

NEAR INFRARED STUDY OF *p*-NITROANILINE SINGLE CRYSTALS: VIBRATIONAL ANALYSIS IN 4200–5200 AND 7000–12000 cm^{-1} REGIONS AND THE ANHARMONICITY CONSTANTS OF CRYSTAL FREQUENCIES

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(Received January 27, 1971)

Using the observed frequencies and polarization directions, an attempt has been made to give assignments of absorption transitions in *p*-nitroaniline (*p*-NA) crystals in the regions of 4200–5200 and 7000–12000 cm^{-1} . On the basis of a triatomic molecule approximation for the $-\text{NH}_2$ group the anharmonic constants of $-\text{NH}_2$ symmetric and antisymmetric stretching and symmetric bending vibration were calculated.

In the previous paper [1] we have made the assignments for *p*-NA single crystals in the fundamental frequency range. For further investigation of the anharmonicity constants and their possible relation to the problem of intermolecular interactions in this solid [2], however, it was necessary to analyse the assignments of the bands also in the region of combination vibrations and second overtones. The infrared absorption spectrum of *p*-NA in 4200–5200 cm^{-1} range has been described only in a few papers. In particular, Whetsel, Robertson and Krell [3] reported about combination tones of $-\text{NH}_2$ bending- and stretching vibrations occurring between 5100 and 5040 cm^{-1} , but the spectra were taken for a number of aniline derivatives only in CCl_4 solutions. Other assignments are not known in this nor in the second overtone regions (7000–12000 cm^{-1}).

Experimental

The spectra of single crystal plates cleaved along (101) of a thickness of about 0.1 mm have been recorded in ordinary (Fig. 1) and in polarized radiation at several temperatures (Fig. 2). Figure 3 presents a spectrum in the range of second overtones, $3\nu_{\text{NH}_2}$, made for a polycrystalline sample of greater thickness. For the sake of comparison, the spectrum of *p*-NA in purified chloroform has also been measured (Fig. 4). The solution and crystal

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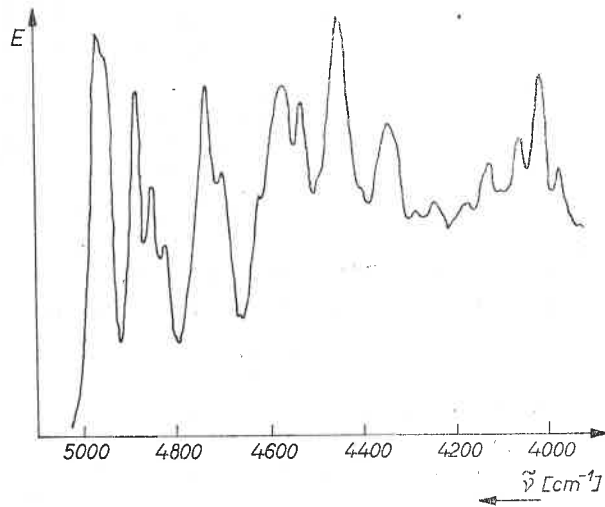
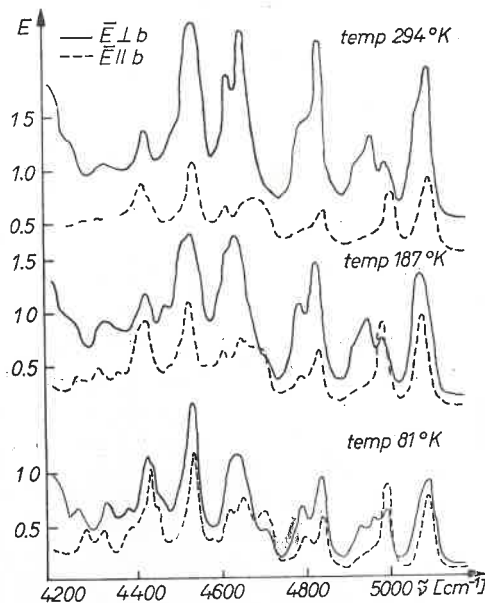


Fig. 1. Spectrum of *p*-NA single crystal plate in ordinary light



ig. 2. Spectrum of *p*-NA single crystal plate ($d = 0.24$ mm) in polarized radiation at several temperatures

spectra for unpolarized radiation were recorded with a Unicam SP-700 spectrometer equipped with a quartz prism. The spectral slit width, automatically controlled at a constant energy level of the outgoing radiation, changed in the limits of $18\text{--}43\text{ cm}^{-1}$.

Polarized crystal spectra were made with a spectrophotometric assembly whose optical part consisted of a monochromator equipped with an LiF prism (Carl Zeiss, Jena) and two Iceland spar polarizers. The apparatus worked with a chopped light beam (400 cps) and an

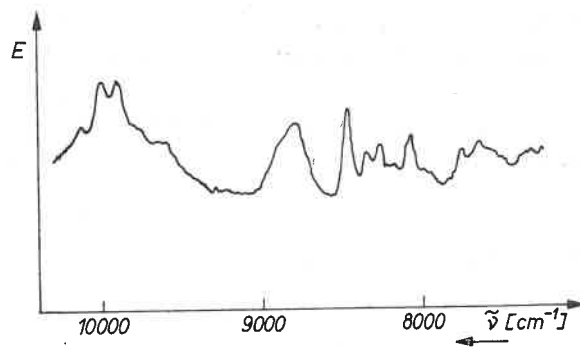


Fig. 3. Spectrum of polycrystalline *p*-NA plate

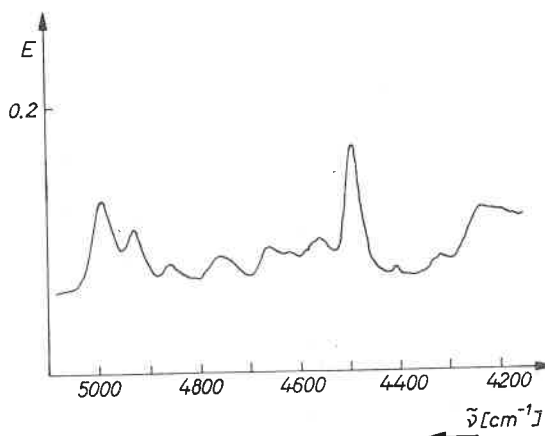


Fig. 4. Spectrum of a solution of *p*-NA in chloroform

a. c. amplifying device. The crystal sample was exactly aligned with its principal optical planes between crossed polarizers (zero output signal). For low temperatures a cryostat was used. It was built at the Department of Physical Chemistry in Wrocław, and employed the following cooling media: liquid air or liquid nitrogen (81 or 77 °K, respectively), and a mixture of solid carbon dioxide and acetone (187 °K).

Vibrational analysis

The absorption bands in the 4200–5200 cm^{-1} region arise primarily as combination tones of the symmetric or antisymmetric $-\text{NH}_2$ stretching vibration with other vibrations of the molecule. They can also be found in the spectrum of a solution but at somewhat lower frequencies.

The values of the crystal shift, $\Delta\nu = \nu_s - \nu_c$, where the subscript “s” denotes the solution and the subscript “c” the crystal, are compiled in Table I for various types of transition. It can be seen from column I that the ν_{NH_2} frequencies show an abnormally high shift in comparison with other fundamentals. This clearly indicates that the frequencies

given in column 2 must be some sort of combination of ν_{NH_2} with other frequencies because their crystal shifts are comparable with that of ν_{NH_2} but are much smaller than for overtones, column 3.

The analysis of the frequencies of combination tones in solution was based on the values for fundamentals discussed earlier [1] and on the spectra measured for *p*-chloroaniline in

TABLE I

The frequencies of absorption bands of *p*-NA in solution and in single crystal [cm^{-1}]

Mode of vibration	Fundamentals			Combination tones*			Overtones			
	ν_s	ν_c	$\Delta\nu$	ν_{CHCl_3}	ν_c	$\Delta\nu$	Mode of vibration	$\nu_{\text{C}_6\text{H}_5}$ [12]	ν_c	$\Delta\nu$
$\nu_{\text{NO}_2}^{\text{as}}$	1507 CCl ₄	1510	-3	5065	5044	21	$2\nu_{\text{NH}_2}^{\text{as}}$	6974	6843	131
$\delta_{\text{CC}}^{\text{s}}$	1115 CCl ₄	1120	-5	4993	4969 4939	24 54	$\nu_{\text{NH}_2}^{\text{s}} + \nu_{\text{NH}_2}^{\text{as}}$	6800	6703	97
$\delta_{\text{CH}}^{\text{s}}$	1130 CHCl ₃	1137	-7	4893	4907	-14	$2\nu_{\text{NH}_2}^{\text{s}}$	6752	6628	124
$\nu_{\text{CC}}^{\text{s}}$	1600 CHCl ₃	1604	-4	4828	4800	28				
$\delta_{\text{NH}_2}^{\text{s}}$	1622 CCl ₄	1638	-16	4656	4624	32				
$\nu_{\text{NH}_2}^{\text{s}}$	3418 CCl ₄	3371	47	4594	4570	24				
$\nu_{\text{NH}_2}^{\text{as}}$	3510	3484	26	4514	4493	21				

* For assignments cf. Table II

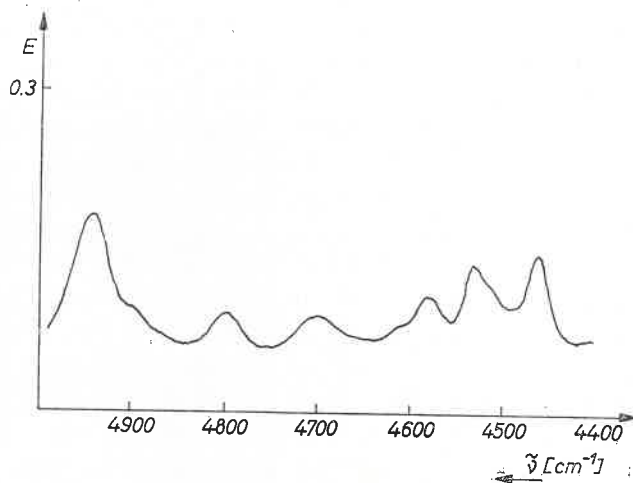


Fig. 5. Spectrum of a solution of *p*-ClA in carbon tetrachloride

CCl_4 solution (Fig. 5). Both molecules belong to the same symmetry group, what manifests itself in the close similarity of their spectra in this region as regards the band shapes and intensities. The main difference is that the frequencies of the *p*-chloroaniline molecule are some 20–50 cm^{-1} lower than those corresponding to the *p*-NA molecule. The values of *p*-chloroaniline fundamentals were taken from a paper by Garrigou-Lagrange [4].

TABLE II

Combination frequencies in solutions of *p*-NA (CHCl_3) and of *p*-CIA (CCl_4) [cm^{-1}]

<i>p</i> -nitroaniline			<i>p</i> -chloroaniline			The most probable assignment
ν_{obs}	Combination of frequencies (calc)	Anharmonicity $\nu_{\text{calc}} - \nu_{\text{obs}}$	ν_{obs}	Combination of frequencies (calc)	Anharmonicity $\nu_{\text{calc}} - \nu_{\text{obs}}$	
5065	3506 + 1625 = 5131	66	5020	3488 + 1620 = 5108	88	$\left. \begin{array}{l} \nu_{\text{NH}_2}^{\text{as}} + \delta_{\text{NH}_2}^{\text{s}} \\ \nu_{\text{NH}_2}^{\text{as}} + \nu_{3a}^{\text{s}} \end{array} \right\} \text{F.I.}^*$
	3506 + 1600 = 5106	41		3488 + 1600 = 5088	68	
4993	3412 + 1625 = 5037	44	4970	3402 + 1620 = 5022	52	$\nu_{\text{NH}_2}^{\text{s}} + \delta_{\text{NH}_2}^{\text{s}}$
4893	3506 + 1447 = 4953	60	4870	3488 + 1426 = 4914	44	$\left. \begin{array}{l} \nu_{\text{NH}_2}^{\text{as}} + \nu_{19b}^{\text{s}} \\ \nu_{\text{NH}_2}^{\text{s}} + \nu_{19a}^{\text{s}} \end{array} \right\} \text{F.R.}$
				3402 + 1496 = 4898	23	
4828	3412 + 1447 = 4859	31	4760	3402 + 1426 = 4828	68	$\nu_{\text{NH}_2}^{\text{s}} + \nu_{19b}^{\text{s}}$
4700	3412 + 1336 = 4748	48				$\nu_{\text{NH}_2}^{\text{s}} + \nu_{\text{NO}_2}^{\text{s}}$
4656	3412 + 1312 = 4724	68	4630	3402 + 1290 + 4692	62	$\nu_{\text{NH}_2}^{\text{s}} + \nu_{\text{CN}}$
4594	3506 + 1180 = 4686	92	4570	3488 + 1170 = 4658	88	$\nu_{\text{NH}_2}^{\text{as}} + \nu_{15}$
4514	3412 + 1180 = 4592	78	4490	3402 + 1170 = 4572	82	$\nu_{\text{NH}_2}^{\text{s}} + \nu_{15}$

*F.r. — Fermi resonance

The results of the analysis of the solution spectra are given in Table II. It is worthwhile to note that, according to Table II, it is possible to explain the frequencies occurring in this spectral region by considering a combination of the same vibration types corresponding to both molecules. This reflects further the fact that the differences of calculated and observed frequencies, $\nu_{\text{calc}} - \nu_{\text{obs}}$, given as a measure of anharmonicity in columns 3 and 6 of Table II, show similar regularities in their behavior.

Using the data given in Table II and taking into consideration also the polarization directions of the crystal bands, a vibrational analysis of the spectrum of crystalline *p*-NA (Table III) was made. Column 2 of this Table gives qualitative data concerning the polarization directions of the observed crystal bands. In this case knowledge of whether $R_{a'/b} > 1$ or $R_{a'/b} < 1$ facilitates differentiation between A_1 and B_1 or B_2 symmetry species, respectively, these symmetries being the only allowed ones in this point group. Here, $R_{a'/b}$ denotes the experimental ratio of the intensities of an absorption band when measured with the electric

Combination frequencies of *p*-NA single crystals [cm⁻¹]

Frequency observed (Fig. 1)	Dichroic ratio (Fig. 2)	Symmetry and deduced assignments	Resulting symmetry	Frequency calculated	Anharmonicity
5057	>1	$A_1 \left. \begin{array}{l} \nu_{\text{NH}_2}^{\text{as}} + \delta_{\text{NH}_2}^{\text{s}} \\ \nu_{\text{NH}_2}^{\text{as}} + \nu_{8a}^{\text{s}} \end{array} \right\} \text{F.r.}$	B_1	3484 + 1638 = 5122	65
			B_1	3484 + 1604 = 5088	31
5044	>1	$A_1 \nu_{\text{NH}_2}^{\text{as}} + \nu_{8b}^{\text{s}}?$	A_1	3484 + 1588 = 5072	28
4969	<1	$B_1 \nu_{\text{NH}_2}^{\text{as}} + \nu_{19a}^{\text{s}}$	B_1	3484 + 1483 = 4963	-6
4939	>1	$A_1 \nu_{\text{NH}_2}^{\text{s}} + \delta_{\text{NH}_2}^{\text{s}}$	A_1	3371 + 1638 = 5009	70
4907	>1	$A_1 \nu_{\text{NH}_2}^{\text{s}} + \nu_{8a}^{\text{s}}$	A_1	3371 + 1604 = 4975	68
4800*	>1	$A_1 \left. \begin{array}{l} \nu_{\text{NH}_2}^{\text{s}} + \nu_{19a}^{\text{s}} \\ \nu_{\text{NH}_2}^{\text{as}} + \nu_{14}^{\text{s}} \\ 3\delta_{\text{NH}_2}^{\text{s}} \end{array} \right\} \text{F.r.}$	A_1	3371 + 1483 = 4854	54
			A_1	3484 + 1400 = 4884	84
			A_1	3 × 1638 = 4914	114
4763	>1	$A_1 \left. \begin{array}{l} \nu_{\text{NH}_2}^{\text{as}} + \nu_{\text{CN}}^{\text{s}} \\ \nu_{\text{NH}_2}^{\text{s}} + \nu_{19b}^{\text{s}} \\ \nu_{\text{NH}_2}^{\text{as}} + \nu_{\text{NO}_2}^{\text{s}} \end{array} \right\} \text{F.r.}?$	B_1	3484 + ~1340 = 4824	61
			B_1	3371 + 1450 = 4821	58
			B_1	3484 + ~1340 = 4824	61
4732	<1	$B_1 \nu_{\text{NH}_2}^{\text{s}} + \nu_{14}^{\text{s}}$	B_1	3371 + 1400 = 4771	39
4625	>1	$A_1 \left. \begin{array}{l} \nu_{\text{NH}_2}^{\text{s}} + \nu_{\text{CN}}^{\text{s}} \\ \nu_{\text{NH}_2}^{\text{s}} + \nu_{\text{NO}_2}^{\text{s}} \end{array} \right\} \text{F.r.}$	A_1	3371 + ~1340 = 4711	87
			A_1	3371 + ~1340 = 4711	87
4570	>1	$A_1 \nu_{\text{NH}_2}^{\text{as}} + \nu_{15}^{\text{s}}$	A_1	3484 + 1188 = 4672	102
4494	<1	$B_1 \nu_{\text{NH}_2}^{\text{s}} + \nu_{15}^{\text{s}}$	B_1	3371 + 1188 = 4559	66
4365	<1	$B_1 \nu_{\text{NH}_2}^{\text{s}} + \delta_{\text{NH}_2}^{\text{as}}$	B_1	3371 + 1057 = 4428	61

* Splits at lower temperature into three components.

vector E of the radiation perpendicular and parallel to the b -axis. More rigorous calculations and a comparison with structural data will be presented elsewhere [2].

The symmetries predicted from the values of the dichroic ratio (column 3 of Table III) agree with those obtained from assignments (columns 5 and 4, respectively), except for two cases. The frequency at 5057 cm⁻¹, corresponding to a very intense band, can be assigned to two combinations: $\nu_{\text{NH}_2}^{\text{as}} + \delta_{\text{NH}_2}^{\text{s}}$ or $\nu_{\text{NH}_2}^{\text{as}} + \nu_{8a}^{\text{s}}$. Both are of identical resulting symmetry (B_1) and of similar frequency. Therefore, they do enter into a Fermi resonance causing an enhancement of the intensity of the resulting transition. It is assumed that a similar situation occurs for three other frequencies corresponding to the absorption band at 4763 cm⁻¹. However, the symmetry of these bands according to their polarization is A_1 , while the resulting symmetry of the combination is B_1 . It is possible that in these two cases an inversion of intensities occurs owing to the combined action of the Fermi resonance and a weak intermolecular hydrogen bonding between amine- and nitro- groups of neighbouring

molecules. This would also inverse the dichroic ratio. The effect of the hydrogen bonding on band frequencies and intensities was discussed by Whetsel and collaborators in their papers on the near infrared spectra of solutions of aromatic amines [5, 6].

Anharmonicity constants

In order to calculate the anharmonicity constants, the following expression was used for the i -th normal frequency of the anharmonic oscillator [7]:

$$\nu_i^{\text{obs}}(1, 0, 0, \dots) = \nu_i + 2x_{ii} + 1/2 \sum x_{ik} + \dots \quad (1)$$

where ν_i^{obs} is the i -th fundamental frequency observed in the spectrum, ν_i is the corresponding harmonic frequency, and x_{ik} are the anharmonicity constants [cm^{-1}], where $i \neq k$. In equation (1) the x_{ik} constants can be interpreted for $i \neq k$ as interaction constants of the i -th frequency with all other vibrations of the molecule. While it is not very difficult to calculate x_{ik} for a diatomic molecule, for a polyatomic one it is a tedious, and sometimes unaccomplishable, task. However, in the case of the p -NA molecule it seems it is reasonable to treat the $-\text{NH}_2$ group separately as a triatomic molecule and consider only the interactions between the three characteristic vibrations of such a molecule. They are: symmetric and antisymmetric stretching vibrations and symmetric deformation vibrations. They occur at the following frequencies: 3371, 3484, and 1638 cm^{-1} , respectively. The other three vibrations of a $-\text{NH}_2$ group attached to the benzene ring are of much lower intensity than those listed above, what is argument in favour of this simplification.

A similar approximation was used with success by Henry and Siebrand [8] in the case of the benzene molecule. They showed that the overtones of CH-stretching vibrations can be reproduced accurately on the assumption that the six local oscillators in the benzene molecule vibrate independently. The authors could describe the anharmonicity of the vibrations by means of one constant of such a local mode instead of using $1/2 N(N+1)$ constants corresponding to an N -atomic molecule. Also Bernstein [9] and Boobyer [10, 11] have made a similar assumption earlier for molecules containing only one C-H bond, which were then treated as diatomic molecules.

In the approximation discussed above for the $-\text{NH}_2$ group it is possible to write expressions like (1) for fundamentals, overtones and combination frequencies of its three vibrations, which can be denoted as follows:

$$\begin{aligned} \nu_1(1, 0, 0) &\equiv \nu_{\text{NH}_2}^s = 3371 \text{ cm}^{-1} \\ \nu_2(0, 1, 0) &\equiv \nu_{\text{NH}_2}^{as} = 3484 \text{ cm}^{-1} \\ \nu_3(0, 0, 1) &\equiv \delta_{\text{NH}_2}^s = 1638 \text{ cm}^{-1} \end{aligned} \quad (2)$$

Therefore, Eq. (1) takes the form:

$$\begin{aligned} \nu_1^{\text{obs}}(1, 0, 0) &= \nu_1 + 2x_{11} + 1/2x_{12} + 1/2x_{13} \\ \nu_2^{\text{obs}}(0, 1, 0) &= \nu_2 + 2x_{22} + 1/2x_{12} + 1/2x_{23} \\ \nu_3^{\text{obs}}(0, 0, 1) &= \nu_3 + 2x_{33} + 1/2x_{13} + 1/2x_{23} \end{aligned} \quad (3)$$

for fundamentals,

$$\begin{aligned}
 \nu^{\text{obs}}(2, 0, 0) &= 2\nu_1 + 6x_{11} + x_{12} + x_{13} \\
 \nu^{\text{obs}}(0, 2, 0) &= 2\nu_2 + 6x_{22} + x_{12} + x_{23} \\
 \nu^{\text{obs}}(0, 0, 2) &= 2\nu_3 + 6x_{33} + x_{12} + x_{23} \\
 \nu^{\text{obs}}(3, 0, 0) &= 3\nu_1 + 12x_{11} + 3/2x_{12} + 3/2x_{13} \\
 \nu^{\text{obs}}(0, 3, 0) &= 3\nu_2 + 12x_{22} + 3/2x_{12} + 3/2x_{23} \\
 \nu^{\text{obs}}(0, 0, 3) &= 3\nu_3 + 12x_{33} + 3/2x_{13} + 3/2x_{23}
 \end{aligned} \tag{4}$$

for 1st and 2nd overtones, and

$$\begin{aligned}
 \nu^{\text{obs}}(1, 1, 0) &= \nu_1 + \nu_2 + 2x_{11} + 2x_{22} + 2x_{12} + 1/2x_{13} + 1/2x_{23} \\
 \nu^{\text{obs}}(0, 1, 1) &= \nu_2 + \nu_3 + 2x_{22} + 2x_{33} + 2x_{23} + 1/2x_{12} + 1/2x_{13} \\
 \nu^{\text{obs}}(1, 0, 1) &= \nu_1 + \nu_3 + 2x_{11} + 2x_{33} + 2x_{13} + 1/2x_{12} + 1/2x_{23} \\
 \nu^{\text{obs}}(2, 1, 0) &= 2\nu_1 + \nu_2 + 6x_{11} + 2x_{22} + 7/2x_{12} + x_{13} + 1/2x_{23} \\
 \nu^{\text{obs}}(1, 2, 0) &= \nu_1 + 2\nu_2 + 6x_{22} + 2x_{11} + 7/2x_{12} + x_{23} + 1/2x_{13} \\
 \nu^{\text{obs}}(1, 0, 2) &= \nu_1 + 2\nu_3 + 6x_{33} + 2x_{11} + 7/2x_{13} + x_{23} + 1/2x_{12}
 \end{aligned} \tag{5}$$

for combination frequencies.

In order to ascertain that the assignments are correct we can make use of the approximate expression

$$\frac{\nu^{\text{obs}}}{\nu} = \nu_i + (v+1)\alpha_e \nu_i \tag{6}$$

which can be derived from (3) and (4) by neglecting the terms with $i \neq k$. In (6), $\alpha_e = -\frac{x_{ii}}{\nu}$, and ν is the quantum number of the transition. According to (6), a linear dependence is expected to hold between ν^{obs}/ν , and $(v+1)$. Neglecting x_{ik} with $i \neq k$, we introduce a small error of

TABLE IV

Frequencies of $-\text{NH}_2$ fundamentals and overtones [cm^{-1}]

Transition	ν^{obs}	ν	$\frac{\nu^{\text{obs}}}{\nu}$	$\nu+1$	α_e^{mean}
$\nu^s(1, 0, 0)$	3371	1	3371	2	$1.57 \cdot 10^{-2}$
$\nu^s(2, 0, 0)$	6628	2	3314	3	
$\nu^s(3, 0, 0)$	9787	3	3262	4	
$\nu^{as}(0, 1, 0)$	3484	1	3484	2	$1.54 \cdot 10^{-2}$
$\nu^{as}(0, 2, 0)$	6843	2	3421	3	
$\nu^{as}(0, 3, 0)$	10120	3	3373	4	
$\delta^s(0, 0, 1)$	1638	1	1638	2	$1.14 \cdot 10^{-2}$
$\delta^s(0, 0, 2)$	3245	2	1622	3	
$\delta^s(0, 0, 3)$	4800	3	1600	4	

little significance, because the x_{ik} change the constant term of the straight line (ν_i) very little. Experimental frequencies are collected together with quantum numbers in Table IV, and the results according to (6) are presented in Fig. 6.

On the basis of data given in Table IV and Fig. 6 we can confirm the assignment of the frequency 6628 cm^{-1} to the 1st overtone of symmetric stretching of the $-\text{NH}_2$ group, made by Lady and Whetsel [12].

In the 5400 to 7200 cm^{-1} spectral region there remains a band of unknown origin at 6387 cm^{-1} . However, as reported by Lady and Whetsel [12], this band disappears in the

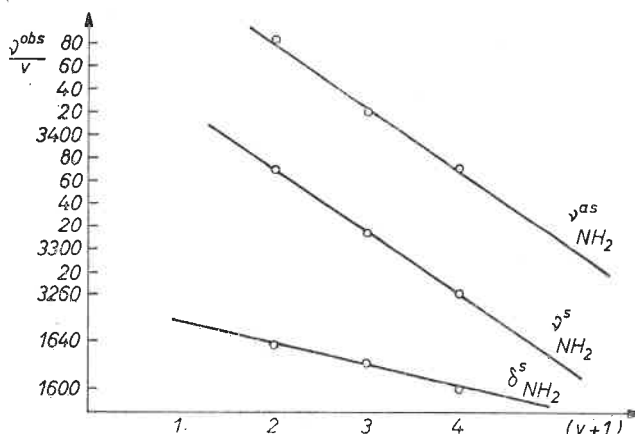


Fig. 6. Relation between ν^{obs}/ν and $(\nu+1)$ acc. to Eq. (6)

spectrum of deuterated derivatives of aniline. Therefore, it has to be associated with $-\text{NH}_2$ group vibrations, and may be of form $2\delta^s + \nu^s$ or $2\delta^s + \nu^{as}$. In order to decide between these two possibilities, we can make use of mean anharmonicity constants, x_{ii} , and harmonic frequencies, ν_i , calculated from (3-5) and given in Table V.

TABLE V

Anharmonicity constants of $-\text{NH}_2$ group vibrations

i	ν_i [cm^{-1}]	x_{ii} [cm^{-1}]	x_{1i} [cm^{-1}]	x_{2i} [cm^{-1}]
1	3574	-54	-54	-121
2	3693	-55	-121	-55
3	1750	-19	-70	-78

The result is given in the last two rows of Table VI beside the results obtained for all other observed frequencies. A comparison shows that with the assignment of 6487 cm^{-1} to a $\nu^s + 2\delta^s$ transition the agreement between observed and calculated frequencies is closer. The polarization of this band, which correspond to a transition of A_1 symmetry, also confirms this assignment.

Observed and calculated frequencies on the basis of the data of Table V

Mode of vibration	Notation of transition	Frequency observed	Frequency calculated	$\Delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}}$
ν_s^s	(1, 0, 0)	3371	3371	—
ν^{as}	(0, 1, 0)	3484	3484	—
δ^s	(0, 0, 1)	1638	1638	—
$2\nu^s$	(2, 0, 0)	6628	6633	-5
$2\nu^{as}$	(0, 2, 0)	6843	6857	-14
$2\delta^s$	(0, 0, 2)	3245	3238	7
$3\nu^s$	(3, 0, 0)	9787	9787	0
$3\nu^{as}$	(0, 3, 0)	10120	10120	0
$3\delta^s$	(0, 0, 3)	4800	4800	0
$\nu^s + \nu^{as}$	(1, 1, 0)	6703	6733	-30
$\nu^s + \delta^s$	(1, 0, 1)	4939	4939	0
$\nu^{as} + \delta^s$	(0, 1, 1)	5044	5044	0
$2\nu^s + \nu^{as}$	(2, 1, 0)	9904	9875	29
$2\nu^{as} + \nu^s$	(1, 2, 0)	10000	9986	14
$2\delta^s + \nu^s$	(1, 0, 2)		6469	18
$2\delta^s + \nu^{as}$	(0, 1, 2)	6487	6566	-79

A weak intermolecular hydrogen bonding affects, of course, the anharmonicity of the vibration of the $-\text{NH}_2$ group. This effect in the crystal spectrum will be discussed in better detail in a separate paper.

The authors would like to express their sincere thanks to Dr A. Sucharda-Sobczyk for making the very precise spectrophotograms on a UNICAM SP-700 spectrophotometer at the Laboratory of Instrumental Chemical Analysis of the Wrocław Technical University.

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