# VIBRATIONAL SPECTRA AND DYNAMICS OF CONFORMATION AND HYDROGEN BONDING OF N-METHYLACETAMIDE.
## I. CONFORMATIONAL DYNAMICS OF THE CH$_3$CONHCH$_3$ MOLECULE AND NH OUT OF PLANE BAND SPLITTING

F. FILLAUX and M.H. BARON

*Laboratoire de Spectrochimie Infrarouge et Raman, CNRS, 94320 Thiais, France*

The infrared spectra of CH$_3$CONHCH$_3$ and CH$_3$CONDCH$_3$ have been investigated as low-temperature crystals, pure liquids and solutions in various solvents in the 400–800 cm$^{-1}$ range. A new assignment of the bands associated with the NH group is given. Multiplets of $\gamma$ NH and $\gamma$ ND fundamentals have generally been observed and have been interpreted in terms of a double minimum potential function of the $\gamma$ NH mode with a tunnelling between two minima. The potential functions of $\gamma$ NH and $\tau$ CN modes are similar and can be combined to give a potential surface with four minima corresponding to four molecular conformations. The influence of the hydrogen bonding on the $\gamma$ NH splitting and barrier height is discussed.

## 1. Introduction

The unusual breadth and structure of the AH stretching band of hydrogen bonded systems has attracted many spectroscopists for a long time. Various band shaping mechanisms such as crystal fields effect, proton tunnelling along the hydrogen bond, Fermi resonances between the $\nu$ AH fundamental and different combinations and overtones, anharmonic coupling between AH and hydrogen bond stretching motions, and structural disorder were suggested [1–4]. The relative importance of different factors appears to depend on the physical state of the hydrogen bonded system as well as on the strength of the hydrogen bond [5].

In these papers (parts I and II [6]) a new $\nu$ AH band shaping mechanism is proposed. It is, like the existing quantitative theories [4], of the strong coupling type. However, the more or less complicated structure of the AH stretching band can be explained by coupling of intramolecular modes alone. In the particular case of N-methyl-acetamide reported here the coupling involves essentially NH stretching, NH out-of-plane bending, and CN torsional modes. Since the NH stretching band structure appears closely related to the $\gamma$ NH (and $\tau$ CN) band splitting resulting from the conformational dynamics of this molecule we shall discuss in the first part of this series the low frequency (400–800 cm$^{-1}$) region characteristic of $\gamma$ NH motions and in the second part the high frequency (3500–2000 cm$^{-1}$) NH (ND) stretching range. A study of the spectral region below 200 cm$^{-1}$ where the CN torsional mode gives rise to bands observed in Raman and neutron inelastic scattering has already been published [7, 8].

## 2. Experimental

### 2.1. Sample preparation

CH$_3$CONHCH$_3$ (Prolabo) was dried and sublimated under vacuum. The deuterated compounds CD$_3$CONHCH$_3$, CH$_3$CONHCD$_3$ and CD$_3$CONHCD$_3$ were obtained by the condensation of the appropriate methylamine and acetyl chloride solution in methylene chloride. The

products distilled over potassium carbonate were sublimed in vacuum after drying. The compounds were checked to be spectroscopically pure and NMR data showed deuteration better than 99%.

N deuterated compounds were obtained from the corresponding N hydrogenated compounds by successive hydrogen exchange with $CH_3OD$.

All the deuterated compounds: acetic-acid ($CD_3COOD$), methylamine hydrochloride ($CD_3NDCl$) and methanol ($CH_3OD$) were commercial products obtained from CEA (France).

### 2.2. Spectra

The infrared spectra were recorded using a Beckman IR 12 or a Perkin–Elmer 225 spectrometer. The spectral slit width was about $2 \, cm^{-1}$. The samples were examined as thin crystalline or liquid films between CsI windows. Solutions were in cells of various thickness equipped with KBr or CsI windows.

The Raman spectra were recorded using a Coderg T 800 instrument with triple monochromator and the 5145 Å exciting line of an $Ar^+$ laser. The spectral slit width was $2 \, cm^{-1}$. The samples were sublimed in vacuum directly into glas tubes of 1 mm diameter. For low temperature experiments a Coderg cryostat was used with a flow of gaseous nitrogen at boiling nitrogen temperature. A Meric cryostat was used for temperatures between liquid nitrogen and liquid helium. In this case, the sample temperature was measured from the intensity ratios of the Stokes and anti-Stokes lines.

### 2.3. Calculations

All the calculations were performed on a PDP 11/34 (Digital Equipment Corporation). The program used for calculating the potential functions is similar to the one already described [6] and refers to the known matrix elements for the hamiltonian [9, 10].

For out-of-plane NH deformation, it was considered that only the hydrogen atom was involved (reduced mass: 1 amu for H and 2 amu for D) and that the giration radius was 1 Å in each case.

## 3. Results and discussion

The assignment of N-methylacetamide (NMA) proposed by Miyazawa et al. [11–13] is based on the assumption that the CONH group is planar. The corresponding vibrations are divided into in-plane A′ (amide A, B, I–IV) and out-of-plane A″ (amide V–VII) modes, their frequencies being all above $200 \, cm^{-1}$. A recent investigation of NMA crystal by neutron inelastic scattering (NIS) [8] and Raman spectroscopy [7], however, has identified two $CH_3$ torsional modes at 165 and $154 \, cm^{-1}$, and two CN torsional modes near 127 and $164 \, cm^{-1}$. The presence of the latter (amide VIII band) in this range implies that the rest of the spectrum must be reinterpreted. Besides, the assignment of the amide VI band to a CO out-of-plane bending motion [14] appears questionable since the corresponding strong infrared absorption near $600 \, cm^{-1}$ disappears on deuration of the NH group while the force field predicts only a slight frequency shift [15].

We have thus investigated in some detail the infrared spectra of low temperature solids of $CH_3CONHCH_3$ and $CH_3CONDCH_3$ (NMA-*d*) and of their solutions in various solvents in the $400–800 \, cm^{-1}$ region where $\gamma$ NH and skeletal bending modes are expected. Our interpretation is different from that of previous authors [10–15] and implies a non-planar peptide group.

### 3.1. Infrared spectra of crystalline NMA

#### 3.1.1. Crystal structure and symmetry considerations

The crystal of NMA at $-35°C$ is orthorhombic and belongs to the $Pnma \equiv D_{2h}^{13}$ space group with four molecules, occupying general positions, per unit cell. There are infinite chains of molecules bonded by medium-strong NH...O hydrogen bonds of 2.825 Å [16]. The factor group analysis of NMA crystal shows that each of the 30 intramolecular vibrations will be split into four components, two infrared active being expected for A′ ($B_{1u}$, $B_{3u}$) and only one ($B_{2u}$) for A″ modes. The same result is obtained in the isolated chain ($C_{2v}$ factor group and $Z = 2$)

approximation suggested by Itoh and Shimanouchi [17].

### 3.1.2. Assignment of the bands in the 400–800 cm$^{-1}$ region

In the 400–800 cm$^{-1}$ region of NMA, skeletal bending and $\gamma$ NH vibrations are expected. The former are but little affected by deuteration of the NH group and by temperature lowering and are identified near 439 and 630 cm$^{-1}$ (fig. 1, table 1). The 630 cm$^{-1}$ band (amide IV) splits into two components when going from liquid to crystal as expected for an in-plane mode while the 439 cm$^{-1}$ band, also due to an A' vibration ($\delta$ CC) [15], remains single.

All the other bands in this region, i.e. the bands at 601 and 725 cm$^{-1}$ in the spectra of liquid NMA and those at 609, 619, 749, 759 and 805 cm$^{-1}$ of the low temperature crystal disappear on deuteration, are temperature sensitive and must thus be due to the NH group (table 1). The 609–619 cm$^{-1}$ doublet and the 805 cm$^{-1}$ band are strong and are assigned to NH out-of-plane. The former cannot be due to a CO out-of-plane motion as suggested previously [11] and the $\gamma$ CO band has been identified at 220 cm$^{-1}$ [7]. It cannot be interpreted in terms of combinations in Fermi resonance with the $\gamma$ NH at 805 cm$^{-1}$ either since the

only suitable combinations can be derived from $\delta$ CC mode of A' species at 439 cm$^{-1}$ and $\gamma$ CO and $\tau$ CN modes of A" species at 220 and 160 cm$^{-1}$, respectively. In such case the resulting combination bands should have frequencies in the 600–650 cm$^{-1}$ range, i.e. in between $\gamma$ NH and $\gamma$ ND frequencies, and their intensities are expected similar for both $CH_3CONHCH_3$ and $CH_3CONDCH_3$ which is not observed: the 609–619 cm$^{-1}$ doublet is found only in the spectrum of NMA (fig. 1). The 749–759 cm$^{-1}$ doublet, on the other hand, is weak and is believed to be due to the $\gamma$ NH + $\tau$ CN combinations, the numerical values of which are very close (609 + 140 and 619 + 140 cm$^{-1}$) to those of the observed frequencies. Finally, a weak absorption near 500 cm$^{-1}$ which disappears on deuteration is also likely to be a combination but no assignment is proposed. Three $\gamma$ NH fundamentals and two $\gamma$ ND analogs have thus been resolved in the spectra of crystalline $CH_3CONHCH_3$ and $CH_3CONDCH_3$, respectively (fig. 1 and table 1). This splitting cannot be interpreted by a crystal field effect which should not be operative for A" vibrations. Anyway, two bands at 536 and 568 cm$^{-1}$ assigned to $\gamma$ ND modes (table 1) persist in the spectrum of an isotopically diluted crystal containing about 10% of ND in 90% of
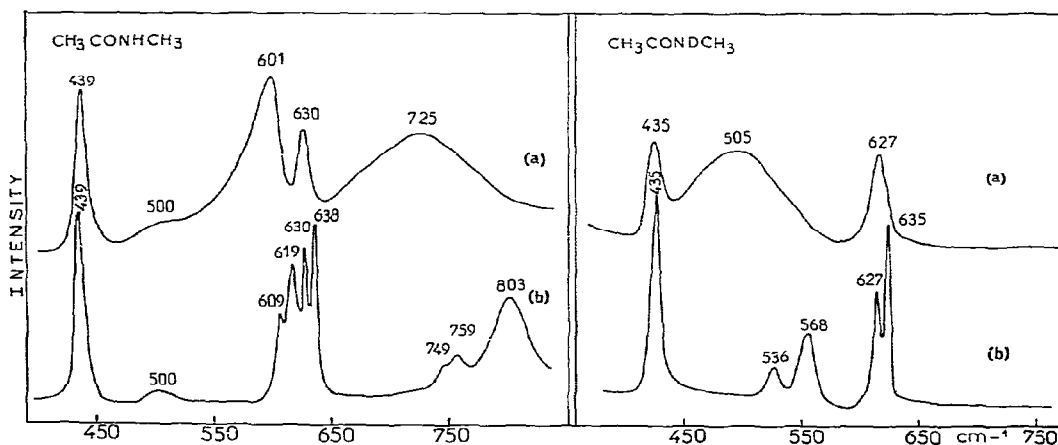


Fig. 1. Infrared spectra of NMA and NMA-$d$ between 400 and 750 cm$^{-1}$. (a) Liquid state at room temperature, (b) crystalline state at the temperature of liquid nitrogen.

Table 1
Infrared frequencies (cm$^{-1}$) of CH$_3$CONHCH$_3$ and CH$_3$CONDCH$_3$ in the 400–800 cm$^{-1}$ region

| CH$_3$CONHCH$_3$ | | CH$_3$CONDCH$_3$ | | Assignment | |
| --- | --- | --- | --- | --- | --- |
| liquid (300 K) | crystal (90 K) | liquid (300 K) | crystal (90 K) | type of motion | transitions |
| 439 s | 439 s | 435 s | 435 s | $\delta$CC | |
| 500 sh | 500 w | | | Combination | |
| | | 505 s, b | $\begin{cases}536\ w\\568\ m\end{cases}$ | $\gamma$ ND | $\begin{cases}0\to2+1\to2\\0\to3+1\to3\end{cases}$ |
| 601 s, b | $\begin{cases}609\ ms\\619\ s\end{cases}$ | | | $\gamma$ NH | $\begin{cases}1\to2\\0\to2\end{cases}$ |
| 630 ms | $\begin{cases}630\ s\\638\ s\end{cases}$ | 627 ms | $\begin{cases}627\ s\\635\ s\end{cases}$ | $\delta$ CO | |
| | $\begin{cases}749\ w\\759\ w\end{cases}$ | | | $\gamma$ NH + $\tau$CN | |
| 725 s, vb | 805 s | | | $\gamma$ NH | $0\to3+1\to3$ |

s: strong; m: medium; w: weak; v: very; b: broad; sh: shoulder.

NH. The same is true of two widely separated $\gamma$ NH bands at 601 and 725 cm$^{-1}$ in the spectrum of isotopically diluted (10% of NH in 90% of ND) pure liquid NMA. In order to account for these $\gamma$ NH and $\gamma$ ND multiplets the following model is proposed.

### 3.1.3. Conformation of the CH$_3$CONHCH$_3$ molecule

The basic assumption about the NMA molecule is that the CONH group is not planar and that the NH (ND) out-of-plane bending mode has to be described by a suitable double minimum potential function [25]. The subsequent tunnelling between the two minima splits the $\gamma$ NH levels and the resulting transitions $(0\to2,\ 1\to2,\ 0\to3$ and $1\to3)$ give rise to the observed multiplets.

The corresponding potential function is of the form $V = a\theta_N^2 + b\exp(-c\theta_N^2)$, where $V$ is the potential energy (cm$^{-1}$) and $\theta_N$ the internal coordinate (rad) defined according to Ramachandran et al. [18] and characterising the deviation from the planarity of the bonds around the nitrogen atom. The coefficients are $a = 21277$ cm$^{-1}$, $b = 31785$ cm$^{-1}$ and $c = 0.89$. The barrier height is 1060 cm$^{-1}$ ($\approx 13300$ J/mol) and the energy minimum is calculated for $\theta_{min} = 32°$.

Under these conditions the 609 and 619 cm$^{-1}$ frequencies can be assigned to $1\to2$ and $0\to2$ transitions (calc. 609 and 619 cm$^{-1}$) while the broad band near 805 cm$^{-1}$ corresponds to overlapped $1\to3$ and $0\to3$ transitions (calc. 793 and 803 cm$^{-1}$) (table 1). Only $1\to2$ and $0\to3$ transitions are infrared active if the first derivative of the dipole moment $(\partial\mu/\partial x)$ alone is considered. However, if the amplitude of the motion is large enough, the second term $\partial^2\mu/\partial x^2$ is no longer negligible and $0\to2$ and $1\to3$ transitions may become very strong. Some other phenomena like quasi-symmetrical potential functions, mechanical and electrical couplings can also contribute to the intensities [19, 20].

The two $\gamma$ ND bands at 536 and 568 cm$^{-1}$ can be interpreted similarly: the former corresponds to $0\to2$ and $1\to2$ (calc. 519.6 and 518.9 cm$^{-1}$) and the latter to the $0\to3$ and $1\to3$ (calc. 552.2 and 551.5 cm$^{-1}$) transitions.

The internal torsional mode ($\tau$ CN) around the C–N bond of the CONH group splits into two components at 127 and 164 cm$^{-1}$ in the crystal. This splitting has also been interpreted in terms of a potential function involving two minima ($\Delta\omega \pm 10°$) separated by a weak barrier indicating a non-planar molecular skeleton of NMA [7]. The potential functions of the $\tau$ CN and of $\gamma$ NH modes can be combined (neglect-
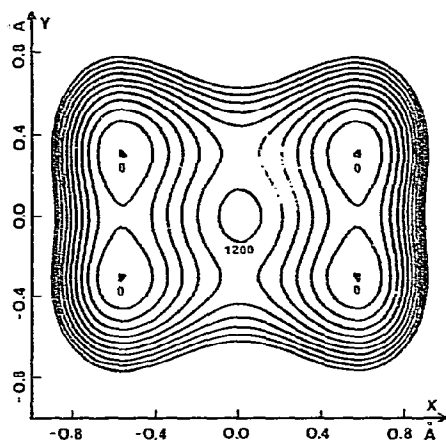
Fig. 2. Four minimum potential function for NMA in crystalline state. $X = R\theta_N$ and $Y = \rho \Delta\omega$. Isoenergy curves are separated by 200 cm$^{-1}$. Energy values in cm$^{-1}$.

ing coupling terms) to define a potential surface represented in fig. 2. There are four minima corresponding to four molecular conformations shown in fig. 3. Each conformation is defined by two angles $\Delta\omega$ and $\theta_N$ and can switch over to another conformation by tunnel effect. The potential surface of fig. 2 is somewhat different from those calculated by various quantum mechanical molecular orbital methods [21, 22] which indicate either only one central minimum or two minima. It must be noticed, however,
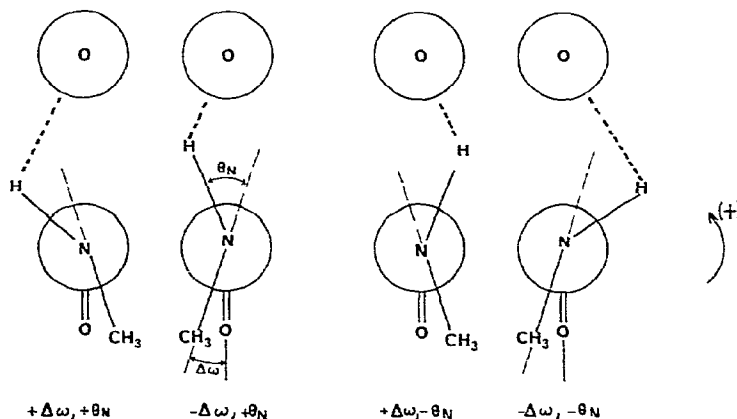
that these calculations concern isolated molecules in vacuum while the experimental results given here are related to the crystalline state.

### 3.2. Infrared spectra of liquid NMA and of its solutions in various solvents

The NH out-of-plane frequency is very sensitive to molecular interactions [5] and we studied the corresponding $\gamma$ NH and $\gamma$ ND absorption bands of pure liquid NMA and of its solutions in different solvents in order to find out if and how the conformational dynamics of this molecule depends on the environment.

#### 3.2.1. Observed spectra

The spectra of solutions of NMA and NMA-$d$ are shown in figs. 4, 5 and 6 and the corresponding $\gamma$ NH and $\gamma$ ND frequencies and their isotopic ratios are given in table 2. As expected the $\gamma$ NH (ND) frequency increases when going from relatively inert solvents or weak proton donors to stronger proton acceptors, i.e. in the opposite direction as that of $\nu$ NH (ND) frequencies investigated under the same conditions [23, 24].

Two main cases can be distinguished. The first comprises relatively inert solvents such as carbon disulphide or benzene (fig. 4). When the



Fig. 3. Conformations of self-associated crystallized NMA corresponding to the four energy minima relative to the internal coordinates $\theta_N$ and $\Delta\omega$. The angles are positive counterclockwise.

Table 2
Out-of-plane NH (ND) frequencies (cm$^{-1}$) and isotopic frequency ratios of $CH_3CONHCH_3$ and $CH_3CONDCH_3$ in various solvents

| Solvent | Concentration (M l$^{-1}$) | $\gamma$ NH [a] | | $\gamma$ ND | $\gamma$ NH/$\gamma$ ND [b] | |
|---|---|---|---|---|---|---|
| cyclopentane | 0.03 | 418 | 470 | 322 | 1.30 | 1.40 |
| carbon disulfide | 0.02 | 470 | NO | S.A. | – | – |
| benzene | 0.1 | 485 | NO | 365 | 1.34 | – |
| methylene chloride | 0.2 | 498 | NO | 373 | 1.34 | – |
| chloroform | 0.2 | 495 | NO | 370 | 1.34 | – |
| nitromethane | 0.2 | 541 | SA | 410 | 1.32 | – |
| acetonitrile | 0.1 | 660 | 570 | 450 | 1.47 | 1.27 |
| diethyl-ether or tetrahydrofuran | 0.2 | 690 | 589 | 471 | 1.47 | 1.25 |
| pure liquid | – | 725 | 601 | 505 | 1.44 | 1.19 |

[a] SA solvent absorption; NO not observed.
[b] Two $\gamma$ NH/$\gamma$ ND values are given when two $\gamma$ NH bands are observed.

concentration of NMA is lowered a monomer $\gamma$ NH band appears in the 460 to 500 cm$^{-1}$ range while the $\gamma$ NH bands near 600 and 700 cm$^{-1}$ ascribed to self associated species disappear (fig. 4, table 2). The same, i.e. existence of a single through broad $\gamma$ NH monomer band, is true of the solutions in weak proton donors such as chloroform and methylene chloride interacting mainly with the carbonyl group of NMA: $\gamma$ NH (ND) mode gives rise to a strong broad band near 500 (370) cm$^{-1}$ (fig. 5, table 2). The $\gamma$ NH/$\gamma$ ND isotopic frequency ratios yield

values of about 1.34 expected for pure out-of-plane NH and ND modes.

The second group contains relatively stronger proton acceptors such as acetonitrile and ether, their spectra being similar to those of pure liquid of NMA and NMA-$d$ (figs. 6 and 1) associated by NH...O hydrogen bonds. There are two $\gamma$ NH bands, one in the 570–601 cm$^{-1}$ region and the other in the 660–725 cm$^{-1}$ range while only one $\gamma$ ND band has been observed in each case (fig. 6). There are thus two isotopic frequency ratios for each system and the obser-
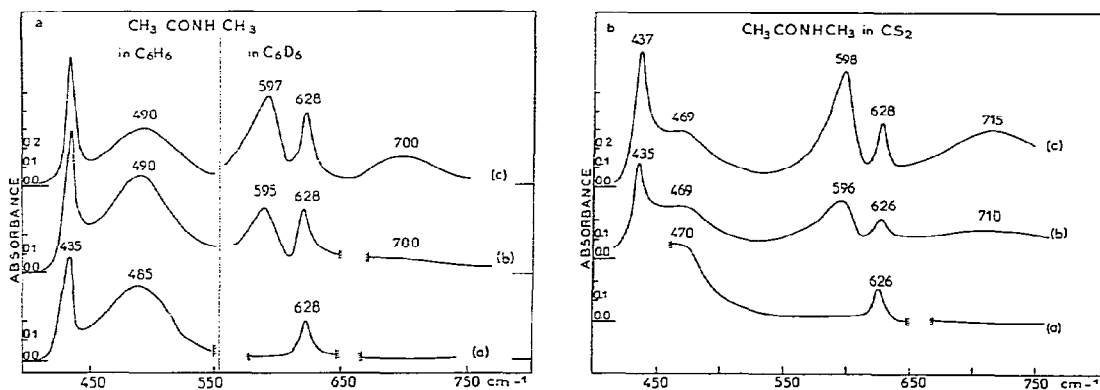


Fig. 4. Infrared spectra of NMA at various concentrations in benzene (a) 0.1 M l$^{-1}$, thickness 230 μ; (b) 0.2 M l$^{-1}$, thickness 110μ; (c) 0.6 M l$^{-1}$, thickness 110μ and carbon disulfide (a) 0.02 M l$^{-1}$; thickness 2000μ; (b) 0.09 M l$^{-1}$, thickness 500μ; (c) 0.2 M l$^{-1}$, thickness 300μ.
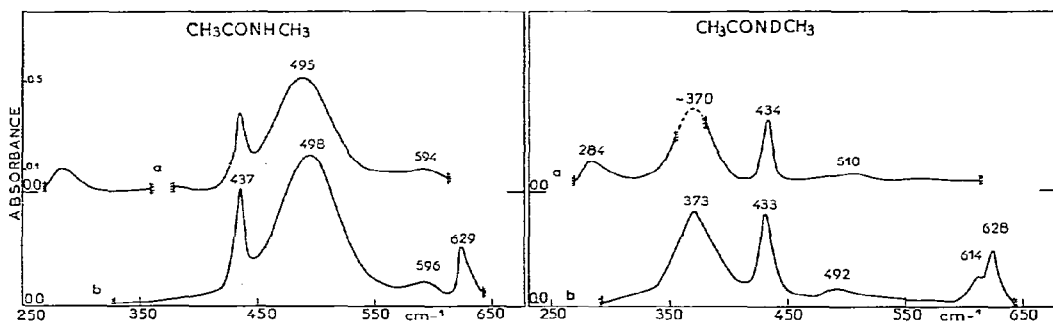
Fig. 5. Infrared spectra of NMA and NMA-*d* in: (a) chloroform, (b) methylene chloride. For each case, the concentration is 0.2 M l$^{-1}$ and the thickness is 39 μ.
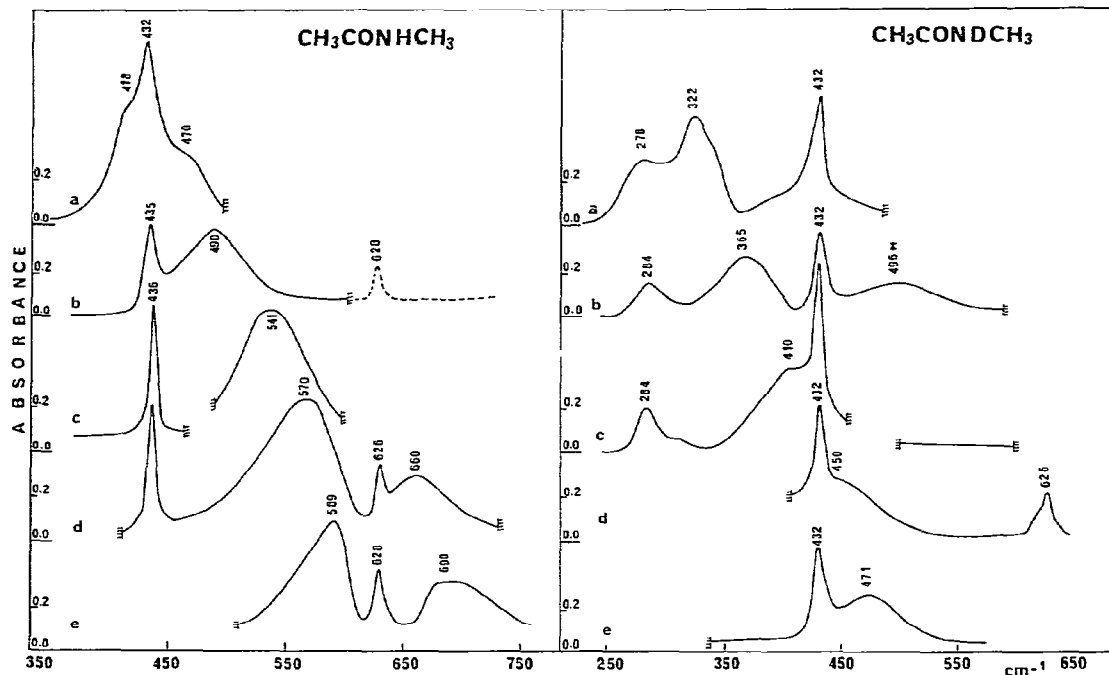


Fig. 6. Infrared spectra of NMA and NMA-*d* in various proton acceptor solvents: (a) cyclopentane (concentration 0.03 M l$^{-1}$, thickness 5000 μ); (b) benzene (C$_6$H$_6$ or C$_6$D$_6$, concentration 0.2 M l$^{-1}$, thickness 230 μ); (c) nitromethane (concentration 0.1 M l$^{-1}$, thickness 39 μ); (d) acetonitrile (concentration 0.1 M l$^{-1}$, thickness 230 μ); (e) diethyl ether (for NMA) and tetra-hydrofuran (for NMA-*d*) (concentration 0.2 M l$^{-1}$, thickness 39 μ). Band with * is due to a little amount of NMA in NMA-*d*.

Table 3

Out-of-plane NH and ND transitions, frequencies $(cm^{-1})$ and potential functions of pure liquid and solutions of NMA in proton acceptor solvents

| | $\gamma$ NH | | Potential functions $(cm^{-1})$ | $\gamma$ ND frequency | | $\theta$min[a] | $H$ $(cm^{-1})$ |
|---|---|---|---|---|---|---|---|
| | frequency obs. and calc. | transition | | calc. | obs. | | |
| pure liquid | $10^{b)}$ | $0 \rightarrow 1$ | $3334\,\theta_N^2 + 2708 \exp(-4.96\,\theta_N^2)$ | 0.9 | – | | |
| | 601 | $0 \rightarrow 2$ | | 481 | | 31 | 1110 |
| | 725 | $0 \rightarrow 3$ | | 502 | 505 | | |
| ether | $10^{b)}$ | $0 \rightarrow 1$ | $2355\,\theta_N^2 + 2093 \exp(-7.01\,\theta_N^2)$ | 1.0 | | | |
| | 590 | $0 \rightarrow 2$ | | 465 | 471 | 30 | 1144 |
| | 690 | $0 \rightarrow 3$ | | 481 | | | |
| acetonitrile | $10^{b)}$ | $0 \rightarrow 1$ | $1998\,\theta_N^2 + 1902 \exp(-7.80\,\theta_N^2)$ | 1.0 | | | |
| | 570 | $0 \rightarrow 2$ | | 447 | 450 | 30 | 1134 |
| | 660 | $0 \rightarrow 3$ | | 462 | | | |

[a] $\theta_{min}$: angle in degrees corresponding to the minimum of potential energy; $H$: barrier height.

[b] Arbitrary value (not observed).

ved values are considerably different from the "normal" ones (table 2). The case of cyclopentane is more complicated since the $\gamma$ NH and skeletal bending absorptions overlap, however, two shoulders near 418 and 470 $cm^{-1}$ are likely to be due to two $\gamma$ NH fundamentals.

### 3.2.2. Interpretation

Existence of two $\gamma$ NH bands in the spectra of solutions and of pure liquid NMA and the

resulting isotopic frequency ratios different from those expected for a harmonic oscillator can be interpreted in terms of potential function with double minimum of the form already used for the crystal. The potential functions calculated for NMA when two $\gamma$ NH bands have been observed are given in table 3. The $\gamma$ ND frequencies calculated from these functions are in good agreement with the experimental data assuming that the two expected bands are not

Table 4

Out-of-plane NH and ND deformation: potential functions and frequencies calculated for weakly hydrogen bonded NMA. The barrier height was assumed to be 1100 $cm^{-1}$ in every case

| Potential function $(cm^{-1})$ | Transition | Frequency $(cm^{-1})$ | | $\theta_{min}$[a] |
|---|---|---|---|---|
| | | $\gamma$ NH | $\gamma$ ND | |
| $756\,\theta_N^2 + 1327 \exp(-15.0\,\theta_N^2)$ | $0 \rightarrow 1$ | 10 | 1.3 | |
| | $0 \rightarrow 2$ | 422 | 322 | 28 |
| | $0 \rightarrow 3$ | 463 | 329 | |
| $1157\,\theta_N^2 + 1482 \exp(-10.9\,\theta_N^2)$ | $0 \rightarrow 1$ | 10 | 1.3 | |
| | $0 \rightarrow 2$ | 490 | 378 | 28 |
| | $0 \rightarrow 3$ | 550 | 388 | |
| $1651\,\theta_N^2 + 1718 \exp(-8.5\,\theta_N^2)$ | $0 \rightarrow 1$ | 10 | 1.0 | |
| | $0 \rightarrow 2$ | 540 | 421 | 30 |
| | $0 \rightarrow 3$ | 620 | 435 | |

[a] $\theta_{min}$: angle in degrees corresponding to the minimum of potential energy.

resolved. The calculated $\theta_{N\min}$ is sensitive to the $0 \rightarrow 1$ transition frequency which could be only estimated and the results given in table 3 are only indicative. However, this is not the case of the barrier height which is rather typical of the 2–3 level splitting. The barrier height has been found to be practically the same when going from pure liquide to ether or acetonitrile (table 3); several functions with a constant barrier height have thus been calculated for various rather weak hydrogen bonds and are given in table 4.

In the $\gamma$ NH versus $\gamma$ ND frequency plot shown in fig. 7, calculated and experimental values are compared. In the case of weak interactions where only one band frequency is observed – except for cyclopentane – the experi-
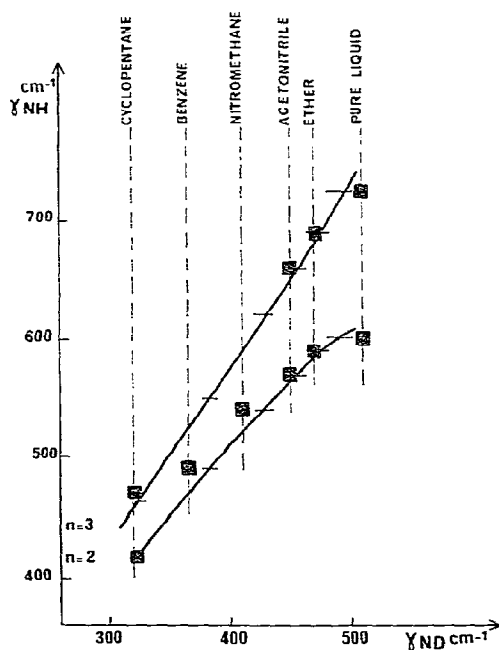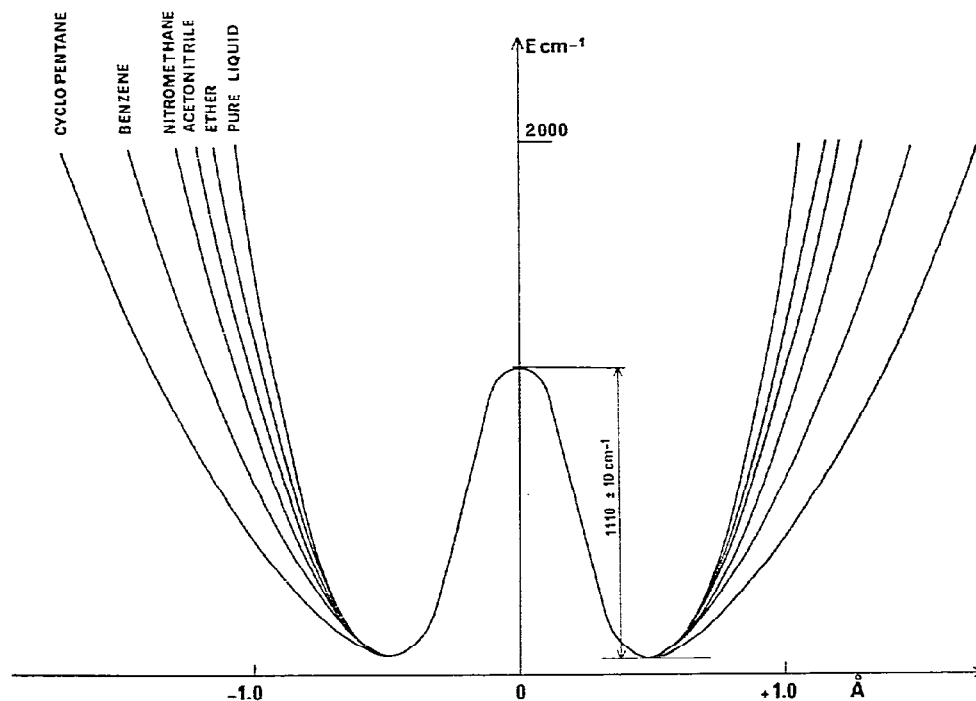
mental points are located between the two theoretical curves which is consistent with overlapping of the two expected components. The potential curves and energy levels of NMA in various solvents shown in fig. 8 illustrate how the hydrogen bond perturbs the parabolic part of the potential function but not the barrier height. Simultaneously with the increasing of the hydrogen bond strength as the $n = 2$ and $n = 3$ energy levels climb up the top of the barrier the splitting increases and the corresponding bands can be resolved.

## 4. Conclusions

Three out-of-plane NH and two out-of-plane ND fundamentals have been identified in the spectra of crystalline $CH_3CONHCH_3$ and $CH_3CONDCH_3$, respectively. They are interpreted as a consequence of conformational dynamics of a non-planar CONH group: the $\gamma$ NH vibration has to be described by a double minimum potential function, the subsequent tunnelling between the two minima splits the $\gamma$ NH levels, and the resulting transitions give rise to the observed multiplets. Similar conclusions can be reached for pure liquid N-methylacetamide and for its solutions in various solvents, proton donnor and acceptor. Their increasing NH...X hydrogen bond strength increases the $\gamma$ NH splitting but does not influence the barrier height between the two minima. Hydrogen bond does not appear to stabilize any configuration at the expense of the other. This conclusion suggests that this interaction is poorly sensitive to deviations from linearity of the three atoms N-H...O. This is consistent with crystal data collected for various hydrogen bonded systems which indicates a wide distribution of the N-H...O angle [26].



Fig. 7. $\gamma$ NH versus $\gamma$ ND frequency plot for various solvents. ▨ Experimental data. The continuous lines correspond to calculated data for potential functions with double minimum. Curves $n = 2$ and $n = 3$ correspond to $0 \rightarrow 2$ and $0 \rightarrow 3$ transitions, respectively.

## Acknowledgement

1/102          Fig. 8. Potential functions calculated for NMA in various solvents.

# References

[1] G.L. Hofacker, Y. Maréchal and M.A. Ratner, in: The hydrogen bond – recent developments in theory and experiments, Vol. 1, eds. P. Schuster, G. Zundel and C. Sandorfy (North-Holland, Amsterdam, 1976) p. 295.

[2] D. Hadzi and S. Bratos, in: The hydrogen bond – recent developments in theory and experiments, Vol. 2, eds. P. Schuster, G. Zundel and C. Sandorfy (North-Holland, Amsterdam, 1976) p. 563.

[3] Y. Maréchal in: Molecular interactions, eds. H. Ratajczak and W.J. Orville-Thomas (Wiley and Sons, New York, 1980) p. 232.

[4] S. Bratos, J. Lascombe and A. Novak, in: Molecular interactions, eds. H. Ratajczak and W.J. Orville-Thomas (Wiley and Sons, New York, 1980) p. 301.

[5] A. Novak, Struct. Bonding 18 (1974) 177.

[6] F. Fillaux, Chem. Phys. 62 (1981) 287, part II of this series.

[7] F. Fillaux, M.H. Baron, C. de Loze and G. Sagon, J. Raman Spectry. 7 (1978) 246.

[8] F. Fillaux and J. Tomkinson, Chem. Phys. 26 (1977) 295.

[9] E. Heilbroner, H. Rutishauser and F. Gerson, Helvet. Chim. Acta 42 (1959) 2285 and 2304.

[10] S.I. Chan and D. Steiman, J. Chem. Phys. 39 (1963) 545.

[11] T. Miyazawa, S. Shimanouchi and S. Mizushima, J. Chem. Phys. 29 (1958) 611.

[12] T. Miyazawa, J. Mol. Spectry. 4 (1960) 155.

[13] T. Miyazawa, in: Poly-$\alpha$-amino acids, protein models for conformational studies, ed. G.D. Fasman (Dekker, New York, 1967) p. 69.

[14] B. Schneider, H. Horeni, H. Pivcova and J. Honzl, Coll. Czeckhos. Chem. Commun. 30 (1965) 2196.

[15] M. Rey-Lafon, M.T. Forel and C. Garrigou-Lagrange, Spectrochim. Acta 29 A (1973) 471.

[16] J.L. Katz and B. Post, Acta Cryst. 13 (1960) 624.

[17] K. Itoh and T. Shimanouchi, Biopolymers 5 (1967) 921.

[18] G.N. Ramachandran, A.V. Lakshminarayanan and A.S. Kolaskar, Biochim. Biophys. Acta 303 (1973) 8.

[19] R.L. Somorjai and D.F. Hornig, J. Chem. Phys. 36 (1962) 1980.

[20] J.L. Wood, J. Mol. Struct. 17 (1973) 307.

[21] A.S. Kolaskar, A.V. Lakshminarayanan, A.V. Saraty and V. Sasisekharan, Biopolymers 14 (1975) 1081.

[22] V. Renugopalakrishnan and R. Rein, Biochim. Bio-
phys. Acta 434 (1976) 164.

[23] M. Rey-Lafon, J. Lascombe and M.L. Josien, Ann.
Chim. 8 (1963) 493.

[24] F. Fillaux and C. de Loze, J. Chim. Phys. 69 (1972)
36.

[25] F. Fillaux, M.H. Baron and C. de Loze, in: Peptides,
Proceedings of the Fifth American Peptide Symposium,
eds. M. Goodman and J. Meienhofer (Wiley and Sons,
New York, 1977) p. 303.

[26] T. F. Koetzle and M.S. Lehmann, in: The hydrogen
bond – recent developments in theory and experi-
ments, Vol. 2, eds. P. Schuster, G. Zundel and C. San-
dorfy (North-Holland, Amsterdam, 1976) p. 457.