

Systematic Interpretation of Raman Spectra of Organic Compounds

IV—Nitrogen Compounds

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The Raman spectra of 79 nitrogen containing organic compounds have been recorded. The frequencies of amines, pyridines, cyanides, amides and nitro-compounds are reported and correlations with the structure have been established by means of computer searching. The collected data have been incorporated into an interpretation system for C, H and O compounds, and difficulties in the interpretation of the data are reviewed. A further extension of the system is discussed.

INTRODUCTION

Systematic interpretation of vibrational spectra has proved to be very useful, especially for a beginner.¹ Interpretation procedures for Raman spectra of organic compounds have been developed up till now by Schrader and Meier,² and by us.³

The most recent system³ is suitable for a variety of C, H and O compounds, and as the results are quite satisfying we decided to extend it to nitrogen compounds.

As a start a limited number of classes of compounds has been selected, viz amine-, pyridine-, cyanide-, amide-, and nitro compounds.

It was expected that the nitrogen compounds would not require too many modifications to the CHO system. Depending on the results a further extension would be considered.

EXPERIMENTAL

Raman spectra were recorded on a Spectra-Physics model 700 spectrophotometer equipped with a Spectra-Physics model 165 argon ion laser as a lightsource. The 488 nm line was used as excitation wavelength with a continuous output power of 200 mW. The spectrophotometer was calibrated daily on indene, resulting in an overall wavenumber accuracy of $\pm 2 \text{ cm}^{-1}$ (readability included). Spectra were run in two parts, i.e. from 0–2000 cm^{-1} and from 2000–4000 cm^{-1} . Sensitivity was adjusted in such a way that the most intense peak in the spectral region had an intensity between 85 and 95% (scale divisions). Intensity is indicated as weak (02–20%), medium (20–50%) and strong (50–95%). Further details can be found in Ref. 1.

SPECTRAL DATA

The nitrogen atom can be present in a number of structural elements such as amine, amide etc., which

may be correlated with certain bands in the Raman spectra.

To find the correlations a computer program INTVA has been developed. This programme searches in any preselected file of spectral data for frequency intervals that all compounds have in common. A file must be composed of compounds having (at least) one common structural element. Limits for (minimum/maximum) intensity and (maximum) interval width can be set at will.

As all possible intervals are found, those that are not clearly correlated with the structural element should be omitted.

The results are discussed successively below:

Amines

In the Raman spectra of all primary and secondary amines at least one weak band shows up in the region 3442–3211 cm^{-1} , caused by the N—H stretching vibration(s).⁵ A second weak band is observed for all primary amines in the same region. Dollish *et al.*⁴ refer to these bands as being strong. The discrepancy is due to the fact that these authors use an indistinct intensity criterion. This once more emphasizes that one should use well defined scanning conditions.

The C—N stretching vibrations in tertiary amines⁶ do have bands in the region 1070–1031 cm^{-1} and 871–841 cm^{-1} . However these intervals are hardly useful for interpretation purposes as other structural elements have peaks in these regions as well.

In the class of cyclic aliphatic amines, piperidines can be detected from $\nu(\text{N—H})$ around 3330 cm^{-1} and two ring skeletal vibrations between 990 and 730 cm^{-1} .⁷ Pyrrolidines show a strong skeletal breathing vibration, already mentioned by Tschamler and Voetter,⁸ in the range 903–872 cm^{-1} . The ring breathing vibrations of normal aliphatic five membered ring is found in about the same region. For primary pyrrolidines $\nu(\text{N—H})$ lies between 3303 and 3297 cm^{-1} .

In the region 2804–2735 cm^{-1} the so called Bohlmann bands are characteristic for the majority of the aliphatic and alicyclic amines. The appearance of these bands is ascribed as a combined effect of Fermi resonance and at least one C—H bond trans to the lone

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pair of the nitrogen atom. No bands show up in case the lone pair is conjugated.⁹

A methyl group attached to the nitrogen atom can be recognized from a band in the range 2815–2775 cm⁻¹. Methylene to nitrogen shows a useful band around 1465 cm⁻¹.

In β -olefinic amines neither $\nu(\text{N-H})$ nor $\nu(\text{C=C})$ has been shifted compared with aliphatic $\nu(\text{N-H})$ and olefinic $\nu(\text{C=C})$. The same holds for the amine group and the triple bond.

Primary anilines display very characteristic bands in the regions 3387–3348 cm⁻¹, $\nu_{\text{as}}(\text{N-H})$, and 3229–3211 cm⁻¹, $\nu_{\text{s}}(\text{N-H})$, (less intensive). For secondary anilines¹⁰ only one band is observed in the region 3402–3398 cm⁻¹.

Pyridines

Pyridines show two rather characteristic $\nu(\text{C=C})$ bands in the interval 1599–1560 cm⁻¹, somewhat lower than benzene derivatives.¹¹ They are useful for identification purposes. Detection of substitution of the pyridine nucleus is very difficult although at least one intensive band is present in one of the regions 1073–1030 cm⁻¹, 1003–988 cm⁻¹ and 786–715 cm⁻¹. Too few compounds have been studied so far to draw a reliable conclusion.

Cyanides

Cyanides show a very intensive $\nu(\text{C}\equiv\text{N})$ in the range 2246–2219 cm⁻¹ (Ref. 15) where also non terminal acetylenes might show a band. In aliphatic nitriles $\nu(\text{C}\equiv\text{N})$ is found in the region 2246–2234 cm⁻¹, whereas in aromatic nitriles it is found between 2234 and 2219 cm⁻¹.

Amides

All aliphatic amides are characterized by a carbonyl attached to a nitrogen atom. These compounds show two peaks which are useful for identification, $\nu(\text{C=O})$ in the region 1669–1623 cm⁻¹ (medium intensity) and a $\nu(\text{C-N})$ in the range 1431–1405 cm⁻¹ (weak to medium)⁴. The $\nu(\text{N-H})$ of primary and secondary amides is found as a weak band(s) in the interval 3348–3200 cm⁻¹.

Nitro compounds

Much work on aliphatic nitro compounds has been done by Geiseler *et al.*^{12,13}. The nitro group is characterized by its asymmetric N—O stretching vibration between 1560 and 1544 cm⁻¹ (weak) and its symmetric one at 1386–1358 cm⁻¹ (strong to medium). Difference between primary and secondary compounds can be made through the more precise values in Table 1.

Some naphthyl compounds show a strong $\nu(\text{C=O})$ band in the same region but can be detected from other $\nu(\text{C=C})$ bands around 1600 cm⁻¹.

Aromatic nitro compounds show a weak $\nu_{\text{as}}(\text{N-O})$ in the interval 1522–1512 cm⁻¹ and a strong $\nu_{\text{s}}(\text{N-O})$ in the range 1348–1336 cm⁻¹. The data compiled from the recorded spectra by means of the programme INTVA are presented in more detail in Table 1.

THE INTERPRETATION SYSTEM

In extending an interpretation system to a new class of compounds two stages can be distinguished:

- (A) adaptation of the existing system such that the new compounds do not produce wrong answers,
- (B) addition of the new *I*(nformation)-elements.

Table 1. Nitrogen correlations. The frequency intervals include the given wavenumbers

aliphatic —NH ₂	3392–3360/02	3342–3302/02		
aromatic —NH ₂	3387–3348/02	3229–3211/02		
aliphatic —NH—	3345–3300/02			
aromatic —NH—	3404–3398/02	1606–1600/30		
piperidine NH	3346–3321/02	2684–2656/02	990–912/10	881–730/40
pyrrolidine NH	3303–3297/02	973–965/02	903–872/50	
—C—N—C—	2788–2706/20			
CH ₃ —N—	2815–2775/02			
—CH ₂ —N—	1484–1476/02	1130–1109/02		
—CH ₂ —N—CH ₂ —(or CH ₃)	2805–2794/02	1480–1454/02	1068–1030/15	
formamide	1669–1656/30	1417–1410/15		
pivalamide	1635–1623/10	1413–1407/02		
prim. amide	3348–3300/02	3172–3150/02	1674–1650/10	1431–1410/10
sec. amide	3342–3200/02	1669–1623/10	1419–1405/02	1252–1246/25
tert. amide	1647–1635/10	1413–1409/10		
pyridine	1599–1560/02	1276–1210/15	1073–1036/30	786–715/50
			1579–1558/02	1003–988/40
aliphatic —C≡N	2246–2234/50			
aromatic —C≡N	2234–2219/50	1602–1597/20		
prim. aliphatic NO ₂	1560–1551/02	1386–1380/25	916–896/02	
sec. aliphatic NO ₂	1555–1544/02	1376–1358/25	865–841/02	
aromatic —NO ₂	1522–1512/02	1348–1336/50	813–787/25	

In stage (A) Q (question)-elements are modified and added to overcome wrong answers. It is the aim to preserve all existing information in the system, but it may be necessary to sacrifice an I -element.

The 79 nitrogen compounds have been passed through the CHO system; 16 wrong reports were obtained. Addition of 6 Q - and the removal of 1 I -element proved to be sufficient to overcome these mistakes. Then the system was suitable for the N-compounds though it did not yet establish any specific nitrogen information.

The aim of stage(B) is to add as much as possible new structural elements. This can be reached by adding Q -elements based upon specific intervals (selecting *all* compounds with a certain functionality and *no* others), pseudo-specific intervals (selecting *almost all* compounds and *no* others), and selective intervals (selecting *all* compounds with *some* others) in that order.

As all useful intervals for the N-functionalities have been found already (Table 1) only those which are (pseudo)specific have to be traced. A programme SELEC has been developed to do so.

From the intervals of the 21 N-functionalities only one proved to be specific (aromatic nitro compounds) and two pseudo-specific (primary aliphatic amines and primary anilines), regarding the total file of 606 compounds. Hence the addition of selective intervals was inevitable. However this brought about wrong answers for some CHO compounds.

There are two possibilities to overcome this: (1) omit information, and (2) making use of pre-information to by-pass certain Q -elements (and thus I -elements). On applying both possibilities it appeared that the system could be extended with 20 I -elements at the cost of 49 new Q 's.

In Table 2 the values of the number of different I 's (ΣI) and Q 's (ΣQ) and the ratio $\Sigma Q/\Sigma I$ have been summarized in the different stages of incorporation.

Although the ratio $\Sigma Q/\Sigma I$ (being a measure for the efficiency of a system) did not rise very much, 2.0 to 2.1, the (sub)value 2.9 for the added Q 's and I 's is rather high.

To get insight in the reliability of the system two tests have been done. In the first test all compounds have been passed through the system in which each interval was broadened with 2 cm^{-1} to both sides. As can be

Table 2. Values of the total number of different information-elements (ΣI), question-elements (ΣQ) and the ratio $\Sigma Q/\Sigma I$, in the three stages of the incorporation

	ΣQ	ΣI	$\Sigma Q/\Sigma I$
CHO system	321	159	2.0
Stage (A)	327	158	2.1
Stage (B)	376	178	2.1
Increase	55	19	2.9

seen in Table 3 the total number of collected I -elements (I_{tot}) increased with 93 and the percentage wrong answers with 1.4%. In the second test the minimum intensity limit was set at 10% for all intervals. I_{tot} decreased from 3259 to 2655 whereas the percentage wrong answers increased from 0.5 to 2.5%. These figures indicate that the system is reliable.

GENERAL REMARKS

The extension of an interpretation system with a new class of compounds is usually attended with the introduction of new functionalities. As each functionality is allied with at least one frequency interval, the chance on interference increases progressively with the number of functionalities. There are two possibilities to prevent such interference, both coupled with some disadvantages;

- (1) addition of still more Q -elements to by-pass, on condition that they do not interfere,
- (2) removal of I -elements (and the allied Q 's).

The disadvantage of (1) is that with the growth of ΣQ , the chance of mistakes increases, and thus the reliability decreases. At the same time the system becomes less surveyable and consequently harder to modify. The disadvantage of possibility (2) is that the information content of the system decreases.

We intend to extend the system[†] but in view of the above mentioned remarks it seems useful to set out rules and procedures first. The development of INTVA and SELEC should be regarded as a step in that direction.

[†] Up till now the system contains 376 Q - and 178 I -elements. A FORTRAN IV programme of the system is available on request.

Table 3. Influence of intensity and wavenumber variation. Values of the numbers of collected I -elements (I_{tot}), the average numbers of I_{tot} per compound (I_{tot}/n) and the percentage wrong answers, split up for the different chemical classes.

(a) The CHON system, (b) the system with intervals broadened with 2 cm^{-1} to both sides and (c) the system with the minimum intensity limit of each interval set at 10%

		CH	OH	—O—	C=O	COOH	COOC	N	total
Number of compounds	n	167	122	67	49	22	100	79	606
Standard system	I_{tot}	881	656	364	281	78	521	478	3259
	I_{tot}/n	5.3	5.4	5.4	5.7	3.5	5.2	6.0	5.4
	% fault	0.6	0.2	0.3	0.7	2.6	0.8	0.4	0.5
Intervals broadened	I_{tot}	898	680	379	282	79	537	493	3352
	I_{tot}/n	5.4	5.6	5.7	5.8	3.6	5.4	6.2	5.5
	% fault	2.2	1.5	2.4	2.1	3.8	1.5	1.8	1.9
Minimum intensity 10%	I_{tot}	702	509	295	243	77	465	364	2655
	I_{tot}/n	4.2	4.2	4.4	5.0	3.5	4.7	4.6	4.4
	% fault	3.1	1.2	2.4	1.7	5.2	1.7	3.8	2.5

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