

Dynamics of Crystalline *N*-Methylacetamide: Temperature Dependence of Infrared and Inelastic Neutron Scattering Spectra

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N-methylacetamide may be viewed as a simple model for polypeptides. Unusual intensities have previously been observed in its amide vibrational spectra and were attributed to contradictory causes, namely, Fermi resonance, vibrational polarons, and dynamic proton transfer along the H bond. We report the first inelastic neutron scattering study of three specifically deuterated derivatives at different temperatures along with new infrared spectra. The analysis of the librations in the INS spectra indicates a degeneracy between the N–CH₃ methyl torsional mode and another degree of freedom assigned to one component of the skeletal torsion. No direct evidence for a methyl–methyl coupling is observed. However $\gamma(\text{CO})$ appears strongly coupled to the motions of the neighboring C–CH₃ group. A new absorption band (“X”) is observed at approximately 1590 cm^{−1} in the IR spectrum of the amide-1/amide-2 region. This calls into question the previous assignment of a band at ~1600 cm^{−1} as the overtone of $\gamma(\text{NH})$. In addition, all observed peaks in the amide-2 region shift to higher frequency on cooling so that none of them could be assigned to the $\nu(\text{NH})$ mode, as previously proposed. Previous theoretical explanations of the anomalous amide spectra of *N*-methylacetamide based on either Fermi resonance or the proton-transfer model are therefore in disagreement with our new experimental data.

Introduction

Crystalline *N*-methylacetamide (CH₃–NH–CO–CH₃, or NMA) has been the subject of a great deal of attention in conjunction with efforts to develop plausible theories for the anomalous behavior of certain amide vibrations. These are revealed in the optical spectra by strong anharmonicity and unexpected sidebands¹ or anomalous intensity observed in the 1500–1800 cm^{−1} range of inelastic neutron scattering (INS) spectra.² It has an orthorhombic structure (space group *Pnma*, or *D*_{2h}¹³) at temperature less than ~10 °C at which a structural transition occurs.³ Parallel chains of >N–H···O=C< hydrogen bonds link the amide groups of neighboring molecules. This gives the system some one-dimensional character, and like acetanilide (ACN),⁴ it may be viewed as one of the simpler models for polypeptides and proteins.

On the basis of the analysis of INS intensity and of the variation of the vibrational spectra with momentum transfer,⁵ it has been suggested that an ionic representation (N^{δ−}···H^{δ+}···O^{δ−}) of the hydrogen bond would be more realistic than the normally accepted covalent model (N–H···O) and that the proton would experience a local double-minimum potential arising from dynamic exchange between the amide-like (OCNH) and the imidol-like (HOCN) forms of the peptide unit. This proton transfer to the oxygen atom would imply a weakening of the strength of the N–H stretching mode, which would be found at around 1600 cm^{−1} instead of 3200 cm^{−1}, as classically expected.

However, this description is debated, first, on the basis of energetic arguments, which question the existence of a quasi-symmetric NHO bond in such a crystalline structure,⁶ second, from the lack of observations of proton transfer in crystallized peptides,⁷ and third, because no infrared band with the expected frequency shift with temperature could be found in the 1400–1800 cm^{−1} range⁸ and because our study of the electric field gradient tensor at the nitrogen atom, deduced from the splitting of the ¹³C NMR spectra, demonstrates similarities between NMA and ACN and indicates that both substances have a similar electronic density distribution along the hydrogen bond.⁹ Since the neutron crystallographic structure of ACN¹⁰ proves that the amide proton is in a single-well potential in the N···O direction, the above-reported similarities are thus an indirect indication of an analogous situation for NMA. On the other hand, this NMR study has also shown important dynamic disorder in NMA down to 220 K, which has no equivalent in ACN.⁹ Since this discussion depends on indirect measurements, a structural study of NMA by single-crystal neutron diffraction is in progress.

Another attempt to explain the unusual features of the amide spectra in these crystals is the “polaron” (vibrational polaron) theory in which a dynamic localization of the vibrational energy is created by coupling an internal mode to a lattice phonon. This model has been widely developed and applied to the issue of the anomalous amide-1 vibration in acetanilide⁴ and has been also proposed as an interpretation of the unconventional band in the amide-2 region for NMA.¹ The “polaron” theory predicts that the intensity of the IR absorption band related to the localized vibration (or self-trapped mode or “polaron”) has a strong temperature dependence,^{1,4} in reasonable agreement with the measured variation.^{1,12}

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To make progress in the understanding of these mechanisms in the dynamics of NMA, it is useful to determine which oscillators may be coupled. The former X-ray crystallographic structure³ reported an unusually short $C_3 \cdots C'_1 = 3.51$ Å methyl–methyl contact along the *c* axis (normal to the H-bonded chains lying in the *a* direction), suggesting an interleaving of hydrogen atoms of the two methyl groups, as would result from a relative rotation of 60°. In such a case, the methyl torsional modes of adjacent molecules should be coupled also.

With this aim we have investigated the temperature dependence of the inelastic neutron scattering (INS) spectra of NMA and its partially deuterated derivatives, with special attention for the torsional modes of the methyl groups. These new measurements are reported below for three compounds: pure NMA, $CD_3NHCOCCH_3$ (or N- CD_3), and $CH_3NHCOCDC_3$ (or C- CD_3). The spectra are then deconvoluted and fitted with Gaussians, and the assignments are discussed in light of their evolution with temperature.

In the following section, we consider the infrared data briefly presented in ref 8 and discuss the origin of the absorption bands in the ranges 1500–1700 and 3000–3300 cm^{-1} and also in the range of amide-5 and -6 modes, or N–H and C=O out-of plane bending around 800–750 and 600–650 cm^{-1} respectively.

The existence of couplings between the methyl librations and the amide modes is debated, and the question of dynamic or structural disorder at low temperature is also evoked. The open question of the existence of proton transfer is examined in light of these new data.

Experimental Details

The INS spectra of the three isotopic derivatives of NMA were collected at six temperatures between 20 and 150 K on the filter difference spectrometer (FDS) at Manuel Lujan Jr. Neutron Scattering Center of Los Alamos National Laboratory. The useful range of energy transfer was 80–1600 cm^{-1} with a relative resolution ($\Delta E/E$) of about 2%. The measured data are a convolution of the scattering law of interest with a resolution function. The deconvolution procedure is achieved with the aid of either of two algorithms, the Mezei method or a Maxent reconstruction to determine the frequency distribution.¹³

The three powdered samples have been synthesized by CDN Isotopes (Vaudreuil, Quebec) with a purity greater than 99%. Infrared spectra were collected with a Bruker IFS 113 V Fourier transform spectrometer with a resolution of 0.5 cm^{-1} . The measured spectra were fitted to Lorentzian bands with a nonlinear optimization analysis program.

INS Spectra

Librations and External Modes. The deconvoluted spectra in the range 90–200 cm^{-1} are presented in Figure 1 at different temperatures. The bands are fitted with Gaussians, and the resulting energy of the different components at 20 K are summarized in the Table 1 along with the proposed assignments.

By comparison of the spectra of the three isotopomers (Figure 2), bands 1 (148 cm^{-1}) and 3 (170 cm^{-1}) can be assigned to the methyl torsions $\tau(N-CH_3)$ and $\tau(C-CH_3)$, respectively. The corresponding librations in the deuterated compounds are shifted and are found at approximately 130 and 115 cm^{-1} for $\tau(C-CD_3)$ and $\tau(N-CD_3)$, respectively. These assignments are in agreement with those proposed in ref 2.

Component 2 of these spectra, observed in the range 160–163 cm^{-1} , in the three isotopic derivatives is tentatively assigned to the skeletal torsion $\tau(C-N)$. Figure 2 shows, however, that the band at 148 cm^{-1} does not totally vanish in the N- CD_3

TABLE 1

sample	temp (K)	frequency (cm^{-1})	assignt	band number in figures
NMA ($CH_3NHCOCCH_3$)	20	148	$\tau(N-CH_3) + \tau'(C-N)$	1 + 2'
		160	$\tau'(C-N)$	2
		168	$\tau(C-CH_3)$	3
C- CD_3 ($CH_3NHCOCDC_3$)	20	148	$\tau(N-CH_3) + \tau'(C-N)$	1 + 2'
		161	$\tau'(C-N)$	2
		130	$\tau(C-CD_3)$	
N- CD_3 ($CD_3NHCOCCH_3$)	20	147	$\tau'(C-N)$	2'
		163	$\tau'(C-N)$	2
		175	$\tau(C-CH_3)$	3
		115	$\tau(N-CD_3)$	

isotope; about half the intensity (2') is still present, which may indicate an accidental degeneracy of the $\tau(N-CH_3)$ mode with another vibration, since there is no doubt as to the effective degree of deuteration of the samples. The frequencies of all the components of this band shift by about 15 cm^{-1} in the range 20–150 K, which is greater than that of the lattice modes observed at lower energy (Figure 3).

The integrated intensities of the different bands deduced from the fit are plotted as a function of temperature in Figure 4. They are normalized to the value at 20 K and compared with the temperature dependence of the intensity of the band corresponding to the methyl libration in ACN.¹⁴ The intensity of component 1 is obtained by subtracting, after proper adjustments, the intensity of the band at 148 cm^{-1} in the N- CD_3 isotope from the total intensity of the band at the same frequency, (1) + (2'), in normal NMA.

Figure 4 shows that the intensities of components 1, 2, 2', and 3 do not show the same dependence on temperature. Within the experimental accuracy, the evolution of components 1 and 3, both assigned to the two methyl librations, is similar to the temperature dependence of the methyl torsion intensity in ACN. These intensities can be fitted with an exponential law of the form $\sim 1 - \exp[-W/(k_bT)]$, where *W* may be estimated to be about 50 K.

Components 2 and 2', on the other hand, have a temperature dependence roughly of the form for a Debye–Waller factor. This suggests that both are related to the $\tau(C-N)$ skeletal torsion. The splitting could be the result of in- and out-of-phase librations in crystalline chains. Within the accuracy of the fits, the width of each component shows no significant change with temperature.

In Figures 1 and 2 we also observe a band at ~ 100 cm^{-1} in the NMA spectra and at ~ 95 cm^{-1} for the other samples. This band shows a larger energy shift with temperature (~ 10 cm^{-1}) than the neighboring peaks in this frequency range. So this maximum may well be related to the “H-bond strain” mode. Relatively intense bands are found also at approximately 85, 65, and 57 cm^{-1} , with a moderate shift with temperature, and assigned to lattice phonons.

Internal Vibrations. The INS spectra in the range 500–900 cm^{-1} for the three derivatives are shown in Figure 5 at different temperatures. The main features of these spectra are the amide-6 or C=O out-of-plane bending mode, $\gamma(CO)$, observed at about 600 cm^{-1} and the amide-5, or N–H out-of-plane bend, $\gamma(NH)$, at 768 cm^{-1} . $\gamma(CO)$ is intense in pure NMA and in the N- CD_3 isotope but much weaker in the C- CD_3 compound. This suggests a strong protonic character for this mode by means of coupling to the protons in the neighboring

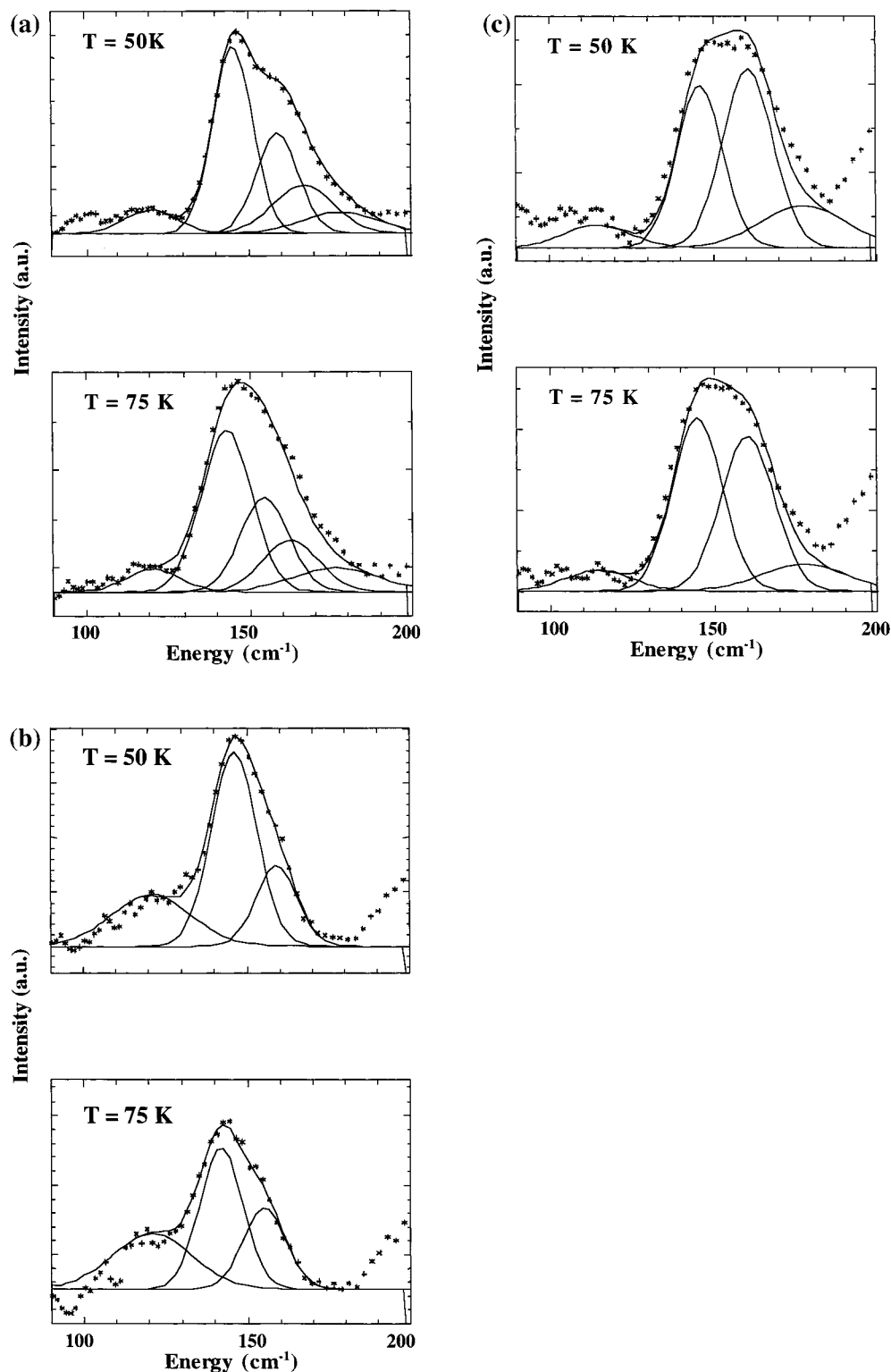


Figure 1. INS spectra of the methyl librations at two temperatures: (a) in NMA; (b) in the C-CD₃ isotopomer, where the C-CD₃ torsional mode is around 130 cm⁻¹; (c) in the N-CD₃ isotopomer. The N-CD₃ torsional mode is at about 115 cm⁻¹.

C-CH₃ group. Moreover, the frequency of this vibration in the C-CD₃ isotopomer is lower by about 20 cm⁻¹ than in other samples. No decrease of its intensity at low temperature was observed (Figure 5), in contradiction with previous observations.² The amide-4 vibration, or $\delta(\text{CO})$, observed at about 640 cm⁻¹ has weak intensity in the INS spectra of the three samples and appears poorly coupled to vibrations of the neighboring protons.

The $\gamma(\text{NH})$ mode is rather intense, as expected, with a larger width and a more asymmetrical shape in normal NMA than in

the deuterated compounds. A small shoulder at about 730 cm⁻¹ appears in all three samples. Methyl rocking modes can clearly be identified by selective deuteration at 1020 and 1120 cm⁻¹ for N-CH₃ and C-CH₃, respectively, in agreement with previous assignments.² We also observe broad intensity in the amide-2 and amide-1 regions.

Infrared Spectra

The IR spectra in the region of the amide-1 and amide-2 modes for pure NMA at different temperatures⁸ are shown in

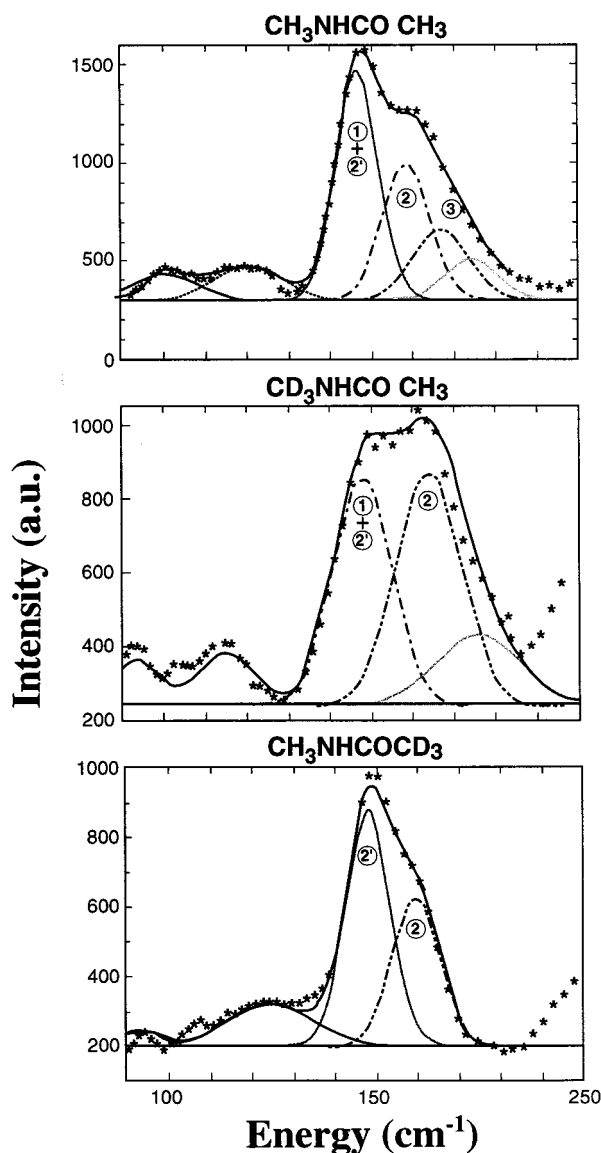


Figure 2. Comparison of the INS spectra of the three samples at 20 K. Bands 1 and 3 are assigned to the $\tau(\text{N}-\text{CH}_3)$ and $\tau(\text{C}-\text{CH}_3)$ methyl torsions, respectively, indicated by arrows. Bands 2 and 2' are assigned to the $\tau(\text{CN})$ torsion.

Figure 6. The bands were fitted with Lorentzians, and the temperature dependence of the resulting frequencies is plotted in Figure 7. All these bands shift to higher frequencies on cooling except the mode at 1643 cm^{-1} , which is firmly assigned¹⁵ to amide-1, or $\nu(\text{CO})$, and is nearly unchanged by N deuteration.¹⁶ None of the observed bands could be assigned to a $\nu(\text{NH})$ mode, as proposed² by Fillaux et al., because the frequency of the $\nu(\text{NH})$ mode would be expected to decrease on cooling.

The assignment of the other peaks in this region is currently under discussion. Band A (Figure 6) at about 1535 cm^{-1} , whose intensity is strongly temperature-dependent, has been attributed either to a Fermi resonance involving¹⁵ the first overtone of $\gamma(\text{NH})$ or to a vibrational polaron.¹ Band B, at 1555 cm^{-1} , is commonly assigned to amide-2, or $\delta(\text{NH})$. Band C, at about 1600 cm^{-1} , was assigned¹ to the first overtone of $\gamma(\text{NH})$ because of its apparently large shift with temperature down to 80 K.

However, our spectra have much improved resolution, extend to lower temperature, and thereby show the existence of a new band (named X at approximately 1590 cm^{-1}). In our new analysis, band X, like band C, has only a moderate blue shift

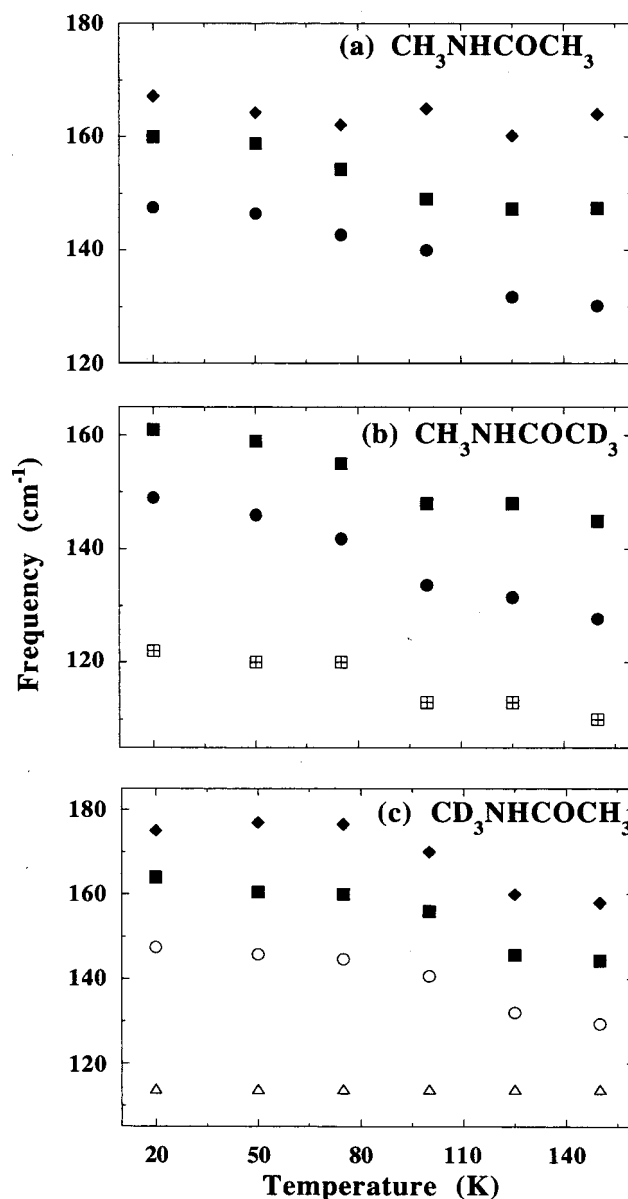


Figure 3. Temperature dependence of the energy of the methyl torsions in the three compounds.

with decreasing temperature. As a result, it is no longer reasonable to assign band C to the first overtone of $\gamma(\text{NH})$. This again raises the question of the assignment of the first overtone of $\gamma(\text{NH})$ as well as that of a possible occurrence of Fermi resonance. The former may perhaps be identified with band A.

Additional regions of the IR spectra are shown in Figure 8, corresponding to amide-6, $\gamma(\text{CO})$, at about 600 cm^{-1} ; amide-4, $\delta(\text{CO})$, at 640 cm^{-1} ; and amide-A,B in the region $3000\text{--}3300\text{ cm}^{-1}$ at different temperatures. None of these bands exhibit the decrease of intensity at low temperature described in ref 2 as temperature tuning between the amide and imidol forms.

The amide-5 region, $750\text{--}820\text{ cm}^{-1}$, is also displayed in Figure 8. The shift to higher energy observed on cooling is important: about 30 cm^{-1} between room and liquid helium temperatures, which is more than twice the shift of the amide-5 mode in acetanilide.¹⁷ This may be explained by the slightly stronger character of the hydrogen bond in NMA and by the larger lattice contraction with temperature.^{3,10} The line width also increases strongly with increasing temperature, which

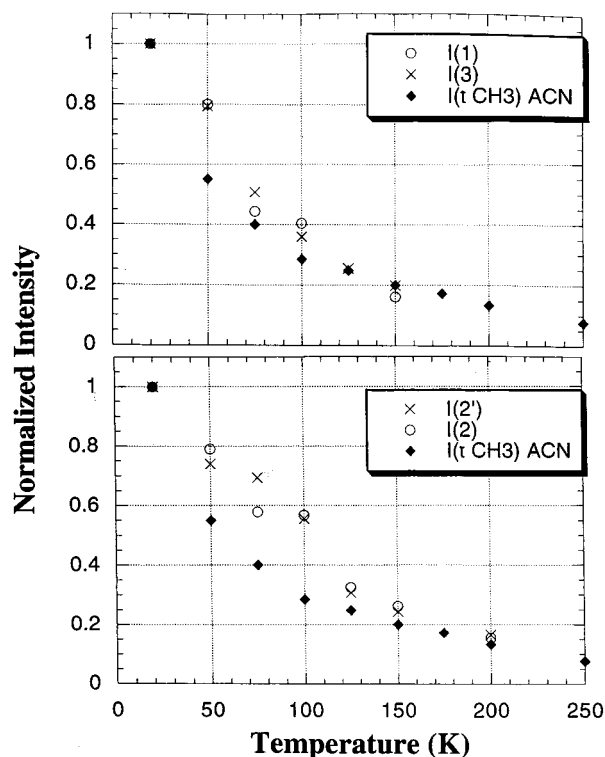


Figure 4. Temperature dependence of the normalized, integrated intensities of the components 1, 3 and 2'. All of them are compared to the variation with temperature of the intensity of the methyl libration in ACN.

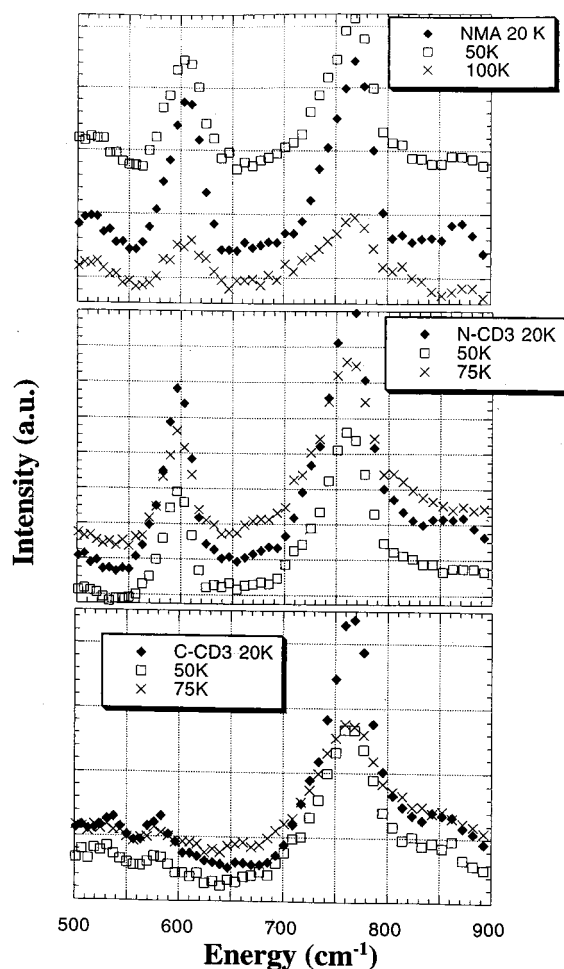


Figure 5. INS spectra of internal modes at three temperatures for the three isotopomers.

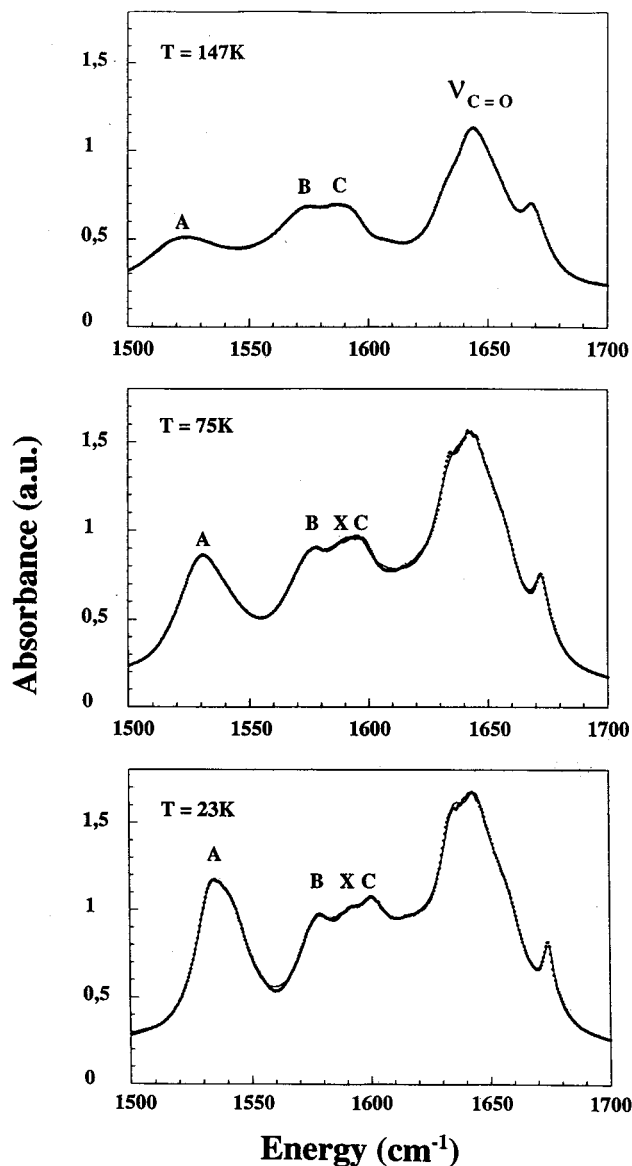


Figure 6. Infrared spectra of NMA in the frequency range of amide-1 and amide-2.

indicates significant anharmonicity that is not observed in the behavior of amide-4 or amide-6.

In the amide-A,B spectra we do not observe (Figure 8) the broad band at 3200 cm⁻¹ described in ref 2. The frequency shift of the mode at 3250 cm⁻¹ (amide-A) is >20 cm⁻¹ between 20 K and room temperature. It cannot therefore be assigned to an overtone of $\nu(\text{CO})$ unless a strong Fermi resonance were present. This large shift seems to be in better agreement with the conventional assignment to the fundamental $\nu(\text{NH})$ vibration. Moreover, the relationship between the NH stretching and the out-of-plane bending in NMA (as it is in ACN) agrees very well with the correlation curve shown by Novak for 44 compounds.¹⁸ The overtone of $\delta(\text{NH})$ may be identified in the amide-B group at around 3100 cm⁻¹. Finally, it is also important to note, as previously observed,² that most of the IR bands related to amide vibrations are split into two components.

Discussion

NMA is a fascinating model system for which a number of important questions remain to be addressed. These include the following: (1) the nature of the disorder in the high- and low-

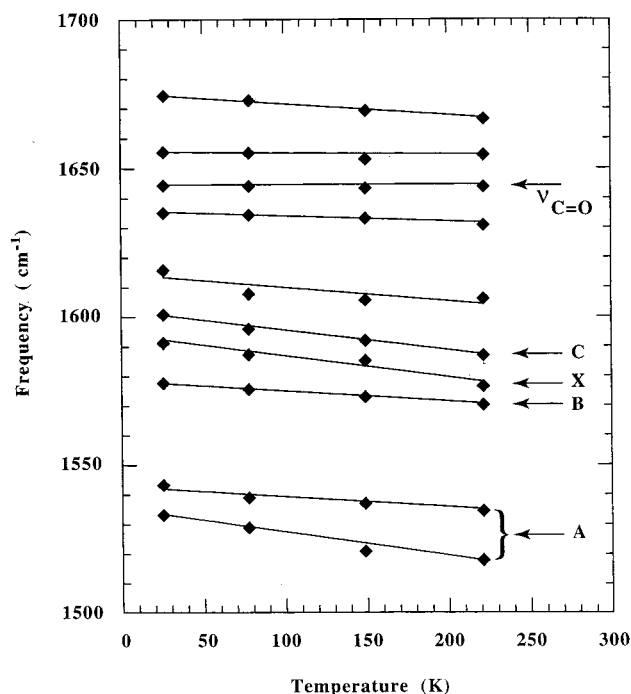


Figure 7. Frequency vs temperature of the bands A, B, C, X, and amide-1.

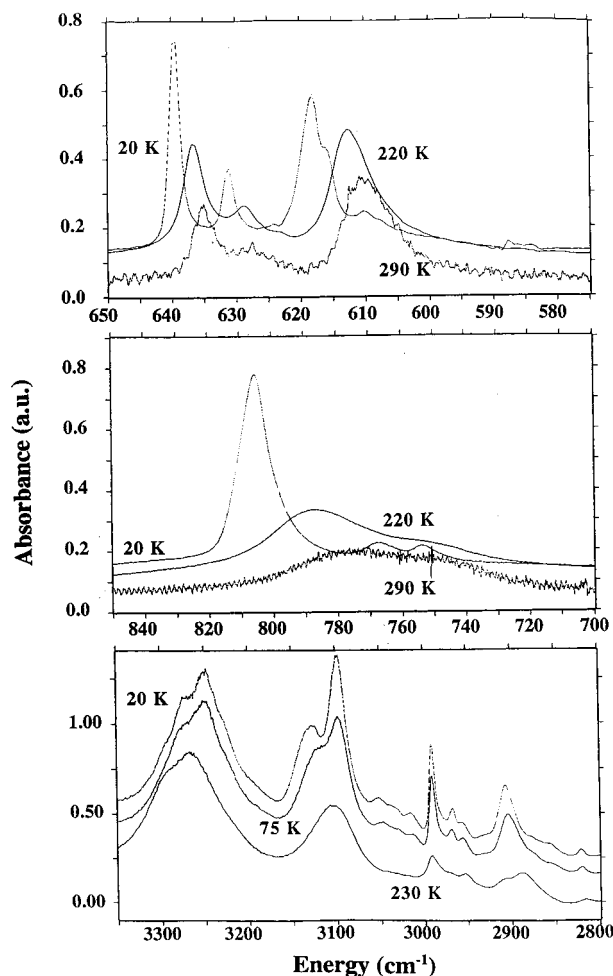


Figure 8. Infrared spectra of NMA in the frequency ranges of amide-6 and amide-4; amide-5; amide-A,B.

temperature phase observed⁹ in our ¹³C NMR studies (is it related to the existence of hydrogen-bonded chains of unequal

length or to random hopping of the methyl protons?); (2) the mechanism of the structural phase transition; (3) possible coupling of the end-to-end methyl groups along the *c* axis normal to the direction of the H bonds; (4) coupling of the amide modes to methyl torsions; (5) the central question of relevance for the dynamics of some biomolecules, namely, the possible existence of a "polaron" (self-trapped state), or alternatively, of proton transfer along the N...O' direction, and the corresponding unexplained intensities in the optical and neutron spectra in the range 1500–1700 cm⁻¹.

The present measurements of the temperature dependence of the INS spectra made it possible to assign the frequencies of the methyl and skeletal torsional modes (Table 1) found at the same frequencies in the three isotopomers. This assignment is at variance with one previously reported,² which suggested a downshift of about 10 cm⁻¹ for $\tau(\text{CN})$ in the C-CD₃ isotope.

The isotopic ratio deduced from the libration frequencies in the deuterated homologues is about 1.29, which indicates that both methyl groups are hindered rotors; some coupling with other vibrational degrees of freedom is likely to be present as well. This is consistent with the previous observation² that the torsional dynamics could not be accounted for with a harmonic potential. If we assume that the rotational potential has 3-fold symmetry, we can estimate the rotational energy barriers to be approximately 500 and 620 cm⁻¹ for N-CH₃ and C-CH₃, respectively. With these values and the calculations by K. Hetch and D. Dennison¹⁹ we can obtain an order-of-magnitude estimate of the rotational ground-state tunnel splitting, namely, 1 and 0.2 μeV , respectively.

The temperature dependence of the intensities of the librations of the two methyl groups in NMA gives no indication for a possible methyl-methyl coupling because both obey the same temperature dependence as the ACN methyl torsional mode (Figure 6), which is not coupled to another methyl group. If the search for a coupling between methyl librations were to be further pursued, the rotational tunneling transitions need to be measured with high-resolution neutron scattering or NMR to determine if the ground state is split into two or four sublevels.

On the questions surrounding the amide vibrations and the frequency of the N-H stretching mode, i.e., the conventional value of 3250 cm⁻¹ or the assignment² by Fillaux et al. at 1580 cm⁻¹, we wish to comment as follows. The presence of the "X" band at 1590 cm⁻¹ in the infrared and the deconvolution of the spectra demonstrate that the energy shift with temperature of all components in this frequency range (amide-1, amide-2, or 1500–1700 cm⁻¹) is only moderate (see Figure 7). The large shift reported in ref 1 for band "C" is therefore certainly in error. As a consequence, band "C" can no longer be assigned to the overtone of the $\gamma(\text{NH})$ vibration, which is difficult to identify. If, however, this overtone is band A, at 1535 cm⁻¹, as previously assigned,¹⁵ the interpretation of band A as the "polaron"¹ is called into question. Nevertheless, the first overtone of $\gamma(\text{NH})$ thus identified would then have a very large shift to higher frequencies on cooling, about twice the shift of the fundamental (about 60 cm⁻¹), and this is not evident in our spectra.

On the other hand, the strong increase of intensity of band A, attributed to temperature tuning of the Fermi resonance,¹⁵ should then be associated with an interacting vibrational mode, namely, $\delta(\text{NH})$ and the amide-1, but this is not observed in the infrared spectra. It should also be remembered that Fermi resonance is known to occur for free molecules as well as in the spectra of solids. The anomalous intensities and the vibrational sidebands observed in the amide spectra of ACN

and NMA, however, are found only in crystals with chains of hydrogen-bonded molecules, and this could be the signature of nonlinear excitations created by coupling of excitons to lattice vibrations.

Moreover, in this frequency range none of the infrared bands shift to lower energy with decreasing temperature (Figure 7) and could therefore not be assigned to the $\nu(\text{NH})$ vibration at 1580 cm^{-1} as proposed in ref 2. The only band that shows a very negligible downshift, at 1650 cm^{-1} , corresponds to $\nu(\text{CO})$, or amide-1, and has been shown to be unchanged upon N deuteration.¹⁶ There are additional observations that do not support the hypothesis of a dynamic proton transfer proposed by Fillaux et al.² We do not observe the decrease in intensity described in ref 2 for the amide-1 band at low temperature or the very large width. Our spectra (Figure 8) do not show either the decrease in intensity described in ref 2 for amide-6 and amide-A,B at low temperature or the very wide band at about 3200 cm^{-1} .

Our new infrared data, however, clearly demonstrate that the dynamics of the amide group in NMA has behavior comparable to that in ACN with a slightly stronger H bond. This is consistent with our ^{13}C NMR measurements⁹ and neutron diffraction data²⁰ and does not support the hypothesis of a proton transfer along the $\text{N}\cdots\text{O}'$ direction.

At this point of our investigations both Fermi resonance and proton transfer are called into question by our new measurements as valid explanations for the unconventional intensities. The applicability of polaron theory, however, cannot be decided in a completely straightforward manner. Polaron theory and the proton-transfer model have in common the existence of a nonharmonic potential for the amide proton, and in this sense, they could be considered as nonlinear excitations. To make further progress in resolving these issues, we plan to examine each of these theories in more detail by carrying out polarized Raman scattering studies on single crystals.

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