Journal of Molecular Structure, 101 (1983) 275—286
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

A MATRIX INFRARED STUDY OF MONOMERIC FORMAMIDE

MARKKU RÄSÄNEN

Department of Physical Chemistry, University of Helsinki, Meritullinkatu 1 C, SF-00170 Helsinki 17 (Finland)

(Received 17 February 1983)

ABSTRACT

Infrared spectra of formamide have been recorded between 4000 and 200 cm^{-1} in Ar, Kr, Xe, N_2 and CO matrices. The fundamentals of monomeric formamide are assigned, the assignment of the low-frequency bands differing from that presented previously. The spectra of the deuterated species $DCONH_2$, $HCOND_2$ and $DCOND_2$ in Ar matrices were also recorded and the fundamentals are assigned. "Complexation" of formamide with CO or N_2 is found to shift the NH_2 rocking and torsional bands in particular. The complexation of formamide with nitrogen, especially its influence on the NH_2 torsional band, has been studied with the aid of ab initio 4-31G calculations. Three of the lowest energy configurations of the 1:1 complexes are presented. In rare-gas matrices, two overtone bands of the very intense torsional band have been found and these indicate only a very slight mechanical anharmonicity in this motion. The large difference between the torsional frequencies of the deuterated compounds HCONHD and HCONDH is discussed.

INTRODUCTION

Formamide ($HCONH_2$, FA) is the simplest molecule containing the N—C=O grouping, important in peptide chemistry, and thus its structure and spectroscopic properties have been the object of numerous studies. Despite the smallness of this molecule there is still controversy concerning the vibrational assignment and structure of this molecule.

The Raman [1] and infrared [2] spectra of FA and its several isotopes have been recorded in the liquid state and these data have been used in constructing a force field for FA [2]. The near-infrared spectra of FA and its deuterated isomers have been studied [3] in chloroform solutions and the anharmonic force field based on these frequencies calculated. Itoh and Shimanouchi [4] studied the IR-spectrum of solid FA, and they concluded that FA and its deuterated homologues do not possess any intramolecular vibrational transitions below 400 cm^{-1}.

Comparison of the gas-phase IR data [5] with results obtained in the liquid state [2] shows large differences between these spectra. The NH_2 stretching frequencies are different in different solvents [6], as are also the νCH frequencies in different electrolyte solutions [7] (the considerable νCH frequency shift on complexation with cations is suggested to be due to the

0022-2860/83/$03.00

trans lone-pair effect). Thus it can be deduced that the experimental force fields contain large intramolecular influences and are useless for comparison with the ab initio calculated force fields.

Five of the lowest frequency fundamentals of FA observed in different phases are listed in Table 1. It can be seen that the assignment of the bands $r\mathrm{NH_2}$, $w\mathrm{NH_2}$, δ OCN and $\tau\mathrm{NH_2}$ is quite different in different studies.

The only previous matrix infrared study on FA deals with the argon matrix spectrum of $HCONH_2$ [8]. The low-frequency data were analysed by fitting the NH_2 wagging or "inversion" mode to a double minimum potential. However, these matrices were contaminated by the decomposition products of FA [8] and the argon used obviously contained a small amount of N_2 (the argon matrix spectra of ref. [8] can be reproduced by adding 1—2% of N_2 to Ar). There are large differences between the argon and nitrogen matrix spectra of FA, as will be discussed later in this paper. Amides are obviously analogous to alcohols, where specific interactions have been found to shift the OH torsion in N_2 and CO matrices to a large extent [9].

The far-infrared gas spectrum of FA [10] has been assigned in terms of the amino inversion fundamental, its overtones and hot bands.

Evans studied the vapour spectrum of FA in the 2700—3700 cm^{-1} region [11] and concluded that the molecule is planar or only slightly nonplanar. An early microwave study resulted in a nonplanar structure with the $C—NH_2$ group being slightly pyramidal [12], while the latest microwave results suggest that the FA molecule is essentially planar without any potential hump at the planar configuration [13].

The ab initio calculations on the STO-3G minimal basis set level favour a

TABLE 1

Collected values for the five lowest frequency fundamentals of formamide in different phases

Wavenumber (cm^{-1})					Phase	Ref.
δCH(oop)	$r\mathrm{NH_2}$	δOCN	$w\mathrm{NH_2}$	$t\mathrm{NH_2}$		
1044	1167	675	1065	787	gas	5
1030	1152		1053	765		
1019				756		
1056	1090	600	750	—	liquid	2
1040	678?	573	327	612	Ar-matrix	8
		564	322	605		
			303			
1053	1095	608	—	—	liquid	1
1057	1133	649	825	—	solid, —65°C	4
1041		633				
1063	1140	657	843	675	solid, —165°C	4
1047	1133	635				
1050	1126	563	288	602	$CHCl_3$	3
	NH_2 inversion		289		gas	10

non-planar structure [14, 15], whereas both the 4-21G [16] and 4-31G [14, 15] calculations indicate a planar structure. From more extensive calculations it has been concluded that the potential well of FA with respect to inversion at nitrogen is very flat and occurs in the vicinity of the planar structure [15].

The internal rotation barrier of FA is, according to NMR [17], 70—89 kJ mol^{-1}, and the ab initio calculated values are quite close to these values [18]. PCILO supermolecule calculations suggest that the internal rotation barrier increases with increasing solvent polarity [19], and ab initio calculations indicate an increase of the barrier with increasing dielectric constant of the solvent [20].

There exist both semiempirical [21, 22] and ab initio [14, 16, 23] calculated force fields for FA. The 4-31G field [14] does not reproduce the experimental low-frequency fundamental values [8] of 289 cm^{-1} (NH_2 wagging) and 602 cm^{-1} (NH_2 twisting). This force field gives a high value (584 cm^{-1}) for the lower frequency vibration, this being related to a mode which should be expressed as an "NH_2 out-of-plane bending" rather than wagging [14]. On the other hand, the ab initio calculations of vibrational frequencies of FA indicate [23] that the low-frequency spectrum of monomeric FA in particular is incompletely studied experimentally.

In the present study the experimental vibrational spectrum of monomeric FA is reassigned using the published ab initio out-of-plane [16] force field as well as the N_2 complexation shifts on the vibrational bands.

EXPERIMENTAL

Formamide (Merck, p.a.) was distilled in vacuum and dried over molecular sieves before use. CD-deuterated FA was purchased from Merck Sharp & Dohme, and it was used without further purification. The ND_2 compounds were prepared by direct exchange with heavy water (from Stohler, USA) and were distilled under reduced pressure. The D_2O addition and distillation procedure was repeated at least five times so that the final extent of deuteration of the amide exceeded 90%. FA is hydrolysed in aqueous solution over a wide pH range [24], and to avoid the residue of the hydrolysis products the deuterated FA was distilled before use.

The vapour pressure of FA is too low to allow the compound to be handled by usual vacuum-line methods. The matrices were prepared by flushing a small amount of molecular sieves, wetted with FA, with the matrix gas under reduced pressure. The gas mixture thus formed was then sprayed onto the cold CsI window of the cryocooler (Displex CS-202) at temperatures between 15 and 20 K. The M/A (matrix/absorber) ratio could be varied by varying the sample temperature; accurate ratios could not be obtained but they were typically between 500 and 1000. During the spray on the gas mixture was occasionally heated to about 300°C in order to reduce the amount of association, but this did not have any influence on the matrix sample.

Thus it can be concluded that collisions in the gas mixture at room temperature suffice to break the FA associates. The spectra were recorded with a Perkin-Elmer 621 spectrophotometer, calibrated against standard gases. When recording the spectra, the matrix temperature was 13 K.

RESULTS AND DISCUSSION

The spectra of FA in Ar, Kr, Xe, N_2 and CO matrices are shown in Fig. 1 and the observed wavenumbers in Table 2. Only the bands of the monomer are included; results on the association of FA in matrices will be published in a later paper.

The assignment presented in Table 2 is in accordance with previous assignments in the region 3700—1200 cm^{-1}. However, a few comments concerning the matrix data in this region will be made.

Comparing the NH_2 stretching frequencies in different hosts it is seen that Xe shifts these bands to lower frequencies even more than nitrogen, the shift being similar to that found for the strongly complexing CO matrix. On the other hand, the low-frequency part of the spectrum is very similar in all rare-gas matrices studied but the spectra in interacting media (N_2 and CO) differ considerably from those in the solid rare gases. In the case of methanol [9] specific complex formation has been found in N_2 and CO matrices. In the case of maleimide [25] nitrogen has been found to interact specifically with the NH group. The bands showing the largest Ar to N_2 or CO shifts in the spectra of FA are due to rocking and torsion of the NH_2 group, which indicates that the amino group acts as the most important complexing group in FA.

In the course of matrix preparations it became apparent that the extent of the self-association in the samples diminished considerably when going from rare gases to N_2 and especially to CO. This indicates that the van der Waals complexes between FA and N_2 or CO occur at energies comparable to those for self-association of FA.

The CH stretching band has in all matrices studied an additional component at lower frequencies, at about 2760 cm^{-1}. This splitting of the νCH band is ascribed to the interaction between the νCH fundamental level and the first overtone level of the CH in-plane bending.

The broad band at 1304 cm^{-1} found only in nitrogen matrices occurs in parallel with the downward shift of the CH stretching band (about 20 cm^{-1}) compared with other matrices, and thus an interaction between νCN and $2 \times \omega NH_2$ is obvious.

To gain information on the influence of nitrogen complex formation on the lowest-frequency mode, structures for a few 1:1 complexes between nitrogen and FA were calculated on the 4—31G basis set level, using the programme GAUSSIAN 76. For the FA molecule the 4—31G optimised geometry was used [18], and the bond length of the nitrogen molecule was 1.098 Å (the experimental value). The intermolecular coordinates were optimised, and the three lowest-energy configurations are shown in Fig. 2. In these cases the N_2 molecule was found to be on the extension of the N—H or C=O bonds, being almost parallel or perpendicular to these bonds in the FA molecular plane. Complex formation in the lowest-energy configuration was found to increase the NH_2 torsional force constant by about 10% compared to the value found for the free FA molecule on this basis set.

The ab initio calculated out-of-plane force field [16] was taken to reproduce the observed out-of-plane frequencies. The torsional coordinate was that of Pietilä and Stenman [26], developed for planar torsions. The experimental planar geometry [13] was used for FA in the calculation. The most important results were that this force field produced the observed frequencies with only slight modifications in the diagonal constants, and that the NH_2 wagging mode has a higher frequency than the NH_2 torsion. The resulting out-of-plane force field is given in Table 3.

The large intensity of the lowest-frequency fundamental band, the τNH_2 band, can be understood with the aid of the results of Williams et al. [27]. They found that perturbations in the N—C=O bond resonance system are encountered upon rotating the NH_2 group out of the molecular plane, which probably causes electrical anharmonicity to the NH_2 torsional transitions.

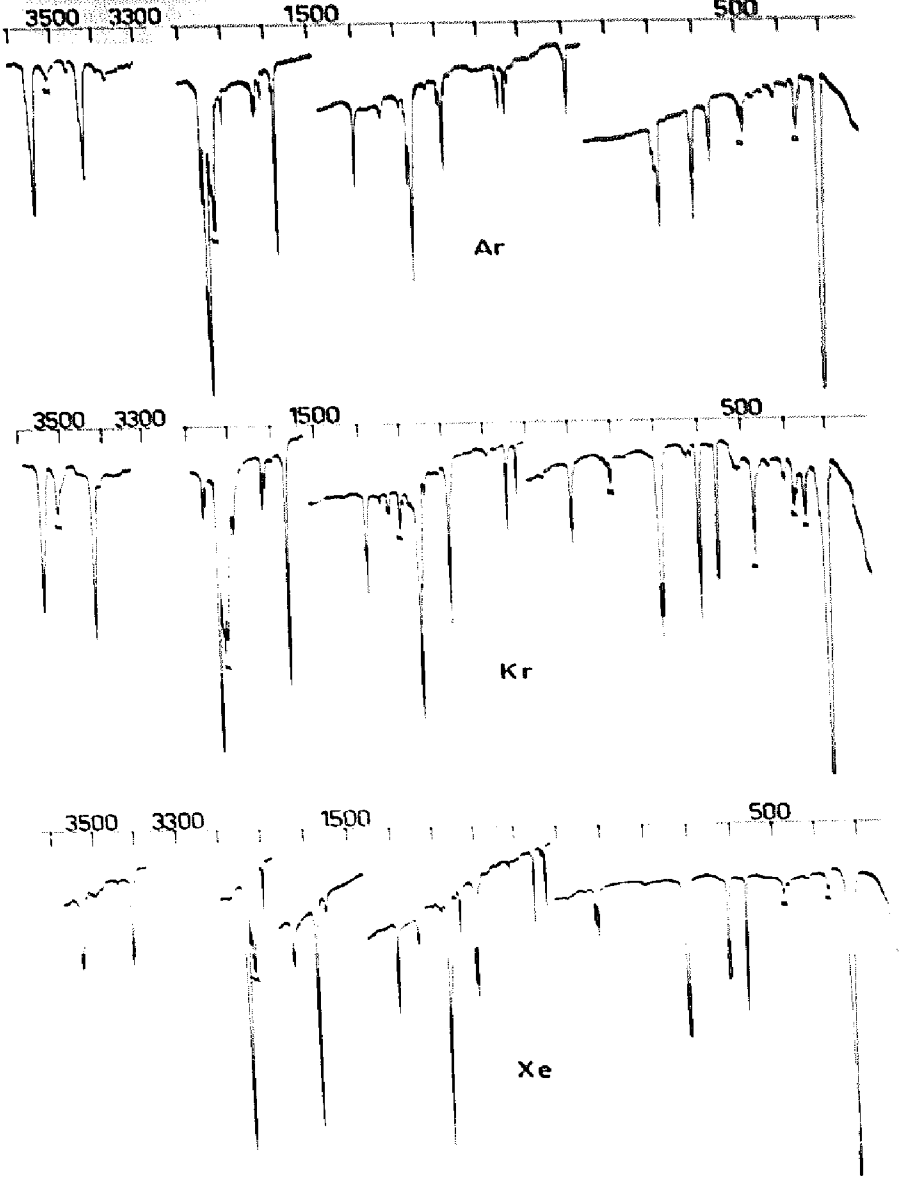
According to the present study the first and second overtones of the NH_2 torsion are of considerable intensity in rare-gas matrices. Overtones occur rather seldom in low-temperature matrices. The frequencies imply that there is only slight mechanical anharmonicity in this motion; the intensity is rather due to electrical anharmonicity.

Evans [5] assigned the $r NH_2$ fundamental of FA in the gas phase at 1167 cm^{-1}. In rare-gas matrix spectra this band can be found at about 1190 cm^{-1} but no fundamental is found in this region in N_2 or CO matrices. This band is shifted due to complex formation to lower frequencies, in N_2 to 830 cm^{-1} and in CO to 948 cm^{-1}. It is to be noted that in the CO matrix spectra the NH_2 rock, wag and torsion fundamentals are split into at least two bands. This fine structure may indicate several well-defined complex structures between FA and CO molecule(s).

It was also found that the NH_2 torsional band broadens reversibly in the temperature range 13—25 K in N_2 and CO matrices, but not in rare-gas matrices. In the case of methanol [9] similar broadening in the OH torsional band was observed and was suggested to be due to rapid vibrational relaxation caused by coupling of the τOH mode with complex modes. The reversibility of the NH_2 torsion band of FA could arise from similar causes.

The deuterated formamides

The fundamental frequencies of the deuterated formamides in Ar are given in Table 4. The spectra of the ND_2 species were, however, complicated in certain regions by the presence of the partially deuterated species NHD and NDH.


3500
3300
1500
500
Ar
3500
3300
1500
500
Kr
3500
3300
1500
500
Xe

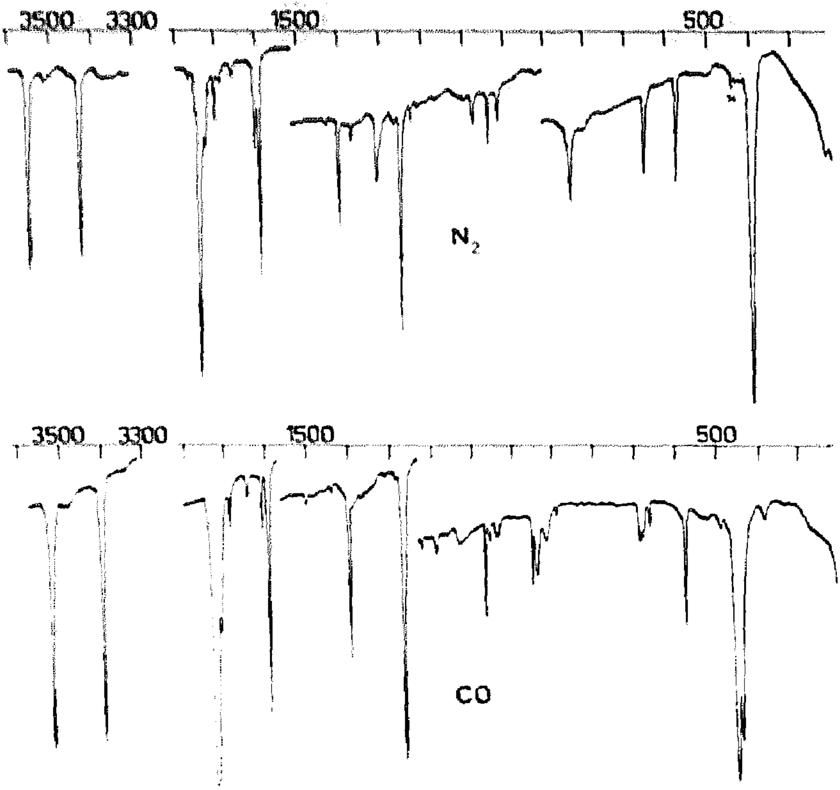


Fig. 1. The matrix infrared spectra of formamide in Ar, Kr, Xe, N_2 and CO matrices. The spectra were recorded at 13 K. The starred peaks are due to associated species.

The νCO band of the C-deuterated species is a doublet with a peak separation of about 30 cm^{-1}. In the case of formic acid similar splitting was observed [28] in the spectra of C-deuterated species and this was explained by Fermi resonance between the νCO fundamental and the CD out-of-plane wagging overtone. For perdeuterated FA this is also the most reasonable explanation. In the case of $DCONH_2$ the third overtone of the NH_2 torsion shifts the CD out-of-plane bending band up to about 970 cm^{-1}, and thus the splitting of the νCO band originates from the interaction of the νCO fundamental with the combination level $r NH_2 + \delta OCN$.

It is difficult to assign with certainty the $r NH_2$ band of perdeuterated FA. There are two candidates, a medium intensity band at 1102 cm^{-1} and a very weak band at 910 cm^{-1}. According to our tentative normal coordinate calculations the ND_2 rocking motion is very much a mixed motion, strong

TABLE 2

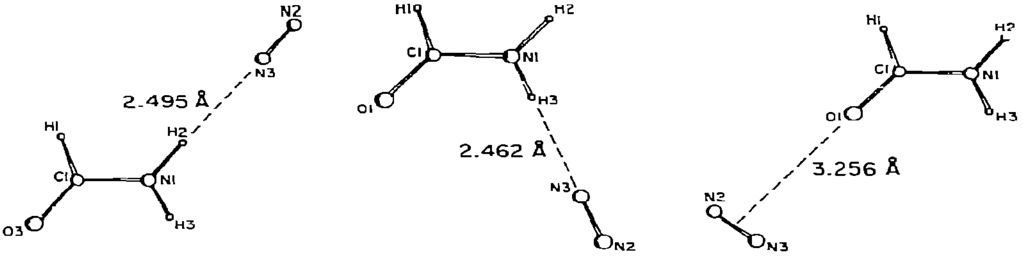
The observed frequencies (cm^{-1}) for formamide in Ar, Kr, Xe, N_2 and CO matrices. The spectra were recorded at 13 K and the frequencies are believed to be accurate to ± 1 cm^{-1}

Argon	Krypton	Xenon	Nitrogen	Carbon monoxide	Assignment
3561 sh	3549 m	3535 m	3554 s	3525 s	$\nu_a NH_2$
3553 sh			3548 sh		
3548 m					
3436 sh	3426 m	3411 m	3431 s	3401 s	$\nu_s NH_2$
3431 sh			3426 sh		
3427 m					
2884 m	2864 m	2851 s	2872 s	2883 w,sh	νCH
2870 w				2870 m	
2779 vw	2761 w	2753 m	2765 w	2765 w,br	$\nu CH + 2 \times \delta CH$
2766 w	2757 w				
1752 w					
1748 w					
1745 vs			1737 vvs	1718 vvs	$\nu C{=}O$
1740 vvs	1739 vvs	1731 vvs	1732 s		
1731	1731	1722	1727	1707	ass.
1728	1725	1718	1723		
1723	1718	1714	1720		
1720	1715				
1699 w	1696 w	1689	1697 w	1682 w	^{13}C
1579 s	1576 s	1574 s	1586 s	1588 s	δNH_2
1577 s					
1400 m	1395 w	1389 m	1396 m	1397 sh	δCH
	1392 m			1395 m	
1334 vw	1341 w	1342 w			$\tau NH_2 + \gamma CH$
	1338 w	1340 w			
			1367 w?		
			1304 m,br		$2 \times \omega NH_2 + \nu CN$
	1311 w				ass.
1271 m	1270 vs	1268 vs	1248 vs	1267 vs	νCN
1261 vs	1263 sh			1262 sh	
		1238 w	1225 vw	1223 vvw	?
				1187 vw	
1194 vw	1195 m	1196 m	839 w,sh	948 m	$r NH_2$
1185 m		1193 m	830 m,br	935 w,br	
1179 vw				909 vw,br	
1052 vvw	1053 m	1052 m	1072 w,br*	1065 m	γCH *probably
1047 w	1028 w	1025 w	1035 w	1055 vw	due to
1035 w^a			1012 w,br*		association
1027 vvw					
890 sh	901 w	908 w			$3 \times \tau NH_2$
889 w		903 w			
694 sh	698 m	707 sh	650 m	690 vw	ωNH_2
686 sh	692 m	705 m		685 vw,br	
682 m		702 m		678 vw,br	
680 m					
608 w,sh	611 m	610 m			$2 \times \tau NH_2$

TABLE 2 (continued)

Argon	Krypton	Xenon	Nitrogen	Carbon monoxide	Assignment
604 m					
600 w,sh					
564 m	571 m	567 m	576 m	579 m	δOCN
311 w	313 vvs	319 vvs	402 sh,m	456 vs	τNH_2
306 m		316 vvs	396 vvs	445 vs	
303 vvs					

[a]Intensity varies from sample to sample.



6.59 (4.37) 6.21 (3.79) 4.08 (2.23)

Fig. 2. Three lowest-energy configurations of 1:1 complexes between FA and N_2 (intermolecular coordinates optimised). In all cases the N_2 molecule is in the FA plane. The interaction energies in kJ mol^{-1} are indicated below the figures (the values obtained with the supermolecule correction are in parentheses).

contributions coming from δND_2, δCD and νCN, and the τND_2 frequency is predicted to be about 1100 cm^{-1}. Thus the band at 1102 cm^{-1} is assigned to the ND_2 rocking mode of the perdeuterated species.

Figure 3 shows the torsional region of a sample containing almost equal amounts of the species $HCONH_2$, HCONHD, HCONDH and $HCOND_2$. For other primary amides similar differences in the torsional bands of the partially *N*-deuterated species have been observed [29]. Table 5 includes the

TABLE 3

The out-of-plane force field of formamide. The off-diagonal constants are those from ref. 16. The coordinates are: S_1 = CH oop bending, S_2 = NH_2 wag and S_3 = NH_2 torsion

Coordinate				ν(calc.)	PED
S_1	0.4071[a]			1038	0.95 S_1
S_2	−0.02	0.1046		677	0.99 S_2
S_3	0.011	0.0180	0.0769	307	0.89 S_3

[a]Force constants in mdyn Å rad^{-2} = 10^{-18} J rad^{-2}.

TABLE 4

Fundamental frequencies (cm^{-1}) for deuterated formamides. The bands marked by an asterisk are uncertain due to the presence of partially *N*-deuterated species as well as the very low intensities of the bands

$DCONH_2$	$HCOND_2$	$DCOND_2$	Assignment
3547	2663	2665	$\nu_a NH_2, ND_2$
3429	2498	2499	$\nu_s NH_2, ND_2$
3424			
2156	2886	2264	$\nu CH, CD$
	2873	2253	
1738	1737	1734	$\nu C=O$
1710	1732	1703	
1699			
1580	1086	1031	$\delta NH_2, ND_2$
1141	1406	946	$\delta CH, CD$
1243	1297	1309	νCN
	1306	1302	
1173	955*	1102*	$r NH_2, ND_2$
1164			
974	1033*	864	$\gamma CH, CD$
960			
688	480	476	$\omega NH_2, ND_2$
682	470	473	
679			
558	565	461	δOCN
305	221	221	$\tau NH_2, ND_2$

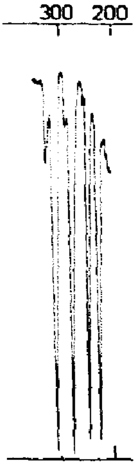


Fig. 3. The torsional region of the spectrum of an FA sample in Ar (containing almost equal amounts of the partially *N*-deuterated species).

TABLE 5

Observed torsional frequencies of partially *N*-deuterated formamides in Ar and N_2 matrices and monofluoro- and monochloroacetamide in Ar

Ar		N_2		Ar		
FA	CD-FA	FA	CD-FA	MFAA	MCAA	
303	305	396	397	354	357	NH_2
270	270	350	349	298	303	NHD
239	240	311	310	286	285	NDH
221	221	295	294	265	265	ND_2

torsional frequencies found for formamides and for monofluoro- and monochloro-acetamides [29].

It was thought that the changes in the frequencies could be due to differences in the reduced moment of inertia for the internal rotation between the NHD and NDH species. Since the torsional barrier of FA is quite high, about 80 kJ mol^{-1} [17], this effect can be estimated by using the high barrier harmonic approximation [30], with eigenvalues $E_v = N(V_N F)^{1/2}$ (v + 1/2). The term F contains the reduced moment of inertia for internal rotation. The potential V_N is taken to be the same for all isomers and thus relative values for the torsional frequencies can be obtained.

This calculation gives for the NHD_t (D in *trans* position to C=O) and NHD_{cis} species a torsional frequency difference of about 7 cm^{-1}, which is much less than the observed difference for FA of 31 cm^{-1}. In the case of the halogenated acetamides the moment of inertia for the internal rotation is so large that this calculation does not predict any difference for the torsional frequencies of the two partially deuterated species.

In all cases the internal rotation axis was chosen to be coincident with the C—N bond axis. Deviations from this in the real motion could partly explain the discrepancy between the calculated and observed results for the internal rotation in partially *N*-deuterated species.

On the other hand, the intramolecular interaction between the C=O and $N—H_{cis}$ groups [18, 23] could be responsible for the lowest-frequency vibration being described as $N—H_t$ out-of-plane bending [14]. Thus, if the contribution to the NH_2 torsion of the NH_t group is larger than that of the NH_{cis} group, we are able to assign the higher frequency torsion peak of the partially *N*-deuterated amides as arising from the NHD_{cis} species.

REFERENCES

1 C. H. Smith and R. H. Thompson, J. Mol. Spectrosc., 42 (1972) 227.
2 I. Suzuki, Bull. Chem. Soc. Jpn., 33 (1960) 1359.
3 Y. Tanaka and K. Machida, J. Mol. Spectrosc., 63 (1976) 306.
4 K. Itoh and T. Shimanouchi, J. Mol. Spectrosc., 42 (1972) 86.
5 J. C Evans, J. Chem. Phys., 22 (1954) 1228.

6 J. Bukowska, Spectrochim. Acta, Part A, 35 (1979) 985.
7 J. Bukowska and K. Miaskiewics, J. Mol. Struct., 74 (1981) 1.
8 S. T. King, J. Phys. Chem., 75 (1971) 405.
9 J. Murto and M. Ovaska, Spectrochim. Acta, Part A, 39 (1983) 149.
10 E. L. Hansen, N. W. Larsen and F. M. Nicolaisen, Chem. Phys. Lett., 69 (1980) 327.
11 J. C. Evans, J. Chem. Phys., 31 (1959) 1435.
12 C. C. Costain and J. M. Dowling, J. Chem. Phys., 32 (1960) 158.
13 E. Hirota, R. Sugisaki, C. J. Nielsen and G. O. Sørensen, J. Mol. Spectrosc., 49 (1974) 251.
14 Y. Sugawara, Y. Hamada, A. Y. Hirakawa, M. Tsuboi, S. Kato and K. Morokuma, Chem. Phys., 50 (1980) 105.
15 N. R. Carlsen, L. Radom, N. V. Riggs and W. Rodwell, J. Am. Chem. Soc., 101 (1979) 2233.
16 G. Fogarasi, P. Pulay, F. Török and J. E. Boggs, J. Mol. Struct., 57 (1979) 259.
17 B. Sunners, L. H. Piette and W. G. Schneider, Can. J. Chem., 38 (1960) 681; H. Kamei, Bull, Chem. Soc., Jpn., 41 (1968) 2269; T. Drakenberg and S. Forsen, J. Phys. Chem., 74 (1970) 1.
18 L. Radom and N. V. Riggs, Aust. J. Chem., 33 (1980) 249.
19 H.-J. Hofman and G. Peinel, J. Mol. Struct., 91 (1983) 289.
20 A. J. Duben and S. Miertus, Chem. Phys. Lett., 88 (1982) 395.
21 A. Balazs, Acta Chim. Acad. Sci. Hung., 108 (1981) 265.
22 A. Annamalai and S. Singh, J. Chem. Phys., 77 (1982) 860.
23 C. W. Bock, M. Tratchman and P. George, J. Mol. Spectrosc., 89 (1981) 76.
24 J. Hine, R. S.-M. King, W. R. Midden and A. Sinha, J. Org. Chem., 46 (1981) 3186.
25 A. J. Barnes, L. LeGall, C. Madec and J. Lauransan, J. Mol. Struct., 38 (1977) 109.
26 L.-O. Pietilä and F. Stenman, Comment. Phys.-Math., 48 (1978) 145.
27 J. O. Williams, C. van Alsenoy and L. Schäfer, J. Mol. Struct., 76 (1981) 171.
28 R. L. Redington, J. Mol. Spectrosc., 65 (1977) 171.
29 M. Räsänen, to be published.
30 A. V. Cunliffe, in W. J. Orville-Thomas (Ed.), Internal Rotation in Molecules, Wiley, New York, 1974, p. 217.