

## Infrared induced conformational change in the two strong hydrogen bonded complexes 2–1 between dimethyl ether and hydrogen iodide in nitrogen matrix

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**Abstract**—The IR spectra of the complexes between dimethylether (DME) and hydrogen iodide in nitrogen matrices were reinvestigated with careful attention to the temperature and IR radiation effects upon the higher aggregates. Irradiation using a broad band IR source was found weakly active leading to a nearly stationary population of the two  $(\text{DME})_2 \text{H}^+ \text{I}^-$  species. Irradiation with  $\text{CO}_2$  laser lines induced a conformational interconversion of both aggregates to non-hydrogen-bonded forms. The breaking of the strong hydrogen bond was principally governed by irradiation in the range  $2600\text{--}1500 \text{ cm}^{-1}$  corresponding to the  $\delta \text{CH}_3$  region whereas the reverse process was observed by increasing temperature above 27 K under the annealing limit or irradiation below  $1100 \text{ cm}^{-1}$ . No accurate evidence was found for the occurrence of photochemical proton transfer between the centrosymmetrical and asymmetrical cations characterizing the two investigated complexes.

### INTRODUCTION

THE PROTON transfer process between two interacting molecules is one of the most interesting problems in the hydrogen bonding phenomenon. It is governed both by the proton affinities of the opposing groups (Ref. [1] and others cited therein) and by environmental effects [2]. Recently it has been shown that the reaction proton transfer takes place in the electronically excited state of the neutral clusters formed in free jet-cooled supersonic expansion [3] or isolated in low temperature rare gas matrices [4]. Besides, recent studies in matrices showed that a large class of hydrogen bonded systems involving HI as proton donor were IR photosensitive (Refs [5, 6] and others cited therein). In this view, it could be expected that a single quantum of excitation of a  $(\text{B})_n(\text{HI})_m$  cluster vibrational mode could induce proton motion by a structural change in a part of the cluster as was recognized by the end of the 1970s [7, 8]. In this paper, we explore this idea showing the effects of monochromatic  $\text{CO}_2$  laser or broad band (globar) irradiation on the two strong hydrogen bonded 2–1 complexes involving dimethylether (DME) and hydrogen iodide, previously identified in nitrogen matrices as ion pairs  $(\text{DME})_2 \text{H}^+ \text{I}^-$  [9]. The first one, IR photosensitive, was characterized by a centrosymmetrical potential function for the proton, whereas the second one showed a proton potential function probably of the symmetrical double minimum type. The one-to-one complex was not accurately identified but it was not surprising as since that time it has been observed that complexes of HI with weak to medium strength bases quickly dissociate in the beam of the spectrometer at low temperature [6]. Also we briefly reinvestigated the DME–HI system trapped in nitrogen, and then we give results on the irradiation of the two cations  $(\text{DME})_2 \text{H}^+ \text{I}^-$ .

### EXPERIMENTAL

Most of the experiments were performed in Paris with some complementary ones done in Siegen. Thus two cryostats have been used in this work: a conventional liquid helium cryostat

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capable of maintaining constant temperatures between 10 and 50 K for 6 to 8 h and a closed cycle Air Product displacer refrigerator, model 202A. The gas mixtures were prepared by standard manometric techniques and sprayed through a dual jet system onto the cold window (ICs or gold copper mirror) maintained at 17 K, at 5 mmol/h. Dimethyl ether (purchased from Fluka) was dried over sodium then quickly distilled and outgassed by condensation and thawing cycles under vacuum. Nitrogen for the matrices (Air Liquide N50) was used without further purification. Infrared spectra were recorded either with a Perkin-Elmer model 580 spectrometer at  $0.9\text{ cm}^{-1}$  resolution with a frequency accuracy of  $0.4\text{ cm}^{-1}$  or in some cases with a Bruker 113V FTIR spectrophotometer at  $0.5\text{ cm}^{-1}$  resolution. Infrared irradiations of the sample were carried out with the 1500 K global source of the spectrometers using broad band filters listed in Table 3 and with CW  $\text{CO}_2$  lasers. The first one (Paris), home built (6 mm diameter), was used at a laser power of about  $300\text{ mW cm}^{-2}$  while the second one (Siegen), an Apollo Lasers Model 570  $\text{CO}_2$  laser, was used at 1.5 W with a Si plate.

## RESULTS AND DISCUSSION

### 1. Identification of $(\text{DME})_m(\text{HI})_n$ species

**One-to-one complex.** At high dilution in HI and DME-H6 (typically HI/DME/Air 1/1/1500), the spectrum recorded at 11 K after deposition at 20 K did not show the characteristic band of a hydrogen-bonded HI molecule ( $\nu_s$ ). Only new weak doublets at  $1094.5\text{--}1093.0\text{ cm}^{-1}$  and at  $919.4\text{--}917.2\text{ cm}^{-1}$  appeared, respectively, in the  $\nu_{as}$  COC and  $\nu_s$  COC mode regions of the DME-H6 molecule. Significant changes occurred when the previous sample was recorded at 29 K. A new weak broad absorption was observed at  $1950\text{ cm}^{-1}$ . In addition, in the  $\nu_{as}$  and  $\nu_s$  COC region, features as previously reported decreased with appearance of new bands respectively at  $1087\text{--}1084\text{ cm}^{-1}$  and  $906\text{ cm}^{-1}$ . All these new bands vanished when the sample was again cooled to 11 K and exposed to the light of the spectrophotometer for 2 h. Figure 1 summarizes the observed typical effects which were completely reversible. Substitution of HI by DI showed a different trend. After deposition and recording at low temperature a broad band centred at about  $1380\text{ cm}^{-1}$  ( $\nu_s$ ) was observed and appeared insensitive to IR irradiation. These overall

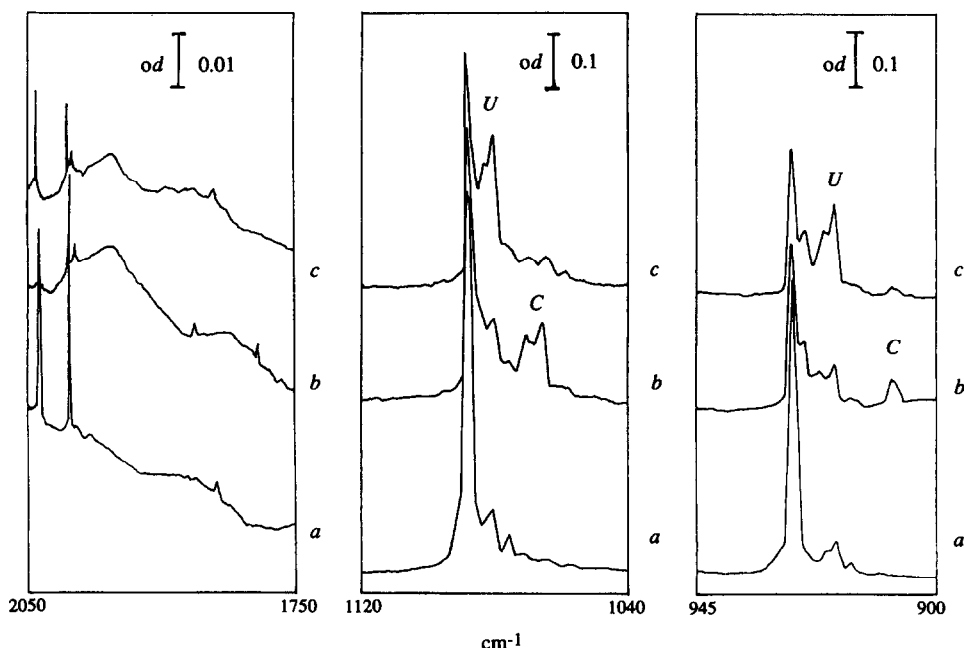


Fig. 1. Spectral changes for a  $\text{DME}/\text{HI}/\text{N}_2 = 1/1/1500$  mixture in the  $2100\text{--}1800\text{ cm}^{-1}$  and  $1200\text{--}900\text{ cm}^{-1}$  domains. (a) after deposition at 20 K in the dark, recording temperature  $T_s = 11\text{ K}$ ; (b) after 5 min warming at 29 K in the dark, recording temperature  $T_s = 29\text{ K}$ ; (c) as for (b), followed by 2 h irradiation in the beam of the 580 Perkin-Elmer spectrometer at  $T_s = 11\text{ K}$ .

Table 1. Characteristic vibration frequencies ( $\text{cm}^{-1}$ ) of the one-to-one complex DME:HI in nitrogen matrix

Mode	DME monomer	DME:HI complex	
		U form	C form
$\nu_s$ COC	925.0*	919.4–917.2	906
$\nu_{as}$ COC	1096.8†	1094.5–1093	1087–1084
$\nu_s$ HI	—	2237‡	1950

\* Weak satellites at 928, 920 and 915  $\text{cm}^{-1}$ .

† Weak satellites at 1098 and 1089.2  $\text{cm}^{-1}$ .

‡ Close to HI monomer band.

observations are similar to those described for the other 1–1 hydrogen bonded complexes trapped in inert matrices with HI as proton donor. The band at 1950  $\text{cm}^{-1}$  is the HI stretching mode ( $\nu_s$ ) of the hydrogen bonded complex (C) which photodissociates through a new orientation of HI [10] in a non-hydrogen-bonded pair U characterized by a HI frequency close to that of free HI and some weak shifted bands of complexed DME. Experimental results are collected in Table 1. Some irradiation experiments carried out with filters led to the conclusion that, as observed for HI–acetone [11] and the HI–ethylene oxide [12] systems, the C→U barrier height is greater than 1400  $\text{cm}^{-1}$ , the vibrational excitation efficiency being the  $\nu_{\text{HI}}$  mode. Due to the barrier height, photodissociation of the isotopic (DME)· · · DI doesn't occur. The reversible U→C conversion observed by the thermal process at 30 K would imply a barrier height of about 3 kJ/mol as previously reported.

*Higher aggregates.* After progressive increasing of the temperature above 27 K for samples relatively diluted in both dopants (typically HI/DME/N<sub>2</sub> 1/2/1000) new bands appeared in the spectra. Careful comparison of the different spectra as displayed for examples in Fig. 2 allowed us to distinguish four distinct new species (referred to hereafter as Ag<sub>1</sub>, Ag<sub>2</sub>, Ag<sub>3</sub>, Ag<sub>4</sub>) mainly characterized by absorption groups which appeared at about: (i) 660, 1200  $\text{cm}^{-1}$ ; (ii) 1015, 830  $\text{cm}^{-1}$  (iii) 830, 1300, 1800  $\text{cm}^{-1}$ ; and

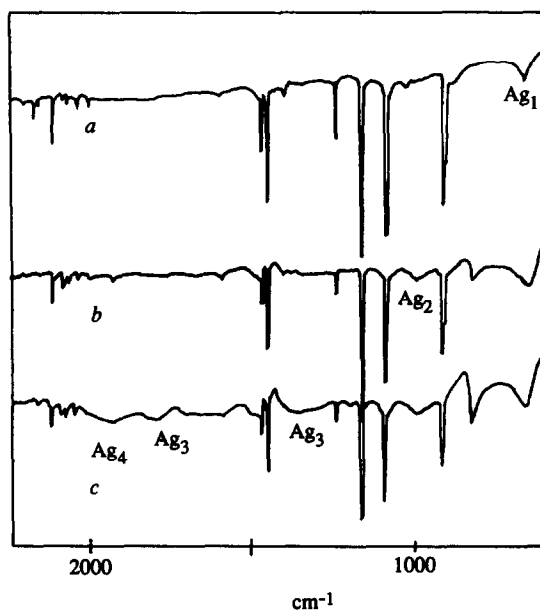


Fig. 2. Typical spectra for DME/HI/N<sub>2</sub> samples 1/2/1000 recorded at 11 K either after deposition or various warming up temperatures showing the appearance of different aggregates. (a) After deposition; (b) after warming at 27 K and recooling at 11 K; (c) after warming at 30 K and recooling at 11 K.

Table 2. Frequencies ( $\text{cm}^{-1}$ ) and tentative assignment of the characteristic absorptions of the different  $(\text{DME})_m(\text{HI})_n$  aggregates in nitrogen matrix

$\text{Ag}_1^*$	$\text{Ag}_2^\dagger$	$\text{Ag}_3^\ddagger$	$\text{Ag}_4^\S$	Assignment
			1900	$\nu(\text{IH})_2 \cdot \cdot \text{O}$
		1800		$\nu(\text{HI})_n \cdot \cdot \text{I}^-$
1456.9				$\delta(\text{CH}_3)$
1208.0				$\delta(\text{OHO})(?)$
1165.0				$\nu_{\text{as}} \text{COC} + \tau // (\text{CH}_3) + \tau \perp (\text{CH}_3)$
1092.5		980		$\nu_{\text{as}} \text{COC}$
919.7–917.2	833	833–817	886	$\nu_s \text{COC}$
	1000	1300		$\nu(\text{O} \cdot \cdot \text{H} \cdot \cdot \cdot)^+$
690–660				$\nu(\text{OHO})^+$

\*  $\text{Ag}_1$ : symmetrical  $(\text{DME})_2\text{H}^+\text{I}^-$  cation.

†  $\text{Ag}_2$ : asymmetrical  $(\text{DME})_2\text{H}^+\text{I}^-$  cation.

‡  $\text{Ag}_3$ : asymmetrical  $(\text{DME})_2\text{H}^+\text{I}^- (\text{HI})_n$  cation.

§  $\text{Ag}_4$ :  $(\text{DME})_2\text{HI}$  complex.

(iv)  $1900 \text{ cm}^{-1}$  with different relative intensity according to the annealing process. These observations bring new insight upon those previously described in the first paper [9] where strong annealings were made upon more concentrated samples. Thus new assignment of obtained spectra is tentatively proposed.

As previously reported, the  $660 \text{ cm}^{-1}$  absorption is the antisymmetric hydrogen stretch of the symmetrical  $\text{O} \cdot \cdot \text{H}^+ \cdot \cdot \text{O}$  cation ( $\text{Ag}_1$ ) characterizing a nearly perfect proton sharing between the two oxygen atoms. This band ( $\text{FWHM} = 60 \text{ cm}^{-1}$ ), recorded in the absence of  $\text{CO}_2$  impurity in our sample, is composed of two unresolved components about  $660$  and  $690 \text{ cm}^{-1}$ . The higher frequency component was not observed when  $\text{CD}_3\text{OCD}_3$  was used in place of  $\text{CH}_3\text{OCH}_3$  denoting that the band broadening can be due to a combination involving complexed low  $\text{CH}_3$  modes enhanced by Fermi resonance. The DME submolecule in the cation appeared very weakly perturbed. Only features at  $917.2 \text{ cm}^{-1}$  and at about  $1500 \text{ cm}^{-1}$  appeared as shoulders of respectively  $\nu_s \text{COC}$  stretching and methyl bending of the isolated DME molecule.

Weak broad absorption centred at  $1000 \text{ cm}^{-1}$  showed a complex structure with two shoulders at  $990$  and  $1010 \text{ cm}^{-1}$ . It grew in concert with the  $830 \text{ cm}^{-1}$  feature so much that annealings were weak without appearance of HI dimers increasing. With strong annealing or more concentrated samples as in Ref. [9] ( $\text{DME}/\text{HI}/\text{N}_2$  1/1/200), the  $830 \text{ cm}^{-1}$  band grew stronger with the appearance of new bands at  $1300$  and  $1800 \text{ cm}^{-1}$ , whereas the  $990 \text{ cm}^{-1}$  shoulder of the  $1000 \text{ cm}^{-1}$  band became prominent. These results suggest formation of an asymmetrical cation  $(\text{DME})_2\text{H}^+$  with two different anions:  $\text{I}^-$  ( $\text{Ag}_2$ ) and  $\text{I}^- (\text{IH})_n$  ( $\text{Ag}_3$ ), the last one generated by strong annealing or more concentrated samples. In regard to the symmetrical cation ( $\text{Ag}_1$ ), the asymmetrical cations have a hydrogen atom tipped towards one of the two oxygen atoms, the proton transfer being more important in the case of the higher aggregate  $\text{Ag}_3$ . Thus the two strongest broad bands about  $1000$  and  $1300 \text{ cm}^{-1}$  could be assigned to the proton motion in  $\text{Ag}_2$  and  $\text{Ag}_3$ , whereas the  $1800 \text{ cm}^{-1}$  band could be responsible for the  $(\text{HI})_n$  absorption. In these cations, the COC stretching modes are expected to be strongly shifted. Consequently the  $\nu_s \text{COC}$  band is located at  $830 \text{ cm}^{-1}$  while the weaker  $\nu_s \text{COC}$  feature probably falls in coincidence with the  $\nu_s$  absorption of  $\text{Ag}_2$ . At higher dilution, the centrosymmetric cation ( $\text{Ag}_1$ ) is favoured relative to the asymmetrical cation ( $\text{Ag}_2$ ), whereas at high concentration, the asymmetrical ( $\text{Ag}_3$ ) cation becomes the major species, the nonequivalent position of  $\text{I}^-$  being stabilized by aggregation with HI.

At last, the broad band at  $1900 \text{ cm}^{-1}$  in the HI region and the weak feature at  $886 \text{ cm}^{-1}$  in the  $\nu_s \text{COC}$  stretching region were identified as the 1:2  $\text{DME} \cdot \cdot (\text{HI})_2$  species ( $\text{Ag}_4$ ) by comparison with the HI-acetone system [11]. As for the 1:1 complex this species disappeared in the beam of the spectrophotometer and after long deposition at  $20 \text{ K}$  in the dark, it was not always observed.

All band positions are listed Table 2.

## 2. Irradiation effects upon the two $(\text{DME})_2\text{H}^+\text{I}^-$ cations $\text{Ag}_1$ and $\text{Ag}_2$

The experiments to be discussed were performed at 11 K either after deposition or after sample warming between 27–29 K then recooling at 11 K. Two kinds of irradiation experiments were carried out: polychromatic irradiation with the full light of the spectrometer source using also several broad band pass filters and monochromatic irradiation in the 10  $\mu\text{m}$  region of the  $\text{CO}_2$  lasers.

**Polychromatic irradiation.** Figure 3 shows the difference spectrum after irradiation for 12 h in the beam of the spectrophotometer (Bruker) of a  $\text{HI}/\text{DME}/\text{N}_2$  1/1/500 sample previously annealed at 27 K and recooled at 11 K. All the aggregate bands were sensitive to the irradiation and decreased in intensity with correlated intensity increase of DME complexed bands at 922.8, 1095.9 and 1167.1  $\text{cm}^{-1}$ . However the observed effects were very weak and after irradiation, a nearly similar stationary population for the two cations was observed. Other experiments were performed using several filters to study the influence of different spectral regions on the photoprocess. Results are summarized in Table 3. Again no noticeable changes were observed and thus did not allow direct kinetic studies. From the observations in Table 3, several remarks can be made: (i) except for the irradiation with filter 1, the two cations showed the same behaviour; (ii) exposition to the range 2600–1500  $\text{cm}^{-1}$  led to the loss of  $\text{Ag}_1$  and  $\text{Ag}_2$ , whatever growth of the two species occurred after irradiation below 2000  $\text{cm}^{-1}$ ; (iii) the observed effect seemed to depend on the matrix history; thus irradiation with filter 4 gave observations in variance: decreasing in intensity of the overall bands when the irradiation was performed just after deposition or increasing the intensity of the same bands when the irradiation was performed after irradiation with filter 2.

**Monochromatic irradiation.** Samples were irradiated using the possible coincidence between the absorption band frequencies of aggregates with the same  $\text{CO}_2$  laser lines emission of the  $00^{\circ}1-(10^{\circ}0, 02^{\circ}0)$  transitions such as: R34 (1086.9  $\text{cm}^{-1}$ ), R22 (1079.8  $\text{cm}^{-1}$ ), R46 (990.6  $\text{cm}^{-1}$ ), R50 (992.5  $\text{cm}^{-1}$ ), R38 (986.5  $\text{cm}^{-1}$ ), R34 (984.3  $\text{cm}^{-1}$ ), R28 (980.9  $\text{cm}^{-1}$ ), R6 (966.2  $\text{cm}^{-1}$ ) and P8 (955  $\text{cm}^{-1}$ ).

Significant successful irradiations were registered only with R22, R46, R50, R38 and R34  $\text{CO}_2$  emission lines.

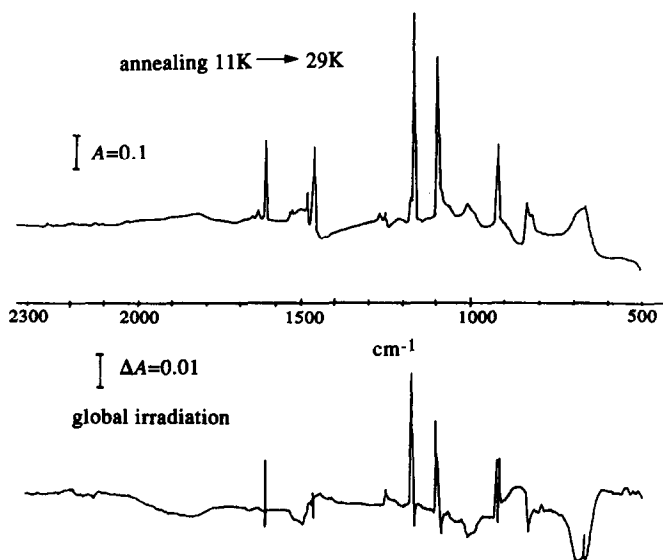


Fig. 3. Infrared spectra of a  $\text{DME}/\text{HI}/\text{N}_2 = 1/1/500$  sample. Upper trace: spectrum recorded at 11 K after annealing to 29 K for 10 min. Lower trace: difference spectrum after-before global irradiation for 18 h (both spectra recorded at 11 K).

Table 3. Characteristics of the filters used in irradiation experiments with the spectrometer beam (Perkin-Elmer) and main observations in the 1100–600  $\text{cm}^{-1}$  region after irradiation; +: small cation population increase; -: small cation population decrease

Filters	Characteristics		Effects		
	Transmission range ( $\text{cm}^{-1}$ )	Transmission percentage	1000 $\text{cm}^{-1}$ band	830 $\text{cm}^{-1}$ band	690–660 $\text{cm}^{-1}$ band
1	>2000	62%	+	+	-
2	2600–1500	70%	-	-	-
3	<2000	60%	+	+	+
4	1200–400	58%	-	-	-†

\* Effect observed after irradiation with filter 2.

† Effect observed after deposition.

A sequence of photolysis with filter 2 and R46 is illustrated (Fig. 4) in the 1050–550  $\text{cm}^{-1}$  spectral region. In the initial spectrum no sensitivity to the beam irradiation with filter 2 is shown in Fig. 4a. Photolysis at 990.6  $\text{cm}^{-1}$  gave the spectrum in Fig. 4c. Characteristic bands of  $\text{Ag}_1$  and  $\text{Ag}_2$  aggregates strongly increased. In the higher frequency spectral region, the 1800  $\text{cm}^{-1}$  absorption of  $\text{Ag}_3$  species also appeared. Furthermore the HI monomer absorption at 2237  $\text{cm}^{-1}$  decreased in intensity without change in the dimer  $(\text{HI})_2$  absorptions. Subsequent photolysis of the sample in the beam of the spectrophotometer with filter 2 resulted in the spectrum Fig. 4d, nearly identical to that in Fig. 4a. Observed effects, also obtained with the R50, R38 and R34  $\text{CO}_2$  lines, were not due to a temperature effect: the laser heating was less than 1 K and a similar trend arose at lower laser power by introducing two silicon filters which reduce the intensity. Similar experiments with previous  $\text{CO}_2$  lines were also carried out by inserting the filter 4 which allows only observation of the 1100–600  $\text{cm}^{-1}$  region, between the  $\text{CO}_2$  source and the sample. In this case, the 906  $\text{cm}^{-1}$  feature associated to the hydrogen-bonded C form of the one-to-one DME–HI complex was observed. After irradiation, it showed no significant change in intensity leading to the conclusion that the observed photoprocess did not proceed through the one-to-one (C) DME–HI complex. The

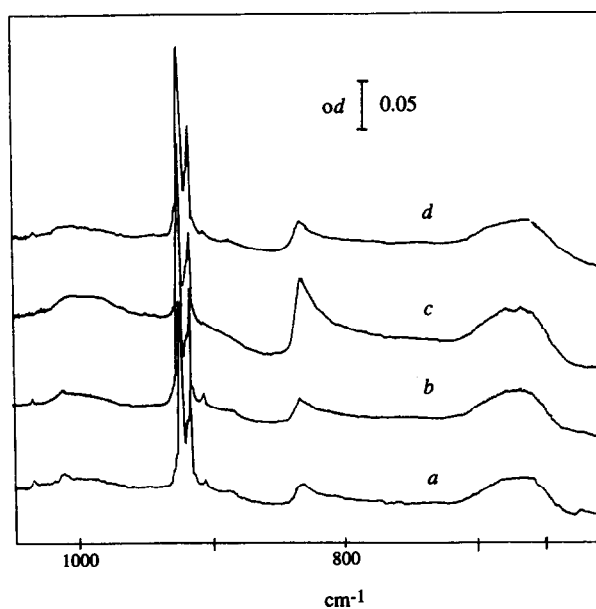


Fig. 4. Spectral changes for a DME/HI/ $\text{N}_2$  1/2/1000 mixture in the 950–650  $\text{cm}^{-1}$  domain. (a) After deposition at 20 K in the dark, recording temperature  $T_s = 11$  K; (b) after 30 min irradiation in the beam of the spectrophotometer with filter 2; (c) as for (b) followed by irradiation with  $\text{CO}_2$  laser line at 990.6  $\text{cm}^{-1}$ ; (d) as for (c) after irradiation in the beam of the spectrophotometer with filter 2.

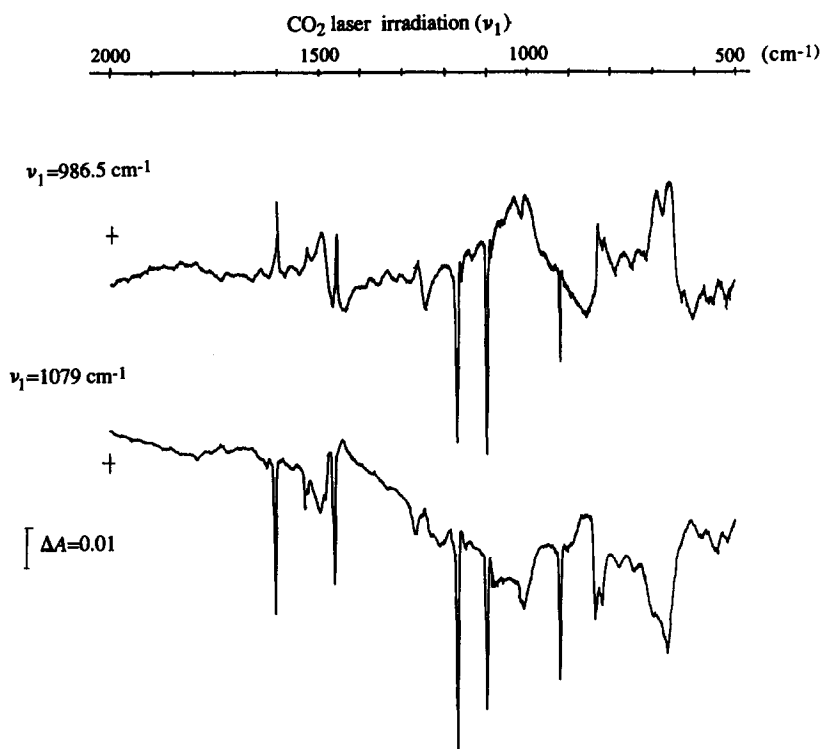


Fig. 5. Difference spectra after-before irradiation by CO<sub>2</sub> laser lines at  $\nu_1 = 986.5$  and  $1079 \text{ cm}^{-1}$ . Same sample as for Fig. 3.

intensity changes in the  $\nu_s$  COC region showed an intricate behaviour and did not allow accurate integrated intensity measurements, because the overlap of the  $925 \text{ cm}^{-1}$  feature (DME monomer) with the three lines at  $923$ ,  $920$  and  $917 \text{ cm}^{-1}$  associated at different species as discussed below.

As illustrated, Fig. 5, the reverse photochemical effect was obtained using the R22 line ( $1079.8 \text{ cm}^{-1}$ ). The HI/DME/N<sub>2</sub> 1/1/500 sample was firstly irradiated with the R38 line then irradiated with the R22 line. The fraction of aggregates which grew with the first irradiation disappeared with the second irradiation, the observed conversion indicating that the absorption coefficients for irradiated modes were of the same order of magnitude, under the experimental conditions used. Careful analysis of the two difference spectra given in Fig. 5 allowed the identification of complexed DME bands assignable to Ag<sub>1</sub> from their behaviour upon IR irradiation. Thus four modes were seen to be sensitive to complexation and belong to the Ag<sub>1</sub> aggregate:  $1456.9 \text{ cm}^{-1}$  (CH<sub>3</sub> bending),  $1165 \text{ cm}^{-1}$  ( $\nu_{as}$  COC + CH<sub>3</sub> rocking),  $1092.5 \text{ cm}^{-1}$  ( $\nu_{as}$  COC) and  $917.2 \text{ cm}^{-1}$  ( $\nu_s$  COC); they are weakly red shifted with respect to that of the monomer DME. New bands belonging to the transformation product of Ag<sub>1</sub> appeared at  $1167.1$ ,  $1095.9$  and  $922.8 \text{ cm}^{-1}$ . As previously mentioned the only relatively well resolved band at  $917 \text{ cm}^{-1}$  cannot unfortunately allow accurate measurements of the disappearance of Ag<sub>1</sub> because it is closed to that characterizing the U form of the one-to-one complex DME-HI.

**Photolytic process.** The most interesting observation resulting from the experiments is that a weak fraction of both cations disappears upon irradiation without appearance of significant new product bands. They reappear upon temperature increase below the annealing limit or under selective irradiation. This phenomenon is similar to that observed for one-to-one complexes involving HI and various bases, although the considered complexes of higher stoichiometries arise from strong hydrogen bond interaction. Hydrogen breaking converts the aggregates Ag<sub>1</sub>, Ag<sub>2</sub>, Ag<sub>3</sub> in non-hydrogen-bonded forms U<sub>1</sub>, U<sub>2</sub>, U<sub>3</sub> with nearby metastable minima. Species U' are only spectroscopically identified by some of the weak shifted DME vibrational modes at  $1167.1$ ,

1095.9 and 922.8  $\text{cm}^{-1}$ , the HI mode being located very close to the monomeric line. After deposition in the dark at 20 K the two forms Ag and U' coexist. Temperature increase upon 27 K or irradiation at low temperature lead to other different steady states, the rigidity of the host lattice and the low thermal bath energy preventing the return to the previous equilibrium. Thus, the intriguing spectroscopic and dynamical information obtained after irradiation with filter 4 depends on the previous distribution of Ag and U' forms.

The Ag  $\rightarrow$  U' conversion, under our experimental conditions, is observed principally with irradiations in the 2500–1500  $\text{cm}^{-1}$  region implying efficient excitation of  $\delta$  CH<sub>3</sub> modes of the complexed base submolecule in the complex. However excitation with the CO<sub>2</sub> laser line at 1079  $\text{cm}^{-1}$  which is resonant with the  $\nu_s$  mode of the Ag<sub>2</sub> complex lead also to the disappearance of Ag<sub>2</sub> and Ag<sub>1</sub>, suggesting an Ag<sub>1</sub>  $\rightarrow$  Ag<sub>2</sub> exchange process by a tunnelling mechanism which requires more study. The barrier height to induce the conformational change Ag  $\rightarrow$  U' in the aggregates seems lower than that observed for the photodissociation of the one-to-one complex. The possibility of a DME bond rotation not an HI rotation cannot be ruled out.

The U'  $\rightarrow$  Ag back conversion is observed upon temperature increase above 27 K and also by irradiation below 1200  $\text{cm}^{-1}$  at low temperature proving an efficient vibrational excitation of the  $\nu_{as}$  COC and  $\nu_s$  COC modes of the U' species. The energy gained by the U' species is probably greater than the U  $\rightarrow$  Ag barrier; such an efficiency was also observed in the U pair conversion to the hydrogen-bonded one-to-one CH<sub>3</sub>OH:HI complex [13] upon excitation of the CO stretching mode of U. Monochromatic irradiation at 986  $\text{cm}^{-1}$  in the broad band associated with Ag<sub>2</sub> also induces U  $\rightarrow$  C photoconversion. This surprising result is probably due to the existence of a combination mode involving a low torsional CH<sub>3</sub> mode of U' and which falls in coincidence with the  $\nu_s$  band assigned to Ag<sub>2</sub>.

Absorption coefficients of the modes implied in the Ag  $\rightarrow$  U' and U'  $\rightarrow$  Ag conversion appear of the same order of magnitude and global irradiation which contains all wavelengths is nearly without effect on the steady state obtained after deposition in the dark or after warming at 27 K.

The observed photoconversion is complex and depends upon intramolecular and intermolecular energy migration from the DME modes to the reaction coordinate. More frequency selective measurements should be necessary for complete understanding of it.

The proton transfer between Ag<sub>1</sub> and Ag<sub>2</sub> was not accurately observed although the results obtained after irradiation with filter 1 seemed to indicate that excitation in CH<sub>3</sub> stretching modes of DME could induce the proton delocalization.

The recent purchase of a tunable laser could allow us to resolve the unanswered questions about this system or other similar systems such as HI–acetone or HI–ethylene oxide for which formation of similar aggregates can be now better understood in the light of the present work.

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## REFERENCES

- [1] P. Schuster, in *Intermolecular Interactions: from Diatomics to Biopolymer* (Edited by B. Pullman), Chap. 4, p.425. Wiley, New York (1980).
- [2] L. Schriver, A. Schriver and J. P. Perchard, *J. Am. Chem. Soc.* **105**, 3843 (1983).
- [3] C. Jouvet, C. Lardeux-Dedonder, M. Richard-Viard, D. Solgadi and A. Tramer, *J. Phys. Chem.* **94**, 5041 (1990).
- [4] C. Crepin and A. Tramer, *Chem. Phys.* **156**, 281 (1991).
- [5] A. J. Barnes, L. Schriver, A. Schriver and J. P. Perchard, *J. Molec. Struct.* **240**, 239 (1990).
- [6] L. Schriver, A. Schriver and J. P. Perchard, *J. Molec. Struct.* **222**, 141 (1990).
- [7] R. E. Miller, *J. Phys. Chem.* **90**, 3301 (1986).



- [8] H. Graener, T. Q. Ye and A. Laubereau, *J. Chem. Phys.* **91**, 1043 (1989).
- [9] A. Loutellier, L. Schriver, A. Burneau and J. P. Perchard, *J. Molec. Struct.* **82**, 165 (1982).
- [10] Y. Hannachi, B. Silvi and J. P. Perchard, *Chem. Phys.* **154**, 23 (1991).
- [11] L. Schriver-Mazzuoli, *J. Chem. Soc. Faraday Trans. 2* **85**, 607 (1989).
- [12] P. Bernadet, L. Schriver-Mazzuoli, A. Schriver and J. P. Perchard, *J. Phys. Chem.* **92**, 7024 (1988).
- [13] N. Bakkas, A. Loutellier, S. Racine and J. P. Perchard, *Chem. Phys.* **166**, 167 (1992).