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Comparison of the proton and deuteron transfer in the hydrogen (deuterium) iodide–ammonia or trimethylamine systems trapped in argon and nitrogen

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Abstract—Infrared spectra of ND_3/HI, NH_3 or ND_3/DI and $N(CH_3)_3/DI$ mixtures trapped in Ar or N_2 have been recorded in order to complete our previous work [*J. Am. chem. Soc.* **105**, 3843 (1983)] on NH_3/HI and $N(CH_3)_3/HI$ trapped in various matrices. The same matrix effect on the rate of deuteron transfer has been evidenced but the deuteron appears to be significantly more completely transferred than the proton.

INTRODUCTION

In a previous paper we reported an i.r. study of strongly hydrogen-bonded complexes between hydrogen iodide and trimethylamine TMA or ammonia in various matrices [1]. We have shown that the rate of proton transfer is strongly matrix-dependent. This conclusion has been confirmed by A. J. BARNES *et al.* in their recent reinvestigation of the ammonia and amines/hydrogen chloride and bromide complexes in argon and nitrogen [2–4].

The present paper deals with the effect of H/D isotopic substitution on the strength of the intermolecular bond, and more precisely in this case of strong interaction, with the relative state of delocalization of the proton and deuteron between the two acceptor sites N and I. Such H/D effects evidenced for strongly hydrogen-bonded systems AH . . . B in the liquid and solid states have been shown to depend on the potential function for the proton (deuteron) [5]. In the case of the asymmetric hydrogen bond type for which the proton possesses two wells of different depths (the deeper one near A), the ν_{AH}/ν_{AD} isotopic frequency ratio is lower than for the free AH(D) group and can reach a value close to unity [6]. In the case of the symmetric hydrogen bonding type characterized by a potential function with either a single central flat minimum or a double minimum with very low barrier, the frequency isotopic ratio is higher than $2^{1/2}$ [7, 8].

EXPERIMENTAL

The apparatus and technique were identical with those used earlier [1]. Separate mixtures of deuterium iodide + matrix gas and base + matrix gas were prepared by a standard manometric technique and sprayed simultaneously onto a caesium iodide window maintained at 17 K for N_2 and 20 K for Ar (spray rate 10 mmol/h). The i.r. spectra were recorded at 10 K on a Perkin–Elmer model 225 or Perkin–Elmer model 580 i.r. spectrometer calibrated using standard gases. DI was prepared by hydrolysis of red phosphorus and iodine mixture and purified by trap to trap distillation under vacuum at 213 K. NH_3 (Matheson), ND_3 (Matheson 99% D enriched) and TMA (Matheson) were purified by condensation at liquid nitrogen temperature (to remove volatile impurities) followed by one thawing–recondensing cycle.

RESULTS

DI-*trimethylamine system*

Figure 1 shows the i.r. spectra obtained when (D + H)I (D/H ratio = 2) and TMA are codeposited with a large excess of argon or nitrogen (molar ratios of 1:400 for each dopant). Bands due to uncomplexed TMA and to HI–TMA complexes are readily identified by comparison with previous matrix isolation studies [3, 4]. The most prominent band due to the DI–TMA 1:1 complex in argon displays a two component pattern at 1580 and 1605 cm^{-1} whereas in nitrogen there is a strong broad absorption with multiple component structure, centred at 1710 cm^{-1} (FWHM = 60 cm^{-1}). The observed bands are summarized in Table 1.

DI-*ammonia system*

DI–ND_3–Ar. Infrared spectra of (D + H)I/A (D/H ratio ~ 10) and ND_3/Ar (D/H ratio ~ 12) mixtures codeposited at 20 K over a range of concentrations from 1/1/600 to 1/1/300 are shown in Fig. 2. New absorptions not present in the spectra of the parent molecules are observed at 1685 (w) 1310 (m) 1005 (s) 690 and 670 (s) (separated by a transmission window) 482 (m) and 264 cm^{-1} (m). The relative intensities of these bands do not remain constant over the range of studied concentrations. Systematic studies at various DI/ND_3 molar ratios show that the bands at 1685 and 482 cm^{-1} increase in intensity with respect to the others at higher concentration in ND_3; they are assigned to the 1:2 complex with a centrosymmetrical cation $(NDN)^+$, the hydrogenated counterpart having been previously characterized at 686 cm^{-1} [1]; the other bands which predominate at high dilution in both dopants are assigned to the 1:1 complex.

DI–NH_3–Ar. Trace c of Fig. 2 shows a typical spectrum of the matrix obtained by codeposition of natural ammonia and deuterium iodide ($DI:NH_3$:Ar 1/1/400; DI/HI ratio ~ 10). The spectrum is dominated

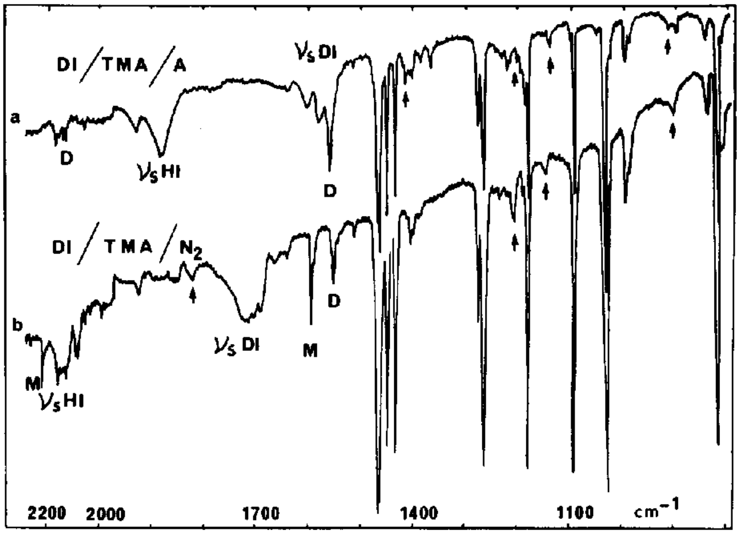


Fig. 1. Infrared spectrum of (a) a mixture of TMA and DI in an argon matrix at an overall concentration of 1/1/400, (b) a mixture of TMA and DI in a nitrogen matrix at an overall concentration of 1/1/400. M, D are respectively monomeric and dimeric lines of free DI or HI. The new bands not present in parent molecules are marked by arrows.

Table 1. Frequency (cm^{-1}) and relative integrated intensity (I) of i.r. bands assigned to the DI:$N(CH_3)_3$ complex embedded in argon and nitrogen

Ar		N_2	
ν (cm^{-1})	I	ν (cm^{-1})	I
		1840	
1605		1725 sh	
1588	1	1707	1
1580		1695	
1417	0.02	1670	0.02
1205 1198	0.02	1206 1202	0.04
1144 1140	0.02	1150	0.02
917 903	0.03	910	0.03

by a strong band at 1256 cm^{-1} previously assigned to the ν_s of HI–NH_3 complex (the 1000 cm^{-1} region is unfortunately overlapped by NH_3 absorptions). The relative intensity of this band is abnormally high with regard to the initial D/H ratio and suggests an exchange between DI and NH_3 in the matrix. Accordingly bands observed at 1320, 1280, 1175, 1135 and 280 cm^{-1} are assigned to mixed isotopic NH_xD_{3-x}:H(D)I species ($x = 1, 2$). Narrow absorptions at 540, 510 and 490 cm^{-1} which decrease in intensity in the more dilute matrices are probably due to larger aggregates; they appear as the counterpart of the bands at 737, 680 and 640 cm^{-1} previously observed in concentrated HI/NH_3/Ar matrices [1].

DI–ND_3–N_2. Experiments performed with DI and ND_3 in nitrogen are illustrated in Fig. 3 (traces a and b). For a DI/HI ratio of about 5 and in the presence of

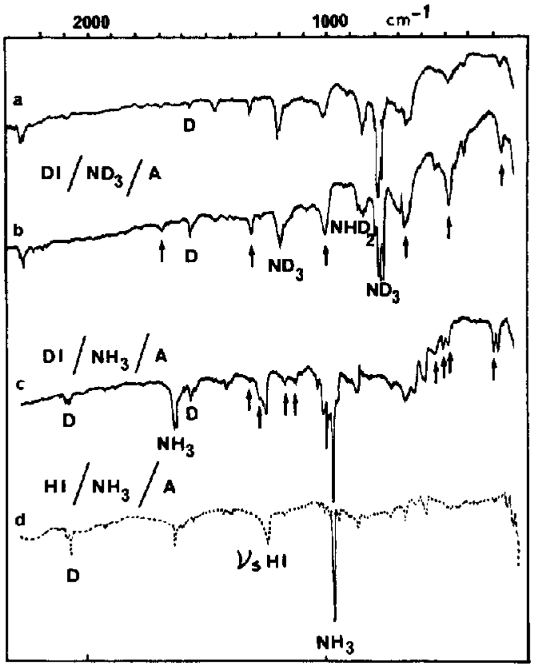


Fig. 2. Comparison of i.r. spectra in argon matrices of (D_3) ammonia–deuterium iodide mixtures (a) 1:1:300, (b) 1:1:600 and (c) (H_3) ammonia and deuterium iodide mixture 1:1:400. Dashed line: i.r. spectrum of (H_3) ammonia and HI mixture for comparison (1:1:600). The new bands not present in parent molecules are marked by arrows. D: dimeric lines of free DI or HI.

ND_3 and NHD_2 (with only a small amount of NH_2D) one observes a strong doublet at 1540–1530 cm^{-1} and weaker bands listed in Table 2. The band at 500 cm^{-1} which increases in intensity with respect to the other ones upon annealing and in the presence of an excess of

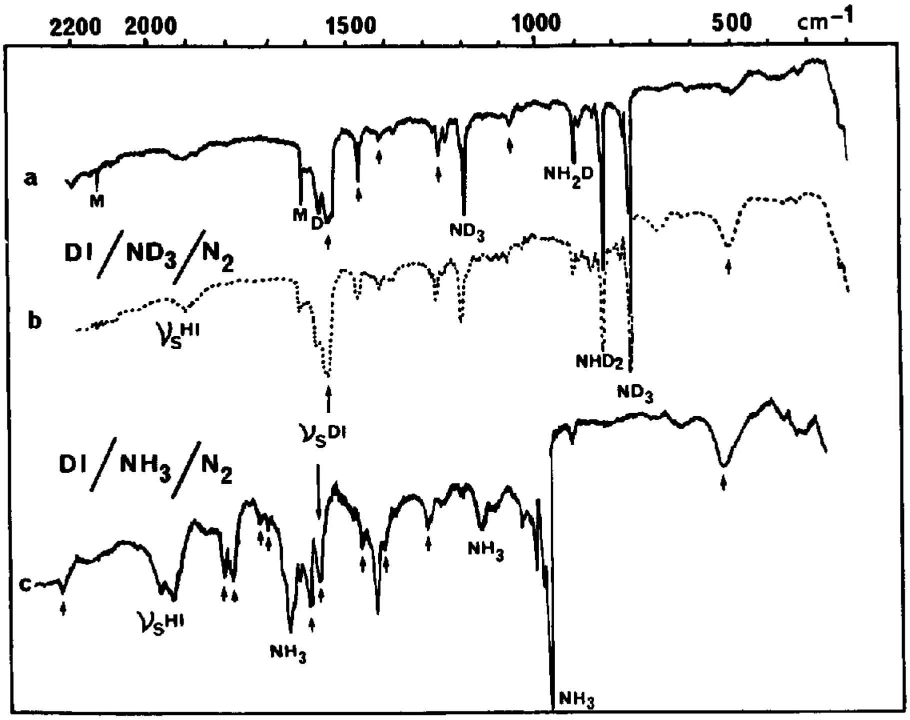


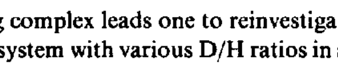
Fig. 3. Comparison of i.r. spectra, in nitrogen matrices, of (D_3) ammonia deuterium iodide mixture 1:1:400 (a) after deposition, (b) dashed line after annealing at 30 K and (c) (H_3) ammonia deuterium iodide mixture (1:1:300). The new bands not present in parent molecules are marked by arrows.

Table 2. Assignment of the main i.r. bands observed for DI/ND_3 mixtures in argon and nitrogen

Assignment	Ar ν (cm^{-1})	N_2 ν (cm^{-1})
ND_3 asym. stretch.		2520
$DI(ND_3)_2$ complex	1685	
ND_3 asym. deformation	1310	1370–1330
N . . . D . . . I asym. stretch.	1005	1540–1530
N . . . D . . . I bend	690–670	1255 (?)
ND_3 sym. deformation		1068
$DI(ND_3)_2$ complex	482	500
$DI{-}ND_3$ complex	264	

ND_3 is assigned to the deuteron axial motion along the NI axis of the 1:2 complex (corresponding frequency for the proton: 690 cm^{-1}).

$DI{-}NH_3{-}N_2$. For a DI/HI molar ratio greater than 10, and typically $(D+H)I/NH_3/N_2 = 1/1/300$ the spectra display (Fig. 3c) strong bands at 1940, 1792, 1770, 1580, 1550, 520 cm^{-1} together with weaker features at 2470, 1705, 1685, 1450, 1390, 1280 and 235 cm^{-1}. The following remarks can be made about these spectra: (i) only a small amount of NH_2D is present, as characterized by a very weak band at 905 cm^{-1}, (ii) the intensity ratio of the DI/HI monomer bands (free species) is larger than 10 while that for ν_s (1:1 complexes, respectively, at 1550 cm^{-1} and 1940 cm^{-1}) is of the order of 0.2, (iii) the structure of ν_s (HI) band undergoes a considerable modification with respect to that of ν_s (HI) band observed in the spectra of $HI{-}NH_3{-}N_2$ mixtures [1]. These observations can be understood in terms of a fast H/D intermolecular exchange in the matrix between NH_3 and DI in neighbouring positions;



$$\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{H{-}N}}}\ldots\mathrm{D{-}I}\rightleftharpoons\underset{\mathrm{D}}{\overset{\mathrm{H}}{\mathrm{H{-}N}}}\ldots\mathrm{HI}.$$

Such an isotopic exchange seems to be efficient only within the 1:1 complex. Indeed, the 520 cm^{-1} band responsible of the $(NDN)^+$ cation is present without a counterpart in the hydrogenated species at 690 cm^{-1}. The significant changes observed in the 2000–1700 cm^{-1} region by replacement of an H atom by a D atom in the ammonia submolecule of the HI containing complex leads one to reinvestigate the HI-ammonia system with various D/H ratios in ammonia.

$HI{-}NH_xD_{3-x}{-}N_2$. Typical spectra displayed in Fig. 4 throw new light on the presence in the spectra of $HI/NH_3/N_2$ samples of two strong bands at 1967 and 1847 cm^{-1}, both assigned previously to ν_s (HI) of the 1:1 complex trapped in two different sites. The main observations, using partially deuterated ammonia are as follows: (i) with a weak D content (predominant species NH_3 and NHD_2) the two strong bands in the range 1800–2000 cm^{-1} are always present but with different relative intensities; furthermore two new sharp features at 1795 and 1772 cm^{-1} appear, (ii) at an

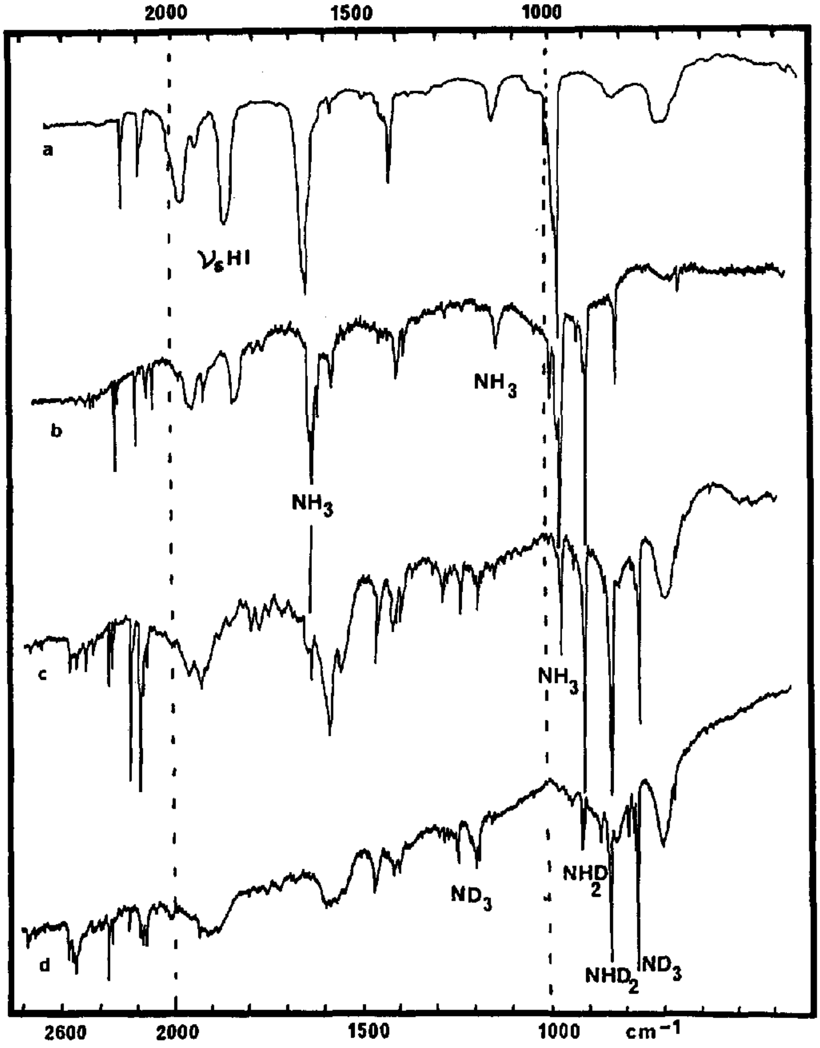


Fig. 4. Infrared spectra of mixtures of ammonia and hydrogen iodide in nitrogen matrices at various D ammonia contents (overall concentration of 1:1:250) (a) natural ammonia, (b) NH_3, NH_2D, (c) NH_2D, NHD_2, ND_3, (d) NHD_2, ND_3.

intermediate D content (predominant species NH_2D, NHD_2) the 1967–1847 cm^{-1} doublet is replaced by a strong band at about 1940 cm^{-1} (FWHM: 100 cm^{-1}) together with the 1795–1772 doublet which increases in intensity, (iii) with a high D content (predominant species NHD_2 and ND_3) all these features vanish and only one broad band is observed at about 1910 cm^{-1} (FWHM = 120 cm^{-1}).

In the other spectral regions, many new absorptions due to NH_xD_{3-x} ($x = 0$–3) species engaged in the 1:1 species are observed and can be assigned (in particular for a weak D content, i.e. $x = 2$) from the known features of the HI–NH_3 complex:

HI:NH_2D: the stretching and the bending modes involving ND are unambiguously measured at 2470 and 1280 cm^{-1}, respectively, whereas the NH_2 antisymmetric and symmetric bending modes are located at 1580 and 1412 cm^{-1}, respectively. The weak band at 1435 cm^{-1} close to the one at 1420 cm^{-1} of the hydrogenated species may thus be assigned to the N ... H ... I bending mode. In the low frequency region weak bands at 240–220 cm^{-1} (250 cm^{-1} with NH_3), probably arise from ammonia librational modes.

HI:NHD_2 and HI:ND_3: the spectra are more complex and more difficult to assign because of the exchange between HI and ND_3 in the matrix; such an exchange is suggested by the similarity between the spectrum c of Fig. 4 and that of DI:NH_3 (Fig. 3c). Accordingly the broad absorption at 1590–1530 cm^{-1} should be assigned to the NH bending mode overlapping the ν_s(DI) mode. The 2520 cm^{-1} line may plausibly be assigned to the antisymmetric stretching ND_2 mode while the 1390 cm^{-1} feature should be a

Table 3. Assignment of the main i.r. bands observed for HI : NH_xD_{3-x} complex in a nitrogen matrix

Assignment	$x = 3$	$x = 2$	$x = 1$ or 0
NH asym. stretch	3390	3385	3355
ND stretch		2470	
ND asym. stretch			2520
N . . . H . . . I asym. str (ν_s)	1967	1940	1910
combination involving NH asym. bend.	1847	1795 1772	1726 1705 (very weak)
NH asym. def.	1638	1580	
N . . . H . . . I bend.	1420	1435	1390
NH sym. def.	1411	1412	
ND def.		1282	
NH_xD_{3-x} HI librational mode	250	240–220	

candidate for the N . . . H . . . I bending mode. Assignments discussed above are summarized in Table 3.

DISCUSSION

In order to clarify the discussion, we shall analyse the results in two sections, the first one devoted to the comparison of H/D transfer in the various matrices, the second one to the effects of H/D substitution in ammonia on the 1:1 HI–NH_3 complex in nitrogen.

Deuteron motion along the N . . . I *axis*

The asymmetric stretching mode of the deuteron, ν_s (DI), in the 1:1 complex with TMA and ND_3 is easily identified as the strongest absorption not assignable to the parent molecules. It occurs at 1725 and 1603–1580 cm^{-1} with TMA and at 1540 and 1000 cm^{-1} with ND_3 in nitrogen and in argon respectively.

For the DI–TMA system, the other bands of the complex are similar in both matrices and are assigned to perturbed TMA vibrations. Available data do not allow us to locate the bending mode of the deuteron. For the DI–ND_3 system, a tentative assignment is given in Table 2 on the basis of the one proposed for HI–NH_3 in argon and nitrogen matrix. Note that the reassignment proposed by BARNES for the N . . . H . . . I bending mode in argon at 875 cm^{-1} instead of 590 cm^{-1} [4] agrees well with the observation of its deuterium counterpart at about 660 cm^{-1}.

Results relative to the bands confidently assigned to ν_s (DI) call for three important remarks: (i) there is a large matrix dependence on the deuteron delocalization and for the same matrix a rate of deuteron transfer increasing with the proton affinity of the base, as previously reported for the proton, (ii) for the DI/TMA/N_2 system, the ν_s (DI) frequency at 1725 cm^{-1} is higher than that of free DI (1604 cm^{-1}) which proves that the deuteron is substantially transferred to the base. In other terms, the nature of hydrogen bonding in the complex is rather of the ion pair type $-N^+-D \ldots I^-$ than deuteron sharing $-N \ldots D \ldots I$, (iii) the ratio of transfer is larger for the deuteron than for the proton. This conclusion is clearly evident if the ν_s frequencies are compared to that of the monomers: for example for the TMA and N_2 matrix ($\nu_s - \nu_{free}$) is negative for HI but positive for DI. The same conclusion is reached if one considers the $\nu_s(H)/\nu_s(D)$ isotopic ratio for the different systems where the bridge proton is seen preferentially attached to the nitrogen atom. In every case this ratio is found to be of the order of 1.2, typical of fairly strongly H-bonded OH . . . O and NH . . . N systems with a stretching frequency of ca 2100 cm^{-1} and implies a weakening of the H-bond on deuteration [6]. It is the existence of a weaker ND . . . X than NH . . . X interaction which leads to the observed effect (greater deuteron than proton transfer).

Effect of progressive deuteration of ammonia on the spectral properties of the 1 : 1 *complex between ammonia and* HI *in nitrogen*

A strong doublet at 1967 and 1847 cm^{-1} characterizes the N . . . H . . . I asymmetric stretching mode (ν_s) of the HI:NH_3 complex. This doublet shows different changes in width, relative intensity and frequency of its components upon deuteration of ammonia. Upon full deuteration, it is replaced by a single broad band at about 1910 cm^{-1}. These observations suggest the existence of a Fermi resonance between ν_s and a combination mode involving a bending mode of ammonia. This resonance weakens as ammonia is more completely deuterated. A probable assignment for this combination is the asymmetric bending mode and the librational mode at 1638 cm^{-1} and 250 cm^{-1}, respectively, for NH_3; upon isotopic substitution both shift to lower frequencies (for NH_2D 1580 and 230 ± 10 cm^{-1}) so that the coincidence with ν_s is no longer acute. Such a combination has previously been observed by FALK *et al.* [9, 10] in some ammonium salts at liquid nitrogen temperature and taken as a criterion of hydrogen bonding. This, together with the observation of the symmetric bending mode between 1400 and 1100 cm^{-1} depending on the H/D ratio, shows that the ammonia molecule in the 1:1 complex has lost its individuality and behaves as the ammonium ion as far as bending modes are concerned.

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