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Fluorescence excitation and dispersed emission spectra of tetrahydroisoquinoline are presented here. Two bands at 36 781 and 36 884 cm^{-1} are confirmed from the spectral hole burning studies as two origins for two conformers. These bands correspond to the inequivalent twist conformers with the hydrogen atom attached to the nitrogen atom at axial and equatorial positions, respectively. The former is found to be the most stable one. SVL spectra are explained on the basis of two theoretically calculated low-frequency vibrations. These correspond to the butterfly and puckering motions of the benzene chromophore, respectively. © *2001 American Institute of Physics.*
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I. INTRODUCTION

The conformational behavior of various flexible biologically relevant molecules has been studied intensively, both theoretically and experimentally,[1] for the last two decades. The factor which controls the conformational landscape involves a subtle balance between through-bond and through-space interactions within a molecule; this balance is further modified by nonbonded interactions with the environment. The effect of these interactions has recently been reported by many,[2–4] including us.[5] The van der Waals, nonbonding and H-bonding interactions not only determine molecular architecture, but also lead to an understanding of electronic charge distribution, pathways for electron and proton transfer, and solvent sensitivity of molecular fluorescence in fluid solutions, membranes, proteins, micelles, and other particles at interfaces.

Among the innumerable studies, the nitrogen-containing aromatic species have received special attention, as they are basic chromophores of proteins and peptides. Their conformational behaviors are interesting. The *trans* form of formanilide[2] (*N* phenyl fomamide) is found to be more stable than the *cis* form by about 2.5 kcal/mol in S_0, while the relative stabilities get reversed in S_1. In the case of acetanilide,[2] only the *trans* isomer is found under jet-cooled condition, but on *N*-methyl substitution,[2] the *cis* form is found in abundance. In *N*-benzylformamide,[3] the *trans* form

is the most stable conformer, stabler by more than 4.5 kcal/mol over the *cis* form. The conformational landscapes of coumarin derivatives and their hydrated clusters have been extensively studied by Topp *et al.* Both coumarin 153[6] and coumarin 337[6] have two conformers with the *syn* form as the most stable one compared to the *anti* form. Their relative stabilities and the nitrogen-inversion mode frequencies are quite different for the two species. However, in the case of coumarin 151[7,8] and coumarin 152A[7] only one species is found. In many of these molecules relaxation rates are found to be considerably different for the bare molecule and its 1:1 complex with water. The various conformers of phenylalanine[9] have been investigated by Simons *et al.* Three of the four most stable conformers are stabilized by intramolecular hydrogen bond; the latter links the carboxylic acid to the amino group and thereby provides a pathway for proton transfer. 2-pyridone and its hydrated clusters have been investigated by many. Recently,[4] the spectrum has been explained on the basis of two conformers in the S_1 state, but only one form in the S_0 state. Indoles and their derivatives[10] which bear similarity to tryptophan have also received close attention.

In the present study we have chosen tetrahydroisoquinoline (THIQ) for jet-spectroscopic investigations. The molecule seemed attractive to us for the following reasons.

(1) Photophysical properties of this molecule in condensed phase have earlier been investigated by us.[11] Flipped intramolecular charge transfer has been found to occur before emission in suitable condensed phases. As the polarity

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of the medium is increased, an exciplex-type broad band emerges on the long wavelength side of the emission band; however, the absorption band remains unperturbed. This has been explained in the following way: THIQ has a lone pair in the equatorial position in the ground state—a configuration where electron transfer from :NHR lone pair to phenyl ring is nearly impossible; this explains the absence of a charge transfer band in the ground state. However, if a configuration with the lone pair in axial position is preferred in the excited state, an exciplex between the -:NHR and the benzene ring may be formed in the excited state leading to a broad emission on the red side in a polar solvent. In view of this interesting observation,[11] we decided to investigate this molecule in detail by jet spectroscopy.

(2) The bare molecule THIQ can exist in a number of symmetry-inequivalent conformations. It seemed to us a worthwhile exercise to compare the experimentally observed relative stabilities, absorption frequencies, and vibronic frequencies of conformers with corresponding theoretically calculated quantities.

THIQ

THIQ (axial hydrogen form)

TA

THIQ (equatorial hydrogen form)

TE
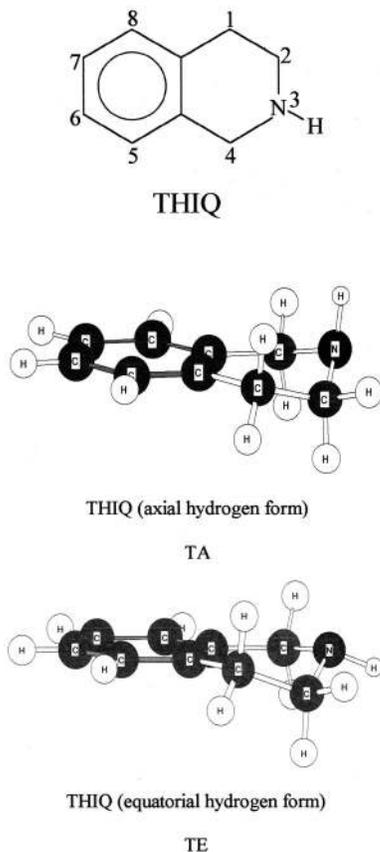
(3) We wanted to compare the spectra of THIQ with that of other similar molecules, such as tetrahydronaphthalene (THN)[12] and tetrahydroquinoline (THQ),[13] which have similar skeletons, or N-benzyl formamide,[4] which has similar lack of conjugation between the N-lone pairs and the phenyl π system.

II. EXPERIMENT

The compound THIQ obtained from Aldrich is of 99% purity but, due to its strong hygroscopic nature it is dried and

purified time and again before receiving the spectrum for the bare molecule. The details of our supersonic jet experimental setup is described elsewhere.[14] In brief, the sample is heated to about 100 °C to increase sample vapor pressure and then expanded with helium and argon as carrier gas into a vacuum chamber through a 0.5-mm-diam orifice of a pulsed nozzle valve (General Valve Corp.) with a frequency of about 10 Hz. The background pressure of the chamber during the experiment is maintained at about 4×10^{-5} Torr by the operation of a 6 in. oil diffusion pump (Varian) backed by a mechanical rotary pump. The output of the dye laser (Molectron), pumped by a Nd:YAG laser (Quanta Ray DCR-11), is frequency doubled by a KDP crystal. The second harmonic output crossed the jet at about 15 mm downstream of the nozzle orifice. The laser induced fluorescence is collected perpendicular to both the laser and the jet directions. The signal is detected by an EMI–9813 QB photomultiplier after passing the emitted light through an optical filter and an aperture to eliminate the scattered laser light and then averaged by a boxcar averager (PAR model −64). The normalized output from the boxcar is then recorded in a PC. Dispersed fluorescence spectra of selected single vibronic levels are recorded with the help of a 20 in. monochromator (Jobin Yvon). For the slit width employed by us, the resolution is around 30 cm^{-1}. The principle and the setup for hole-burning spectroscopy have been described earlier.[15]

III. RESULTS AND DISCUSSION

A. 0–0 band

Four conformers of this molecule, two bent and two twisted, are possible. These are produced by out-of-plane puckering of adjacent carbon (C_2) and nitrogen (N) atoms. Note that the inversion at the nitrogen center does not produce any additional distinct conformers. Unlike tetrahydronaphthalene (THN)[12] or sym-hexahydropyrene (HHP),[5] where the corresponding four conformers may be grouped into two symmetry-equivalent pairs, all four conformers of THIQ are inequivalent and all of them, in principle, can leave a signature in the spectrum under favorable conditions. To assign the conformers, whose signatures appear in the spectra, we take recourse to a number of arguments, including ones pertaining to hole-burning spectroscopy and semiempirical calculations.

The longest wavelength band, supposedly a 0–0 one, shown in Fig. 1, is observed at 36 781 cm^{-1} in THIQ, while it is at 36 791 cm^{-1} in tetrahydronaphthalene (THN). Compared to corresponding 0–0 bands of tetrahydroquinoline THQ[13] (32 450 cm^{-1}), aniline[16] (34 021 cm^{-1}), benzotriazole (BZT)[17] (34 917.8 cm^{-1}), and indole[10] (35 231 cm^{-1}), the THIQ 0–0 band shows a consistent blueshift. This closeness of 0–0 transitions of THN and THIQ (which is also corroborated by vertical transition energy calculations of these two molecules), and the marked blueshifts from 0–0 bands of THQ, indole, etc., are presumably consequences of the conjugation of the lone pair on the nitrogen atom with the π cloud of aromatic chromophore in the latter set of molecules (THQ, indole, aniline, BZT, etc.) and nonconjugation in the former set (THN, THIQ). However, as will be seen later, the
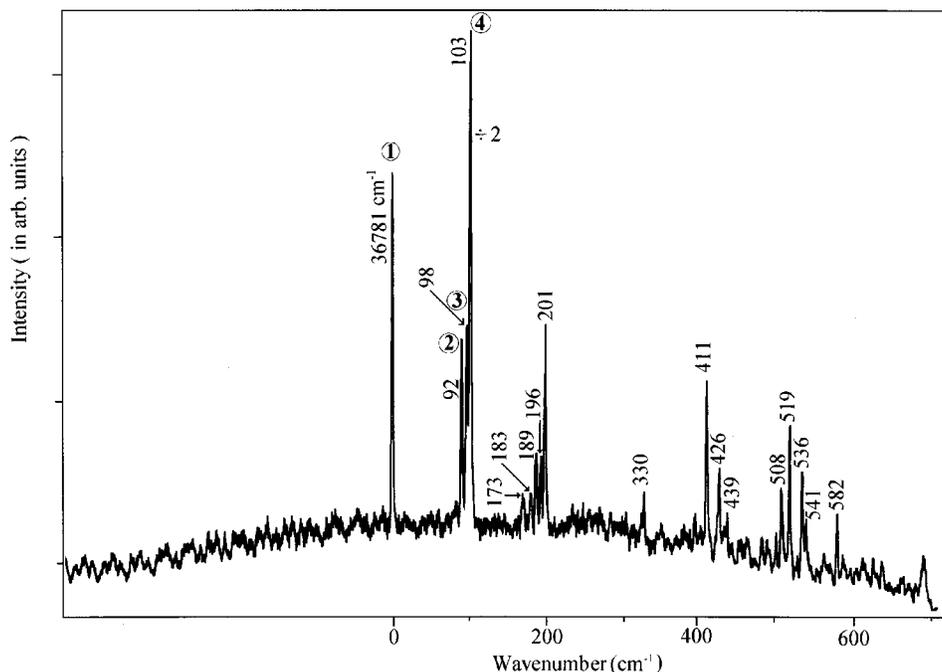
FIG. 1. Laser induced fluorescence excitation spectrum of THIQ in supersonic jet seeded in He.

position of the lone pair in equatorial or axial configuration is significant, even though to a small extent.

There are three very close lying bands at 92, 98, and 103 cm^{-1} on the blue side of the band origin in Fig. 1. All of these cannot be ascribed to the vibronic feature of this molecule in the excited S_1 state. Molecules close to THIQ in structure, like THN and THQ, show different vibronic features. The observed two low-frequency bands at 100 and 110 cm^{-1} from the origin in THQ have been ascribed to CH_2 puckering motions in the twisted configuration. In THN only one low-frequency vibronic band at 95 cm^{-1} from the origin band, corresponding to the twisting motion of adjacent carbon atoms, is observed. It may be noted that none of the structurally similar molecules exhibit this kind of bunching of three low-frequency bands around 100 cm^{-1} from the 0–0 band. Theoretical calculations for the ground state show that there are only two such low-frequency bands close to 100 cm^{-1}. We guessed, therefore, that at least one of them was an origin (0–0) transition of a different conformer. We looked for their response to the variation of laser intensity following the prescription of Levy *et al.* for conformer identification[18]—a technique that has also been successfully used by Topp *et al.*[6] Note that bands 1 and 4 are of unequal intensity. Suppose the transition originates from a common initial state (i.e., the same conformer) and this difference in intensity arises from a difference in transition probabilities to two different vibronic levels of the S_1 state. In that case, if the laser power is increased the strongest band should saturate first and the relative intensity of the weaker band should start increasing afterwards. The rate of increase of intensities of the two bands with laser power should have been different, if the band at 36 884 cm^{-1} was a vibronic feature over the 0–0 band at 36 781 cm^{-1}; but this is not what is observed. So we conclude that the two bands in the FE spectra arise from different initial states; that is, these are conformer bands. It is difficult to extend the same argument for bands 1, 2, and 3 as

their observed intensities are close and they should reach saturation at the same time even if they involve the same ground state. We, therefore, conclude conservatively that at least two conformers are contributing to the observed jet spectrum.

Further experimental confirmation came from dispersed emission spectra, corresponding to excitations at these four bands. Small *et al.* and Pratt *et al.*,[19(a),19(b)] argued that the 0–0 SVLs should have a strong (0–0 band) origin in the dispersed emission spectra relative to the vibronic bands; in contrast, vibronic band SVLs might be expected to have a relatively weak origin band relative to the total intensity in the vibronic manifold. Following this argument, we find that the band at 92 cm^{-1} (Fig. 2) should better be assigned as a vibronic band. However, in the case of the band at 98 cm^{-1} in the FE spectrum, the same conclusion is not so obvious, for the dispersed emission spectrum exhibits that intensities of the 0–0 band and the vibronic manifold are comparable. From these observations we conclude that the origin band and the one at 103 cm^{-1} from it are definitely 0–0 bands for two different conformers, while band 2 is a vibronic band over origin band 1. The identity of band 3, however, cannot be decided only on the basis of SVLs. The band at 201 cm^{-1} is clearly a vibronic band either on band 1 or on band 4.

We have taken the help of two-color spectral hole-burning (SHB) spectroscopy. When the probe laser is scanned while the pump is fixed at the origin transition (36 781 cm^{-1}), dips at 92 and 98 cm^{-1} are observed as this identifies band 3 as a vibronic one in Fig. 3. The hole-burnt spectra of the band at 36 884 cm^{-1} show dips at frequencies different from those observed for SHB of band 1. This corroborates our conclusion drawn from the SVLs and the intensity saturation measurements. The band at 201 cm^{-1} is a vibronic band over the origin band 4. The FE spectrum of the two conformers are shown in Fig 3.
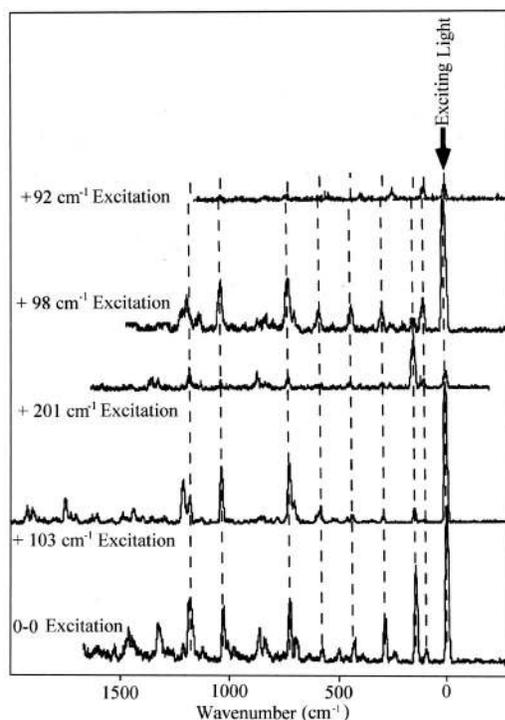
FIG. 2. Dispersed emission spectra of different bands (origins are appropriately shifted to a common one).

B. Possible structures of the two conformers and the assignment of the two band origins

To assign the structure and determine the stability of the conformers of the bare molecule in the ground state we resorted to theoretical calculations. *Ab initio* calculations of such a large molecule are beyond the scope of our computational facilities and, hence, we went for semiempirical calculations. For ground state energy calculations AM1 and PM3 Hamiltonians [MOPAC-5.0] are used and molecular mechanics (MM2) results are also compared with. For vertical transition energy calculations we invoke configuration interaction, the maximum number of configurations being limited to 1500 in

the program used. A potential energy curve (PEC) is generated by the relative movement of the nitrogen atom and its neighboring carbon atom (C_2). In moving from the twisted to the bent conformer, the out-of-plane coordinate of nitrogen atom is changed in small steps and the carbon atom (C_2) is held fixed in optimized position and vice versa. The rest of the atoms search freely for the global minima. The optimized energy in all these configurations is used to draw the PEC of the ground state shown in Figs. 4 and 5.

The lowest S_0 energy conformer obtained is TA, a structure twisted at the $N–C_2$ bond with the hydrogen atom of the NH group in the axial position. The other conformers, two bent and another twisted, lie higher in energy. One of the bent structures, has a lower energy than the twisted equatorial hydrogen conformer (TE), but it is located in a very shallow potential and is highly unstable. In MOPAC- AM1 and PM3 calculations if the molecule is placed close to this shallow well, it easily crosses over to its optimized twisted form (TA). The relative stabilities of the two stable conformers, as obtained in various ways are given in Table I. The vertical transition energies calculated with the TA and TE forms are also given. The calculated vertical transition energy is about 145 cm^{-1} less for the TE form than the more stable TA form.

In a jet one deals with unrelaxed populations. Nevertheless, Cable *et al.*[2] estimated the energy difference $E_{cis} - E_{trans}$ of formanilide from the observed relative intensities of corresponding bands of *cis*- and *trans*-isomers, using the Boltzmann distribution law and assuming a temperature corresponding to the reservoir (373 K); their estimated energy difference ($E_{cis} - E_{trans}$) of 2.5 kcal/mol was close to the value of 2.4 kcal/mol calculated with 3-21 G basis set. Such a procedure perhaps can only be justified in the presence of a high barrier and the absence of conformational relaxation during cooling in the jet stream. Ruoff *et al.*[20] and Felder *et al.*[21] dealt with the problem of relaxation of conformational isomers in seeded supersonic expansion and suggested a simple test for conformational relaxation. If the intensity ratio of the two conformer bands is the same in He jet and Ar jet, the barrier may be assumed to be large enough ($\geqslant 1$
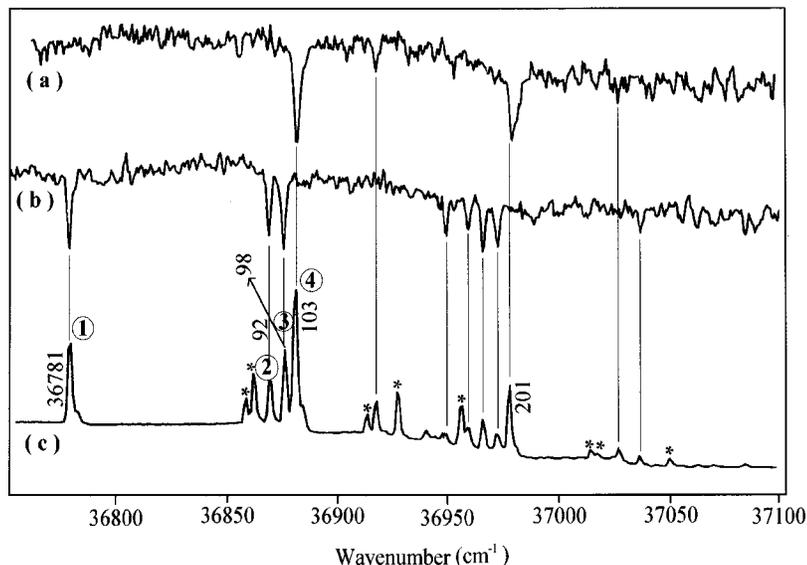

FIG. 3. Hole burnt spectra with pump fixed at (a) 36 884 cm^{-1} and (b) 36 781 cm^{-1}, respectively, are compared with (c) LIF spectrum. The bands due to water clusters are marked with an asterisk.
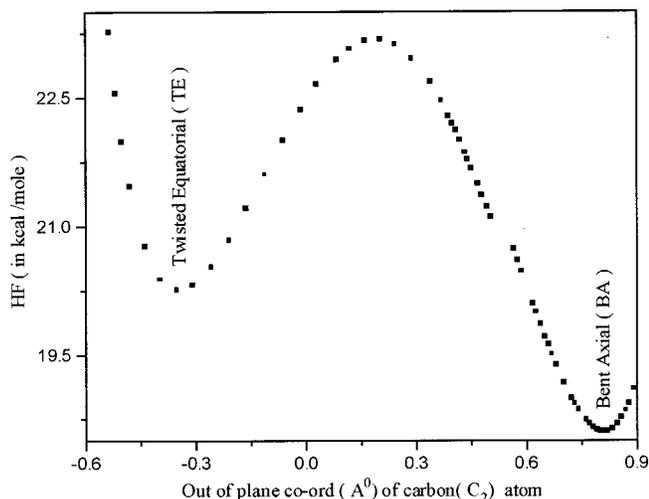
FIG. 4. Potential energy curve (PEC) of THIQ with respect to the out-of-plane movement of the carbon atom with the nitrogen atom fixed at the optimized geometry of the lowest energy conformer.

kcal/mol) to prevent conformational relaxation. In our case, the FE spectra of THIQ is insensitive to the nature of the carrier gas, indicating a barrier larger than 1 kcal/mol. Our semiempirical calculations estimate the barrier between the potential wells to be ~3 kcal/mol. Indeed, in respect of many of these parameters, the molecule THIQ closely resembles acroline.[20] In spite of our lack of accurate information of the potential energy surface and the dynamics in the jet, we attempted a rough estimate of the difference in stabilities of the two conformers from the observed intensity ratios of the two bands. In this case the chromophore in the two forms is the same and hardly perturbed by the nonconjugated N center; hence, one can expect that the 0–0 transition probabilities are the same for the two conformers, TA and TE. The intensity ratio of bands 1 and 4 should therefore be a good measure of the population difference. If we assume a large enough barrier to prevent conformational relaxation and an
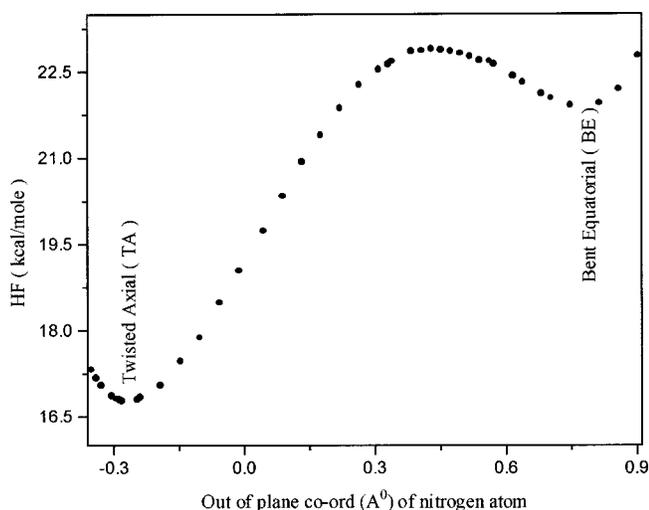

FIG. 5. Potential energy curve (PEC) of THIQ with respect to the out-of-plane movement of the nitrogen atom with the carbon atom fixed at the optimized geometry of the lowest energy conformer.

TABLE I. Relative stabilities and transition energies of the two twisted forms of THIQ.

(A) Stability (relative to TA)		
(I) Theory (method used)	Axial (TA)	Equatorial (TE)
MM2	0	+0.33 kcal/mol
MOPAC [AM1]	0	+3.31 kcal/mol
MOPAC [PM3]	0	+1.92 kcal/mol
(II) Experiment ($T = 373$ K)	0	+0.84 kcal/mol
(B) Transition energy (relative to TA)		
(I) Theory	0	-145 cm^{-1}
(II) Experiment	0	-103 cm^{-1}

equilibrium reservoir temperature of 373 K, we get an energy difference of 0.84 kcal/mol using the Boltzmann distribution law. Since the effective temperature at the time when the conformational relaxation ceases and the rapid vibrational relaxation in the two potential wells begins should be less than the reservoir temperature, our estimated value of the energy separation may be considered as an upper limit.

All the semiempirical calculations suggest that the conformer having axial hydrogen in twisted configuration (TA) is the most stable one and has to be assigned to the more intense band 4. This is in agreement with the transition frequency calculations which predict that the origin of TA form should appear at the blue side of the origin band of the TE form. The observed separation between the origin bands is 103 cm^{-1}, which may be compared with 145 cm^{-1} calculated theoretically. We, therefore, assign band 1 to the TE form and band 4 to the TA form.

C. Vibronic bands

1. S_0 state

The ground state vibronic frequencies are probed by SVL spectra. The SVL spectrum for excitation of band 1 (TE) at 36 781 cm^{-1}, shown in Fig. 6 exhibits two low-frequency vibrations of 95 and 145 cm^{-1} out of which the band at 145 cm^{-1} is much more intense and generates a
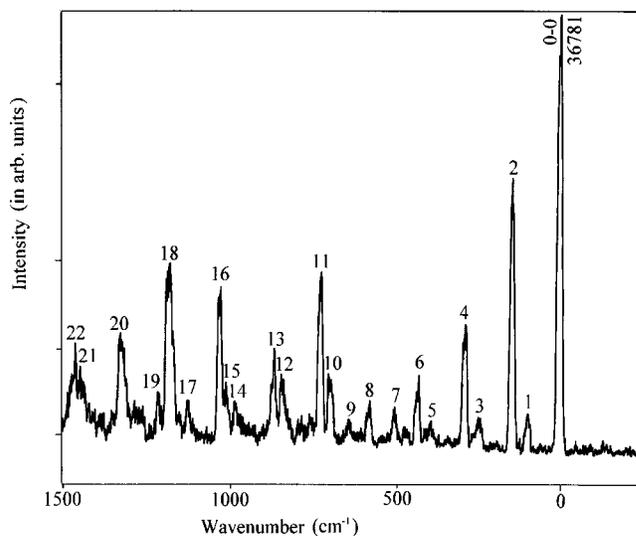

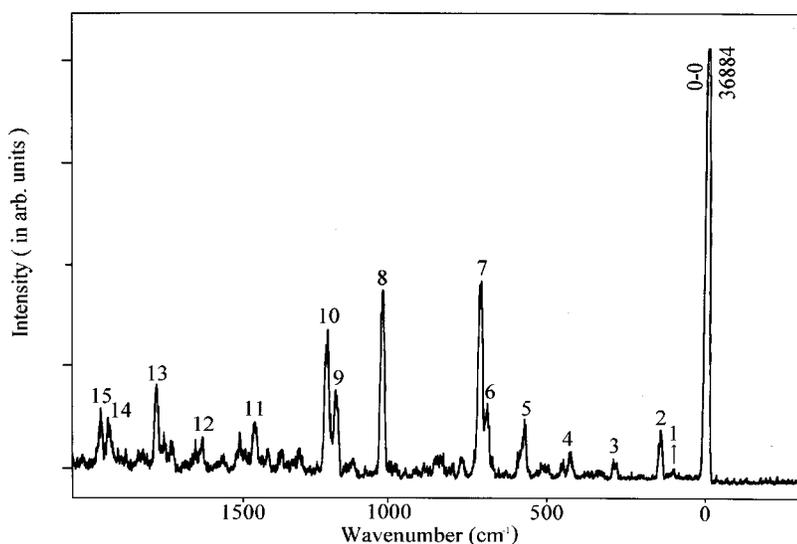FIG. 6. Dispersed emission spectra of THIQ when excited at 36 781 cm^{-1}.

FIG. 7. Dispersed emission spectra of THIQ when excited at $36\,884$ cm^{-1}.

sequence of overtones. Not only are the first three quanta of the low-frequency mode of 145 cm^{-1} observed with decreasing intensities starting with the origin band, the same sequence rides over other false origins as well. Figure 7 exhibits the SVL spectrum of band 4 at 36 884 cm^{-1}; only one nearly harmonic progression of 145 cm^{-1} appears in the spectra of the TA form. The 95 cm^{-1} band appears very feebly. This sequence of harmonics, however, is weaker than that of the TE form. Indeed, if after separating the two spectra by the hole-burning technique (Fig. 3) we compare the laser excitation (or absorption) spectra of TA and TE conformers, we find that the intensities are more in the vibronic manifold for the TE conformer (Fig. 6). Apparently, the geometry of the TE form is affected more (compared to the TA) on excitation of the π electrons of the benzene chromophore; this leads to greater intensity in the vibronic manifold. This is understandable in a general way, as the N-lone pair of the

TE form is more exposed to the benzene ring, and any perturbation such as optical excitation in the π cloud affects the nitrogen lone pair, thus inducing a vibration in which the displacement of the nitrogen atom is a major component.

We have calculated the S_0 frequencies (Table II) and the nature of displacement vectors of the soft modes of THIQ and other similar molecules. Both AM1 and PM3 Hamiltonians yield consistent results regarding the vibrational frequencies in S_0 and S_1. The two low-frequency modes (ν_1 and ν_2) are calculated to be at 93 and 138 cm^{-1} for the TA form and 75 and 135 cm^{-1} for the TE. These numbers are in fair agreement with our observed frequencies. Tables III and IV list the observed low frequencies and corresponding assignments for TA and TE forms. For structurally similar molecules, THQ and THN, the calculated values are {95 and 136

TABLE II. THIQ S_0 vibrational frequencies (cm^{-1}) calculated with MOPAC (AM1 Hamiltonian).

Serial No.	Twisted axial (TA) form	Twisted equatorial (TE) form
1	93	75
2	136	134
3	246	226
4	294	254
5	379	380
6	425	424
7	465	467
8	503	503
9	518	514
10	626	625
11	675	652
12	687	684
13	805	803
14	871	843
15	878	882
16	910	909
17	924	918
18	955	960
19	963	984

TABLE III. S_0 vibrational frequencies (cm^{-1}) and their assignments, obtained from SVL on excitation at band (1) (36 781 cm^{-1}).

Band No.	Observed freq.	Assignment
1	95	ν_1
2	144	ν_2
3	245	$\nu_2 + \nu_1$
4	287	$2\nu_2$, $3\nu_1$
5	392	$\nu_1 + 2\nu_2$
6	429	$3\nu_2$
7	501	ν_{ring}
8	580	$4\nu_2$
9	640	$\nu_2 + \nu_{ring}$
10	699	ν'_{ring}
11	725	ν''_{ring}
12	846	$\nu_2 + \nu'_{ring}$
13	867	$\nu_2 + \nu''_{ring}$
14	986	$2\nu_2 + \nu'_{ring}$
15	1017	$2\nu_2 + \nu''_{ring}$
16	1034	ν'''_{ring}
17	1134	$\nu'''_{ring} + \nu_1$
18	1190	ν''''_{ring}
19	1224	$\nu'''_{ring} + 2\nu_1$
20	1339	$\nu''''_{ring} + \nu_2$
21	1460	$2\nu''_{ring}$
22	1474	$\nu''''_{ring} + 2\nu_2$

TABLE IV. S_0 vibrational frequencies (cm^{-1}) and their assignments, obtained from SVL on excitation at band (4) (36 884 cm^{-1}).

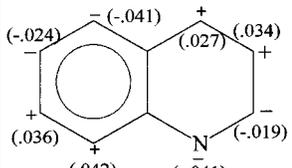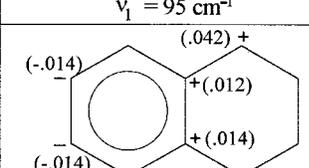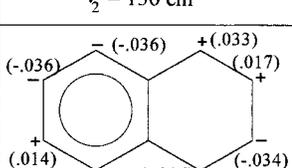| Band No.	Observed freq.	Assignment
1	95	ν_1
2	145	ν_2
3	290	$2\nu_2$
4	435	$3\nu_2$
5	581	$4\nu_2$
6	701	ν'_{ring}
7	725	ν''_{ring}
8	1035	ν'''_{ring}
9	1188	$\nu'''_{ring} + \nu_2$
10	1215	ν''''_{ring}
11	1446	$2\nu''_{ring}$
12	1613	$2\nu''_{ring} + \nu_2$
13	1761	$2\nu''_{ring} + 2\nu_2$
14	1915	$2\nu''_{ring} + 3\nu_2$
15	1939	

cm^{-1}} and {86 and 130 cm^{-1}}, respectively. This means that these modes are not N-specific inversion modes, but are rather out-of-plane puckering frequencies of the skeleton. Our calculated displacement vectors for the normal modes of two (ν_1 and ν_2) low-frequency (out-of-plane movement only) vibrations of the above three molecules are shown in Table V. Interestingly, the two modes are identical in nature

for all three molecules. It indicates that the substitution of carbon with nitrogen does not alter the nature of the modes. The mode ν_1 is essentially a butterfly type of vibration with extended aromatic ring forming one wing of the butterfly. The important point is that the out-of-plane vibration does not disturb the spectrum of the π system. The ν_2, on the other hand, make the chromophore out-of-plane puckered and thereby get coupled to the phenyl ring transitions very effectively.

2. S_1 state

The spectra of the two conformers are disentangled in the SHB spectroscopy. The conformer with the band origin at 36 781 cm^{-1} shows clustered low frequency bands at 92, 98, 171, 182, 189, 196, and 260 cm^{-1}. Since theoretical calculations of excited state are not very reliable, we explain the vibronic features in S_1 by comparing them with S_1—frequencies of similar molecules on the one hand and with its own S_0 frequencies on the other. The low-frequency vibronic bands of the excitation spectra can be explained on the basis of two low-frequency bands of 92 cm^{-1} (ν'_1) and 98 cm^{-1} (ν'_2) corresponding to the S_0, butterfly motion and the out-of-plane puckering motions ν_1 and ν_2, as already discussed. Similar low-frequency vibrations have been observed for S_1 states of structurally related molecules like

TABLE V. Comparison of low-frequency vibrational modes of THIQ, THQ, and THN in S_0.
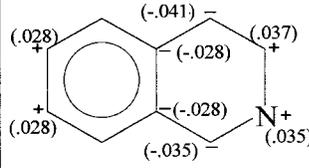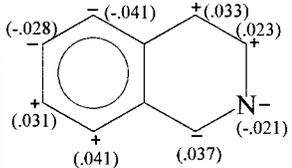
THN and THQ. For example, in THQ these are 100 and 110 cm^{-1}, while for THN the corresponding numbers are 90 and 95 cm^{-1} in S_1. While the vibronic bands at 182, 189, and 196 cm^{-1} can be clearly assigned as overtones or combination bands $2\nu_1'$, $\nu_1' + \nu_2'$, $2\nu_2'$, the band at 171 cm^{-1} has to be identified as a new frequency ν_3' and the one at 260 cm^{-1} as $\nu_3' + \nu_1'$.

One interesting point to note is that while in SVL only ν_2 appears as a sequence, the first overtones of both ν_1' and ν_2' show up in the FE spectrum. This suggests a ground state mode mixing of Duschinsky type in the excited state. It is to be noted further that the general features of the FE spectrum are considerably different from any of the SVL spectra. In particular, a sudden drop in intensities of vibronic bands after 400 cm^{-1} in the FE spectrum is suggestive of an excited surface considerably different from the ground state surface. One possibility is that the barrier for puckering as well as the extent of puckering is considerably lower in the S_1 state compared to that in the S_0 state.

The SHB spectrum of the TA form shown in Fig. 3, with band origin at 36 884 cm^{-1}, show vibronic bands at 98 and 137 cm^{-1} from the band origin. The weak band at 36 cm^{-1} does not appear in the FE spectrum of carefully dried sample and has therefore been ignored. The two frequencies closely match the ground state frequencies for both forms. The reason why these frequencies are not affected in this conformer on excitation in the benzene ring could be that the lone pair directed away from the benzene ring does not interact with the chromophore and hence remains largely unaffected by photoexcitation in chromophore.

IV. CONCLUSION

The FE spectra of tetrahydroisoquinoline (THIQ) shows a bunch of bands at regular intervals with 36 781 cm^{-1} as the origin. SVL and hole-burning spectroscopy confirm the assignment of the two bands at 36 781 and at 36 884 cm^{-1} to the two 0–0 bands of two conformers of THIQ. With the help of semiempirical theoretical calculations we identify the conformers as twisted ones where the hydrogen atom attached to the nitrogen atom is in either axial or equatorial position. The former is found to be the most stable one. SVL spectra exhibit two low-frequency vibrations, one corresponding to butterfly motion and the other to the puckering motion encompassing the chromophore.

The molecule THIQ has two independent centers for H bonding with water—the N atom and the phenyl ring. Additionally, the N-center should behave differently in the two conformers with regard to cluster formation with water. Finally, the molecule being nonplanar, the H-bonding capability of both sides of the N atom may not be the same. The consequence of all these is that the THIQ–water adducts could exist in a number of conformers with characteristic spectral signatures. THIQ shows at least five different origin transitions on the addition of water. These are confirmed from hole-burning studies, which will be published shortly.

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