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TITLE

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ANOMALOUS VIBRATIONAL MODES IN ACETANILIDE :

a F.D.S. incoherent inelastic neutron scattering study

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Extended Abstract

The origin of the anomalous infra-red and Raman modes in acetanilide ($C_6H_5NHCOCH_3$, or ACN)(1) , remains a subject of considerable controversy. One family of theoretical models involves Davydov-like solitons (2) nonlinear vibrational coupling (3), or "polaronic" localized modes (4)(5). An alternative interpretation of the extra-bands in terms of a Fermi resonance was proposed (6) and recently the existence of slightly non-degenerate hydrogen atom configurations (7) in the H-bond was suggested as an explanation for the anomalies.

In this paper we report some new results on the anomalous vibrational modes in ACN that were obtained by inelastic incoherent neutron scattering (INS) . Comparisons of the spectra of ACN and of five deuterated

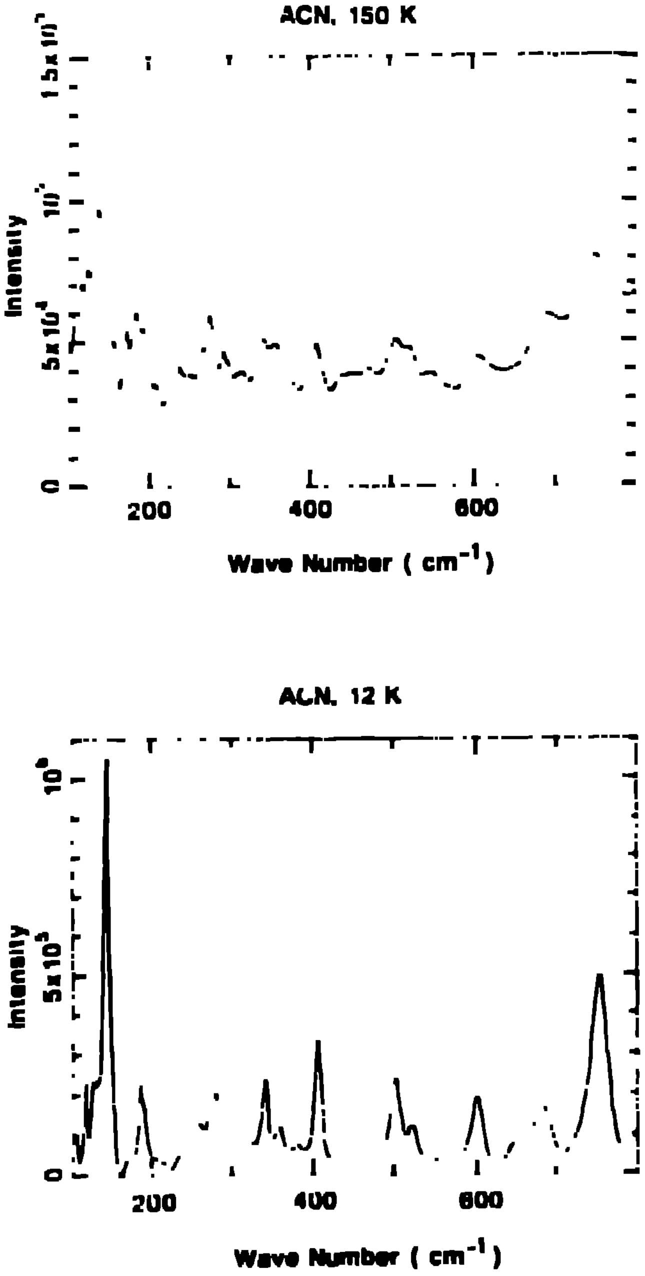

Fig.1 INS spectra of ACN

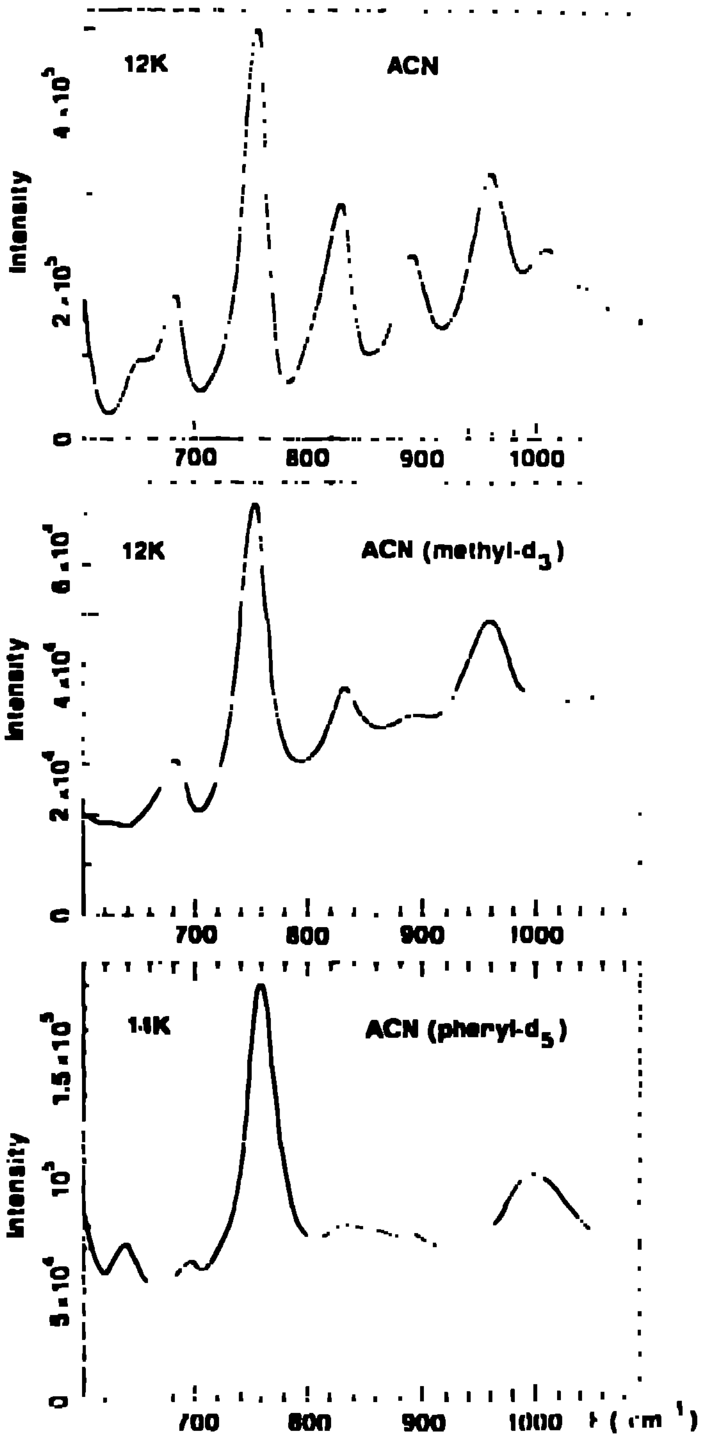

Fig.2 · INS spectra of the γ NH mode derivatives, greatly facilitates assignments of the main features .

The mutual influence of the different chemical groups (amide, methyl group and phenyl ring) are emphasized by means of selective deuterations. The possibility of vibrational coupling between them is discussed.

In addition, the temperature dependence of the γ(NH) modes (out-of-plane bend of the H-bond) and of the methyl torsional modes are described.

These data are then compared to the predictions of the different theoretical models that attempt to explain the anomalies.

The INS data were collected on theFilter Difference Spectrometer (FDS), at Manuel Lujan Jr. Neutron Scattering Center of Los Alamos National Laboratory, between 10K and 300K and deconvoluted ,to determine the frequency distribution . The useful range of energy transfers , was 100 cm^{-1}-1600cm^{-1} (12meV-200meV) with a relative resolution ($\Delta E/E$) of about 2% .

The five deuterated derivatives are :

$C_6H_5NHCOCD_3$: ACN -d_3 ; $C_6H_5NDCOCD_3$: ACN -d_4 ; $C_6D_5NHCOCH_3$: ACN -d_5 ; $C_6D_5NDCOCH_3$: ACN -d_6 ; $C_6D_5NDCOCD_3$: ACN-d_9 .

Comparison of the INS spectra of the various ACN isotopomers is a powerful tool for determining the origin of the modes and their assignments . In addition,direct subtraction ("differential spectroscopy") can be used to highlight the modes of a particular molecular group.

The low temperature spectrum of ACN is displayed in fig. 1 from 100 to 800cm^{-1}. Fig. 2 shows the INS spectrum in the region of γ(NH) at 12K for the three samples that have a protonated amide group. Tentative assignments of the bands are given in table I. These are in agreement with available previous data from Raman and IR spectroscopy .However , the INS do provide new informations : for example ,in amide deuterated derivatives some small peaks at 750 cm-1 may be attributed to out- of-plane C-H bending of the phenyl . In ACN those bands are screened by the N-H bending , and never before identified .

Fig 3 shows the methyl torsional modes at 12 K in three samples. Despite the limited resolution, the methyl mode appears to be split , in agreement with the Raman scattering spectra (8)(9). In the single crystal polarized Raman study (9) with a z(xy)z configuration the methyl torsion was found to gradually split as the temperature is lowered below about 200K . The frequencies of the three

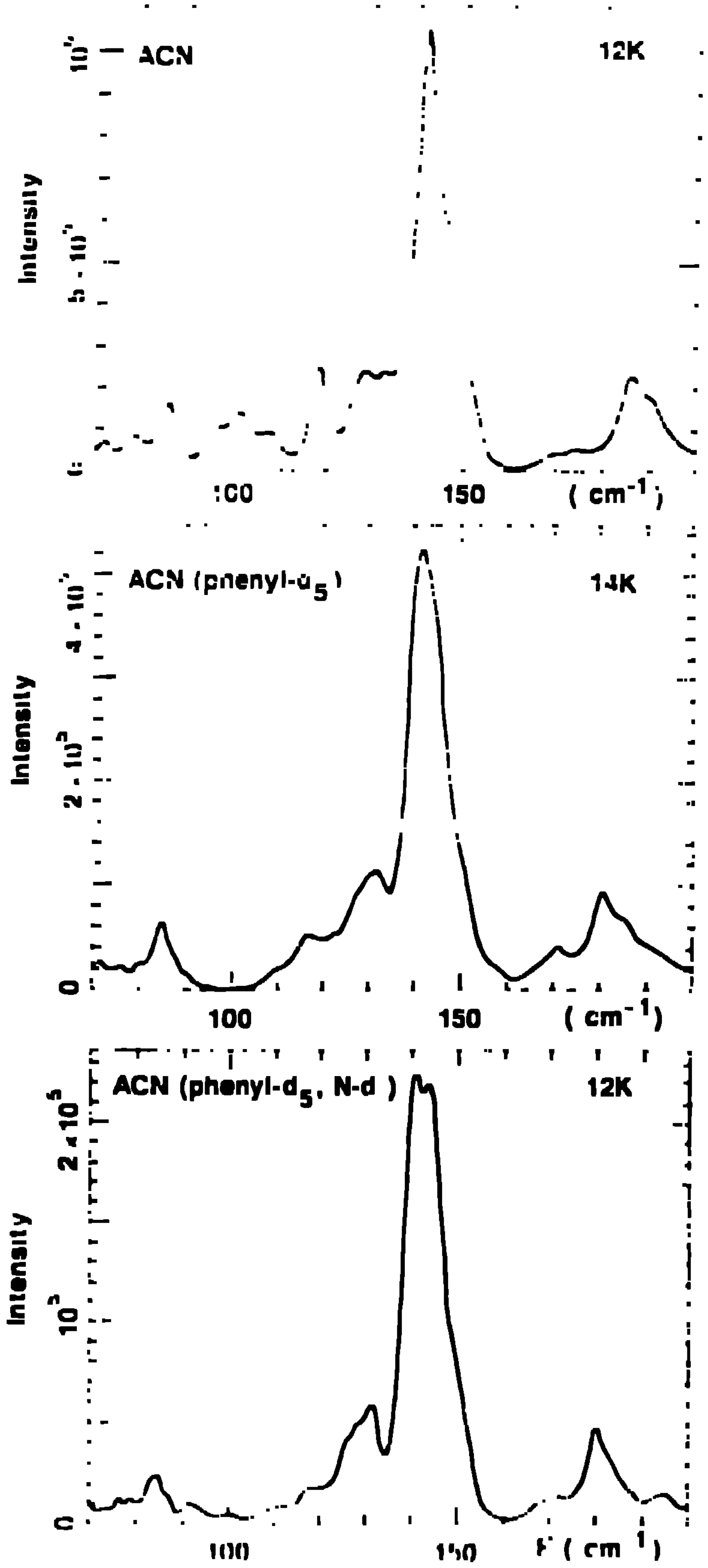

Fig 3   Methyl torsional modes

components as well as the splittings all increase with decreasing temperature . INS studies (10) previously identified the methyl torsion in ACN but the splitting was not observed . In the present work at least three components may be identified in ACN , namely at 142, 146 and 152cm-1 . The effect of deuteration of the phenyl ring is a significant change in the shape and of width of the methyl librational band. In ACN-d_6 the splitting is even more evident, and the relative intensities of the component have changed. These observations clearly demonstrate the influence on the dynamics of the amide and methyl groups on each other.

The frequency shift of the methyl torsions as a function of temperature obtained from our data ,fig.4 , is consistent with the measurements of Johnston et al.(9) . The γ (NH) mode at 754 cm^{-1} is also found to be affected by deuteration of the other groups as shown in Fig.2. This mode undergoes a change in shape and width upon deuteration of the methyl or phenyl group. Similar changes in shape were observed in the corresponding IR absorption bands (11).

Another important feature of these spectra is the temperature dependence of the γ(NH) mode, at 750-770cm^{-1}. The intensity of this mode was observed to increase strongly with decreasing temperature (Fig.1) . Moreover, if one considers the two spectra of ACN-d3 shown in fig 5 , in which there is no longer any contribution from the methyl group. it is apparent that the intensity of the γ(NH) peak increases much more than other peaks with decreasing temperature. So, the unusual intensity increase of the γ(NH) with decreasing temperature is therefore an intrinsic property of this mode .

These observations are in agreement with our IR spectra (11) which indicate an total increase of intensity of the γ(NH) with decreasing temperature of about 20% between 300K and 15K. Similar observations have also been made by Raman scattering in ACN(12).

Data from the different techniques are thus in agreement about this important result , namely that γ(NH) also has an anomalous temperature dependence. So , ACN exhibits not only an anomalous amide mode at 1650cm^{-1} but also another one at 750cm^{-1}.

Among these new results, two of them seem to be especially relevant to the problem of the anomalous modes in ACN :

- observation of the interdependence of the chemical groups, by selective deuteration.
- Anomalous increase of the intensity of γ(NH) with decreasing temperature.

The band corresponding to the methyl torsional transitions is split in three components and is sensitive to the deuteration of other parts of the molecule.This splitting (also observed in the polarized Raman scattering(9)) may be rationalized by a small departure from three-fold symetry for the rotational potential. This could be induced by the low symetry of the steric environment of the methyl group which in turn could be caused by differences in the positions of the hydrogen bond protons . The methyl group would as a consequence occupy energetically inequivalent positions and therefore have different librational frequencies . The change in shape and width of the librational components when the amide or phenyl ring are deuterated could result either from direct vibrational coupling of the methyl torsion with motions of the other groups (or with low frequency phonons) or from a modification of the rotational potentiel by changing the local environment of CH_3.

The former model is consistent with the hypothesis of "polaronic" local modes or solitons (5), while the latter would be related to the assumption of multiple conformations of the molecular chain(7).

The width and shape changes of the bands corresponding to the N-H bending mode upon deuteration of other groups of the molecule could be accounted for by the same mechanisms , i.e. either direct vibrational coupling, or a multiple-well potential for the amide proton .In this latter case , changes in the steric environment affects the shape of this potential , and thus the frequencies and intensities of the transitions to the excited levels.

At this point it is not possible to decide which of these possible explanations is the relevant one.

The second result, which has now been observed by INS , IR , and in Raman scattering is the anomalous thermal behaviour of γ (NH) . It may be expected to provide further important input into the determination of the origin of these anomalies For example,in the case of localized modes (polarons, solitons or coupled oscillators) the temperature dependence of the anomalous intensity should obey a characteristic law $^{I(T)}/_{I(0)} \sim \exp(-T^2/_{\Theta^2})$ (4) while the hypothesis of non degenerate substates for the amide proton would mean either a temperature independent global intensity , or one governed by the Boltzman population of each level.

Our former infrared data (11) indicate that the intensity of the γ(NH) mode of ACN obeys the $\exp(-T^2/\theta^2)$ which would favor the family of models of localized nonlinear excitations.However , former theories of the ACN problem only took into account the anomaly at 1650 cm-1, and the recent observations of new anomalies suggest that the self-trapping mechanism in ACN may be more complex . Further analysis is underway.

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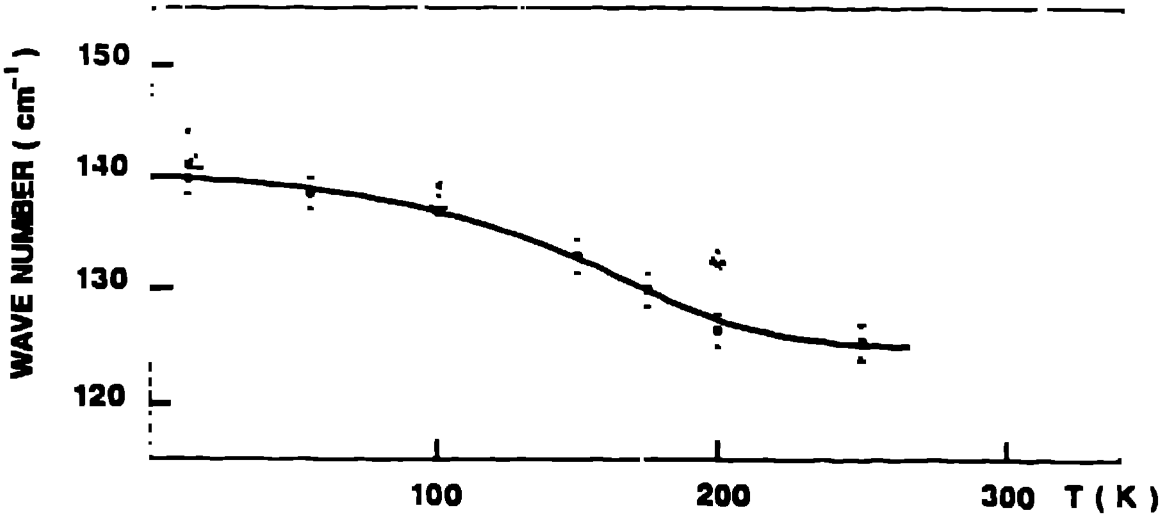
TABLE I

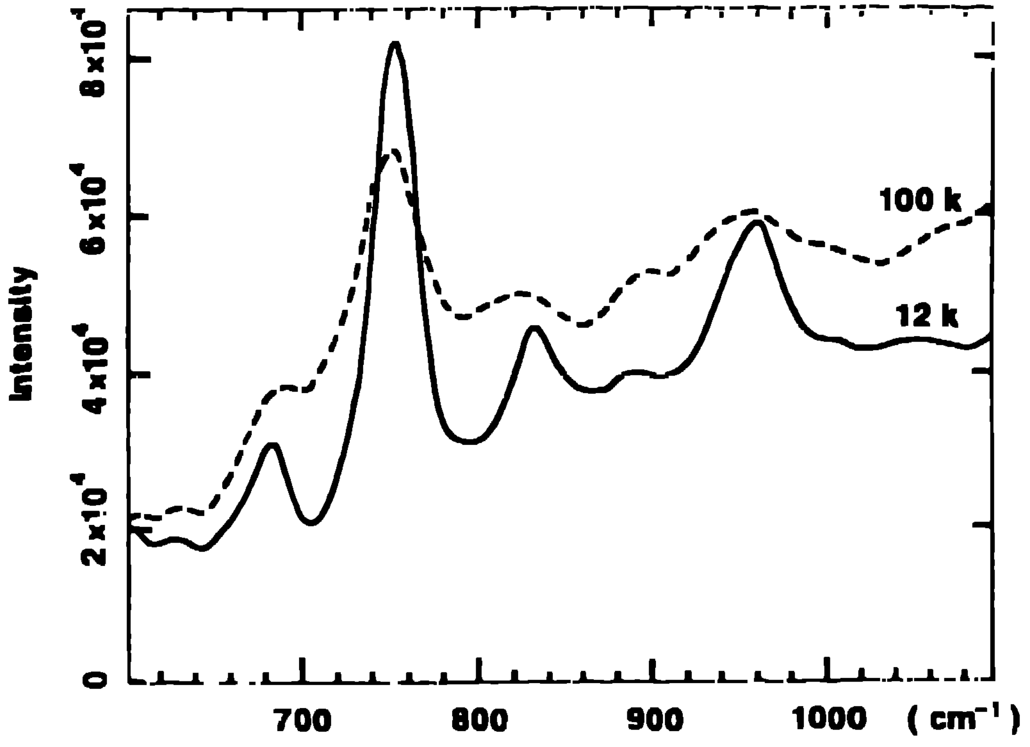
TENTATIVE ASSIGNMENT OF THE INS SPECTRUM OF ACETANILIDE

FREQUENCY(cm $^{-1}$)	ASSIGNMENT	OBSERVATIONS
0-33	Acoustic modes	
35-100	External modes librations.	IR and Raman spectroscopy
	FDS	
130-140	Methyl torsional transitions	(10), (9), sensitive to the deuteration of other group
171		shoulder disappearing at 15K
186	External mode	progressive energy shift with deuteration.
275	Phenyl modes	
345	Methyl modes	
406	(C-C-C) out-of-plane deformation	
502	Methyl modes	
521	(C-C-C) out-of-plane deformation	
600	Methyl modes	
646	Methyl	
683	Phenyl modes ,C-C-H deformation	
754	γ(NH) (out-of -plane bending mode) and γ(CH),Phenyl .	Anomalous modes
829	γ(CH) , Phenyl	
890	Combination band	decreases in ACN-d3 and in $ACNd_5$
959	γ(CH) Phenyl	Breathing modes (1)
1020	Methyl rock	
1140	δ(CH) Phenyl	

Notes: Vibrational modes that involve predominantly methyl group motions appear to be heavily coupled with other modes (see Fig.3). Their precise assignment requires a normal coordinate analysis. γ and δ refer, respectively, to out-of-plane and in-plane bends



- Fig.4 - Frequency shift of the methyl torsions .



- Fig.5 - The γ-NH mode at 12K and 100K in ACN-d3