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Resonance Raman Spectra of Acid-Base Indicators. I. *p*-Aminoazobenzene Derivatives

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Resonance Raman spectra between 1800 and 1000 cm^{-1} of methyl orange and a few other *p*-aminoazobenzene-type acid-base indicators have been investigated at various pH, and a marked spectral change has been observed on the transformation between the acid and the base forms of these indicators. The characteristic Raman frequencies have been assigned by referring to the spectra of related compounds and the deuteration effects. The spectra of the acid form are well elucidated on the basis of the quinoid-type structure.

The color change of acid-base indicators is generally understood as a consequence of the change in molecular structures accompanying various redistributions of electrons on the transformation between the indicator acids and their conjugate bases. Spectroscopic evidence, however, has rarely been obtained for details of such a structure change of indicators. The visible and ultraviolet spectra should reflect the electron redistributions directly, but they are too simple in most cases to afford sufficient information on the complicated structure of indicator molecules. The infrared and ordinary Raman spectra may be informative, but their application is severely restricted by the solvents and the concentrations with which indicators are practically used. These difficulties are expected to be overcome by the recently developed technique of the laser-excited resonance Raman spectra, which seem to be very promising to inquire into the molecular structure of indicators in dilute aqueous solutions. Most of the acid-base indicators show absorption maxima in the spectral region around 500 nm, where two intense excitation lines, 488.0 and 514.5 nm, are available from the Ar$^+$ laser, and rigorous resonances with high sensitivities are expected even at very low concentrations.

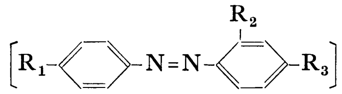
The resonance Raman spectrum of methyl orange in the neutral aqueous solution has been reported by Hacker[1)] and Carey *et al.*[2)] and several bands attributable to the azobenzene structure postulated for the base form have been identified. For any acid-base indicator, however, the pH dependence of the Raman spectrum does not seem to have been investigated. In this paper we report the resonance Raman spectra of methyl orange and a few other *p*-aminoazobenzene type indicators at various pH. The structures of the acid and the base forms of these indicators are discussed by referring to the spectra of related compounds and deuteration effects.

Experimental

Materials. The azobenzene derivatives listed with the abbreviations in Table 1 and two other reference compounds, quinone dioxime and diazoaminobenzene, were obtained from commercial sources, and were recrystallized several times from water or ethanol. *O*-Deuterated quinone dioxime and *N*-deuterated diazoaminobenzene were prepared by the usual exchange reaction with ethanol-*d*.

Measurements. The Raman spectra between 1800 and 1000 cm^{-1} were recorded on a JEOL S-1 laser Raman spectrophotometer with the excitation lines 488.0 nm and 514.5 nm of a Coherent 52G Ar$^+$ laser (2 W). The spectral slitwidth was 12 cm^{-1} and 14 cm^{-1} for the 514.5 nm and the 488.0 nm excitations, respectively. The measurements were made for solid samples of quinone dioxime and its *O*-deuterated compound and for the solutions of the other compounds in various solvents. Each sample was sealed in a 1 mm capillary tube. The pH of the aqueous solutions was adjusted by using 0.1M HCl, 0.1M NaOH and the phthalate buffers.[5)] When the desired solubility was not attained with water alone, suitable amounts of ethanol or acetone-d_6 were added to the solvents. At the concentrations adopted presently, acetone-d_6 shows no interfering Raman band in the region between 1650 and 1100 cm^{-1}, but shows a weak band at 1690 cm^{-1} which may be used as an internal standard. For the measurements of the deuterated compounds, the stock solution of 1M DCl was prepared by mixing the calculated amounts of 20% DCl (Merck) and heavy water in a 1 ml syringe, and was reserved in a sealed ampule. Similarly, 1M NaOD in heavy water was prepared from 40% NaOD (Merck). These solutions were diluted with heavy water to the desired concentration before use.

TABLE 1. STRUCTURE



, ABSORPTION MAXIMUM AND COLOR-CHANGE INTERVAL

Compound	Abbr.	Structure			Absorption Maximum (nm)		Color-change interval (pH)
		R_1	R_2	R_3	Basic form	Acidic form	
Methyl orange	MO	$N(CH_3)_2$	H	SO_3Na	464	508	3.1—4.4[3)]
Methyl red	MR	$N(CH_3)_2$	COOH	H	430	512	4.2—6.3[3)]
Methyl yellow	MY	$N(CH_3)_2$	H	H	440	512	2.9—4.0[3)]
p-Aminoazobenzene	AAB	NH_2	H	H	383	503	1.9—3.3[3)]
Tropaeolin OO	TOO	NHC_6H_5	H	SO_3Na	447	530	1.3—3.0[4)]
Azobenzene	AB	H	H	H	446	—	—

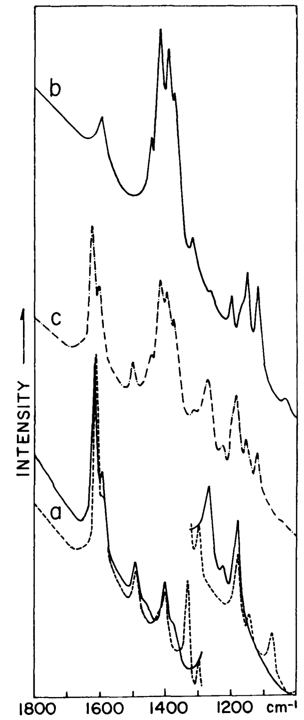


Fig. 1. Resonance Raman spectra of MO: (a) 1×10^{-4} M in 0.1M HCl (solid line) and in 0.1M DCl (broken line), 514.5 nm; (b) 2×10^{-4} M in water, 488.0 nm; (c) 2×10^{-4} M in the phthalate buffer (pH 3.4), 488.0 nm.

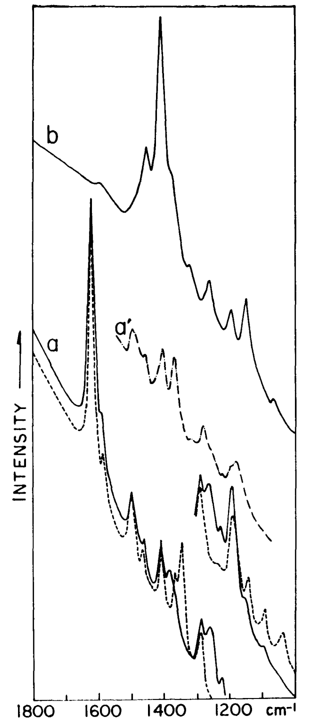


Fig. 2. Resonance Raman spectra of MR: (a) 1×10^{-4} M in 0.1M HCl (solid line) and in 0.1M DCl (broken line), 514.5 nm; (a′) 1×10^{-4} M in a 1: 3 mixture of ethanol and the phthalate buffer (pH 4), 514.5 nm; (b) 2×10^{-4} M in 0.1M NaOH, 488.0 nm.

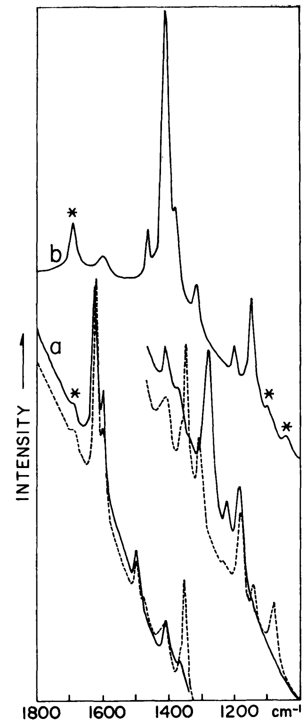


Fig. 3. Resonance Raman spectra of MY: (a) 1×10^{-4} M in a 1:4 mixture of acetone-d_6 and 0.1M HCl (solid line) and in a 1:4 mixture of acetone-d_6 and 0.1M DCl (broken line), 514.5 nm; (b) 2×10^{-4} M in a 1: 4 mixture of acetone-d_6 and water, 488.0 nm.

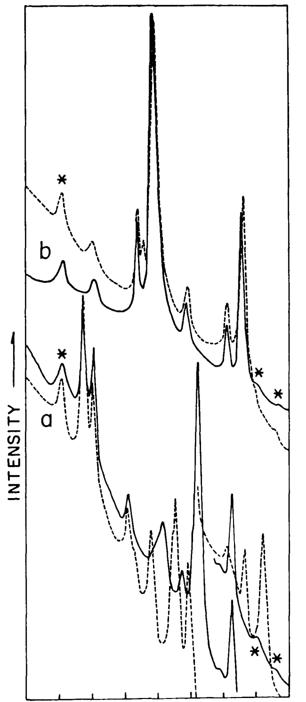


Fig. 4. Resonance Raman spectra of AAB: (a) 5×10^{-4} M in a 1:4 mixture of acetone-d_6 and 0.1M HCl (solid line) and in a 1:4 mixture of acetone-d_6 and 0.1M DCl (broken line), 488.0 nm; (b) 5×10^{-3} M in a 1: 4 mixture of acetone-d_6 and water (solid line) and in a 1: 4 mixture of acetone-d_6 and heavy water (broken line), 488.0 nm.

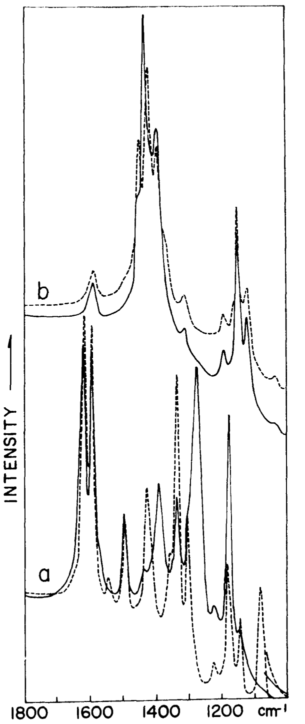


Fig. 5. Resonance Raman spectra of TOO: (a) 1×10^{-4} M in 0.1M HCl (solid line) and in 0.1M DCl (broken line), 514.5 nm; (b) 5×10^{-4} M in water (solid line) and in heavy water (broken line), 488.0 nm.

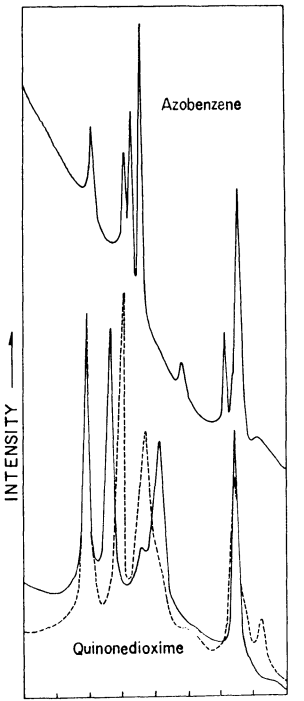


Fig. 6. Resonance Raman spectrum (488.0 nm) of azobenzene in methanol-d_6 (1×10^{-2} M) and Raman spectra (514.5 nm) of solid sample of quinone dioxime (solid line) and its O-deuterated compound (broken line).

The concentration dependence of the Raman intensities was briefly surveyed for MO between 1×10^{-7} M and 1×10^{-3} M, and the optimum concentration was found to be about 1×10^{-4} M for the acid form excited by the 514.5 nm and the 488.0 nm lines and about 3×10^{-4} M for the base form excited by the 488.0 nm line. For the base form, a little higher concentration (about 1×10^{-3} M) was found suitable when the 514.5 nm line was used. The change in the relative intensities of Raman bands on changing the excitation wavelength from 488.0 nm to 514.5 nm was not appreciable and was left out of detailed examination. At the concentrations investigated, no detectable spectral change due to the thermal effect or the decomposition was observed on the prolonged exposure of the samples to the excitation beam. The representative Raman spectra are shown in Figs. 1—6.

The electronic spectra between 380 and 600 nm were recorded on a Shimadzu W-40 spectrophotometer for the same solutions of the indicators as those used for the Raman measurement by using a cell of 1 mm path length. The absorption maxima obtained are given in Table 1. They are essentially the same as those in literatures. The electronic spectra of the indicators in the deuterated solutions, either acidic or basic, were identical with those for the corresponding undeuterated solvents. The infrared spectra of solid samples of diazoaminobenzene and its N-deuterated compound were recorded on a JASCO DS-301 infrared spectrophotometer for Nujol or hexachlorobutadiene mulls (Fig. 7).

Results and Discussion

The yellowish color of any p-aminoazobenzene type indicator in a neutral or a basic solution changes to a reddish color when the solution is acidified to a pH below the color-change interval of the indicator. This color change has been attributed to a change of the molecular structure from an azo-type to a quinoid-type with the protonation to the azo group as shown in Chart 1.[3,6] Such a structure change is expected to give rise to a marked change in the resonance Raman spectra, in which the band intensity is often enhanced for the group vibrations participating in the resonant electronic transition. Previously, Hacker investigated the resonance Raman spectra of a number of azo compounds among which MO in water and MR, AAB, and AB in methanol and CCl_4 were included.[1] The presently recorded spectra for the neutral to alkaline solutions of these compounds are essentially the same as Hacker's result, except the N=N stretching frequency ($\nu_{N=N}$) of MR, for which the present value is about 40 cm^{-1} lower than Hacker's value. Table 2 summarizes the characteristic Raman frequencies of the base form identified by referring to the previous works on the vibrational spectra of azobenzene derivatives.[1,7] By the revision of $\nu_{N=N}$ of MR, a correlation between $\nu_{N=N}$ and the nature of the p-substituent was revealed. If we take the $\nu_{N=N}$ of MO to be the mean value of the doublet frequencies 1395 and 1420 cm^{-1}, the substituents arranged in the decreasing order of $\nu_{N=N}$,

$$H- > C_6H_5NH- > NH_2- > (CH_3)_2N-$$

follow well the order that both the electron donating effect and the pH of the color-change interval (Table 1) increase.

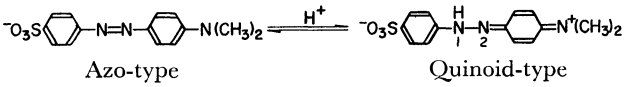


Chart 1

Table 2. Observed frequencies (cm^{-1}) and assignments for the base form

MO	MR	MY	AAB($\Delta\nu$)	TOO($\Delta\nu$)	AB	Assignment
1600 w	1600 vw	1600 w	1600 (0) w	1591 (0) w	1598 m	Benzene ring
1450 w	1460 m	1465 m	1468 (1) m	1455 (0) sh	1475 s	Benzene ring
1420 1395 } vs	1412 vs	1415 vs	1420 (3) vs	1437 (12) vs	1444 vs	N=N str.
1320 w	1325 vw	1320 w	1317 (0) w	1315 (1) w	1318 w	Benzene ring
1200 w	1195 w	1198 w	1193 (0) w	1195 (1) w	1187 m	Benzene ring
1155 m	1150 m	1150 m	1147 (4) m	1150 (1) m	1147 vs	Ph–N str.

$\Delta\nu=\nu$ (in the ordinary solvent) $-\nu$(in the deuterated solvent)

The deuteration of the solvent gives no change in the resonance Raman spectra of the base form of MO, MR, and MY as expected from the azo structure of these indicators containing no active hydrogen. The base form of TOO and AAB in the deuterated solvent gives essentially the same spectra as those in the undeuterated solvent, but the $\nu_{N=N}$ of these compounds are affected a little on the deuteration of the NH or NH_2 group, suggesting a slight coupling of this vibration with the ND or ND_2 deformation vibrations (Figs. 4 and 5).

The resonance Raman spectrum of MO in the 0.1M HCl solution is completely different from that in the neutral solution as shown in Fig. 1. When the pH is adjusted close to the pK_a of MO (3.4 at 25 °C),[8] an intermediate spectral feature between the acid and the base forms is observed in accord with the color change in the visible region (Fig. 1c). The acid form shows no strong Raman band assignable to the N=N stretching vibration near 1420 cm^{-1}, but shows a very strong Raman band at 1624 cm^{-1}, which may be assigned to a stretching vibration of the ring C=C bonds of the quinoid structure. This frequency, however, is appreciably lower than the C=C symmetric stretching frequency of *p*-quinone (1667 cm^{-1} [9,10]), and it is desirable to clarify how far the latter may diminish on replacing both the C=O groups by the C=N– groups. Since the Raman spectra of quinonediimine-like compounds were not found in literatures, we examined the Raman spectra of quinone dioxime and its *O*-deuterated compound, regarding them as the simplest reference compounds. As shown in Fig. 6, quinone dioxime exhibits two strong Raman bands at 1617 and 1544 cm^{-1} assignable to the symmetric C=C and C=N stretching vibrations, respectively. The low-frequency shift of the latter on the *O*-deuteration is quite analogous to the case of the C=N stretching band in the infrared spectrum of quinone monoxime reported by Hadži.[11] Based on this result, the characteristic 1624 cm^{-1} band of MO can be assigned to the C=C stretching vibration. The absence of any strong band assignable to the C=N stretching vibration in the resonance Raman spectrum of MO may be due to the difference either in the substituents on the nitrogen atoms between MO and quinone dioxime or in the sensitivity to the resonance enhancement between the C=C and the C=N stretching vibrations.

The quinoid structure shown in Chart 1 has an active hydrogen atom attached on N_1. If the acid form of MO takes such a structure, the deuteration of this hydrogen by a simple exchange reaction may give rise to a change in the resonance Raman spectrum. In agreement with this expectation, MO in 0.1M DCl shows a much different spectrum from that in 0.1M HCl in the region between 1400 and 1000 cm^{-1} (Fig. 2). In order to clarify the difference in the vibrational frequencies between the Ph–NH–N= and the Ph–ND–N= groups, we examined the effect of the *N*-deuteration on the infrared spectrum of diazoaminobenzene, C_6H_5–NH–N=N–C_6H_5. For this compound, reliable assignments of the Ph–NH–N= group frequencies have been made on the basis of a detailed analysis of various N^{15} isotope shifts in the infrared spectra,[7] but the vibrational spectra of the *N*-deuterated diazoaminobenzene have not yet been reported. Unfortunately, the Raman spectra of diazoaminobenzene could not be recorded because of a very strong fluorescence. According to Kübler *et al.*,[7] the infrared bands at 1520 and 1248 cm^{-1} of diazoaminobenzene arise from the N–H deformation and the Ph–N stretching vibrations, respectively. As shown in Fig. 7, both these bands disappear on the *N*-deuteration, and new bands arising possibly from a coupling which may involve the Ph–N stretching and the N–D deformation vibrations are observed at 1364, 1105, and 1068 cm^{-1} for diazoaminobenzene-*d*. Correspondingly, the resonance Raman band at 1272 cm^{-1} of the acid form of MO is replaced by three bands at 1338, 1145, and 1076 cm^{-1} on changing the solvent from 0.1M HCl to 0.1M DCl. This result is a strong support to the presence of a Ph–NH–N= group in the acid form of MO.

The resonance Raman spectra of MR and MY show marked changes analogous to the case of MO

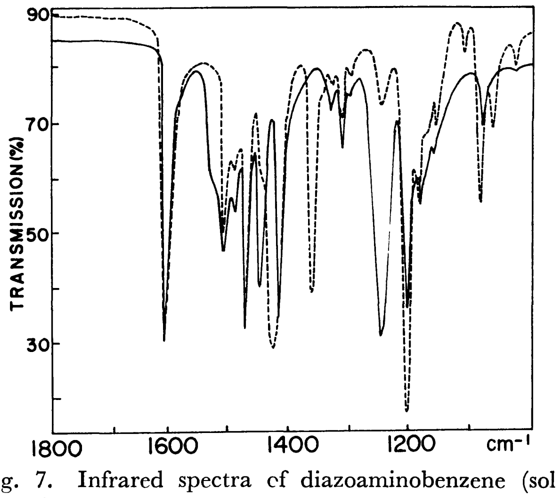


Fig. 7. Infrared spectra of diazoaminobenzene (solid line) and its *N*-deuterated compound (broken line).

not only on the color change from the base form to the acid form but also on the deuteration of the latter. Besides the strongest C=C stretching band around 1620 cm^{-1} and the deuteration sensitive Ph–N stretching band around 1270 cm^{-1}, four bands around 1600, 1500, 1380, and 1180 cm^{-1} are commonly observed for the undeuterated acid forms of MO, MR, and MY. The 1600 and 1500 cm^{-1} bands, which persist in the 0.1M DCl solution, may be assigned to the benzene ring vibrations. The origin of the 1380 cm^{-1} band, which is very weak but is clearly recognized from its disappearance on the *N*-deuteration, is not obvious at this stage. A possible interpretation of this band will be given later. The 1180 cm^{-1} band seems to be the counterpart of the infrared band at 1202 cm^{-1} of diazoaminobenzene due to the N–N stretching vibration,[7] since no effect of the *N*-deuteration is observed in either case. For the quinoid structure of MR, an acid-base equilibrium was suggested from the pH gradient thin layer chromatography.[12] We accordingly measured the resonance Raman spectrum of the acid form of MR at various pH's below the color change interval, and observed a little spectral change around 1400 and 1200 cm^{-1} accompanying the pH change (Fig. 2). This result supports the existence of the equilibrium shown in Chart 2, since the coupled vibrations of the C–O stretching and the OH deformation vibrations of the COOH group[13] and the symmetric stretching vibration of the CO$_2^-$ group[14] are expected to give Raman bands around these frequencies.

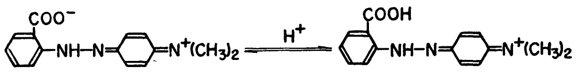


Chart 2

The acid forms of TOO and AAB show similar resonance Raman spectra to that of MO. On changing the solvent from 0.1M HCl to 0.1M DCl, the spectra of these compounds change complicatedly as shown in Figs. 4 and 5, but the characteristic features of the spectral change observed for MO, MR, and MY are recognized also for these compounds. Both TOO and AAB show a band around 1390 cm^{-1} which is replaced by a band around 1430 cm^{-1} on going to the 0.1M DCl solution. The disappearance of the 1390 cm^{-1} band on the *N*-deuteration suggests a common nature between this band and the weak 1380 cm^{-1} band of MO, MR, and MY mentioned above. The high-frequency shift of the latter seems to be obscured by the overlap of a band near 1410 cm^{-1} attributable to the N–CH$_3$ group. For quinone dioxime, an analogous shift of a Ramanb and from 1391 cm^{-1} to 1439 cm^{-1} is observed on the *O*-deuteration. Probably, this band of quinone dioxime corresponds to the b$_{1g}$ C–C stretching band of *p*-quinone[9] and the 1390 cm^{-1} band of TOO and AAB as well as the 1380 cm^{-1} band of MO, MR, and MY may be interpreted on the same basis. The proposed assignments of the resonance Raman bands of the acid form are summarized in Table 3.

According to the present assignment, the quinoid ring C–C stretching frequency for each of the undeuterated and the deuterated acid form increases in almost the same order as the $\nu_{N=N}$ of the base form. This trend is reasonable since both the azo N=N and the quinoid ring C–C bond orders increase on the increase of the azo-type character of the conjugate system, and the electron donation from the amino-nitrogen to the ring opposes this change. For the suructure of the acid form, a resonance hybrid between the quinoid-type and the protonated azo-type has been postulated, the latter being pictured as the azo-type with a hydrogenated and positively charged nitrogen,[15,16] *p*-$(CH_3)_2N-C_6H_4-N=N^+H-C_6H_4-SO_3^-$. The resonance Raman spectra of the acid form as revealed in this work indicate that the quinoid-type is much predominant over the azo-type in this resonance, if any. As suggested by the behavior of the C–C stretching frequency, however, the contribution of the azo-type is not entirely excluded at present. More knowledge on the vibrations of both the quinoid- and azo-type structures seems to be necessary to deal with this hybridization quantitatively.

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TABLE 3. OBSERVED FREQUENCIES (cm^{-1}) OF THE ACID FORM IN THE ORDINARY AND DEUTERATED SOLVENTS AND ASSIGNMENTS

MO		MR		MY		AAB		TOO		Assignments
ord.	deut.	ord.	deut.	ord.	deut.	ord.	deut.	ord.	deut.	
1624 s	1620 s	1623 vs	1621 vs	1623 vs	1620 vs	1630 s	1628 s	1624 vs	1617 vs	C=C str.
1601 sh	1600 sh	1595 sh	1585 vw	1599 m	1595 m	1598 m	1600 m	1594 vs	1593 vs	Benzene ring
1502 m	1500 m	1499 m	1496 m	1499 w	1499 w	1495 m	1495 m	1499 m	1497 m	Benzene ring
1370 sh	1411 m	1385 w	1410 m	1370 vw	1410 w	1386 m	1421 m	1396 m	1430 m	C–C str.[a]
1272 m	1338 m	1288 w	1348 m	1282 s	1350 m	1280 vs	1347 s	1279 vs	1337 s	Ph–N str.
1183 m	1183 m	1190 m	1190 m	1184 m	1184 m	1177 m	1195 w	1178 m	1182 m	N–N str.
—	1145 w	—	1145 w	—	1145 w	—	1140 m	—	1146 w	?
—	1076 w	—	1095 w	—	1084 m	—	1083 s	—	1084 w	?

a) Tentative assignment

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