</sub>	444	860 <sup>b</sup>	0.97 <sup>c</sup>
6a	a <sub>1</sub>	544	542	1.00
NNNH <sub>inv.</sub>	b <sub>1</sub>	604	1239 <sup>b</sup>	1.02 <sup>c</sup>
6b	b <sub>2</sub>	631	626	0.99
16a	a <sub>2</sub>	641	–	–
γ NH	b <sub>1</sub>	713	–	–
11	b <sub>1</sub>	741	1495 <sup>b</sup>	1.01 <sup>c</sup>
1	a <sub>1</sub>	792	778	0.98
17a	a <sub>2</sub>	824	1619 <sup>b</sup>	0.98 <sup>c</sup>
12	b <sub>2</sub>	897	866 (833)	0.97 (0.93)
5	a <sub>2</sub>	900	–	–
17b	b <sub>1</sub>	901	1854 <sup>b</sup>	1.03 <sup>c</sup>
15	a <sub>1</sub>	978	971	0.99
18b	a <sub>1</sub>	1022	1000	0.98
18a	b <sub>2</sub>	1138	1132	1.00
9a	a <sub>1</sub>	1166	1124	0.96
ν <sub>s</sub> NN	a <sub>1</sub>	1204	1154	0.96
13	b <sub>2</sub>	1233	1189	0.96
3	b <sub>2</sub>	1306	1250	0.96
7a	a <sub>1</sub>	1351	1316	0.97
ν <sub>as</sub> NN	b <sub>2</sub>	1382	1304	0.94
14	a <sub>1</sub>	1434	1357	0.95
19b	a <sub>1</sub>	1497	1407	0.94
δ NH	b <sub>2</sub>	1502	1414	0.94
19a	b <sub>2</sub>	1527	1449	0.95
8a	a <sub>1</sub>	1611	1537	0.95
8b	b <sub>2</sub>	1670	1569	0.94
ν <sub>as</sub> CH	b <sub>2</sub>	3208	<sup>d</sup>	–
ν <sub>s</sub> CH	a <sub>1</sub>	3220	<sup>d</sup>	–
ν <sub>as</sub> CH	b <sub>2</sub>	3235	<sup>d</sup>	–
ν <sub>s</sub> CH	a <sub>1</sub>	3239	<sup>d</sup>	–
ν <sub>s</sub> NH	a <sub>1</sub>	3649	3486	0.96

<sup>a</sup> Values in parentheses give alternative assignments.

<sup>b</sup> First (allowed) overtone.

<sup>c</sup> Observed/calculated for the harmonic value.

<sup>d</sup> In this spectral region there are too many bands to give an unambiguous assignment.

by means of ab initio calculations [14,19–22], but the results strongly depend on the chosen basis sets and methods pointing to a small energy difference. Thus, the existence of both tautomers in a supersonic jet cannot be excluded.

By rotationally resolved LIF spectroscopy Berden et al. [11] showed, that the electronic origin at

34917.8 cm<sup>-1</sup> belongs to the 2H tautomer. Because of the relatively high symmetry (C<sub>2v</sub>, cf. the structure in Fig. 3), many vibronic transitions are expected to be forbidden by selection rules. Hence, the large number of bands in the LIF (Fig. 3a) as well as in the R2PI spectrum (Fig. 3b) is surprising and may be due to transitions from both tautomers. The LIF and R2PI spectra show quite different intensities and the electronic origin as well as the lowest-energy vibronic band are not observed in the one-color R2PI spectrum. Therefore we took a two-color R2PI spectrum with an ionization energy of 266 nm shown in the inset of Fig. 3b. The appearance of both bands in the two-color spectrum shows, that in this region the energy difference between the ionic state and the S<sub>1</sub> state is greater than the S<sub>0</sub> – S<sub>1</sub> difference. The vibronic band at 329 cm<sup>-1</sup> blue to the electronic origin is the first one appearing in the one-color spectrum and therefore the ionization potential is determined to be within the range of 8.72–8.74 eV. This value considerably differs from the 9.2 eV given by Katritzky et al. [23].

The next step is to assure via SHB that the spectrum stems from only one tautomer. The most intense band at 0,0 + 480 cm<sup>-1</sup> was chosen for analysis. By scanning the hole burning laser over the electronic origin with an ionization energy of 266 nm, a decrease of the analysis signal at the 0<sub>0</sub><sup>0</sup> wavelength showed that the 480 cm<sup>-1</sup> band belongs to the 2H tautomer. The SHB spectrum in Fig. 3c was recorded via analysis of this intense vibronic band using one-color hole burning. The hole depth at the position of the vibrationless transition clearly shows, that the ionization step contributes little to the irreversible depopulation of the ground state. All bands observed in the excitation spectra are present in the SHB spectrum as well, indicating, that only the 2H tautomer absorbs in this region. Fast nonra-

Table 5

Electronic origins and spectral shifts of 2H-BT(H<sub>2</sub>O)<sub>0–3</sub>

Species	Electronic origin (cm <sup>-1</sup> )	Spectral shift (cm <sup>-1</sup> )
BT	34917.8	–
BT(H <sub>2</sub> O)	35039.2	121.4
BT(H <sub>2</sub> O) <sub>2</sub>	35049.3	131.5
BT(H <sub>2</sub> O) <sub>3</sub>	35071.0	153.2

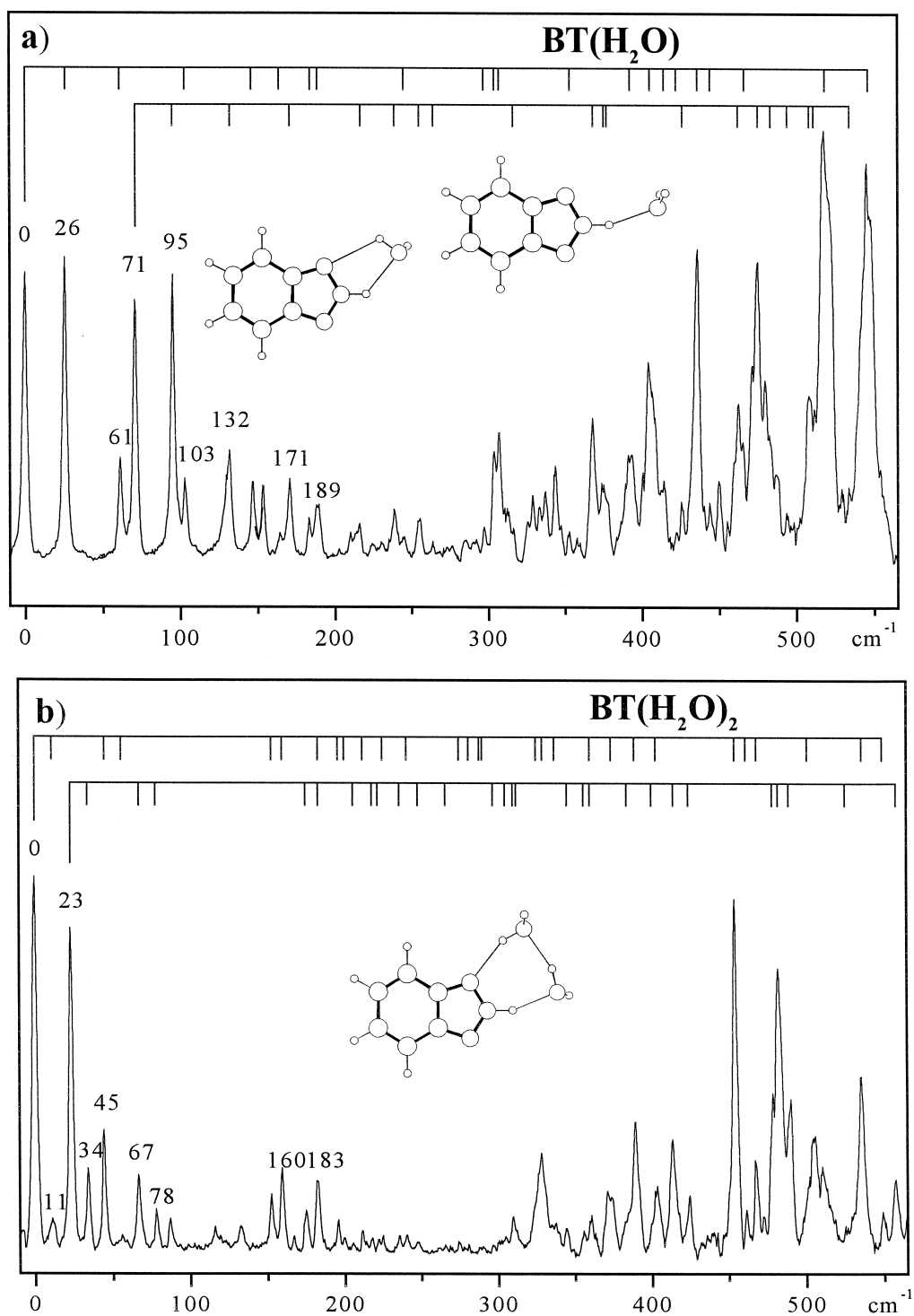


Fig. 5. R2PI spectra of the 2H-BT(H<sub>2</sub>O)<sub>n</sub> clusters with  $n = 1$  (a) and  $n = 2$  (b). Note the two similar band systems which are separated by 71 and 23 cm<sup>-1</sup>, respectively. The inset shows the calculated minimum energy structure of 2H-BT(H<sub>2</sub>O)<sub>1</sub> and 2H-BT(H<sub>2</sub>O)<sub>2</sub>.



diative processes leading to a rapid termination of the LIF and R2PI spectra above  $1200\text{ cm}^{-1}$  favor the hole burning process, so that the SHB spectrum continues to higher frequencies.

As shown by Berden et al. [11] the transition dipole moment of the electronic origin is orientated along the  $b$  (short in plane) axis. The  $S_1$  state ( ${}^1L_a$ ) therefore has  $B_2$  symmetry and only totally symmetric vibronic bands with  $b$ -type rotational contours are expected. Nevertheless, a large number of intense  $a$ -type vibronic bands are observed indicating the presence of  $b_2$  symmetric vibrational transitions. These experimental findings cannot be explained by vibrationally induced dipole moment components along the inertial  $a$  axis. One possible explanation is, that the  $b_2$  modes get their intensity by Herzberg–Teller coupling to a close lying electronic state. This  $S_2$  state has to be the  ${}^1L_b$  state with the transition dipole moment lying along the inertial  $a$  axis ( $A_1$  symmetry).

The observed bands are summarized in Table 3 together with the corresponding band types. Furthermore some assignments are given, that were made by comparison to a normal mode analysis.

In order to obtain information about the  $S_0$  state of 2H-benzotriazole, DF spectra were recorded after excitation of several vibronic bands (Fig. 4). The assignments of the vibrational bands are given in Table 4 and are discussed in more detail in Ref. [14]. The unscaled frequencies obtained by MP2/6-311G(d,p) ab initio calculations are obviously in good agreement with the experimental data. It can be seen, that in the region from  $0\text{--}1700\text{ cm}^{-1}$  all in-plane modes ( $a_1$  and  $b_2$  symmetries) are observed in the spectra. Furthermore almost every out-of-plane vibration can be found as overtone. In the region of the CH vibrations the large number of weak bands prevents an unambiguous assignment. The NH stretch vibration is prominent and can be found at  $3649\text{ cm}^{-1}$  [24]. In addition to the transitions listed in Table 4, a lot of combination bands and overtones of in-plane modes have been assigned.

### 3.3. Benzotriazole–water

R2PI spectra of  $2\text{H-BT}(\text{H}_2\text{O})_n$  clusters with  $n = 1\text{--}3$  were recorded, which absorb in the same spectral region as the monomer. The positions of the electronic origins (Table 5) show a continuous blue

shift, suggesting cyclic cluster structures. The spectra of the two smallest BT–water clusters are shown in Fig. 5. A quite interesting feature is the existence of two similar band systems in both spectra separated by 71 and  $23\text{ cm}^{-1}$ , respectively.

We took an SHB spectrum of  $\text{BT}(\text{H}_2\text{O})$ , which clearly showed, that all transitions share a common ground state level and thus excluded the existence of two different isomers to be responsible for the two band systems. Furthermore the possibility of transitions originating from different torsional levels is disproved. Another explanation for the two similar band systems could be the existence of two close-lying electronically excited states, but this seems unlikely due to the similarity of the vibronic patterns. The different electronic structures would lead to different vibrational frequencies and to perturbations of vibronic states having identical symmetries. So the most probable explanation is, that in both clusters there is a dominant vibration coupling to all other modes. Almost every vibronic transition can be observed in combination with the mode at  $71\text{ cm}^{-1}$  for the  $n = 1$  cluster and at  $23\text{ cm}^{-1}$  for the  $n = 2$  cluster. It should be mentioned, that for the  $n = 3$  cluster there is no such mode, but the appearance of the spectrum is quite similar to that of the individual band systems of the smaller clusters.

Possible structures of  $2\text{H-BT}(\text{H}_2\text{O})$  are the linear and the cyclic cluster which is shown in Fig. 5. Another possible structure is a  $\pi$  hydrogen-bonded cluster. On the HF/6-31G(d,p) level of theory it was not possible to obtain geometry convergence for  $\text{H}_2\text{O}$  interaction with the  $\pi$  system of BT. The linear  $\text{NH}\text{--O}$  structure is a transition state on the HF and MP2/6-31G(d,p) level with an imaginary frequency for  $\text{H}_2\text{O}$  torsion around its  $b$  axis. This motion points to the cyclic form, whose harmonic frequencies are all real but not in agreement with the measured  $S_1$  frequencies. Direct comparison between the calculated and measured  $S_0$  frequencies are not possible yet, because the fluorescence of  $\text{BT}(\text{H}_2\text{O})_1$  is very weak.

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