INFRARED SPECTRUM AND NORMAL COORDINATE
CALCULATIONS OF DEUTERATED ACRYLAMIDE

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: الخلاصـة

تـم قياس طيف الأشعة تحت الحمراء لمسحوق (الأكريلمايد) المهدرج بالهيدرجين الثقيل
(الديتوريم) في حدود (٤٠٠٠) الى (١٨٠) سم ⁻¹ . وقد استُخدمت طريقة مجال قوى تربيعية
عامة لمعالجة الإحداثيات المعيارِّية (العادية) لأكريلمايد المهدرج ، وكذلك استُخدمت طريقة تضاؤل
المربعات الصغرى لتعديل دقة ثوابت القوة . وجرى البحث عن توزيع الطاقة الكامنة في كلّ من
إحداثيات الفراغ التربيعي العام وإحداثيات التماثل وعلاقته بمزج الترددات الهيكلية لأكريلمايد
المهدرج وطبيعة حزم الإمتصاص . هذا وقد حسبت السعة المتوسطة الاهتزازية .

ABSTRACT

The infrared spectrum of deuterated acrylamide as mull was measured in the range 4000-180 cm⁻¹. Normal coordinates treatment of deuterated acrylamide was carried out using general quadratic force field, and the force constants were refined by the damped least-squares method. The potential energy distributions in both general quadratic space and symmetry coordinates are discussed in relation to the mixing of skeletal frequencies for deuterated acrylamide and the nature of the absorption bands. The vibrational mean amplitudes are also calculated.

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INTRODUCTION

Spectroscopic studies have an important role in elucidating the structure of amides. Infrared and Raman spectra, studies of dichroism, band contour studies, and normal coordinate analysis of simple primary, secondary, and tertiary amides and thio-amides and of their deuterated species have enabled various workers [1–9] to assign the skeletal frequencies and to investigate the nature of the amide I, amide II, the amide III absorption bands. Important results have been obtained in assigning the $v(C-N)$ and $v(C=O)$ frequencies which vary considerably from amide to amide. Nuclear Magnetic Resonance (NMR) studies of amides and molecular orbital computations have been used by a few workers in calculating the height of the potential barriers [10–12]. Far infrared spectra of N-methylacetamide and other mono substituted amides were recorded in the liquid state in the $60-250 \, cm^{-1}$ region by Itoh and Shimanouchi [13] and the bands in this spectrum have been assigned as due to hydrogen bonding, torsional and lattice oscillations. Miyazawa *et al.* [14] carried out the normal coordinate analysis of N-methylacetamide and Usha Bai *et al.* [15] that of propionamide. In all these studies the CH_3 and CH_2 groups were treated as point masses — a consideration which obviously neglects the potential energy contributions to the various modes of methyl and methylene group modes thus resulting in an incorrect description of the force field for the entire molecule.

The spectroscopic literature on acrylamide and deuterated acrylamide is rather scarce. Infrared (IR) and Raman spectra with tentative assignments were first reported by Jonathan [16]. However, the IR data were limited to $450 \, cm^{-1}$ for these molecule. Raman polarization measurements and normal coordinate calculations were not performed for these cases [17]. Hence in the present work, we report more complete IR data of deuterated acrylamide along with the results of normal coordinate analysis taking into account the internal modes of the CH_2 and the NH_2 groups.

EXPERIMENTAL DETAILS

The infrared spectrum was recorded on Perkin–Elmer 983 double beam grating spectrophotometer. Unoriented samples were prepared as mulls and KBr discs. N-deuteration was achieved by repeated exchanges with D_2O. The measured spectrum is shown in Figure 1.

NORMAL COORDINATE ANALYSIS

The molecular skeleton is planar to a good approximation and therefore a C_s symmetry can be assumed A representative structure of the molecule is shown in Figure 2. For a C_s structure, the 24 fundamental vibrations fall into 17 in-plane vibrations of the A' species and 7 out-of-plane vibrations of the A" species.
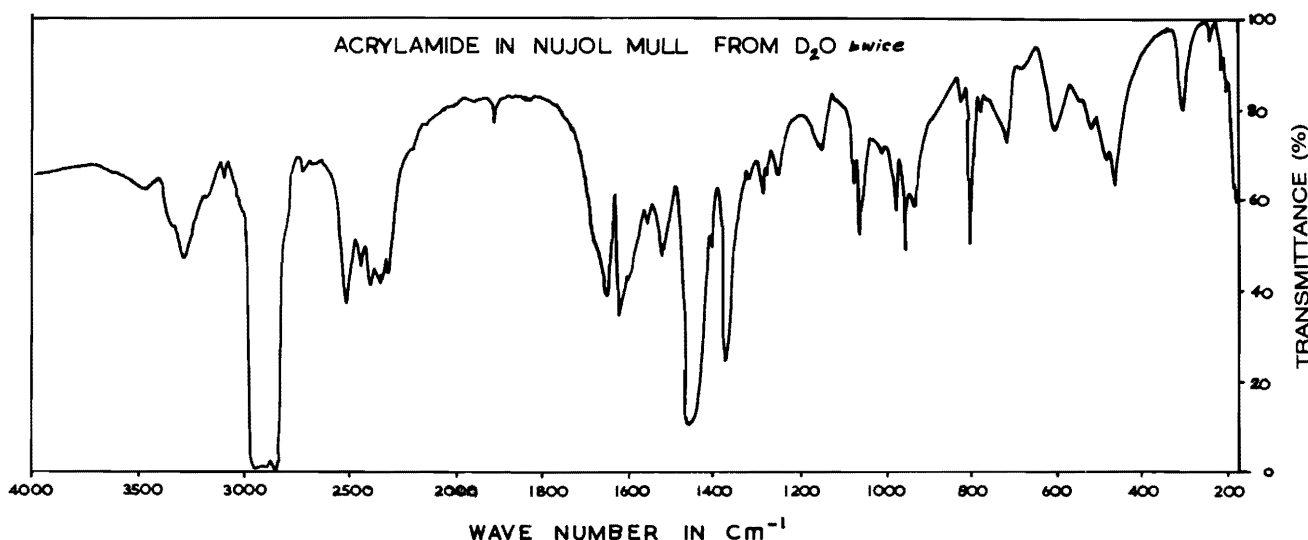

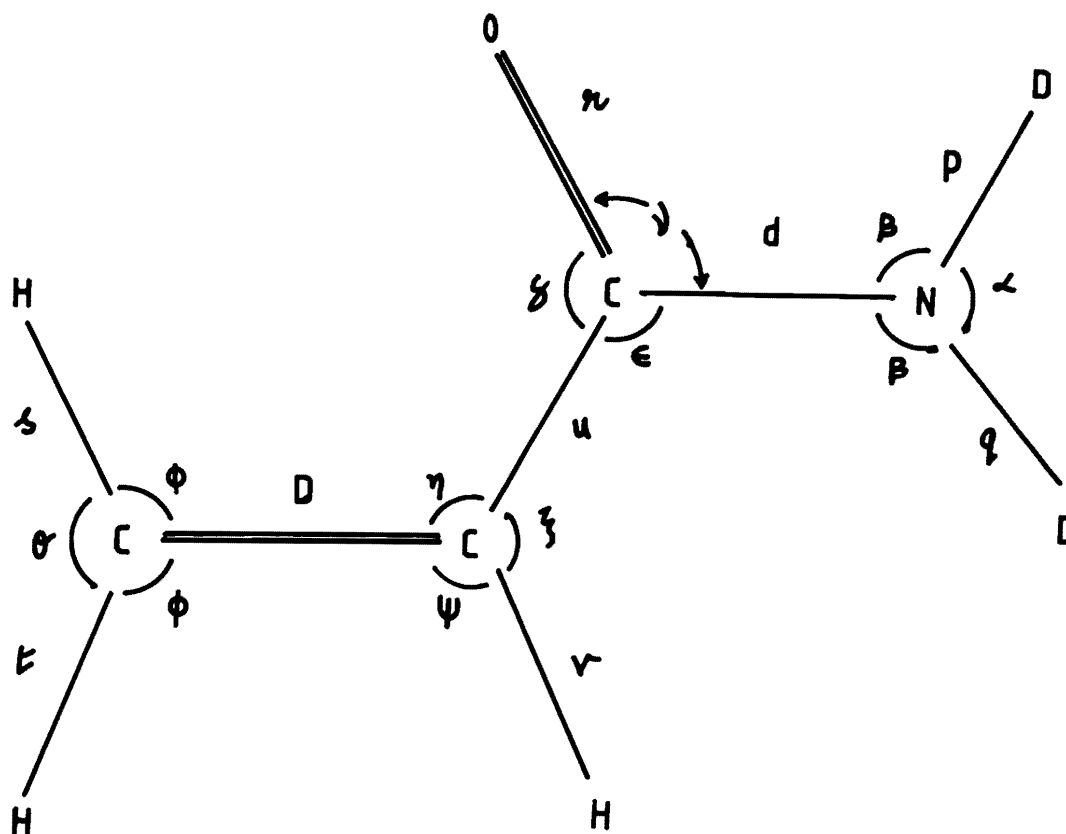*Figure 1. Infrared Spectrum of Deuterated Acrylamide.*

Figure 2. Structure of Deuterated Acrylamide.

In order to ascertain the amount of mixing among the normal modes and to obtain a more accurate description of the fundamental vibrations of deuterated acrylamide, a normal coordinate analysis was undertaken. The analysis of deuterated acrylamide was carried out using general quadratic force field and the force constants were refined by damped least squares method. The calculations were done by the Wilson GF matrix method with the computer program developed by Schachtschneider [18].

The bond lengths used in the present investigation are C$-$N = 1.315 Å, C=O = 1.243 Å, C$-$C = 1.47 Å, C=C = 1.337 Å, N$-$D = 1.02 Å, and C$-$H = 1.07 Å. All the bond angles were assumed to be 120° [19].

The symmetry coordinates used in the calculations are shown in Table 1. The initial force constants

used in the present work are taken from related molecules.

RESULTS AND DISCUSSION

The observed, calculated frequencies and potential energy distributions among the symmetry coordinates for the observed frequencies for deuterated acrylamide is shown in Table 2.

PED in symmetry coordinates is obtained by using the formula $(F_{ki}L_{ki}L_{li}/\lambda_i) \times 100$ and that in internal coordinates by using the formula $[\Lambda^{-i}(Jz)\ \phi] \times 100$. PED in symmetry coordinates which contribute below 10% are not shown in Table 2.

As expected, ND stretching vibrations (around 2530 and 2455 cm^{-1}) and CH stretching vibrations (around 3300 and 3100 cm^{-1}) are pure stretching

Table 1. Symmetry Coordinates for the In-Plane Vibrations of Deuterated Acrylamide.

$S_1 = (1/\sqrt{2})(\Delta p - \Delta q)$ $\nu_{asy}\left(N\underset{D}{\overset{D}{<}}\right)$

$S_2 = (1/\sqrt{2})(\Delta p + \Delta q)$ $\nu_{sy}\left(N\underset{D}{\overset{D}{<}}\right)$

$S_3 = (1/\sqrt{2})(\Delta s - \Delta t)$ $\nu_{asy}\left(C\underset{H}{\overset{H}{<}}\right)$

$S_4 = (1/\sqrt{2})(\Delta s + \Delta t)$ $\nu_{sy}\left(C\underset{H}{\overset{H}{<}}\right)$

$S_5 = \Delta v$ C−H stretch

$S_6 = \Delta r$ C=O stretch

$S_7 = \Delta D$ C=C stretch

$S_8 = \Delta d$ C−N stretch

$S_9 = \Delta u$ C−C stretch

$S_{10} = (1/\sqrt{6})(2\Delta pq - \Delta dp - \Delta dq)$ $N\underset{D}{\overset{D}{<}}$ in-plane deformation (δ)

$S_{11} = (1/\sqrt{6})(2\Delta st - \Delta Ds - \Delta Dt)$ $C\underset{H}{\overset{H}{<}}$ in-plane deformation (δ)

$S_{12} = (1/\sqrt{2})(\Delta uv - \Delta Dv)$ C−H deformation

$S_{13} = (1/\sqrt{2})(\Delta dp - \Delta dq)$ $N\underset{D}{\overset{D}{<}}$ rocking (γ)

$S_{14} = (1/\sqrt{2})(\Delta Ds - \Delta Dt)$ $C\underset{H}{\overset{H}{<}}$ rocking (γ)

$S_{15} = (1/\sqrt{2})(\Delta ru - \Delta dr)$ C−C rocking

$S_{16} = (1/\sqrt{6})(2\Delta rd - \Delta ru - \Delta du)$ $O{\overset{\backslash\backslash}{}}C$−N deformation

$S_{17} = (1/\sqrt{6})(\Delta uD - \Delta uv - \Delta Dv)$ $C=C{\overset{/}{\underset{}{}}}C$ deformation

frequencies as the corresponding force constants contribuctue almost 100% to PED of these modes. In addition to PED confirmation these assignments compare well with their counterparts in earlier work [20].

The medium strong band at 1540 cm^{-1} is assigned to C−N stretching which agrees well with the literature values [21].

The band at 468 and 305 cm^{-1} are predominantly $O{\overset{\backslash\backslash}{}}C$−N and $C=C{\overset{/}{}}C$ deformations respectively.

These values agree well with the literature values [15]. The bands at 1290 and 1250 cm^{-1} are assigned to $N\underset{D}{\overset{D}{<}}$ and $C\underset{H}{\overset{H}{<}}$ in-plane deformation respectively, which agrees well with those for related molecules [2]. Similarly the deformation mode at 1085 cm^{-1} is assigned to C−N deformation.

It is not difficult to assign the other modes of vibration. Some of the vibrations of the A″ species have been assigned by comparing with the assignments in related systems with the help of PED

Table 2. Vibrational Assignments of Deuterated Acrylamide.

Species	Infrared frequency and Intensity cm⁻¹ (observed)	Calculated frequency cm⁻¹	Vibrational assignment	PED (%)
A′	3300 vw	3341	ν C⟨^H_H asym. stretch	$S_3(98)$
A′	3100 w	3120	ν C⟨^H_H symm. stretch	$S_4(99)$
A′	2730 vw	2738	ν C–H stretch	$S_5(100)$
A′	2530 vs	2521	ν N⟨^D_D asym. stretch	$S_1(97)$
A′	2455 ms	2459	ν N⟨^D_D symm. stretch	$S_2(98)$
	2405 w		(1410+985)	
	2360 w		(1578+830)	
	2322 w		(3100−770)	
A′	1655 m	1638	ν C=C stretching	$S_7(61)S_6(15)S_{17}(10)$
A′	1630 ms	1614	ν C=O stretching	$S_6(52)S_7(20)S_{13}(13)$
A′	1540 ms	1549	ν C–N stretching	$S_8(95)$
A′	1410 vw	1428	ρ C⟨^H_H rocking	$S_{14}(54)S_{11}(21)S_5(11)$
A′	1368 ms	1342	ν C=C stretching	$S_9(57)S_{17}(24)$
A′	1290 ms	1278	δ N⟨^D_D in-plane deformation	$S_{10}(45)S_{13}(32)S_{16}(20)$
A′	1250 ms	1229	δ C⟨^H_H in-plane deformation	$S_{11}(51)S_{14}(25)S_{15}(18)$
A′	1085 ms	1098	δ C–N deformation	$S_{12}(45)S_{15}(21)S_{14}(15)$
A′	985 s	997	ρ N⟨^D_D rocking	$S_{13}(44)S_{10}(20)$ $S_{16}(14)S_{14}(10)$
A′	490 w	479	ρ C–C rocking	$S_{15}(49)S_6(12)S_7(29)$
A′	468 ms	448	δ O=C–N deformation	$S_{16}(38)S_{13}(22)S_7(21)$
A′	305 ms	292	δ C=C^C deformation	$S_{17}(34)S_{15}(28)S_{14}(16)$
A″	952 s	941	τ(C=C)	64τ(C=C), 20τ(C–N)

Species	Infrared frequency and Intensity cm⁻¹ (observed)	Calculated frequency cm⁻¹	Vibrational assignment	PED (%)
A″	770 w	745	ω wag H$_2$>C	$60\omega\left(C\begin{smallmatrix}H\\H\end{smallmatrix}\right)$, $10\tau\left(C\begin{smallmatrix}H\\H\end{smallmatrix}\right)$
A″	730 m	710	$\tau(C-H)$	$80\tau(C-H)$, $10\tau(C-N)$
A″	610 w	590	τ twist $C\begin{smallmatrix}H\\H\end{smallmatrix}$	$52\tau\left(C\begin{smallmatrix}H\\H\end{smallmatrix}\right)$, $35\omega\left(C\begin{smallmatrix}H\\H\end{smallmatrix}\right)$
A″	525 vw	512	ω wag $N\begin{smallmatrix}D\\D\end{smallmatrix}$	$65\tau\left(N\begin{smallmatrix}D\\D\end{smallmatrix}\right)$, $24\tau\left(N\begin{smallmatrix}D\\D\end{smallmatrix}\right)$
A″	195 (p)	195	τ twist $N\begin{smallmatrix}D\\D\end{smallmatrix}$	—
A″	245 vw	—	$\tau(C-N)$ deformation	$82\tau(C-N)$

w - weak; vw - very weak; s - strong; m - medium; ms - medium strong; p - predicted.

calculation. They are given in Table 2 along with vibrational assignment and PED.

The calculated and observed frequencies shown in Table 2 are in good agreement, indicating that the force constants obtained are reasonable (Table 3). The C=O and C=C stretching force constants considerably deviate from their values in propionamide indicating a change in the strength of these bonds. The other valence force constants are comparable with those obtained for closely related molecules.

MEAN AMPLITUDE OF VIBRATION

The vibrational mean amplitudes evaluated at 298.16 K for the bonds C=O, C–N, C=C, C–C,

$C-H$, $N\begin{smallmatrix}D\\D\end{smallmatrix}$ and $C\begin{smallmatrix}H\\H\end{smallmatrix}$ of deuterated acrylamide

are 4.013, 4.511, 4.201, 4.725, 8.009, 6.984, and 7.642×10^{-2} Å respectively. These values agree well with those for related molecules [20].

CONCLUSION

A complete vibrational assignment and the analysis of deuterated acrylamide using the frequencies obtained from infrared spectrum is available on the basis of C_s symmetry in the present study.

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Table 3. Initial and Final Sets of Force Constants of Deuterated Acrylamide (in Units of mdyne $Å^{-1}$, mdyne rad^{-1}, mdyne $Å^{-1}$ rad^{-2}).

Types of constants		Parameter	Coordinates involved	Initial	Final
	Stretching	$f_t = f_s$	C–H	5.00	5.13
		f_D	C=C	7.51	7.77
Diagonal		f_u	C–C	2.85	3.69
		f_v	C–H	4.50	4.48
		f_r	C=O	8.71	8.75
		f_d	C–N	5.42	5.54
		$f_q = f_p$	N–D	5.75	5.92
	Bending	f_α	DND	0.25	0.29
		f_β	CND	0.52	0.79
		f_ν	OCN	0.65	0.82
		f_δ	OCC		
		f_ϵ	CCN	0.50	0.61
		f_η	CCC	0.62	0.69
		f_ξ	CCH	0.55	0.57
		f_ψ	C=C–H	0.26	0.28
		f_θ	HCH	0.15	0.20
		f_ϕ	C=C–H	0.25	0.71
Interaction constants	Bond–Bond	f_{du}	CN, CC	0.89	0.90
		f_{ru}	CO, CC	1.51	1.52
		f_{Du}	CC, C=C	0.44	0.44
		f_{Dr}	CH, C=C	1.35	1.35
		f_{dr}	CN, CO	1.61	1.61
Out-of-plane		f_{t1}	C⟨H H	0.87	0.62
		f_1	C⟨H H	0.21	0.31
		f_2	N⟨D D	0.57	0.48
		f_2	N⟨D D	0.38	0.35
		f_{t3}	C–N	0.61	0.66
		f_{t4}	C–H	0.72	0.66
		f_{t5}	C=C	0.95	0.81
		f_{t3}, f_{t4}	CN, CH	0.15	0.06

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