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Structure of hydrated clusters of tetrahydroisoquinoline $[\text{THIQ}-(\text{H}_2\text{O})_{n=1,3}]$ investigated by jet spectroscopy

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The hydrated clusters of tetrahydroisoquinoline have been investigated by laser-induced fluorescence (LIF), UV–UV hole burning, and IR–UV double-resonance spectroscopy in a seeded supersonic jet. Clusters of different sizes and isomeric structures have different 0–0 transitions (origins) in the LIF spectrum. UV–UV hole burning spectroscopy has been used to identify different cluster species and their vibrational modes. The structures of the clusters have been predicted by comparing the observed OH and NH frequencies in the IR–UV double-resonance spectra with the results calculated at different levels of sophistication. It is found that the water molecules form linear and six- and eight-membered cyclic H-bonded structures at the nitrogen center of 1:1, 1:2, and 1:3 clusters, respectively. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1711810]

I. INTRODUCTION

In recent years the spectra of solvated clusters have been extensively investigated with the intention of improving our understanding of microscopic interactions between solutes and solvents, including biological environments.[1–6] In particular, hydrated or ammonated clusters of aromatic molecules provide information on the structures and strengths of hydrogen bonds. Considering the weakness of a hydrogen and/or van der Waal's bond and the numerous possible conformations, the condensed or normal vapor phase is not the appropriate medium for carrying out spectral investigations. The collisionless, ultracold condition of a seeded jet is required for obtaining high-resolution spectra and arriving at unambiguous conclusions.

The collision-free clusters formed in a jet are generally stable, but vary in size and structure. Time-of-flight-mass (TOFM) spectrometry allows size selection, but it does not throw light on the conformation of the species. Various kinds of two-color double-resonance experiments are needed to disentangle the overlapping spectra of different species. The X–H stretching mode is a very sensitive probe for structures of H-bonded clusters and their changes due to proton/hydrogen transfer. These stretching frequencies can be conveniently obtained through IR–UV or stimulated Raman–UV double-resonance spectroscopy.[7–12] Some interesting examples are discussed in the next paragraph.

Zwier and co-workers have investigated several hydrogen-bonded clusters of benzene with a monomer, dimer, trimer, or tetramer of water and proposed the probable structures of the clusters.[13–15] By examining clusters of phenol, Mikami and co-workers[16–18] have investigated the acid-base proton transfer reaction between phenol and a variety of amines. Recently, they have used the double-resonance technique, autoionization-detected infrared (ADIR) spectroscopy, to study the OH vibrational mode of the ionic states of several molecules; this provided information regarding through-bond and through-space interactions.[19,20] The combination of IR–UV and stimulated Raman–UV double-resonance measurements proved to be an excellent method for distinguishing asymmetric and symmetric modes of water in the clusters.[21] The same double-resonance techniques have been used to discriminate different conformational isomers of hydroxy- or amino-substituted phenyl molecules.[22,23] Last, Reimann and co-workers have found an interesting new type of hydrogen bond, called an antihydrogen bond, in benzene–chloroform clusters; here, a blueshift instead of the usual redshift was observed for the asymmetric OH stretch frequency.[24]

Recently, we have identified by laser-induced fluorescence (LIF) and UV–UV hole-burning measurements two low-energy conformers of tetrahydroisoquinoline (THIQ) in a cold jet.[25] As shown in Fig. 1, the two conformers of THIQ are different with respect to the orientation of the N lone pair; that is, the two conformers have the H atom in either an equatorial or an axial orientation. In the present work we discuss hydrated clusters of THIQ. To date, hydrated clusters of a large number of nitrogen-containing aromatic molecules

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(a) Conformer T_A ($\Delta E = 0$ cm^{-1})
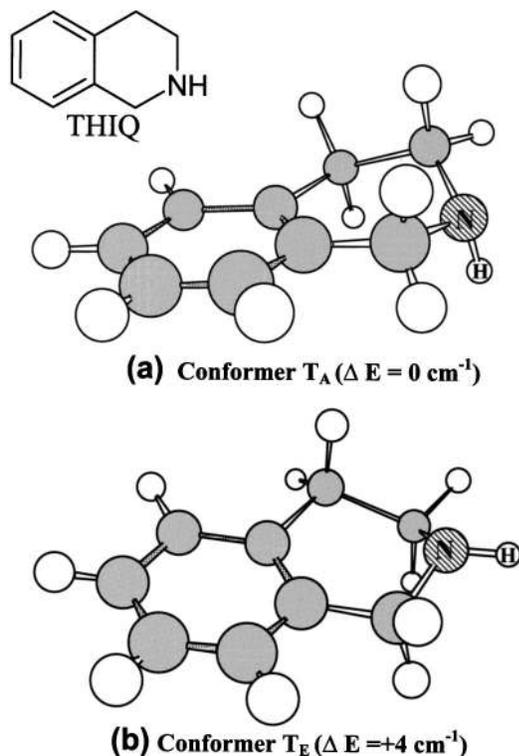

(b) Conformer T_E ($\Delta E = +4$ cm^{-1})

FIG. 1. *Ab initio* (HF/6-31++G) calculated structures of (a) axial (T_A) and (b) equatorial (T_E) conformers of bare THIQ.

have been investigated. In most cases the nitrogen atom is in conjugation with the benzene ring.[26,27] The only exception perhaps is N-benzylformamide (NBF), where, as in THIQ, two conformers of the bare molecule have been observed.[28] The cis conformer of NBF forms 1:1, 1:2, and 1:3 hydrated clusters, all having cyclic H-bonded structures bridging the C=O and NH$_2$ groups. In the 1:1 cluster of the trans conformer, however, water is bound only to the carbonyl group; for the 1:2 cluster, one end of the water chain is bound to the NH group and the other forms a loose bond to the π electrons of the benzene ring. The trans isomer of the 1:3 cluster was not observed in the jet.

The molecule THIQ chosen by us is similar in structure to that of NBF and, therefore, has the potential of forming similar interestingly bridged clusters with water. The THIQ molecule has two independent centres for H-bond formation with the water molecule(s): (i) the N atom and (ii) the benzene ring, which might permit bridge formation. Moreover, the N center should behave differently depending on whether the lone pair is in the axial or in the equatorial orientation. As the saturated ring of THIQ is not planar, the hydrogen-bonding ability of the two sides of the N atom may not be the same. Finally, depending on the configuration of the hydrated cluster, it is possible for any of the N and O atoms to behave as an H donor while the other behaves as an H acceptor or vice versa. All these possibilities may give rise to unexpected spectral features and unusual H bonds.

II. EXPERIMENT

A description of our LIF jet setup has been discussed in our earlier publications.[29,30] In brief, the jet-cooled molecules

and their clusters were generated by the expansion of heated vapors (100 °C) and carrier gases from high pressure to high vacuum. Tunable UV light was generated by frequency-doubling the output of a dye laser (PDL-3) pumped by a Nd:YAG laser (Spectra Physics, DCR-11). The exciting UV light was introduced into the vacuum chamber perpendicular to the molecular beam. The emitted total fluorescence was collected perpendicular to both the molecular beam and the exciting light by a two-lens collecting system. The fluorescence was detected by a PMT (1P 28) and finally processed by a boxcar integrator and personal computer.

UV–UV hole-burning spectroscopy requires two UV light sources[25] and was carried out at Tohoku University. One UV source was generated by doubling the output of a dye laser (ND-6000) pumped by a Nd:YAG (Quanta Ray GCR 230) laser, and the other UV source was generated by doubling the output of a Lambda-Physik dye laser pumped by an excimer laser (Lamda Physik FL 2002). The two counterpropagating light beams were introduced coaxially into the vacuum chamber and crossed the molecular beam. The frequency of the first UV light beam was fixed to a particular LIF excitation line and the constant level of the fluorescence signal was monitored. The frequency of the second laser light beam was scanned, and this source was introduced ~100 ns prior to the first one. If the second light beam is resonant with a vibronic transition of the same excited state the first UV beam is resonant with, the constant fluorescence signal caused by the first UV light beam is reduced due to depopulation of the ground state. It follows, therefore, that LIF bands whose intensities are reduced by the second UV light beam correspond to the same species. Thus the vibronic (S_1) bands of different species can be identified.

For the IR–UV double-resonance spectrum,[31,32] the population of a particular species in its lowest vibrational level of the ground electronic state was monitored by measuring the S_1 fluorescence intensity generated by the probe UV beam. The UV source used was the second harmonic of a XeCl-excimer-laser-pumped dye laser (Lambda Physics FL 2002). Tunable IR light (pump beam) was generated by difference-frequency mixing, where a portion of the second harmonic of an Nd:YAG (Quanta Ray GCR 230) and the output of a dye laser (ND 6000) pumped by the same Nd:YAG laser were mixed in a LiNbO$_3$ crystal. The IR light was introduced ~50 ns prior to the UV light after passing it through a CaF$_2$ window and dichroic mirror in order to eliminate visible light. Both the IR and UV light beams were introduced into the vacuum chamber in a counterpropagating manner and coaxially focused by a lens. The fluorescence was detected by a photo multiplier tube (PMT) and finally processed by a boxcar and a computer in the usual way. When the tunable IR light was resonant with a vibrational transition of a particular species, the ground state [i.e., the lowest vibrational level of the ground electronic state (S_0)] population of that species was depleted. Thus, by scanning the IR source, the ground-state vibrational spectra of the species were obtained one by one.

The compound THIQ was purchased from Aldrich Chemical Co. and was vacuum distilled before use. All the-
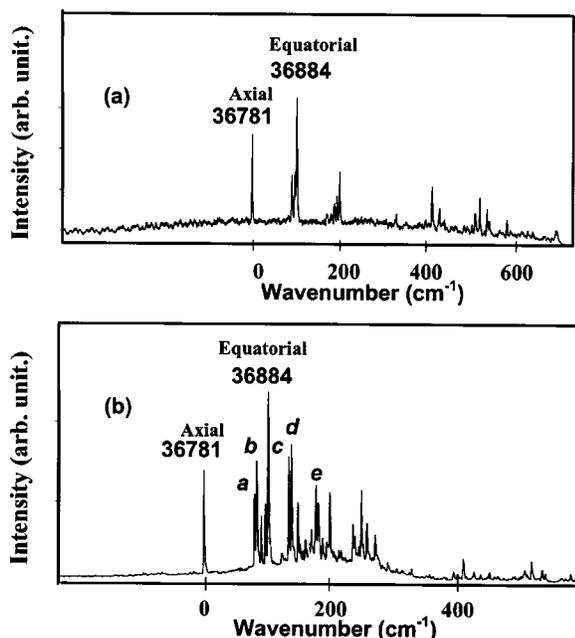
FIG. 2. Laser-induced fluorescence excitation spectra of (a) tetrahydroiso-quinoline and (b) its water clusters in the region of band origins.
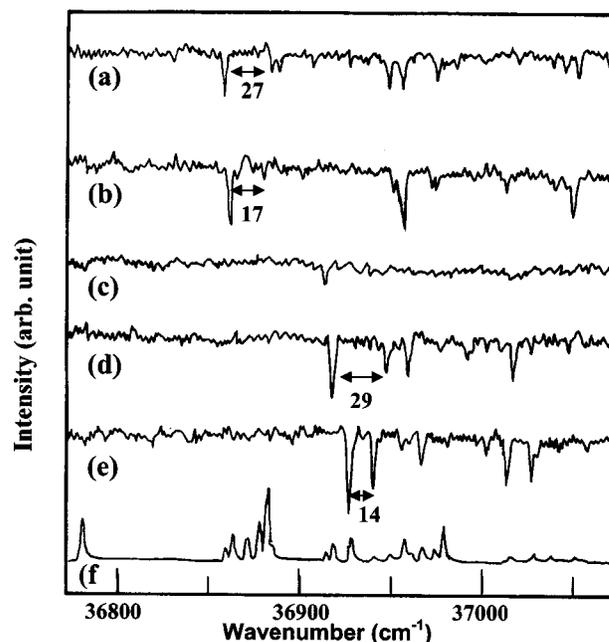

FIG. 3. UV–UV hole-burning spectra of THIQ–water clusters when the UV light source was fixed at the (a) +80 cm^{-1}, (b) +84 cm^{-1}, (c) +135 cm^{-1}, (d) +139 cm^{-1}, and (e) +149 cm^{-1} bands. The frequencies are relative to the 36 781 cm^{-1} band. (f) LIF spectrum of the bare molecule and its water clusters, all together.

oretical calculations were done using the GAUSSIAN 03W program.[33]

III. RESULTS AND DISCUSSION

A. LIF and UV–UV hole-burning measurements

The LIF excitation spectra of both bare THIQ and its water clusters are shown in Fig. 2 and presented in Table I. The 0–0 bands for the two inequivalent conformers having the N–H hydrogen atom in either an axial or an equatorial position are located at 36 781 and 36 884 cm^{-1}, respectively [Fig. 2(a)]. The vibrational modes of the two conformers have also been clearly identified by UV–UV hole-burning spectroscopy.[25] These features of the bare molecules have been discussed in one of our recent publications.[25] When

TABLE I. Assignment of the frequencies observed in the LIF spectrum of hydrated THIQ.

Band number	Band position with respect to 36 781 cm^{-1}	Assignment
1	0	Origin for bare conformer T_A
2	+80	Origin for cluster *a*
3	+84	Origin for cluster *b*
4	+92	ν_1 (butterfly mode) of T_A
5	+98	ν_2 (out-of-plane puckering mode) of T_A
6	+103	Origin for bare conformer T_E
7	+135	Origin for cluster *c*
8	+139	Origin for cluster *d*
9	+149	Origin for cluster *e*
10	+161	⋯
11	+171	⋯
12	+178	⋯
13	+182	$2\nu_1$
14	+189	$\nu_1 + \nu_2$
15	+196	$2\nu_2$

water vapor is introduced in the sample chamber, in addition to the increase of intensity of some weak bands, a number of new bands appear in the LIF spectrum [Fig. 2(b)]. This indicates that these bands are due to the formation of water clusters with the bare molecule. The bare molecule itself is present in the jet as two low-energy conformers, axial and equatorial (Fig. 1), the H-bonding capability of which may differ. It is necessary, therefore, to find out both the number of water molecules in the cluster and the conformer type of THIQ.

The usual way for differentiating clusters of different sizes is to perform time-of-flight mass spectroscopy. However, clusters of the same size but different structures cannot be differentiated by TOFM spectroscopy. Moreover, clusters may disintegrate during the time of flight. We have opted, therefore, to use the combination of hole-burning fluorescence spectroscopy with the IR–UV double-resonance technique and theoretical calculations to identify clusters of the same size but different structures. Each cluster may be treated as a different molecular species with a characteristic electronic transition energy and vibrational spectrum. Figures 3(a)–3(e) show the UV–UV hole-burning spectra obtained when the probe UV beam was fixed at different lines of the LIF excitation spectrum. Analysis of these spectra clearly indicates that the bands at +80, +84, +135, +139, and +149 cm^{-1} with respect to 36 781 cm^{-1} band correspond to the origin transitions of different water clusters. It is also observed that the low-frequency modes for each of these bands are different. The first low-frequency mode in spectra 3(b) and 3(e) occurs at around 15 cm^{-1}. This roughly corresponds with the intermolecular rocking mode of 22 cm^{-1} observed in phenol monohydrates.[34] In spectra 3(a) and 3(d)
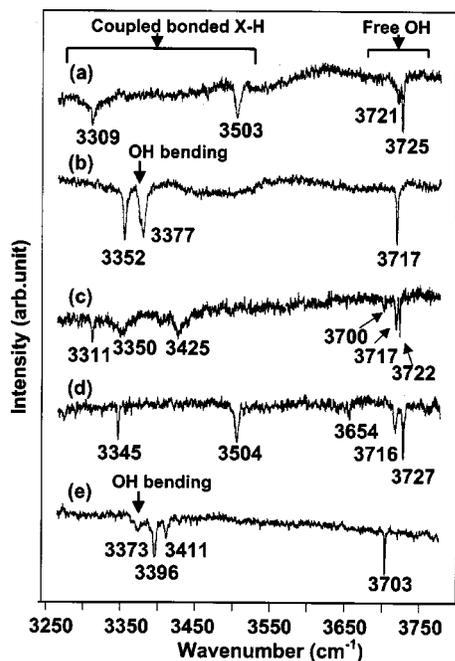
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FIG. 4. IR–UV double resonance spectra of THIQ–water clusters when the UV light was fixed at the (a) $+80$ cm^{-1}, (b) $+84$ cm^{-1}, (c) $+135$ cm^{-1}, (d) $+139$ cm^{-1}, and (e) $+149$ cm^{-1} bands.

FIG. 5. *Ab initio* HF/6-31++G level calculated structures of THIQ–water 1:1 clusters. (a) Linear OH H-bonded conformer X_A and (b) linear NH H-bonded conformer Y_A correspond to the T_A form (axial NH). (d) Linear OH H-bonded conformer X_E and (e) linear NH H-bonded conformer Y_E correspond to the T_E form (equatorial N–H). Cyclic structures (c) Z_A and (f) Z_E were obtained at the AM1 level for the axial and equatorial forms, respectively.

the first low-frequency mode occurs at around 28 cm^{-1}. Our *ab initio* calculations for 1:1 and 1:2 clusters show that this type of low-frequency mode is an intermolecular one where the displacement vectors are at the cyclic hydrogen-bonded site. Spectrum 3(c) is different from the above two pairs. It is evident, therefore, that there are five different 0–0 bands of five different water clusters. On the basis of vibronic features we classify the five spectra in three separate groups—3(a) and 3(d), 3(b) and 3(e), and 3(c)—and try to obtain further structural information from their IR spectra in the S_0 state.

B. IR–UV double-resonance measurements

In the LIF spectrum of THIQ–water clusters, the five 0–0 bands at frequencies $+80$, $+84$, $+135$, $+139$, and $+149$ cm^{-1} relative to the 0–0 band of the THIQ (bare) axial conformer[25] correspond to five different water clusters *a*, *b*, *c*, *d*, and *e*, respectively. The IR–UV double resonance spectra offer us, in effect, the IR spectrum of each of the five species *a*, *b*, *c*, *d*, and *e* in their ground states (Fig. 4, Table II). A casual look at the five IR spectra in the O–H and N–H stretching frequency regions (3200–3800 cm^{-1}) shows that spectra 4(b) and 4(e) are similar; spectra 4(a) and 4(d) are also similar. This spectral pairing arises from the presence of the two nearly identical conformers of THIQ (axial and equatorial). The question of which of the two spectra corresponds to the axial form and which to the equatorial form is addressed in the next paragraph. The second point to note about the spectra is that in the frequency region around 3710 cm^{-1}, which corresponds to the asymmetric OH stretch of free water, the IR spectra of species *b* and *e* have only one band, while *a* and *d* have two bands and *c* has three bands. The number of IR bands in and around 3700 cm^{-1} should be equal to the number of free (non-hydrogen-bonded) OH
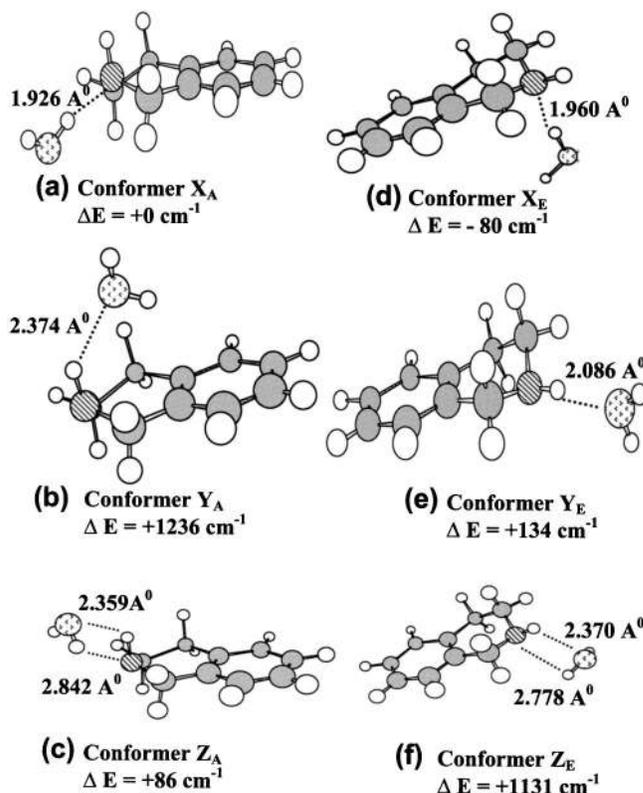
groups of the water clusters. In completely free C_{2v}-symmetric water only one OH frequency (asymmetric stretch $\sim$3756 cm^{-1}) is allowed.[13] However, in a monohydrate one OH is utilized for H bonding with the substrate, while the other OH group remains more or less free; hence, only one narrow-width IR band should appear around 3700 cm^{-1}. On the basis of this argument, we ascribe the spectra 4(b) and 4(e) to the monohydrates of the two conformers. By similar argument we assign spectra 4(a) and 4(d) to dihydrates and 4(c) to a trihydrate.

C. Structures of monohydrates and spectra

In the monohydrates under consideration there are three possible ways of binding a water molecule to either of the two THIQ conformers: (i) the O–H group may form a H bond with the N lone pair [Figs. 5(a) and 5(d)], (ii) the N–H group may form a H bond with the O lone pairs [Figs. 5(b) and 5(e)], and (iii) both the N–H and O–H groups are involved in a cyclic, two-way H-bond formation [Figs. 5(c) and 5(f)]. In the first two cases the hydrogen-bonded X–H stretching mode is expected to be redshifted, intensified, and broadened. Moreover, as the OH bond is more polar than the NH bond, the H-bond interaction should be stronger in OH than in NH. The redshift and bandwidth of the H-bonded OH mode should therefore be larger than that of the H-bonded

NH mode. In the third case both the N–H and O–H bands should be redshifted, intensified, and broadened to varying extents.

In order to determine which of the three cases described above is applicable for the monohydrates of THIQ, calculations were performed to find the lowest-energy structures and the vibrational frequencies of these structures. The vibrational frequencies were then compared to the experimental spectra in order to determine which structures are present in the jet and firmly assigned the modes observed. Calculations of the structures of the conformers of the bare molecule and their water clusters have been performed by semiempirical AM1, *ab initio* (HF,MP2), and density functional theory (DFT) methods. Some relevant calculated results for hydrates are presented in Tables II and III. The bare molecule forms two low-energy inequivalent twist conformers, one with an axial (T_A) and the other with an equatorial (T_E) NH bond (Fig. 1). It is found that the axial form is more stable than the equatorial one at all levels of calculation (Table III), but the difference in energy between the two conformers is indeed very small. From our extensive calculational exercise it emerges that out of several possible 1:1 water–THIQ clusters, the only low-energy conformers are those where the water molecule is positioned near the aliphatic nitrogen atom. The phenyl ring could have been another possible binding site, but the calculated energies of π-bonded water–THIQ conformers are much higher; hence, such conformers are not expected to be populated in the cold jet. It has been observed in the case of NBF clusters that the water molecule forms a hydrogen bond that bridges the lone pair of nitrogen and the π electrons of benzene.[28] However, such a structure is clearly unfavorable in the THIQ cluster, presumably because the distance between the two possible hydrogen-bonding sites, the N atom and the phenyl ring, is large.

Figures 5(a) and 5(d) show three types of calculated N-bonded low-energy structures of 1:1 clusters of the two conformers. In computer-generated structures of type X_A or X_E, the OH of water molecule forms a linear hydrogen bond with the lone pair of nitrogen of THIQ [Figs. 5(a) and 5(d)]. As expected, frequency calculations for X-type structures predict a free OH, a slightly shifted, weak NH and a largely redshifted, intense OH mode. Monohydrate structures of type Y_A or Y_E where NH is H bonded with the lone pair of oxygen of water are higher in energy compared to linear O–H-bonded structures X_A or X_E and hence should not show up in the jet. Additionally, had these structures been populated, one could expect in the IR spectra a large redshifted NH mode and a weak symmetric OH mode. The observed IR spectrum, therefore, does not favor Y_A- or Y_E-type structure. Semiempirical AM1 calculations, however, favor some low-energy cyclic structures [e.g., Z_A or Z_E of Figs. 5(c) and 5(f)] where the H-bond network is cyclic, presumably due to two-way, admittedly weak, H-bond formation. In these structures the water molecule is placed in such a way that both the NH and OH hydrogens form a hydrogen bond with the other's lone pair which may be best described as a skewed quadrilateral. Although in a Z-type structure the NH mode gains intensity due to coupling with the OH mode, which is in agreement with observations, we could not find any similar

stable conformer at higher levels of calculation [HF/6-31++G, MP2/6-31G(d) or B3LYP/6-31+G(d)]. The strains in the cyclic H-bonded ring of Z structures cause the H bonds to be weak, leading to small redshifts in OH and NH modes, but this is not what is observed. We therefore prescribe an X-type structure for the monohydrate of THIQ.

We assign a pair of redshifted IR bands at 3377 and 3352 cm^{-1} in Fig. 4(b) and another pair at 3411 and 3396 cm^{-1} in Fig. 4(e) to coupled, H-bonded NH and OH modes. Comparing the IR spectra with our calculated results we assign the redshifted band at 3352 cm^{-1} in Fig. 4(b) and 3396 cm^{-1} band in Fig. 4(e) to a coupled, but primarily OH mode, while 3377 cm^{-1} in Fig. 4(b) and 3411 cm^{-1} band in Fig. 4(e) correspond to a coupled, but primarily NH mode. This assignment may be compared with that of cis-NBF–water 1:1 cluster.[28] The OH and NH modes in spectrum 4(b) are 77 and 52 cm^{-1} and, in spectrum 4(e), 33 and 66 cm^{-1}, more redshifted compared to similar modes in the cis-NBF–water 1:1 cluster. This indicates that the hydrogen bond strength in THIQ cluster is greater than that in the NBF cluster. It may also be observed that the H-bonded OH modes in spectra 4(b) and 4(e) are, respectively, 304 and 260 cm^{-1} redshifted from the symmetric OH mode of free water,[13] while the NH modes in spectra 4(b) and 4(e) are only 67 and 33 cm^{-1} redshifted from the NH mode of free ammonia.[16(a)] The comparatively small redshift of the NH mode is presumably due to lower hydrogen bonding power of the NH group than that of the OH group. It may be further pointed out that in spectrum 4(e) the O–H and NH frequency shifts on H-bond formation are slightly less than the corresponding quantities in Fig. 4(b). This means that the H bond is somewhat weaker in species e [spectrum 4(e)] compared to species b [spectrum 4(b)]. The band at 3373 cm^{-1} in the IR spectrum of e is likely to be the overtone of the OH bending mode as has been reported for other clusters.[17,28] The same OH bending overtone appears in spectrum 4(b) also, but only as shoulder on the 3377 cm^{-1} band.

In the LIF spectrum of the bare molecule [Fig. 2(a)], the electronic origin of the equatorial form is blueshifted by 103 cm^{-1} with respect to the axial form.[25] A difference in the blueshifts of the same order may be expected for the two corresponding monohydrates. As the origin of conformer e is 65 cm^{-1} blueshifted relative to the origin of conformer b, we assign conformer b to the axial and e to the equatorial form. The assignment of the monohydrates to the two conformers of THIQ (T_A and T_E) cannot be the other way round. Assigning the LIF band e as the axial monohydrate 0–0 band and LIF band b as the equatorial monohydrate 0–0 band would mean that H bonding has caused a blueshift in the 0–0 band of one conformer and a redshift in the case of the other conformer. On the other hand, our present assignment of the LIF band b to the H-bonded axial T_A form and the LIF band e to the H-bonded equatorial T_E form means that the H-bond strengths in both conformers are similar, though not equal. In the case of the axial form the shift is 84 cm^{-1} to the blue of the axial form of the bare molecule while the corresponding shift for the equatorial form is 46 cm^{-1} to the blue. The lower spectral shift on H bonding for T_E implies that the H-bond strength is lower in T_E compared to that of T_A. This

TABLE II. Experimentally observed and *ab initio* (HF/6-31++G) calculated vibrational modes in relation to the minimum-energy structures of THIQ–water clusters.

FE spectral origins[a] [Fig. 2(b)]	Observed IR frequency (cm^{-1})	Calculated IR frequency (cm^{-1})[b]	Nature of bands	Assignment of the species
0	Not observed	3458(3)	NH mode	THIQ (axial), T_A
103	Not observed	3480(2)	NH mode	THIQ (equatorial), T_E
84 (b)	3717	3717(128)	OH (free)	THIQ–$(H_2O)_1$ (axial) Conformer X_A
	3377	3420(3)	NH/OH coupled mode	
	3373	3188 (1594×2) (97[c])	Overtone of OH bending	
	3352	3377(770)	OH/NH coupled mode	
149 (e)	3703	3710(102)	OH (free)	THIQ–$(H_2O)_1$ (equatorial) Conformer X_E
	3411	3443(12)	NH/OH coupled mode	
	3396	3412(513)	OH/NH coupled mode	
	3373	3208 (1604×2) (149[c])	Overtone of OH bending	
80 (a)	3725	3746(146)	OH (free)	THIQ–$(H_2O)_2$ (axial) Conformer C_A
	3721	3743(81)	OH (free)	
	3503	3467(326)	OH/NH coupled mode	
	3309	3375(131)	NH/OH coupled mode	
	⋯	3238(1043)	OH/NH coupled mode	
139 (d)	3727	3746(120)	OH (free)	THIQ–$(H_2O)_2$ (equatorial) Conformer C_E
	3716	3741 (94)	OH (free)	
	3654	⋯	⋯	
	3504	3465(329)	OH/NH coupled mode	
	3345	3392(148)	NH/OH coupled mode	
	⋯	3250(862)	OH/NH coupled mode	
135 (c)	3722	3747(116)	OH (free)	THIQ–$(H_2O)_3$ (equatorial) B_A/B_E
	3717	3735(102)	OH (free)	
	3700	3730(77)	OH (free)	
	3425	3387(449)	OH/NH coupled modes	
	3350	3356(668)		
	3311	3329(451)		
		3097(1157)		

[a]In relation to the 36 781-cm^{-1} band.
[b]Calculated frequencies are multiplied by a factor of 0.9094 to correlate with the observed free OH mode. Numbers in the parentheses are IR intensities (km/mol).
[c]Calculated IR intensity for the OH bending fundamental transition.

is consistent with the conclusion made before.

Figure 6 shows the relative frequencies and intensities of the experimental and simulated IR spectra obtained by AM1 calculation for three types of structures of the axial con-

former. The correlation between the experimental frequencies and the ones simulated by AM1 calculation is indeed poor. On the other hand, if *ab initio* (HF/6-31++G, MP2/6-31G) or density function theory [DFT, B3LYP/6-31+G(d)]

TABLE III. Calculated energies for different conformers of THIQ and its water clusters by AM1, various *ab initio* and DFT methods.

Type of species	Method of calculation	Calculated energy difference (ΔE cm^{-1}) with respect to the conformer T_A or X_A or C_A or B_A, as applicable			
THIQ		$E(T_A)-E(T_A)$		$E(T_E)-E(T_A)$	
	AM1	0	⋯	+1149	⋯
	HF/6-31++G	0	⋯	+4	⋯
	MP2/6-31G	0	⋯	+162	⋯
	B3LYP/6-31+G(d)	0	⋯	−3	⋯
THIQ (H$_2$O)$_1$		$E(X_A)-E(X_A)$	$E(Y_A)-E(X_A)$	$E(X_E)-E(X_A)$	$E(Y_E)-E(X_A)$
	AM1	0	+158	+1099	+1094
	HF/6-31++G	0	+1236	−80	+1343
	MP2/6-31G	0	+1222	−135	>10000
	B3LYP/6-31+G(d)	0	+1428	−68	+1627
THIQ (H$_2$O)$_2$		$E(C_A)-E(C_A)$	$E(D_A)-E(C_A)$	$E(C_E)-E(C_A)$	$E(D_E)-E(C_A)$
	AM1	0	+393	944	+1934
	HF/6-31++G	0	+1474	−131	+2508
THIQ (H$_2$O)$_3$		$E(B_A)-E(B_A)$	⋯	$E(B_E)-E(B_A)$	⋯
	AM1	0	⋯	+948	⋯
	HF/6-31++G	0	⋯	−175	⋯

methods are used for simulation of IR frequencies of axial (X_A) and equatorial (X_E) forms, the agreement is good as shown in Figs. 7 and 8. The problem regarding relative intensities still persists. The weakness in coupling between NH and OH stretch modes in X-type structures is obviously the cause of the low calculated NH intensity. To explain the IR-band intensities, strong coupling between OH and NH modes needs to be assumed. Some normal modes for the axial 1:1

cluster are shown in Fig. 9. These do demonstrate mode coupling, but stronger coupling is needed to explain observed intensities of IR-active $X\cdots$H stretching modes. The characteristics of the calculated OH and NH modes for the lowest-energy equatorial 1:1 water cluster are similar to that of the axial one.

To summarize, AM1 calculations favor Z-type low-energy structures which are consistent with the intensities of
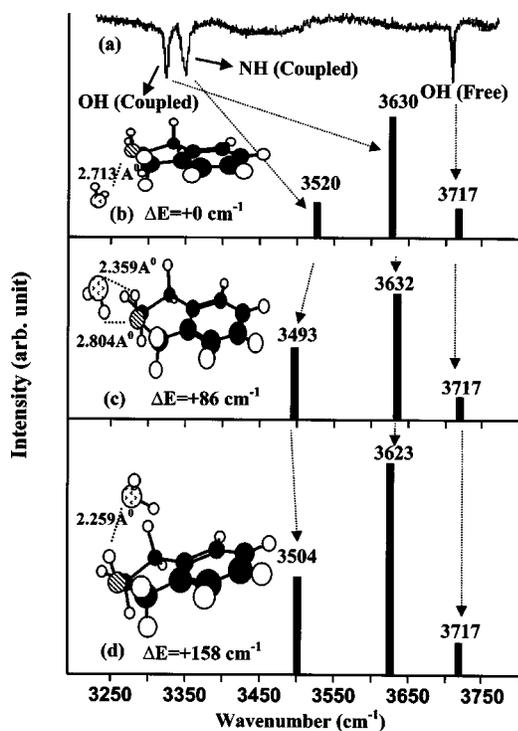

FIG. 6. Comparison between the experimental FDIR spectrum with those obtained at the AM1 level for 1:1 water clusters of the axial conformer. (a) Experimental FDIR spectrum, simulated spectra for (b) conformer X_A, (c) cyclic-hydrogen-bonded ring conformer Z_A, and (d) conformer Y_A. Relative AM1 energies are for against each conformer. Calculated IR frequencies are multiplied by a factor of 1.0384, 1.0407, and 1.0380 for the X_A, Z_A, and Y_A conformers, respectively, to correlate with the observed free OH mode of the axial form.
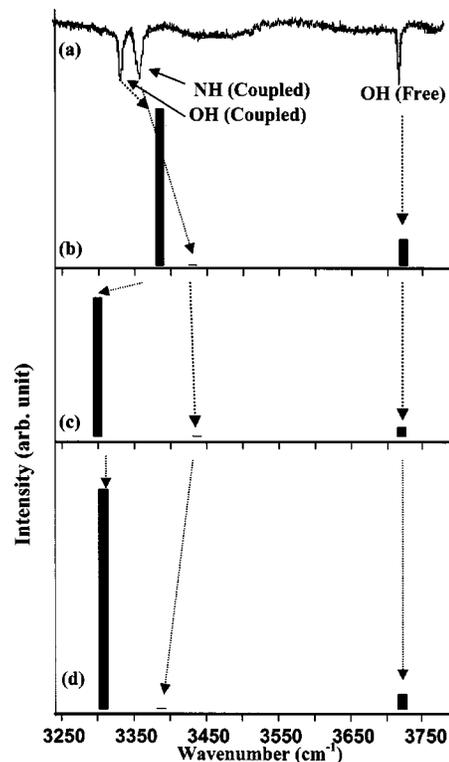

FIG. 7. Comparison between (a) the experimental FDIR spectrum of the axial THIQ–H$_2$O 1:1 cluster with the IR spectra of X_A conformer simulated at (b) HF/6-31++G, (c) MP2/6-31G, and (d) B3LYP/6-31G+(d) levels. Calculated IR frequencies are multiplied by 0.9094, 0.9856, and 0.9763 for HF/6-31++G, MP2/6-31G, and B3LYP/6-31G+(d) levels, respectively.

FIG. 8. Comparison between (a) the experimental FDIR spectrum of equatorial THIQ–H$_2$O 1:1 cluster with the IR spectrum X_E conformer simulated at (b) HF/6-31++G, (c) MP2/6-31G, and (d) B3LYP/6-31G+(d) levels. Calculated IR frequencies are multiplied by a factor of 0.9094, 0.9856, and 0.9763 for HF/6-31++G, MP2/6-31G, and B3LYP/6-31G+(d) levels, respectively.
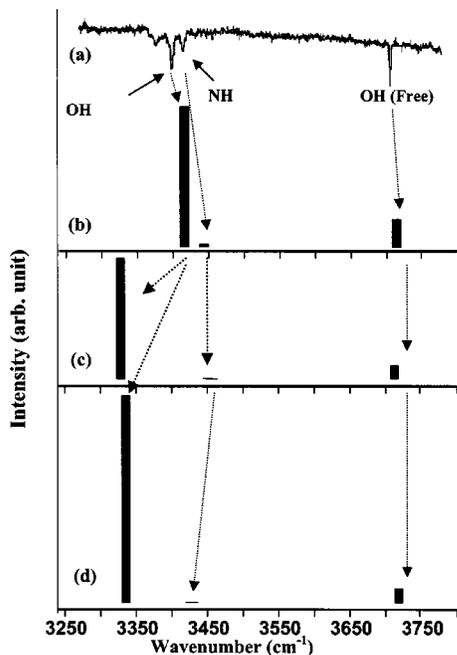
the IR bands, but not their frequencies. On the other hand, *ab initio* and DFT calculations suggest *X*-type structures which explain the frequencies, but not the relative intensities. Additional mode coupling needs to be taken into consideration. *X*-type structure gives the best agreement between experimental and theoretical results and, therefore, is the type of structure assigned to conformers *b* and *c*.

It may be noted that our calculations (HF/6-31++G) indicate an out-of-plane OH-bending mode at about 1595 cm^{-1} (Table II); this IR band is very intense, so its overtone may be expected to appear at 3190 cm^{-1} with moderate intensity, as observed. Last, the calculated distance between the hydrogen of the OH group and the lone pair of the nitro-
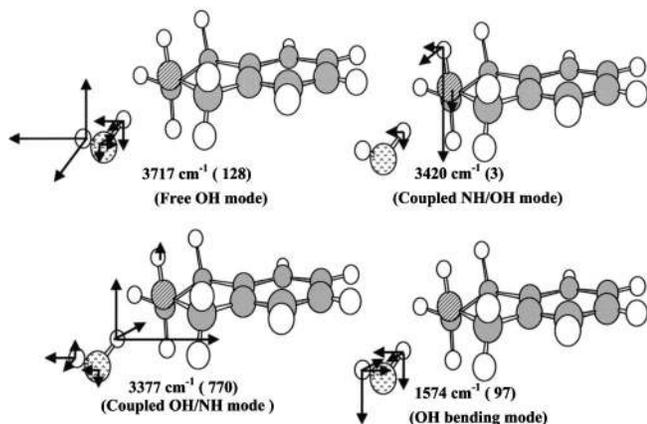

FIG. 9. The calculated (HF/6-31++G) normal-mode displacement vectors for the axial conformer of the 1:1 THIQ–H$_2$O cluster at OH and NH sites. Calculated IR intensities are presented in parentheses.

gen atom of THIQ is smaller in conformer X_A than in conformer X_E (see Fig. 5). Consequently, the redshift of the H-bonded OH mode of conformer X_A should be higher compared to that of conformer X_E. Therefore, our assignment of spectrum 4(b) to X_A and 4(e) to X_E is consistent with the structures calculated.

D. Structures of dihydrates and spectra

In the case of the dihydrates, several studies have shown that the two water molecules prefer to cluster together by forming a hydrogen bond between the two water molecules; the dimeric water then behaves as a unit and utilizes one of the remaining three free OHs to form a bond with the molecule, leaving only two OHs free.[7,32] Since both the spectra 4(a) and 4(d) have two bands around 3720 cm^{-1} corresponding to two free O–H groups, we assign the spectra 4(a) and 4(d) to the dihydrate clusters of the two conformers. Spectrum 4(d) has the expected number of bands (i.e., five total, four for two water molecules and one for the NH moiety), but spectrum 4(a) has one less. This could be due to one of the following reasons: (i) One of the IR bands in the dihydrate spectrum 4(a) may be forbidden for symmetry reasons. (ii) According to the calculated IR frequencies and intensities presented in Table II, there should be one intense IR band just below 3250 cm^{-1}. Such a band has indeed been noticed in the case of the dihydrate of NBF.[28] Unfortunately, the spectra presented in Fig. 4 extend only down to 3250 cm^{-1}. It is possible that this band will show up when the frequency region below 3250 cm^{-1} is covered in the study.

It is worth noting that the characteristic signature of the O⋯H–O unit in a water dimer is a band at around 3500 cm^{-1},[3(a),7] which is redshifted from the free symmetric OH frequency by ~225 cm^{-1}. Indeed, it is satisfying to note that this band characteristic for O⋯H–O is present in the IR spectra 4(a) and 4(d), but not in the spectra 4(b) and 4(e). It may also be noticed that the width of the 3500 cm^{-1} band is distinctly much larger than that of 3720 cm^{-1}. This provides support for the interpretation of the 3500 cm^{-1} band as the H-bond-redshifted O–H⋯O frequency of the water dimer. This 3500 cm^{-1} band, which may be expected in all dihydrates, should not be very sensitive to the molecular substrate to which the water dimer binds itself. In the case of NBF dihydrate, such a band was indeed noticed.[28] An alternative interpretation might be offered that these characteristic frequencies (3500 cm^{-1}) are shifted N–H frequencies; this argument, however, does not hold, as the observed bands are on the higher-frequency side of the free N–H frequency.[16(a)] The narrow bands at 3309 cm^{-1} in spectrum 4(a) and 3345 cm^{-1} in spectrum 4(d) are associated with the H-bond-redshifted, coupled OH or N–H stretch frequency. Finally, there is a weak band at about 3654 cm^{-1} in spectrum 4(d). It is suggestive of a π–H bond between O–H and the phenyl ring. However, in our extensive theoretical exercise we have not been able to generate an appropriate low-energy stable structure whose spectrum contains the 3654 cm^{-1} frequency. Further calculations are required.

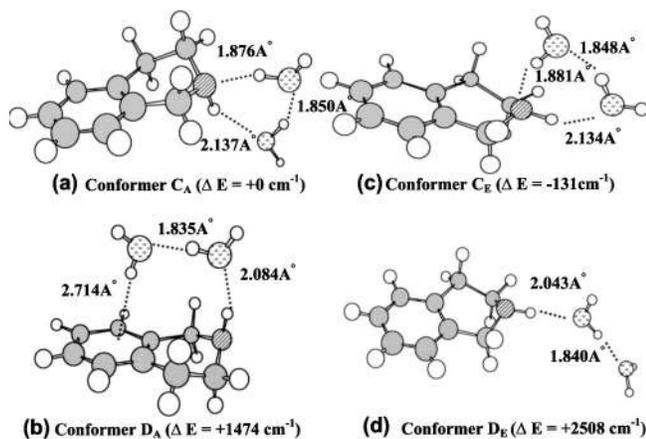In the bare molecule LIF excitation spectrum, we associate the lower-frequency 0–0 band (36 781 cm^{-1}) with the

FIG. 10. *Ab initio* (HF/6-31++G) calculated structure of THIQ–water 1:2 clusters, (a) conformer C_A and (b) conformer D_A corresponding to axial NH; (c) conformer C_E and (d) conformer D_E correspond to equatorial N–H.
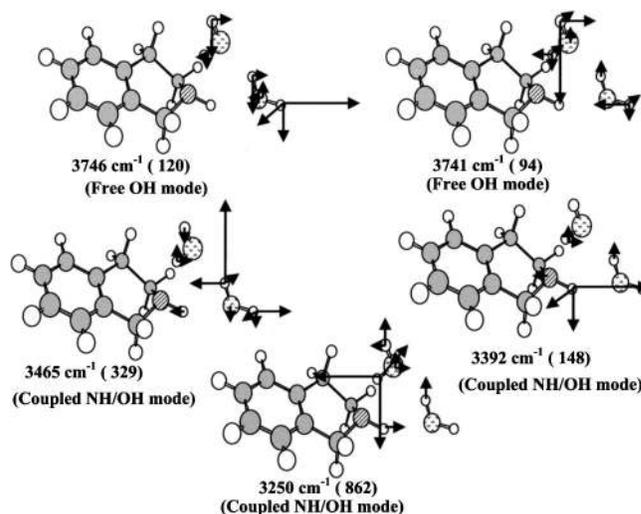

FIG. 11. The calculated (HF/6-31++G) normal-mode displacement vectors for the equatorial conformer of the 1:2 THIQ–H$_2$O cluster at OH and NH sites. Calculated IR intensities are presented in parentheses.

axial conformer and the higher-frequency 0–0 band (36 884 cm^{-1}) with the equatorial conformer. To be consistent, in the case of monohydrate we associate the lower-frequency peak *b* [Fig. 2(b)] with the axial and higher-frequency peak *e* [Fig. 2(b)] with equatorial forms. Similarly, for the dihydrate clusters, peak *a* [Fig. 2(b)] is associated with the axial and peak *d* [Fig. 2(b)] with the equatorial conformer. As in the case of the monohydrates, we assign the IR spectrum 4(a) to the axial dihydrate and spectrum 4(d) to the equatorial dihydrate. These assignments imply that the frequency shift of the 0–0 bands of the hydrates in the LIF spectrum is not a monotonically increasing function of the number of H$_2$O molecules. There is a large blueshift in the 0–0 bands of the LIF spectrum (Fig. 2) on going from the bare molecules to the monohydrates, but the shift is slightly to the red on going from the monohydrate to the dihydrate. This is true for both conformers.

Figure 10 displays several low-energy calculated structures for 1:2 THIO–water clusters. In all of our calculated, low-energy forms of 1:2 clusters, the water dimer is located near the nitrogen atom, such that the hydrogen of the NH group can also form a hydrogen bond with one of the lone pairs of an oxygen of the water dimer. Each of the NH conformers of the bare molecule forms two low-energy structures differing in the location of the water dimer. In the low energy conformer (conformer C_A), which has an axial NH configuration, the water dimer is located in a way such that a six-membered cyclic hydrogen bond network is formed. In this form the nitrogen plays the role of both a proton donor and a lone pair donor. Note that in the cyclic dihydrate structure there are two hydrogen-bonded OH groups, two free OH groups, and one hydrogen-bonded NH group. Energy calculations show that the cyclic structures C_A and C_E are more stable than the corresponding linear structures D_A and D_E. We expect, therefore, that C_A and C_E should be the species present in the cold conditions of the jet.

The IR spectra of conformers C_A and C_E may be expected to consist of two free O–H frequencies, one characteristic O–H$\cdots$O frequency, one N–H$\cdots$O frequency redshifted from the N–H frequency, and one N$\cdots$H–O

frequency redshifted from the O–H frequency, with the extent of the shifts depending on the strength of the H bond. Figure 11 shows vector diagram of five normal modes for the equatorial 1:2 water clusters of THIQ (C_E) in the OH and NH stretching frequency regions. The nature of OH and NH modes for axial conformer (C_A) is similar to that of equatorial (C_E) one. The first two calculated high-frequency modes correspond to the free OH site. The other three calculated modes shown in Fig. 11 are strongly coupled OH and NH modes. Similarly coupled X–H modes were observed in case of 2-pyridone–(H$_2$O)$_2$ clusters.[7] Generally, in a cyclic hydrogen bond network the vibrational modes at hydrogen bond sites show strong coupling. In our case the most redshifted calculated mode corresponds to the H-bonded OH mode with maximum intensity. It is found (Table II) that the redshift of the calculated OH and NH modes in C_A is more than that in C_E. This is consistent with the observed IR spectra of 4(a) and 4(d). Spectrum 4(d) is consistent with the structure C_E. Spectrum 4(a) corresponds to C_A, but it has four bands instead of the expected five. The possible reasons have been discussed before.

E. Structure of trihydrates and its IR spectrum

Spectrum 4(c) has seven bands, the number expected for a trihydrate. One can therefore reasonably expect three free or nearly free –OH groups. There are indeed three bands in the 3710 cm^{-1} region. The structures of the 1:3 clusters were calculated for both conformers. Figure 12 shows the lowest-energy structures for the two conformers. Three H$_2$O groups link up to form a H-bonded cyclic trimer with the NH group included in the cyclic structure, as shown in Fig. 12. As the cyclic structures and strengths of the H bonds at the OH and NH sites for both conformers are similar, the expected number of bands and their IR frequencies are nearly the same. Calculated OH and NH modes for the minimum energy equatorial conformer (B_E) are shown in Table II. Spectrum 4(c) exhibits extensive H bonding with THIQ and is compatible with an (N–H)-included cyclic structure. It has three
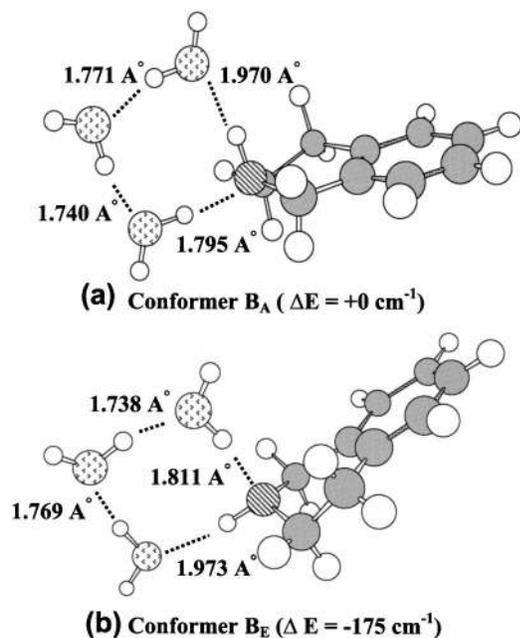
FIG. 12. *Ab initio* (HF/6-31++G) calculated structure of THIQ–water 1:3 clusters, (a) conformer B_A corresponds to axial NH and (b) conformer B_E corresponds to equatorial NH.

free O–H, two O···H–O, one O–H···N, and one O···H–N units. In view of the large bandwidths of the features in spectrum 4(c), we cannot confidently speculate on the structure and spectrum of the trihydrate.

IV. CONCLUSION

In the present work we have produced hydrated clusters of THIQ in a jet and discussed the cluster structures with the help of IR–UV double-resonance spectra and *ab initio* calculations. The free OH and redshifted NH and OH vibrational frequencies have been used to infer the hydrogen-bonded structures of water clusters of different kinds. In the 1:1 clusters it is seen that the water molecule is placed near the nitrogen atom in such a way that it can form a linear *X*-type hydrogen-bonded structure (see Fig. 5) where the OH of water forms a strong hydrogen bond with the lone pair of nitrogen. In the case of 1:2 and 1:3 hydrated clusters, the water dimer and trimer form a cyclic H-bonded framework at the nitrogen center. Instead of forming bridged hydrogen-bonded clusters, as was observed in NBF,[28] the water molecule(s) in THIQ clusters form(s) linear and six- and eight-member cyclic H-bonded structures at the nitrogen center for monohydrated, dihydrated, and trihydrated clusters, respectively.

ACKNOWLEDGMENTS

[1] T. Ebata, A. Fujii, and N. Mikami, Int. Rev. Phys. Chem. **17**, 331 (1998).
[2] C. J. Gruenloh, J. R. Carney, F. C. Hagemeister, C. A. Arrington, and T. Zwier, J. Chem. Phys. **109**, 6601 (1998).
[3] (a) B. Brutchy, Chem. Rev. **100**, 3891 (2000); (b) C. E. H. Dessent and K. Muller-Dethlefs, *ibid.* **100**, 3999 (2000).
[4] C. Jacoby, P. Hering, M. Schmitt, W. Roth, and K. Kleinermanns, Chem. Phys. **239**, 23 (1998).
[5] M. R. Hockridge and E. G. Robertson, J. Phys. Chem. A **103**, 3618 (1999).
[6] C. J. Weinheimer and J. M. Lisy, Chem. Phys. **239**, 357 (1998).
[7] G. M. Floria, C. J. Gruenloh, R. C. Quimpo, and T. S. Zwier, J. Chem. Phys. **113**, 11143 (2000).
[8] T. Ebata, A. Iwasaki, and N. Mikami, J. Phys. Chem. **104**, 7974 (2000).
[9] S. Ishiuchi, M. Saeki, M. Sakai, and M. Fujii, Chem. Phys. Lett. **322**, 27 (2000).
[10] P. M. Felker, P. M. Maxton, and M. W. Schaeffer, Chem. Rev. **94**, 1787 (1994).
[11] T. Ebata, M. Kayano, S. Sato, and N. Mikami, J. Phys. Chem. **105**, 8623 (2001).
[12] B. A. Pryor, P. M. Palmer, Y. Chen, and M. R. Topp, Chem. Phys. Lett. **299**, 536 (1999).
[13] R. N. Pribble and T. S. Zwier, Faraday Discuss. **97**, 229 (1994).
[14] T. S. Zwier, Annu. Rev. Phys. Chem. **47**, 205 (1996).
[15] F. C. Hageister, C. J. Gruenloh, and T. S. Zwier, Chem. Phys. **239**, 83 (1998).
[16] (a) A. Iwasaki, A. Fujii, T. Watanabe, T. Ebata, and N. Mikami, J. Phys. Chem. **100**, 16053 (1996); (b) Y. Matsumoto, T. Ebata, and N. Mikami, J. Mol. Struct. **552**, 257 (2000).
[17] Y. Matsumoto, T. Ebata, and N. Mikami, Chem. Phys. Lett. **338**, 52 (2001).
[18] R. Yamamoto, T. Ebata, and N. Mikami, J. Chem. Phys. **114**, 7866 (2001).
[19] E. Fujimaki, Y. Matsumoto, A. Fujii, T. Ebata, and N. Mikami, J. Phys. Chem. **104**, 7227 (2000).
[20] A. Fujii, E. Fujikami, T. Ebata, and N. Mikami, J. Chem. Phys. **112**, 6275 (2000).
[21] N. Guchhait, T. Ebata, and N. Mikami, J. Phys. Chem. A **104**, 11891 (2001).
[22] N. Guchhait, T. Ebata, and N. Mikami, J. Am. Chem. Soc. **121**, 5705 (1999).
[23] M. R. Hockridges, S. M. Kight, E. G. Robertson, J. P. Simon, J. McCombic, and L. M. Walker, Phys. Chem. Chem. Phys. **1**, 407 (1999), and references therein.
[24] (a) B. Reimann, K. Buchhold, S. Vaupel, B. Brutchy, Z. Havlas, V. Spirko, and P. Hobza, J. Phys. Chem. A **105**, 5560 (2001); (b) P. Hobza, V. Spirko, Z. Havlas, K. Buchhold, B. Reimann, H. D. Barth, and B. Brutschy, Chem. Phys. Lett. **299**, 180 (1999).
[25] A. Chakraborty, N. Guchhait, S. Banerjee, D. N. Nath, G. N. Patwari, and M. Chowdhury, J. Chem. Phys. **115**, 5184 (2001).
[26] T. Nakanaga, K. Kawamata, and F. Ito, Chem. Phys. Lett. **309**, 279 (1997).
[27] Y. Honkawa, Y. Inokuchi, K. Ohashi, N. Nishi, and H. Sekiya, Chem. Phys. Lett. **358**, 419 (2002).
[28] E. G. Robertson, M. R. Hockridge, P. D. Jelfs, and J. P. Simons, J. Phys. Chem. A **104**, 11714 (2000).
[29] S. Banerjee, N. Guchhait, A. Chakraborty, D. N. Nath, and M. Chowdhury, Chem. Phys. Lett. **346**, 387 (2001).
[30] N. Guchhait, Proc.-Indian Acad. Sci., Chem. Sci. **113**, 235 (2001).
[31] N. Guchhait, T. Ebata, and N. Mikami, J. Chem. Phys. **111**, 8438 (1999).
[32] T. Watanabe, T. Ebata, S. Tanabe, and N. Mikami, J. Chem. Phys. **105**, 408 (1996).
[33] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision B.03, Gaussian, Inc., Pittsburgh, PA, 2003.
[34] M. Schutz, T. Burgi, S. Leutwyler, and T. Fischer, J. Chem. Phys. **98**, 3763 (1993).