

STRUCTURE OF MATRIX ISOLATED N-METHYLACETAMIDE

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The infrared spectra ($200\text{--}4000\text{ cm}^{-1}$) of four isotopic species of matrix (argon and nitrogen) isolated monomer N-methylacetamide are interpreted in conformational terms: *cis-trans* isomerism, and pyramidal nitrogen.

1. Introduction

In polypeptides and proteins the peptide group is generally assumed to take up the *trans* configuration (for general reviews see ref. [1]). A number of studies have been devoted to model amides [2–4]. For N-methylacetamide (NMA) the *cis* form has been either not detected or considered as present in low proportion [2,5,6].

The presence of slightly non-planar peptide units has been observed in polypeptides and proteins [7–9]. Calculations show that skew peptide groups increase the flexibility of the chains and therefore the stability range of certain secondary structures [10,11]. The amide group of NMA has been assumed planar [12–18], although some data on similar molecules suggest that in some cases the hydrogen and carbon atoms bound to the nitrogen atom may diverge from planarity [19]. Results of calculations differ according to the method used [20,21].

We have examined the infrared spectra of four isotopic species of NMA (^{14}NMA , the N-deuterated $^{14}\text{NMAd}$ molecule, and the corresponding derivatives substituted by ^{15}N , ^{15}NMA and $^{15}\text{NMAd}$) isolated as monomers in argon and nitrogen matrices. The band assignments and the force field are known for the pure self-associated amide [14–18] and will be used here as a first approximation. The bands will be named as usual after ref. [14]. After having taken into account the possible matrix effects, the obtained data will be discussed with respect to two problems: possibility of

cis-trans isomerism and planarity or non-planarity of the amide group.

2. Problems raised by the matrix technique

The experimental procedure is described in ref. [22].

The matrix medium has several advantages: it brings little perturbation to the molecule, since the shifts of the vibration frequencies $\Delta\nu = \nu_{\text{matrix}} - \nu_{\text{gas}}$ are lower than those observed in "inert" solvents. The absorption bands are very sharp, so that a good resolution may be reached and small isotopic effects may be observed.

However some specific matrix effects may occur and must be considered before any other interpretation, since a common feature of our spectra is that, even at high dilutions, they contain more bands than expected for one molecular species. These splittings may have several causes:

- existence of several trapping sites;
- specific interactions between the matrix and the guest molecule;
- nearest neighbour interactions;
- combinations with external modes;
- hot bands.

There are experimental ways of checking these points and a detailed discussion [22] shows that they are not sufficient to explain the multiplicity of the observed bands.

3. Possibility of *cis-trans* isomerism

In argon and in nitrogen matrices it is possible to distinguish two sets of amide bands. The example of the νNH bands is given in fig. 1: two bands are observed for ^{14}NMA and ^{15}NMA in the two matrices. The isotopic shifts of the two bands are the same ($\approx 8\text{ cm}^{-1}$) and close to those expected for an NH vibrator [23]. There are no hot bands, since the spectrum does not change between 14 and 27 K, except for a reversible broadening of the bands when temperature is increased. The two bands are due neither to multiple trapping site effect nor to nearest neighbour interactions, since the splitting is the same in both matrices and the spectra are not perturbed through annealing. The two bands can be assigned to molecular species A and B; the relative amounts of these species are different in argon and in nitrogen (fig. 1) assuming that the relative absorption coefficients are not modified by the environment.

A similar analysis can be made for the other amide bands in nitrogen matrix [22]; the frequencies are reported in table 1, except for the amide I band which never splits.

Numerous examples exist in the literature whereby several molecular conformations could be observed by

matrix technique, while they could not be spectroscopically distinguished in solution or in the gas phase (for a review see for example ref. [24]).

In NMA isomers may result from rotation around the $\text{C}^1\text{C}'$ and NC^2 bonds* (methyl rotation) or around the $\text{C}'\text{N}$ bond (*cis-trans* isomerism). The A and B forms give amide II bands 13 cm^{-1} apart (table 1) and it is unlikely that the rotation of methyl groups would cause such a frequency shift in a band mostly due to $\nu\text{C}'\text{N}$ vibration.

The spectra may therefore be better explained by a *cis-trans* isomerism. Such an isomerism has been postulated in solution from experimental data [2-4]. The frequency difference between the *trans* and the *cis* νNH bands is about 40 cm^{-1} in carbontetrachloride solutions of NMA [2,4], while the splitting observed in fig. 1 is only 5 cm^{-1} . It is possible to assume that the *cis* form in solution is planar, while the form observed in matrix is a non-planar cisoid form, its νNH higher frequency being justified by the absence of interaction between the oxygen and the proton fixed on the nitrogen.

There is no way of telling which form, *cis* or *trans*, is predominant in argon; it may be supposed that it is

* Carbon atoms are numbered such as $\text{C}^1\text{H}_3\text{C}'\text{ONHC}^2\text{H}_3$.

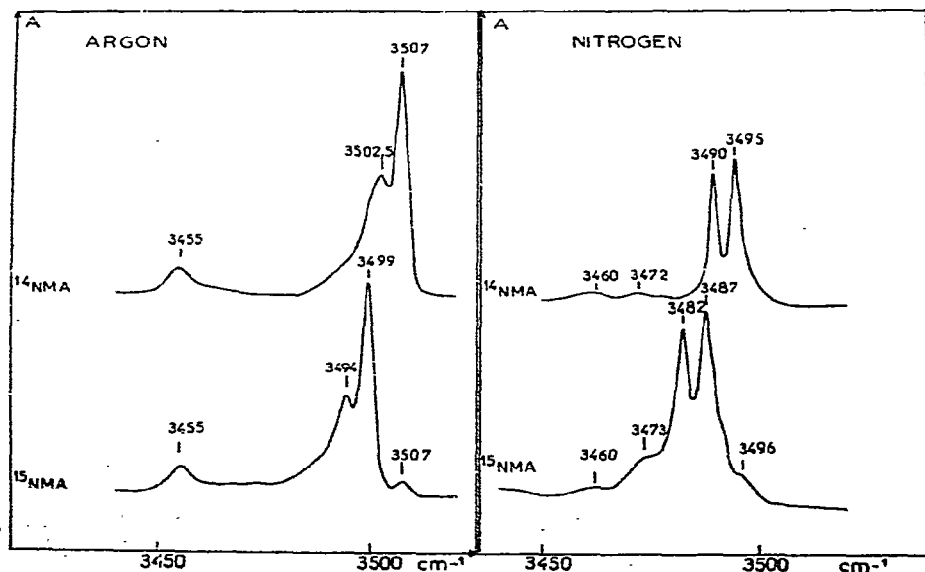


Fig. 1. Spectra of ^{14}NMA and ^{15}NMA in argon and nitrogen matrices. NH stretching region.

Table 1
NMA amide band frequencies characteristic of *cis* and *trans* isomers in argon and nitrogen matrices ^{a)}

<i>Trans</i>		<i>Cis</i>		Assignment
argon	nitrogen	argon	nitrogen	
3507 m	3495 m	3502 w	3490 m	NH stretch
1454 sh 1537 sh 1509 m 1502 m	1511 m	1523 w	1524 m	amide II
1264 m 1252 m	1265 m	1260vwsh	1260vwsh	amide III
≈442 sh ≈437 sh 390.5 s 379 w	439 vs	405 vw	482 w	amide V

^{a)} s: strong; m: medium; w: weak; sh: shoulder; v: very.

the *trans* form, so that the NH stretching frequency be higher for the *trans* than for the *cis* as usually assumed.

4. Pyramidal nitrogen

In nitrogen the bands related to each *cis/trans* isomer are single (table 1) [22,27]. In the argon matrix a salient feature of the spectra is that the bands are still more complex. The example of the amide V/V' band is given fig. 2.

Amide V and V' bands appear in a region where

skeletal vibrations are also expected [18]. Through comparison of the two isotopic species the skeletal bands are identified (fig. 2) at 277/279 and 429/431 cm^{-1} . The weak band at 405 cm^{-1} in ^{14}NMA is due to the amide V and of the *cis* form; the corresponding band of $^{14}\text{NMAd}$ is probably too weak to be observed.

There remains a system of four amide V/V' bands for the *trans* form:

- two amide V' bands at 288 and 297 cm^{-1} correspond to the amide V bands at 379 and 390.3 cm^{-1} (isotopic ratios 1.316 and 1.315);
- two amide V' bands at 326.5 and 336 cm^{-1} cor-

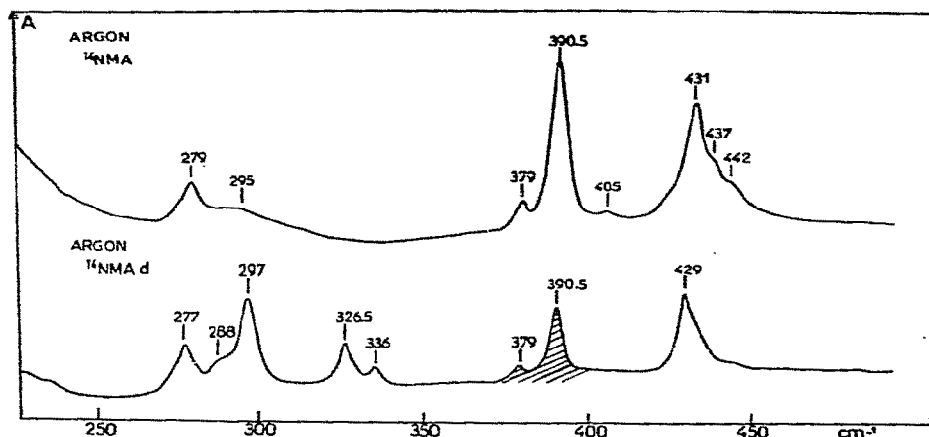


Fig. 2. Spectra of ^{14}NMA and $^{14}\text{NMAd}$ in argon matrix. Amide V/V' region.

respond to the amide V bands which are partially overlapped by the skeletal deformation (431 cm^{-1}) and appear as shoulders near 437 and 442 cm^{-1} .

The distance between the two lower frequency bands of the amide V' mode is nearly equal to that between the higher frequency bands (respectively 9 and 9.5 cm^{-1}). This feature is more difficult to observe for the amide V bands, because of the overlapping with the skeletal band at 431 cm^{-1} . The existence of four bands corresponding to four out-of-plane bending modes of one molecular form may be explained by an NH proton motion through a low potential barrier and subsequent splitting of the NH vibrational levels. Assuming a Somorjai and Hornig type of quasi-symmetrical potential function [25] the theoretical isotopic ratio may vary between 0.97 and 1.4 in agreement with the observed ratio. This theoretical scheme is also consistent with the observed frequencies and intensity characteristics, and with temperature effects which have been observed on the 379 and 370.5 cm^{-1} bands [22].

The amide nitrogen being not planar, the molecular symmetry is not C_s and coupling may occur between the so called δ "in-plane" and γ "out-of-plane" NH bending modes. Tunnel effects may appear for each normal mode involving the δ coordinate and therefore give additional splittings for the related bands (for instance the amide II see refs. [26,27]).

In nitrogen matrix the amide V band of the *trans* form is simple (table 1). It can be deduced that no tunnel effect takes place in this matrix. The amide II region however [26,27] is consistent with a non-planar amide group.

5. Conclusion

The spectral data on matrix isolated NMA lead to the assumption that both *trans* and *cis* forms are present in equal amounts in nitrogen matrix, one of these forms (presumably the *trans* one) being predominant in argon.

The *cis* form is probably not planar in either of the two matrices.

The *trans* form appears different in argon and in nitrogen. In argon the amide group is not planar. The motion of the NH proton may be described through a potential function with two quasi-symmetrical mini-

ma. In nitrogen there is no tunnel effect for the bending motion of the NH mode.

The results show that in matrix isolated monomer NMA the nitrogen doublet is not highly delocalized. Besides the nitrogen and argon matrices although rigid do not force the amide into a well defined conformation. Internal motions of the molecule with large amplitude are still observed.

The question whether such a variety of amide conformations and amide group structures is proper to matrix conditions or does exist in other physical states (or even occur in polypeptides) remains open and is under investigation.

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