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Electronic and Vibrational Spectroscopy of Dihydrogen Bonded 2-Pyridone−Borane−Trimethylamine Complex in Supersonic Jets

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In this paper we present results of laser-induced fluorescence excitation, fluorescence detected infrared and IR−UV hole-burning spectroscopic studies on the 2-pyridone and borane-trimethylamine complex. A relatively small blue shift in the electronic transition accompanied by a large shift in the N−H stretching vibration to a lower frequency suggests the formation of a dihydrogen bonded complex. The structure of the complex is elucidated with the aid of ab initio DFT calculations, which fits the observed spectral shifts.

I. Introduction

Hydrogen bonding has profound impact on structure and reactivity both in chemistry and biology. In last 2 decades, hydrogen bonding involving various unconventional donors and acceptors have been reported in the literature.[1−3] One of these unconventional hydrogen bonds is the hydrogen bonding between two oppositely charged hydrogen atoms, named "dihydrogen bond".[3] This novel electrostatic/dipolar interaction (E−H····H−X) is between a positively charged hydrogen atom connected to an electronegative atom, X, such as oxygen or nitrogen or halogen, and a negatively charged hydrogen atom connected to an electropositive atom, E, such as boron or metal.[3] The existence of dihydrogen bonds in crystals of transition metal complexes and borane-amine adducts is known for more than 10 years. However, only recently we have established the existence of gas-phase dihydrogen bonded complexes between borane-amine adducts and proton donors, such as phenol.[4,5] The main structural features of the dihydrogen bond are the H····H contact distance of less than 2.4 Å (sum of van der Wall radii) and the strongly bent E−H····H angle, with an average around 110°. This bent geometry is in sharp contrast to near linear geometry of conventional hydrogen bonds. Interestingly, it has been found both experimentally[6,7] and theoretically[8] that the two interacting hydrogen atoms in a dihydrogen bond could escape as H_2, leading to dehydrogenation reaction. Apart from the novelty, above-mentioned unusual structure and reactivity, provides motivation to investigate gas-phase dihydrogen bonded complexes. Further, dihydrogen bonded systems gains importance due to its potential application in crystal engineering.[9]

A survey of H····H contact distances between 1.7 and 2.2 Å in crystal structures of many borane-amine adducts reported in the Cambridge Structural Database revels the existence of dihydrogen bond between N−H and H−B groups.[3] In our earlier work, proton donor for the dihydrogen bond was an O−H group. For a better understanding of dihydrogen bonding interaction in the borane−amine adducts, we have taken up spectroscopic investigation of gas-phase dihydrogen bonded complexes with N−H group being the proton donor. 2-Pyridone (2PY) and 2-hydroxypyridine (2HP) are keto−enol tautomers associated with a single proton transfer. Recently, a lot of interest has been generated in these two tautomers and their hydrogen bonded complexes in supersonic jets in order to identify the solvent assisted tautomerization process.[10−14] The infrared spectroscopy of 2PY and 2HP complexes with protic solvents such as H_2O and MeOH suggests the involvement of solvent proton in the tautomerization, however, the process of tautomerization is not complete in binary complexes.[12−14]

In this paper, we report, for the first time, a new gas-phase dihydrogen bonded complex of the type N−H····H−B between 2PY and borane-trimethylamine (BTMA), using electronic and vibrational spectroscopy. Laser-induced fluorescence spectroscopy was used to probe the electronic transition. On the basis of the shift in the electronic transition of 2PY upon complexation, the possible binding site of BTMA to 2PY can be inferred. Infrared spectroscopy is an important tool to identify the hydrogen bonding, due to the fact that the hydride stretching frequency of proton donors is very sensitive to hydrogen bonded structures.[15] In the present case we examine the shifts in the N−H stretching of 2PY moiety upon complexation with BTMA using fluorescence detected infrared (FDIR) spectroscopic technique. Ab initio density functional theory (DFT) based calculations were carried out to determine the structure of the complex. The calculated stabilization energies and the vibrational spectra were compared with the experimental spectra to determine the structure of the dihydrogen bonded complex between 2PY and BTMA.

II. Experimental Section

Details of the experimental setup have been described elsewhere.[16] Briefly, helium buffer gas at 4 atm was passed over BTMA (Kanto chemicals) vapor at 320 K and was mixed with 2PY (Wako chemicals) vapor in a sample compartment heated to 370 K. One of the difficulties associated with this experiment was to maintain different temperatures for the solvent (BTMA) and the solute (2PY). The mixture was expanded supersonically through a 0.8 mm diameter pulsed nozzle. The electronic excitation of 2PY and its cluster with BTMA was achieved using a second harmonic of Nd:YAG laser (Spectra Physics INDI-50) pumped tunable dye laser (Lumonics HD-500; LDS-690 dye). The LIF excitation spectra were recorded by monitoring the total fluorescence with a photomultiplier tube (Hamamatsu, 1P28) combined with a cut off filter (Toshiba UV-D36A), while

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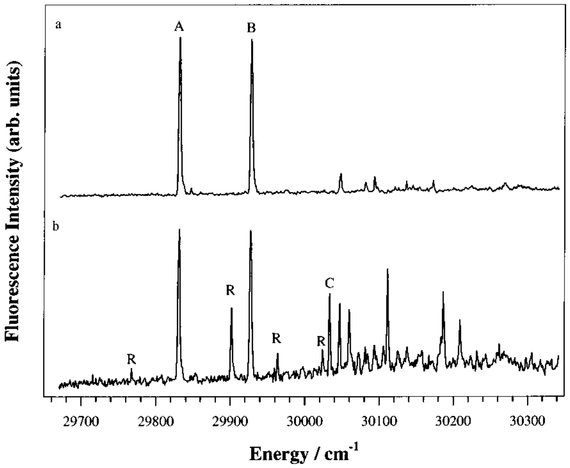

Figure 1. LIF excitation spectrum of (a) 2-pyridone and (b) 2-pyridone in the presence of BTMA. Peaks marked A, B are the two band origins of the bare molecule, C is the cluster with BTMA, and those marked R are some reaction products between 2-pyridone and BTMA.

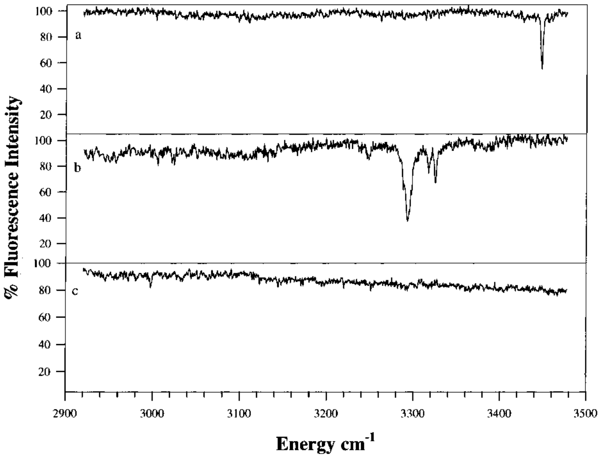

Figure 2. FDIR spectrum of (a) bare 2-pyridone, (b) 2-pyridone-BTMA complex, and (c) one of the peaks marked R in LIF excitation spectrum.

scanning UV laser frequency. The IR spectrum of the complex was obtained by fluorescence detected infrared (FDIR) spectroscopy. In this spectroscopy, the ground-state zero point level population of a particular species is monitored by LIF intensity following an electronic excitation to its $S_1 \leftarrow S_0$ origin band with an UV laser pulse. A tunable IR laser pulse was introduced 50 ns prior to the UV laser pulse. When the IR frequency is resonant with the vibrational transition of the species monitored, the ground-state population decreases, resulting in the depletion of the LIF signal. Thus, the IR spectrum is obtained as a fluorescence dip spectrum. The tunable IR light was generated by difference frequency generation (DFG) between the second harmonic of Nd:YAG laser (Quanta-Ray GCR/230) and the output of Nd:YAG pumped dye laser (Continumm ND 6000; DCM dye; wavelength region 650−665 nm) with a $LiNbO_3$ crystal. The IR−UV hole-burning spectrum was obtained by measuring the $S_1 \leftarrow S_0$ LIF excitation spectrum with and without the IR laser, whose frequency was tuned to the N−H vibrational transition of the 2PY−BTMA complex.

III. Results and Discussion

Figure 1a shows the LIF excitation spectrum of bare 2PY; peaks A and B at 29831 and 29928 cm^{-1} are the two band origins corresponding to two different N−H conformations it adapts in the S_1 state.[10] Figure 1b shows the excitation spectrum in the presence of BTMA. It is clearly evident that many transitions appear after the addition of BTMA. The transition at 30034 cm^{-1}, marked with ‘C’, was assigned to the origin band of 2PY−BTMA complex, based on IR−UV hole-burning spectroscopy, which will be presented latter in this section. This band is blue shifted by 203 cm^{-1} from the corresponding band (band A) of bare 2PY. Accompanied with band origin are several vibronic transitions associated with low-frequency intermolecular modes of the complex. Appearance of vibronic transitions coupled to intermolecular modes is a common feature of gas-phase dihydrogen bonded complexes, and the present case is in accord with the previous results.[4,5] Transitions marked with R are thought to be due to some reaction product between 2PY and BTMA, and will be discussed later.

The hydrogen bonded complexes of 2PY can be split into two categories according to the extent of blue shift in the electronic transition of the complex relative to bare 2PY.[11−13] The first category consists of complexes in which both N−H and carbonyl group are associated with the intermolecular structure forming a cyclic complex. These complexes have a large blue shift in the electronic transition as in the cases of 2PY−H_2O (633 cm^{-1}), 2PY−MeOH (615 cm^{-1}), and 2PY−dimer (944 cm^{-1}). This large blue shift is due to the interaction of the solvent proton with the carbonyl oxygen of 2PY, which gets destabilized upon electronic excitation. The second set consists of complexes in which solvent binds exclusively to the N−H proton. These complexes have much smaller blue shifts, as in the case of dioxane (120 cm^{-1}) and dimethyl ether (131 cm^{-1}). The present 2PY−BTMA complex falls in the second category since the blue shift in the electronic transition is only 203 cm^{-1} and indicates that BTMA interacts primarily with N−H group of 2PY. On the basis of the blue shift in the electronic transition alone, one could infer the formation of a dihydrogen bonded complex between 2PY and BTMA, since the hydrogens attached to boron are the only accessible proton acceptors in BTMA.

Figure 2a shows the FDIR spectrum of bare 2PY in the ring C−H and the N−H stretching frequency region. Only one transition corresponding N−H stretching was observed at 3448 cm^{-1}, which is in good agreement with that reported elsewhere.[12] It is worth noting that no IR activity was found in the ring C−H stretching. Figure 2b shows the FDIR spectrum of 2PY−BTMA complex. Once again no IR activity was found in the ring C−H stretching region. The slightly broad transition at 3293 cm^{-1} was assigned to the N−H stretching of 2PY moiety, which is shifted by 155 cm^{-1} to a lower frequency. This suggests that the BTMA interacts with N−H of BTMA moiety, which is in agreement with the observed electronic blue shift. In the present case, observed shift in the N−H stretching vibration to lower frequency is more than that of 2PY−H_2O (119 cm^{-1}) and 2PY−MeOH (121 cm^{-1}) complexes and less than 2PY−dioxane (226 cm^{-1}) and 2PY−dimethyl ether (250 cm^{-1}).[11] This clearly indicates that BTMA is a relatively strong proton acceptor, and is in accord with similar conclusion drawn in the case of the phenol−BTMA complex.[5] Furthermore, the appearance of two low-frequency intermolecular modes in combination over the N−H stretching is an indication of a strong hydrogen bond between 2PY and BTMA. This situation is very similar to that observed in the case of dihydrogen bonded complex between phenol and borane-dimethylamine.[4]

Shown in Figure 2c is the FDIR spectrum of one of the peaks marked with “R” in the LIF excitation spectrum. Evidently, transition corresponding to neither C−H nor N−H stretches appears, which was rather puzzling. On the other hand, the

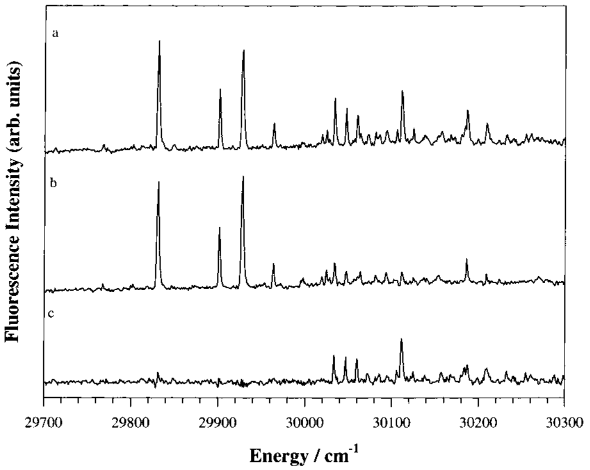

Figure 3. (a) LIF excitation spectrum with IR off and (a) LIF excitation spectrum with the IR laser frequency fixed to the N−H stretching vibration of 2-pyridone-BTMA complex (IR−UV hole-burning spectrum). (c) The LIF excitation spectrum of 2-pyridone-BTMA complex, obtained by subtracting (b) from (a).

electronic transition is in the same energy region of 2PY suggesting that the 2PY chromophore is intact. The similarity of the electronic transition energy and the disappearance of N−H stretching indicates possibility of a reaction between 2PY and BTMA leading to some substitution on the pyridine ring, which did not alter the $S_1 \leftarrow S_0$ electronic excitation. Efforts are on to characterize the reaction product.

IR−UV hole-burning spectroscopy was carried out to determine the origin of numerous bands appearing in the LIF excitation spectrum (Figure 1) and to check the possibility of isomers. IR−UV hole burning spectroscopy has been proved to be an useful technique to separate transitions of belonging to various hydrogen bonded structures.[4,5,17] Figure 3a shows the LIF excitation spectrum, which is identical to that shown in Figure 1b. Trace "b" is the IR−UV hole-burning spectrum, which was recorded by pumping the N−H stretching vibration of 2PY−BTMA complex at 3293 cm^{-1}. It can be seen that apart from the 2PY−BTMA origin band at 30034 cm^{-1} several other transitions have diminished intensities. Trace "c" is the resultant of subtraction of trace "b" from trace "a'", which is the LIF excitation spectrum of 2PY−BTMA complex. This spectrum shows a rich vibronic activity in the low frequency region corresponding to the intermolecular vibrations. Moreover, this also confirms presence of only one isomer of the 2PY−BTMA complex.

A rather small blue shift in the electronic transition and a large shift in the N−H stretching vibration to a lower frequency together with the appearance of low-frequency vibrations in the electronic excitation and in combinations with the N−H stretching vibration suggests the formation of dihydrogen bonded complex between 2PY and BTMA. To elucidate the structure of 2PY−BTMA complex we have carried out ab initio DFT calculations using Gaussian-98.[18] The level of theory used is Becke-3LYP (B3LYP) exchange correlation functional[19] with 6-31++G(*d,p*) basis set, which is a split valence with polarization and diffuse functions on heavy atoms as well as hydrogens. The usage level of this calculation can be rationalized by the fact that many hydrogen bonded structures are well represented at a reasonable computational cost. Moreover, this level of calculation has shown a remarkable agreement with the experiment in the case of a dihydrogen bonded complex reported earlier.[5] The geometries of bare molecules and the complex were optimized under tight binding conditions with no constraints (Gaussian keyword fopt = tight). The nature of the obtained stationary point was confirmed by calculating the vibrational frequencies at the same level of theory. The stabilization energy of the complex was corrected for the zero point energy (ZPE) and the basis set superposition error (BSSE). Though we started from several initial geometries all of them converged to only one minimum, whose structure is shown in Figure 4. The ZPE and BSSE corrected stabilization energy of the complex is −6.84 kcal/mol. This complex has roughly C_s symmetry, in which N−H proton of 2PY forms a dihydrogen bond with negatively charged hydrogen atom attached to boron of the BTMA moiety. In the dihydrogen bond the distance between the two hydrogens is 1.78 Å and the BHH angle is 117.5°. These geometric parameters are in good agreement with other dihydrogen bonded structures reported elsewhere.[3−5] Furthermore, a weak hydrogen bond of length 2.29 Å between a methyl proton of BTMA moiety and the carbonyl oxygen of 2PY gives additional stability. This weak interaction causes slightly larger blue shift in the electronic transition compared to dioxane or dimethyl ether complexes of 2PY.[10] The calculated vibrational frequencies were scaled with a factor of 0.955 to correct for the basis set truncation, partial neglect of electron correlation, and the harmonic approximation. This scaling factor is same as that used earlier for phenol−BTMA complex.[5] The calculated N−H stretching frequencies for bare 2PY and 2PY−BTMA complex are 3442 and 3282 cm^{-1} corresponding to experimental values of 3448 and 3293 cm^{-1}, respectively. The agreement between the calculated and the experimental values is excellent. This corroborates a very good correlation between the calculated and the experimentally observed 2PY−BTMA dihydrogen bonded complex.

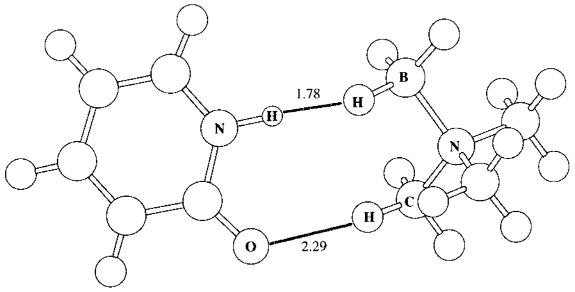

Figure 4. Calculated structure of 2-pyridone-BTMA complex. Distances are in angstroms and the labels B, N, O, and H correspond to boron, nitrogen, oxygen, and hydrogen atoms, respectively. See text for details.

IV. Conclusion

The observed 203 cm^{-1} blue shift in the electronic transition of the 2PY−BTMA complex indicates that the interaction between 2PY and BTMA is largely at the N−H site. The N−H stretching vibration was shifted by 155 cm^{-1} to a lower frequency due to the hydrogen bonding between 2PY and BTMA. These experimental results together with ab initio calculations ascertained the formation of a dihydrogen bonded complex between 2PY and BTMA.

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