

Electronic Spectra of Hydrogen-Bonded Indazole in a Supersonic Free Jet

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Abstract

Fluorescence properties of indazole complexes with various protic molecules in supersonic jets are investigated. Indazole forms hydrogen-bonded complexes with acetic acid, formic acid, water and ethanol in jets and the 0-0 bands are shifted by 256, 243, 274 and 201 cm^{-1} to the red of the 0-0 band of free indazole, respectively. The dispersed fluorescence spectra of these complexes are all similar indicating similar complex structures. Different from the cases of indazole-acid complexes in solution, no spectroscopic evidence was obtained in jets for excited state tautomerization or protonation. On the basis of the analysis of the fluorescence excitation and emission spectra, it is suggested that indazole-acid complexes in jets are bonded by a single hydrogen bond.

Introduction

Indazole is known to form hydrogen-bonded complexes with various molecules and to show interesting fluorescence properties in solution. I have found that indazole undergoes excited state tautomerization from 1H to 2H in acetic acid, showing fluorescence of both tautomer^{1,2} (Figure 1). This tautomerization was

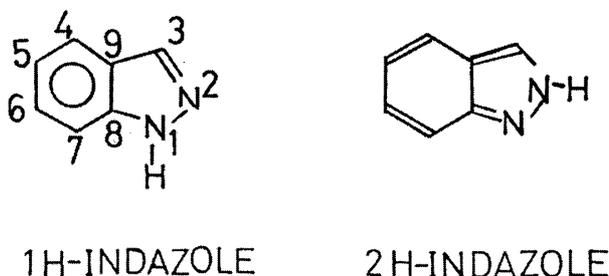


Figure 1. Two tautomers of indazole and the numbering system.

considered to take place via double proton switching in an indazole-acetic acid complex. Furthermore, it was also found that indazole in formic acid is protonated in the ground state and gives rise to a very different fluorescent spectrum. However, the exact natures of the indazole-acid complexes are not known and it was felt that it might be helpful in understanding these fluorescent properties, if I can study the hydrogen-bonded indazole-solvent complexes in isolated conditions.

Recent development of the supersonic expansion technique has proven that this technique, combined with the high resolution laser spectroscopy, is extremely useful to prepare isolated ultra cold molecules³⁻⁶ or complexes⁷⁻¹¹ for which spectral congestion due to hot bands could be avoided. It seems to be very interesting to study the spectral features of the isolated indazole complexes at high resolution and to examine if the proton transfer occurs in the isolated indazole-acid complex as well.

In this paper, I present the fluorescence excitation and dispersed fluorescence

spectra due to the S_1-S_0 transition of indazole and its hydrogen-bonded complexes with various protic molecules including acetic acid in supersonic free jets. On the basis of the obtained spectra I discuss the structures of the complexes in free jets and the difference in the fluorescence properties between the complexes in jets and in solutions.

Experimental

The fluorescence excitation spectra of indazole and hydrogen-bonded indazole in supersonic free jets were observed with the same apparatus as that reported elsewhere¹²⁻¹⁴. The apparatus belongs to Institute for Molecular Science, Okazaki. Indazole was heated in a nozzle chamber to 120 °C and mixed with He. The stagnation pressure was 4 atm. To study indazole complexes with other molecules, the latter were cooled to obtain favorable vapor pressure (-10 °C for formic acid and water, -15 °C for ethanol, and 5 °C for acetic acid). The excitation light source was a frequency-doubled tunable dye laser pumped with a YAG laser (Quantel, bandwidth 0.2 cm⁻¹, pulse duration 15 ns). In the measurement of the fluorescence excitation spectrum, the total fluorescence emission was detected with a photomultiplier (Hamamatsu R1104) through a glass filter (Toshiba L 38). For the SVL fluorescent measurement, the emission was taken through a monochromator (Nikon P-250). The ratio of the emission intensity to the excitation light intensity was recorded using a box-car integrator (PARC model 162) and processed with a microcomputer system. IR spectrum of indazole was taken in a KBr pellet with an IR spectrometer (JASCO IRA-1).

Indazole (Aldrich) was purified by vacuum sublimation. H₂O, ethanol, acetic acid, formic acid (Wako, spectral grade), D₂O and formic acid-d₂ (Aldrich, special grade) were used without further purification. Deuterated indazole was prepared by treating indazole with KOH and D₂O. It was purified by recrystallization from D₂O. In this manner indazole was completely deuterated at the 1 position and partially at the 3 position (see Figure 1).

Results and Discussion

(1) Fluorescence excitation and dispersed fluorescence spectra of free indazole.

Figure 2 shows the fluorescence excitation spectrum of free indazole in a supersonic free jet. It agrees well with the gas phase absorption spectrum reported

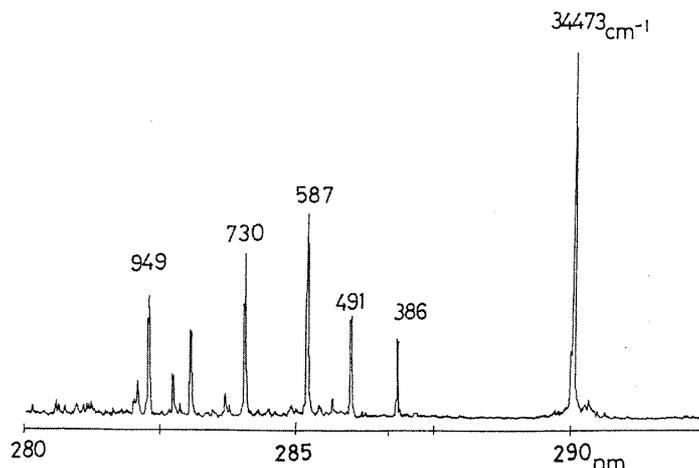


Figure 2. Fluorescence excitation spectrum of indazole in supersonic free jets.

by Byrne and Ross¹⁵ except that the spectral congestion in the latter is removed to show sharp individual vibronic bands. This is due to the disappearance of hot bands and narrower rotational envelopes, which indicates that the vibrational and rotational temperatures are extremely low. The fluorescence excitation spectrum is characterized by an intense 0-0 band located at the same energy (34473 cm⁻¹) as that observed in the gas phase¹⁵. This energy is higher than that in cyclohexane (33864 cm⁻¹)². Figure 3 shows fluorescence spectra of indazole in supersonic free jets obtained by exciting the 0, 0+587, 0+730, and 0+949 cm⁻¹ bands of the excitation spectrum. The vibrational bands in the excitation spectrum correspond to those in the absorption spectrum in the gas phase¹⁵. The vibrational bands obtained in the fluorescence spectrum correspond to those in the gas phase fluorescence reported by Logan and Ross¹⁶. They are summarized in Table 1 together with the vibrational bands in the IR spectra.

Table 1. Vibrational Frequencies of Indazole in the Ground and Excited States.

S ₁ State		S ₀ State		
isolated ^{b)}	Gas Absorption ^{c)}	isolated ^{b)}	Gas Fluorescence ^{d)}	IR
386				
491			624	
587	585	634	778	762
730	727	784	1097	1075
949	944	1104		
975				1357
1362	1361	1354		
		1381		

a) In units of cm⁻¹.

b) Present work.

c) Taken from ref.15.

d) Taken from ref.16.

Correspondence between the vibrational frequencies of the ground and excited states can be made from the observed features of the SVL fluorescence spectra. For example, when the 0+587 cm⁻¹ band in the fluorescence excitation spectrum is excited, the bands displaced to the red by 642, 1264, 1914 cm⁻¹ from the position of excitation (bands 3, 5 and 8, respectively, in Figure 3(b)) appear strongly in the dispersed fluorescence spectrum, where the 1264 cm⁻¹ and 1914 cm⁻¹ bands are the overtone frequencies of the 642 cm⁻¹ fundamental. Therefore, the correspondence between the excited state vibration of 587 cm⁻¹ and the ground state vibration of 642 cm⁻¹ is established. The difference between 642 cm⁻¹ and 634 cm⁻¹ in the 0-0 excitation is presumably due to the spectral resolution (~10 cm⁻¹). Table 1 shows that the vibrational bands in the ground state correspond well with those of the excited state, but the vibrational frequencies of the ground state are larger than those of the excited state.

Many additional vibrational bands appear in the SVL fluorescence spectra. These include the bands in the ground state which are coupled with the vibronic band being excited and, possibly, those coupled with some other bands in the excited state which could be excited isoenergetically. Assignments are given in Figure 3 and Table 2.

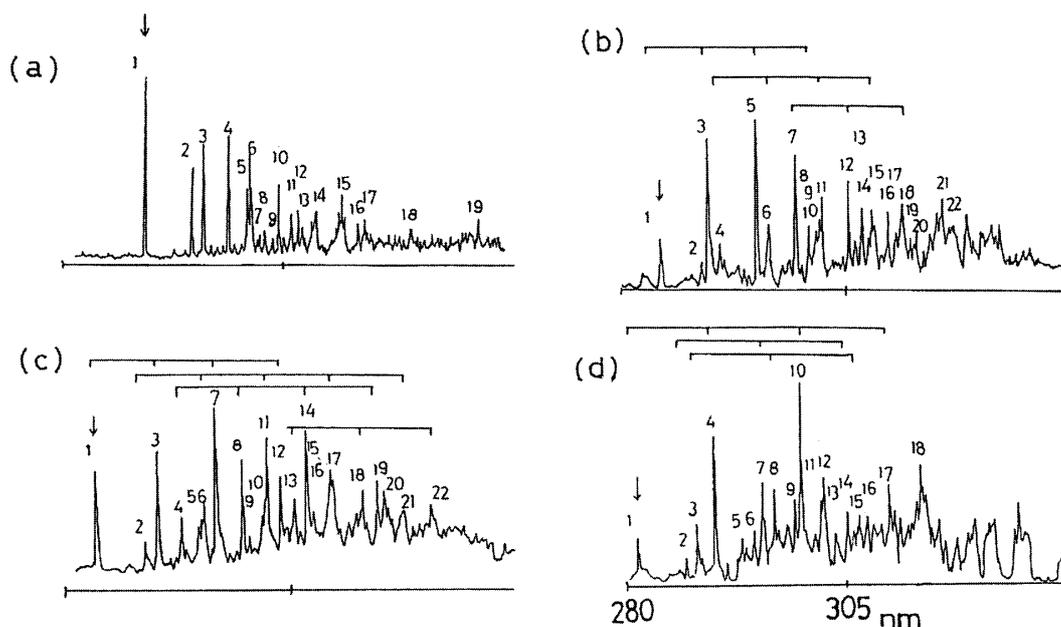


Figure 3. Fluorescence spectra of free indazole in supersonic free jets excited at (a) 0-0, (b) 0-0+587, (c) 0-0+730, (d) 0-0+949 cm^{-1} bands. Arrows indicate the bands being excited.

Table 2. Intramolecular Vibrational Bands in the SVL Fluorescence Spectra of Indazole.

0-0		0-0+587		0-0+730		0-0+949		
Excitation		Excitation		Excitation		Excitation		
Band Label	cm^{-1}							
		Assignment		Assignment		Assignment		
1	0	1	0	1	0	1	0	
2	634	2	560	2	663	2	676	676
3	784	3	642	3	816	3	822	822
4	1104	4	794	4	1125	4	1070	1070
5	1354	5	1264	5	1357	5	1435	
6	1381	6	1415	6	1433	6	1603	
7	1502	7	1749	7	1583	7	1710	676+1040
8	1566	8	1914	8	1909	8	1863	822+1040
9	1656	9	2006	9	1986	9	2127	
10	1731	10	2032	10	2154	10	2200	2 × 1070
11	1875	11	2070	11	2222	11	2451	
12	1960	12	2392	12	2376	12	2481	
13	2011	13	2470	13	2548	13	2635	
14	2183	14	2547	14	2695	14	2754	676+2 × 1040
15	2470	15	2668	15	2769	15	2902	822+2 × 1040
16	2650	16	2853	16	2968	16	2994	
17	2735	17	2950	17	3001	17	3251	3 × 1070
18	3244	18	3025	18	3336	18	3607	
19	3966	19	3114	19	3497	19		
		20	3184	20	3574	20		
		21	3489	21	3781	21		
		22	3589	22	4094	22		

(2) Fluorescence excitation spectra of hydrogen-bonded indazoles

Figures 4(b)~4(e) show the fluorescence excitation spectra of the indazole complexes with acetic acid, formic acid, H₂O and ethanol, respectively, in supersonic jets. When one monitors the whole fluorescence, the bands due to the complex in the excitation spectrum are overlapped by those due to a free indazole. To avoid this complication, the excitation spectra given in Figures 4(b) ~ 4(e) were obtained by monitoring only the 0-0 bands of the complexes so that the emission of the free molecule is not detected.

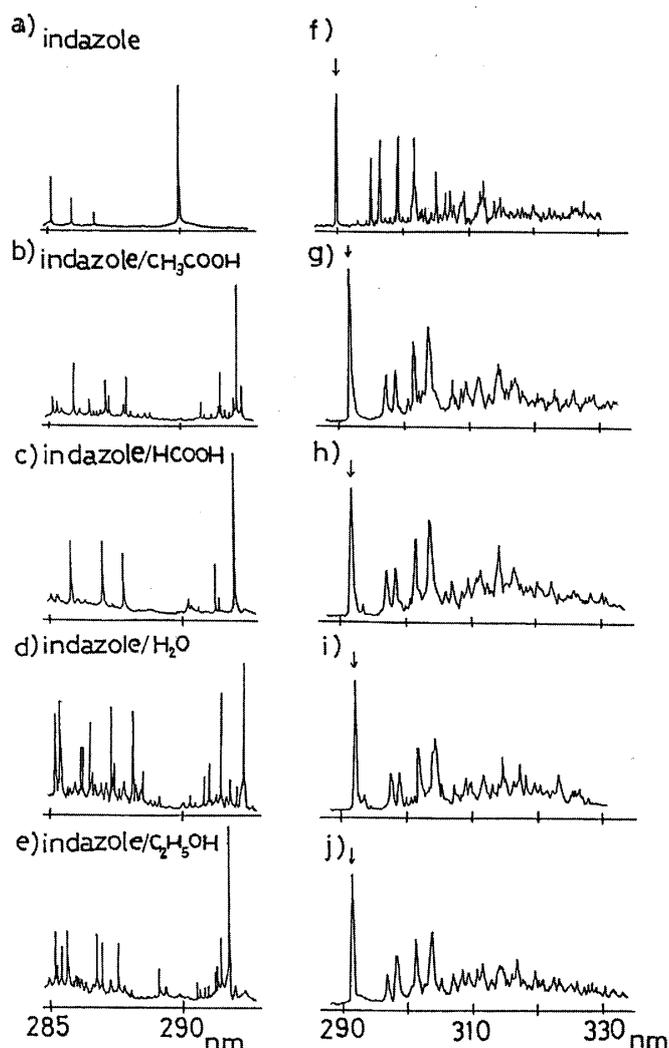


Figure 4. Fluorescence excitation spectra of (a) indazole, (b) indazole-CH₃COOH, (c) indazole-HCOOH, (d) indazole-H₂O and (e) indazole-C₂H₅COOH, and fluorescence spectra of (f) indazole, (g) indazole-CH₃COOH, (h) indazole-HCOOH, (i) indazole-H₂O and (j) indazole-C₂H₅COOH.

The bands appearing at 34217, 34230, 34199, and 34272 cm⁻¹ which are shifted by 256, 243, 274, and 201 cm⁻¹, respectively, to the red of the 0-0 band of free indazole are assumed to be the band origins of the acetic acid, formic acid, H₂O and ethanol complexes, respectively (Table 3). The observed red shift of the electronic origin by the complexation indicates that the stabilization energy due to the hydrogen-bond formation is larger in the excited state than in the ground state. These red shifts are close to 214 cm⁻¹ found in the indole-ethanol complex⁴ and 236 cm⁻¹ in the 3-methylindole-H₂O complex³.

The intramolecular vibrational bands of the indazole complexes in the fluorescence excitation spectra are similar to those of the indazole monomer (Table 4), indicating that the geometry of the excited state does not change so much by complexation. This is true even for the indazole-carboxylic acid complex. It is also to be noted that the relative intensities of the intramolecular bands are not affected so much by complex formation.

Low frequency bands which cannot be seen in the indazole monomer are observed in the fluorescence excitation spectra of the complexes (Table 5). They are assigned to the intermolecular vibrations, since their frequencies are too low to be intramolecular vibrations of the constituent molecules.

Table 3. Electronic Origins of the S_1 - S_0 Transitions of Indazole and its Complexes in Supersonic Jets.

Complex	ν cm ⁻¹	$\nu - \bar{\nu}$ (Indazole) cm ⁻¹
Indazole	34473	0
Indazole-Acetic Acid	34217	-256
Indazole-Formic Acid	34230	-243
Indazole-H ₂ O	34199	-274
Indazole-Ethanol	34272	-201

Table 4. Intramolecular Vibrational Bands in the Fluorescence Excitation Spectra of Indazole and its Complexes.^{a)}

Indazole	Indazole- Acetic Acid	Indazole- Formic Acid	Indazole- H ₂ O	Indazole- Ethanol
491	499	498	498	492
587	596	594	596	593
730	739	739	738	733

a) In units of cm⁻¹.

Table 5. Intermolecular Vibrational Bands in the Fluorescence and Fluorescence Excitation Spectra of indazole Complexes.^{a)}

Indazole- Acetic Acid		Indazole- Formic Acid		Indazole- H ₂ O		Indazole- Ethanol	
S ₁	S ₀	S ₁	S ₀	S ₁	S ₀	S ₁	S ₀
75	65	69	77	31		28	
	122	83		62	69	47	
166	162	206	199	101	97	57	61
256	239		275	152	150	88	
				177		102	
				242	218	124	130
				272	278	281	

a) In units of cm⁻¹.

(3) Fluorescence spectra of the indazole complexes

Figures 4(g) ~ 4(j) show dispersed fluorescence spectra of the indazole complexes in the jets. The excitations are indicated by arrows in the figures. The fluorescence spectra of the indazole complexes are all similar to each other except for the intermolecular vibrations. The 0-0 energies are also very similar in the complexes studied here, being slightly shifted to the red from that of free indazole. The intramolecular vibronic bands are summarized in Table 6. They also show little change upon hydrogen-bond formation. The intermolecular vibrational frequencies are summarized in Table 5, where they are less accurate than those in the excited state because of lower resolution in the fluorescence measurement ($\sim 10 \text{ cm}^{-1}$).

(4) Deuterium effects on the fluorescence and fluorescence excitation spectra of indazole and its complexes in supersonic free jets.

Indazole-d₁ The fluorescence excitation spectrum of indazole-d₁ is shown in Figure 5(a). The 0-0 energy is higher by 8 cm^{-1} than that of indazole-h. The 0-0 band in the fluorescence excitation spectrum of indazole-d₁ shows a doublet. I expect that the relatively weak higher energy band at 34489 cm^{-1} is the 0-0 band of indazole-d₂ which is further deuterated at the 3 position. Higher energy vibronic bands show all doublet structures with spacings of 8 cm^{-1} . Figure 5(b) and 5(c) show the fluorescence spectra obtained by exciting the lower and higher energy 0-0 components, respectively. The frequencies are summarized in Table 7. The intramolecular vibrational bands of these two fluorescence spectra are different in those marked by * in the figure. These bands could be due to the vibrations containing C(3)-H.

Indazole-h-formic acid-d₂ complex The fluorescence and fluorescence excitation spectra of the indazole-h-formic acid-d₂ complex show little change from those of indazole-h-formic acid-h₂. The 0-0 energy and the vibrational structure are all the same. This results would indicate that the hydrogen bonding N(2)...H-O- does not play an important role in the complex formation (see later discussion).

Indazole-d-formic acid-d₂ complex and indazole-d-D₂O complex

The fluorescence excitation spectrum of indazole-d-formic acid-d₂ is shown in Figure 6(a) and the fluorescence spectrum is shown in Figure 6(b). The 0-0 energy of the fluorescence excitation spectrum of indazole-d-formic acid-d₂ is higher by 12 cm^{-1} than that of indazole-h-formic acid-h₂. However, both inter- and intramolecular vibrational frequencies in the fluorescence excitation and fluorescence spectra are not changed much by deuteration (Table 8).

The fluorescence and fluorescence excitation spectra of the indazole-d-D₂O complex are shown in Figures 7(a) and 7(b), respectively. Similar to the formic acid complex, the 0-0 energy is higher by 12 cm^{-1} than that of indazole-h-H₂O complex. Again, the intermolecular and intramolecular vibrational bands are not affected so much by deuteration.

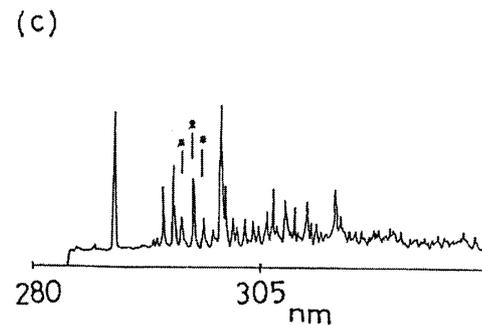
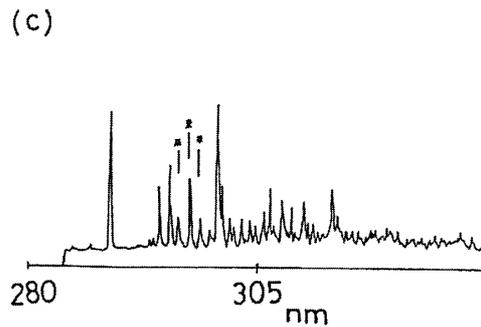
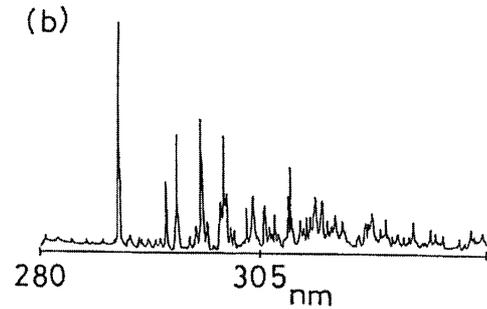
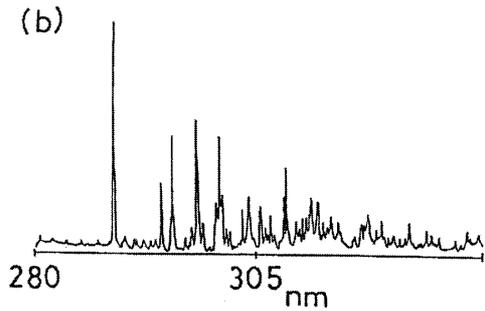
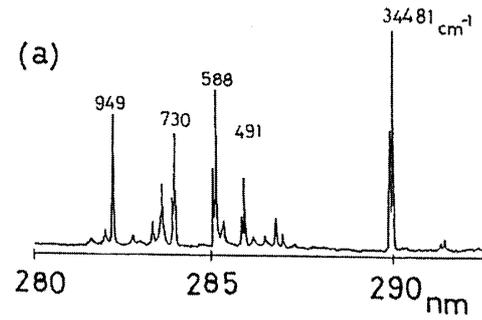
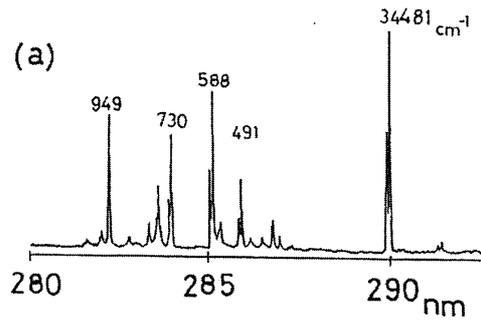


Figure 5.

- (a) Fluorescence excitation spectrum of indazole-d.
- (b) Fluorescence spectrum of indazole-d excited at the 0-0 band.
- (c) Fluorescence spectrum of indazole-d excited at the 0-0+8 cm^{-1} band.

Figure 6.

- (a) Fluorescence excitation spectrum of the mixture of indazole-d and DCOOD.
- (b) Fluorescence spectrum of the mixture of indazole-d and DCOOD.

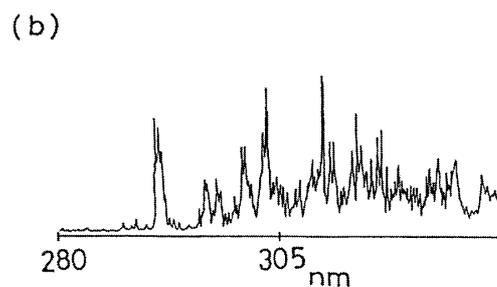
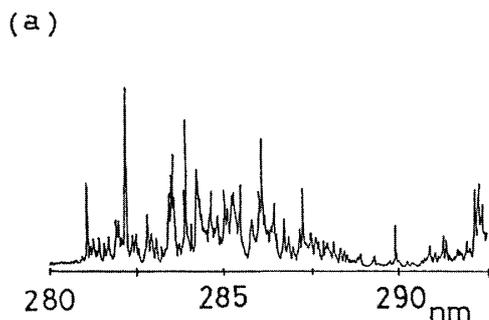


Figure 7. (a) Fluorescence excitation spectrum of indazole-d- D_2O .
(b) Fluorescence spectrum of indazole-d- D_2O .

Table 6. Intramolecular Vibronic Bands in the Fluorescence Spectra of Indazole and its Complexes.^{a)}

Indazole	Indazole-Acetic Acid	Indazole-Formic Acid	Indazole-H ₂ O	Indazole-Ethanol
636	623	612	626	605
784	787	764	774	766
1104	1099	1103	1097	1087
1354	1352	1334	1380	1367
1381				

a) In units of cm⁻¹.Table 7. Effect of Deuteration on the Intramolecular Vibrational Bands of Indazole in Supersonic Free Jets.^{a)}

S ₁		S ₀		
Indazole-h	Indazole-d	Indazole-h	Indazole-d 0-0 Excitation 0-0+8cm ⁻¹ Excitation	
0	0			
	8			
386	386			
491	491			
	498			
587	588	634	617	617
	596			
730	730	784	760	760
	738			
853	853			1007
949	949	1104	1073	1116
975	974			
		1354	1346	1339
		1381		

a) In units of cm⁻¹.Table 8. Effect of Deuteration on Intermolecular Vibrational Frequencies in the Fluorescence Excitation and Fluorescence Spectra of the Indazole Complexes with Formic Acid and H₂O.^{a)}

S ₁		S ₀		S ₁		S ₀	
Indazole-h-Formic Acid-h ₂	Indazole-d-Formic Acid-h ₂	Indazole-h-Formic Acid-h ₂	Indazole-d-Formic Acid-h ₂	Indazole-H ₂ O	Indazole-D ₂ O	Indazole-H ₂ O	Indazole-D ₂ O
69	69	77	64	31	39		
83	88			62	62	69	74
206	202	199	181	101	101	97	137
		275	230	152		150	179

a) In units of cm⁻¹.

(5) Proton transfer in the isolated system and in the solution

Indazole in the acetic acid solution exhibits a fluorescence spectrum with a Stokes-shift which is understood in terms of tautomerization via proton transfer in the excited singlet state². The potential barrier for the tautomerization was estimated to be $\sim 1390 \text{ cm}^{-1}$ from the temperature dependence of the rate constant for the tautomerization. In contrast, the characteristic Stokes shift was not observed for the isolated complex in supersonic jets even for higher energy excitation exceeding 1500 cm^{-1} . This suggests definitely the difference of the potential surface of the free complex in the excited singlet state from that in solution.

It is also to be noted that the fluorescence excitation spectrum of indazole-formic acid complex in supersonic jets is similar to those of the complexes with other non-acidic molecules in spectral shifts and vibrational features. This indicates that indazole and formic acid form a hydrogen-bonded complex in supersonic jets without transferring protons in the ground state. This is in contrast with the behavior in the formic acid solution, where the structureless absorption spectrum and the broad and red-shifted fluorescence spectrum indicate the existence of a protonated cationic species.

The deuterium effect mentioned above provides a further information about the potential surface. The deuteration of indazole and its complexes with formic acid and water causes blue shifts of $8\sim 12 \text{ cm}^{-1}$. These shifts are the results of the difference between reductions of the zero point energies in the ground and excited states. The small shift indicates that the force constants in both states are very similar to each other. Actually, assuming harmonic potentials, the excited state force constant for the proton stretching motion is estimated to be only a few % smaller than that in the ground state.

The intensity distribution would provide further information about the potential. As can be seen in Figure 4, indazole and all its complexes show similar vibrational intensity distributions both in fluorescence and fluorescence excitation spectra, in which intense 0-0 bands appear commonly followed by some vibronic bands with minor intensities. This suggests that the stable conformation in the excited state is not so much different from that in the ground state.

Finally, the difference in the stable conformations of the carboxylic acid complexes between the vapor and solution is to be mentioned. The experimental results presented in the preceding section show that the indazole-carboxylic acid complexes exhibit no appreciable difference in their spectral features in the isolated systems from the 'single-bonded' indazole- H_2O and ethanol complexes. The most plausible explanation for this would be that only a single hydrogen bonding (presumably, $\text{N}(1)\text{-H}\cdots\text{O}$) is formed in the isolated system even for the carboxylic acid complexes. The double proton switching can never occur in this case. This model can account for the spectral similarity observed for all the complexes studied here, and also for the relatively small difference between the ground and excited state potential curves discussed above.

On the other hand, indazole in carboxylic acid solution must be double-hydrogen-bonded to undergo the tautomerization from 1H to 2H. The simplest structure with double hydrogen bonds is a cyclic complex, though the exact structure of the indazole-carboxylic acid complex in solution is not known. A preliminary ab initio calculation¹⁷ predicts that this cyclic structure is more stable than the single bonded structure, though the energy gain by forming a double hydrogen-bonded complex is not large. Therefore, apparent failure to detect double bonded complexes for acids in jets needs an explanation. The above calculation, however, suggests also the

existence of a barrier between the singly and doubly hydrogen-bonded conformations.

If the singly-bonded complex is formed first during the supersonic expansion, there is a chance for the complex to be cooled by successive collisions with helium atoms into the shallower well. It has then no chance to take the doubly-bonded conformation across the barrier.

The main difference between the complexes in jets and in solution seems to be that in acid solution indazole is probably hydrogen-bonded with two or more acid molecules. The tautomerization accompanied by double proton transfer in solution probably involves two or more acid molecules.

Summary and conclusion

I have studied the fluorescence properties of indazole complexes with various protic molecules including carboxylic acid in supersonic jets. Different from the cases of indazole-acid complexes in solution, no spectroscopic evidence for the excited state tautomerization, proton transfer or protonation was obtained in jets. It is concluded that all the protic molecules studied here form single-hydrogen-bonded complexes in jets, preventing the tautomerization via double proton transfer.

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References:

1. M.Noda and N.Hirota, *J.Am.Chem.Soc.*, 105, 6790 (1980).
2. M.Noda, N.Hirota, M.Sumitani and K.Yoshihara, *J.Phys.Chem.*, 89, 399 (1985).
3. R.Bersohn, U.Even, and J.Jortner, *J.Chem.Phys.*, 80, 1050 (1984).
4. J.Hager and S.C.Wallace, *J.Phys. Chem.*, 88, 5513 (1984).
5. Y.Nibu, H.Abe, N.Mikami and M.Ito, *J.Phys.Chem.*, 87, 3898 (1983).
6. J.Montro, J.Jouvet, A.Lopez-Campillo, and B.Soep, *J.Phys.Chem.*, 87, 3582 (1983).
7. Y.Wang and K.B.Esenthal, *J.Chem.Phys.*, 77, 6076 (1982).
8. P.M.Felker and A.H.Zewail, *Chem.Phys.Lett.*, 94, 448 (1983).
9. N.Gonohe, N.Suzuki, H.Abe, N.Mikami, and M.Ito, *Chem.Phys.Lett.*, 94, 549 (1983).
10. H.Abe, N.Mikami and M.Ito, *J.Phys.Chem.*, 86, 1768 (1982).
11. H.Abe, N.Mikami, M.Ito and Y.Udagawa, *J.Phys.Chem.*, 86, 2567 (1982).
12. M.Baba and I.Hanazaki, *Chem.Phys.Lett.* 103, 93 (1983)
13. M.Baba and I.Hanazaki, *J.Chem.Phys.*, 81, 5426 (1984).
14. M.Baba, I.Hanazaki and U.Nagashima, *J.Chem.Phys.*, 82, 3938 (1985).
15. J.P.Byrne and I.G.Ross, *Aust.J.Chem.*, 24, 1107 (1971).
16. L.M.Logan and I.G.Ross, *Acta Phys. Polonica*, 34, 711 (1968).
17. U.Nagashima, Unpublished result.