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A Raman and UV-Vis study of catecholamines oxidized with Mn(III)

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Abstract

A UV-Vis and Raman spectroscopy study of three aminochromes generated through Mn^{3+} oxidation of the dopamine, L-dopa and adrenaline molecules at physiological pH was performed. The UV-Vis spectra of the catecholamines oxidized using Mn^{3+} in buffer solution at pH 7.2 show a band at ca. 300 nm, formed by two transitions at 280 nm and 300 nm assigned to an L_a and L_b transition respectively, and other at ca. 470 nm assigned to an $n-\pi^*$ transition localized in the carbonyl group. This assignment is suggested by the UV-Vis and Raman spectra of *ortho*-aminoquinone generated by MnO_2 oxidation of a dopamine aqueous acidic solution. The resonance Raman spectra of the three chromes at buffer pH 7.2 show a very similar feature and the most intense bands are observed in the spectral range 1100–1800 cm^{-1}. The band around 1680 cm^{-1} for the three compounds is assigned to a ν(C=O) stretching vibration, 1630 cm^{-1} to the ν(C=C) ring mode, two bands at 1423, 1439 cm^{-1}; 1427, 1438 cm^{-1} and 1456, 1475 cm^{-1} are assigned to a $\nu(C=N^+)$ vibration, for aminochrome, dopachrome and adrenochrome, respectively. The excitation profiles for the most intense bands for aminochrome and adrenochrome were obtained. The band assigned to the $\nu(C=N^+)$ present a red shift with respect to the visible band peak, however the band in adrenochrome at 1475 cm^{-1} shows a profile similar to ν(C=O) and ν(CC) modes that reflects the methyl group effect on mixing this mode more effectively with the ν(CC) ring mode.

Keywords: Catecholamines; Manganese; Aminochromes; Resonance Raman

1. Introduction

Parkinson's disease is believed to be caused in large measure by a reduction in level of a catecholamine neurotransmitter, dopamine (4-(2-aminoethyl)benzene-1,2-diol), in the caudade nucleus due to death of more than 80% in the dopamirnegic cells of the substantia nigra.

Graham [1] performed spectrophotometric studies on the pathways by which dopamine, norepinephrine (4-(2-amino-1-hydroxyethyl)benzene-1,2-diol) and adrenaline (4-[1-hydroxy-2-(methylamino)ethyl]benzene-1,2-diol) can be oxidized to aminochrome, noradrenochrome and

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adrenochrome, through exposure to oxygen at basic pH. He proposed that the oxidative process that results in the production of superoxide radicals also promotes the oxidation of the catecholamines to quinone products. Such products polymerize to form neuromelanin, which accumulates progressively with time within the cytoplasm of the neuron. Then this oxidative pathway produces potentially toxic products in the cell. The proposed [1–3] oxidative mechanism is shown in Fig. 1.

Archibald and Tyree [4] have shown that when L-dopa (3-hydroxytyrosine)in a physiological buffer was mixed with Mn(III)-pyrophosphate complex there was an immediate (< 5 s) appearance of visible color, easily discernible from the Mn(III)-pyrophosphate color by its much greater intensity and different visible maximum (476 nm). This final product also presents a band at 302 nm and is stable for at least several hours; the author's assignment was aminochrome, the dehydro-indole-*o*-quinone derivative of dopa. When Mn(III)-pyrophosphate was added to buffered dopamine, the results were identical to those with DL-dopa. The authors noted that if the Mn^{3+} oxidized DL-dopa and dopamine were left in aqueous solution, the solution blackened over several hours, suggesting a slow melanin-like polymerization of the quinones. Another observation was that Mn^{2+} does not react with the catecholamines while Mn^{3+} does so vigorously.

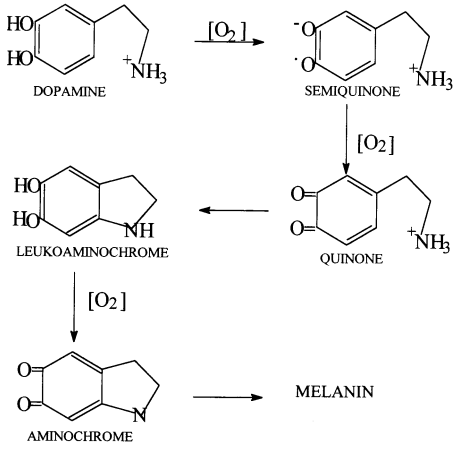

Fig. 1. The proposed oxidative pathway for dopamine.

The resonance Raman spectra can provide important information about the nature of the molecular electronic transitions. The resonance Raman spectrum has the characteristic of presenting a very selective feature because only a few vibrational modes involved in electronic transition are intensified.

Resonance Raman spectra of the aminochromes generated through periodate oxidation of catecholamines, have been reported to have been used as an analytical tool for trace level quantitative determination [5–7]. Also SERRS (Surface-enhanced resonance Raman scattering) [8] and NIR-SERS [9] have been suggested as powerful tools for the quantitative determination of cathecolamines.

In this article, continuing our studies on quinone systems [10] and resonance Raman scattering [11,12], we report a UV-Vis and Raman spectroscopy study of three aminochromes generated through Mn^{3+} oxidation of the dopamine, L-dopa and adrenaline molecules at physiological pH. We also report the Raman and UV-Vis spectra of the *ortho*-quinone derived from adrenaline.

2. Experimental section

2.1. Reagents

Dopamine hydrochloride, L-dopa-free and adrenaline-free bases were supplied by the Sigma (St. Louis, MO) and used without further purification. The 0.01 M phosphate buffer solutions, pH 7.2, were prepared using 0.1 M sodium hydroxide solution and 0.1 M KH_2PO_4 with further dilution. Bi-distilled water was always used. The Mn(III)-pyrophosphate complex in aqueous solution, pH 7, was prepared as reported [4] and is stable for at least 6 months.

The *ortho*-quinones were prepared for the UV-Vis spectra dissolving the MnO_2 dust in stoichiometric quantities (2:1) to obtain a 5.00×10^{-4} M aqueous solution of the catecholamines (pH 1). Hydrochloric acid was used for acidification.

For Raman spectra the *ortho*-quinone samples were prepared using a saturated acid solution of the catecholamines and MnO_2 was added until no more reaction was observed. The adrenaline and L-dopa *ortho*-quinones are unstable in the laser beam and decompose with time.

2.2. Raman measurements

A rotating cell was used to avoid sample decomposition, and the laser beam emerged very close to the glass wall to minimise reabsorption. The compound stabilities were a critical problem for the Raman resonance studies, even using a laser power not exceeding 30 mW on the sample. The chromes are intermediate compounds in the course of the auto-oxidation processes (Fig. 1) with a short lifetime which is no more than 60 min. When the chromes are irradiated with a laser, their respective lifetimes are reduced and it is impossible to measure the six spectra in a sequence, since the total incidence time would be ca. 2 h. To surmount this experimental problem the original procedure of Raman resonance studies was developed but changing the samples after each measurement.

To obtain reproducible spectra it was necessary to use a standard procedure in preparing the samples. All solutions of dopamine, L-dopa and adrenaline were freshly made and kept in the dark until to be used. To 3 cm^3 of the 5×10^{-4} M catecholamine solution, pH 7.2 and O_2 free, was added 250×10^{-6} dm^3 of the 0.035 M Mn(III)-pyrophosphate solution. The solution was bubbled with N_2 for 4 min and centrifuged for 2 min to precipitate the $Mn(OH)_2$ produced by Mn(III) reduction. After the spectrum acquisition using a laser line, a new sample preparation was made for the next laser line.

Good and reproducible spectra were obtained for the aminochrome and adrenochrome using this procedure for the laser lines at 514.5, 501.7, 496.5, 488.0, 476.0 and 457 nm. Two spectra were obtained for each laser line and the intensities were calculated measuring the band area and dividing them by the sulphate standard area. Two experiments were developed in duplicates and the intensities presented correspond the average of two measurements in each radiation excitation.

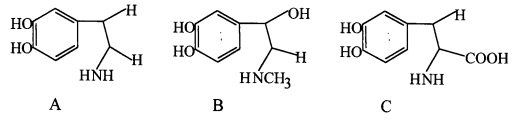

Fig. 2. A schematic structure of the compounds (trivial and systematic name):(A) dopamine, (4-(2-aminoethyl)benzene-1,2-diol), (B) adrenaline, (4-[1-hydroxy-2-(methylamino)ethyl]-benzene-1,2-diol), (C) L-dopa,(3-hydroxytyrosine).

For the dopachrome, the best spectrum was obtained around the maximum absorption band, and its resonance profile is not presented because the signal/noise ratio was very low in 457 nm laser excitation.

2.3. Raman instrumentation

The Raman spectra were obtained in a Jobin–Yvon U1000 Raman spectrometer equipped with a double monochromator and fitted with an RCA high gain photomultiplier tube. The Raman spectra were obtained using Ar^+ ion laser lines (Ion Laser Innova 400-Coherent), with a spectral resolution of 7 cm^{-1}. Spectra were acquired using the Enhanced Prism Software 3.1 (Jobin Yvon Division Instruments) and processed in Labcalc Arithmetic A1.2 (Galactic Industries).

2.4. UV-Vis instrumentation

A DU-7500 Beckmann Spectrophotometer and a Perkin–Elmer Lambda 5 were used to record the ultra-violet and visible spectra.

3. Results and discussion

3.1. UV-Vis study

3.1.1. The catecholamines

In a 0.01 M phosphate buffer solution at pH 7.2 the three compounds show two bands in the UV range: at 220 and 281 nm for dopamine, at 225 and 280 nm for adrenaline, at 222 and 282 nm for L-dopa. Fig. 2 present a schematic structure for the compounds and the Fig. 3(a) the spectra of the L-dopa as exemple.

These electronic transitions are directly related to those of the parent benzene molecule at 183, 203 and 253 nm. In benzene the first band is assignable to a strong allowed $\pi-\pi^*$ (or $B_{a,b}$ in Platt's notation) transition and the last two are the weak symmetry-forbidden transitions L_a and L_b.

We know that substitutions on the benzene ring lower the symmetry and introduce some allowed character into symmetry-forbidden transitions. The perturbation is observable for tyrosine, with a hydroxyl and a methylene substituent, where the L_a and L_b have higher intensity and are red-shifted relative to benzene: 193 nm for the $\pi-\pi^*$ transition and 222–273 nm for the L_a-L_b transitions, respectively. When the perturbation is strong, like the tryptophan molecule with a pyrrole ring fused onto the benzene ring, the two bands L_a and L_b overlap in the 280 nm range and the $\pi-\pi^*$ transition shifts to 218 nm [13].

Considering these arguments we may tentatively assign the transitions at 220 and 280 nm in catecholamines, with two hydroxyl and one aliphatic group substituents, to a $\pi-\pi^*$ and an L_a-L_b coincident transition, respectively.

3.1.2. The chromes

The UV-Vis spectra of the catecholamines oxidized using Mn^{3+} in buffer solution at pH 7.2 show marked modification in the visible region as

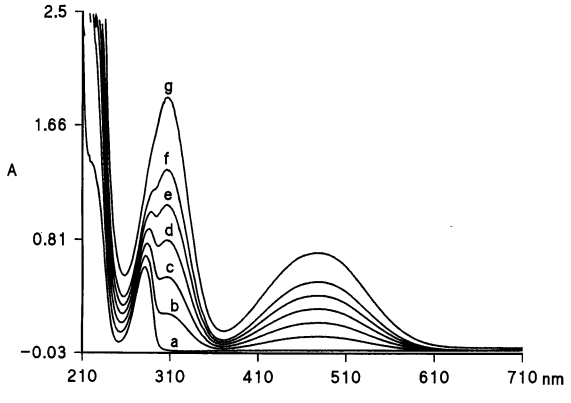

Fig. 3. UV-Vis spectra of: (a) L-dopa 9.6×10^{-5} M in 0.01 M phosphate buffer pH 7.2; (b) (g) L-dopa oxidized during the successive addition of a 0.035 M Mn^{3+}-pyrophosphate solution to the (a) solution, until an excess of Mn^{3+} ion is present.

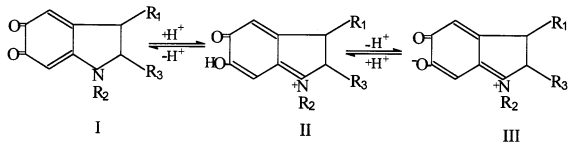

Fig. 4. Acid-base equilibrium suggested for the aminochromes in aqueous solutions at neutral pH where the dipolar ion (III) is the predominant form. For aminochrome R_1=H_2, R_2=H_2 R_3=H_2, adrenochrome R_1=OH, R_2=CH_3, R_3=H_2 and dopachrome R_1=H_2, R_2=H_2, R_3=COOH.

compared to the reagents. Fig. 3(b–g) show the spectra obtained during the Mn^{3+} oxidation for L-dopa. The same spectrum pattern was observed for adrenaline and dopamine during the oxidation processes. During the oxidation a band appears at ca. 300 nm rising progressively in intensity until it overlaps the band at 280 nm that clearly does not change in intensity and finally results in a broad band centered at 307 nm (for dopamine at 301 nm and adrenaline, 303 nm). This broad and intense band is formed by two transitions around the peak at 300 nm. An intense band rises at 475 nm for L-dopa (for dopamine at 473 nm and adrenaline at 478 nm), and is a characteristic electronic transition of the chrome form.

In aqueous solutions at neutral pH, the predominant chrome form would be the dipolar ion III in acid-base equilibrium [1,14] (Fig. 4).

In order to make a tentative assignment of these bands we refer to indole and indole-derivates. First we will consider the band at 300 nm composed of two transitions. In tryptophan, the L_a and L_b transitions overlap, the resulting band having a maximum at 280 nm: since the tryptophan molecule has a very similar structure to the chromes, these latter are expected to show the same effect. The details of the nature of L_a and L_b can be understood using the indole assignation.

In a recent study on the electronic transitions of indole and its methyl and methoxy derivatives [15], the bands at 287 and 265 nm are assigned to a $1L_b \leftarrow 1A_1$ and a $1L_a \leftarrow 1A_1$ transition, respectively. The separation between these two transitions is sensitive to the substitution site. The presence of a substituent in position 3 lowers the energy of the L_a transition whereas substitutions

in positions 5 and 6 lower the L_b transition energy. In the chrome molecule positions 5 and 6 have a carbonyl group, and thus a similar shift is expected.

Considering these observations we assigned the band at 280 nm to the L_a transition and that at 300 nm to the L_b. Taking these arguments into consideration, the carbonyl group substitution on indole in positions 5 and 6 seems to be much more effective in changing the L_a and L_b transitions in terms of intensities and frequencies as compared with substitution on position 3. This is the case of adrenaline where position 3 is occupied by a hydroxyl group and the same spectrum pattern is observable.

The bands at 480 nm can be assigned to an $n-\pi^*$ transition localized in the carbonyl group where the ring pyrrole formation caused a delocalization effect over the indole structure, lowering the transition energy, and consequentely leading to a red shift for this transition. This assignment is suggested by the spectrum of *ortho*-aminoquinone (Fig. 5) generated by MnO_2 oxidation of a dopamine aqueous acidic solution (Fig. 6)

A close analysis of the spectra as functions of time allows us to see an intense band at 225 nm and a weak band at 280 nm (Fig. 5(a)). After a few minutes a shoulder at 293 nm rises gradually until it has the same intensity as the 280 nm band, and an intense band at 386 nm appears (Fig. 5(b–e)).

The band at 225 nm can be assigned to a $\pi-\pi^*$ transition and the 293 nm band to the overlapped L_a and L_b transitions. The band in the visible region, 395 nm, is $n-\pi^*$ transition due to the carbonyl group attached to benzene ring, and is a characteristic band for the identification of the *ortho*-quinone family [16]. This band disappears when the solution is neutralized to pH 7. At this pH the aminochrome is readily formed by a nucleophilic nitrogen attack on the benzene ring resulting in an indole-like structure [17].

3.2. Raman study

3.2.1. The Raman spectra

The resonance Raman spectra of the three chromes at buffer pH 7.2 show a very similar feature (Fig. 7).

Table 1 gives the observed wavenumber (cm^{-1}) for the three compounds. The most intense bands are observed in the spectral range 1100–1800 cm^{-1}. The in-plane-skeleton vibrations and the carbonyl group vibration should fall within this region.

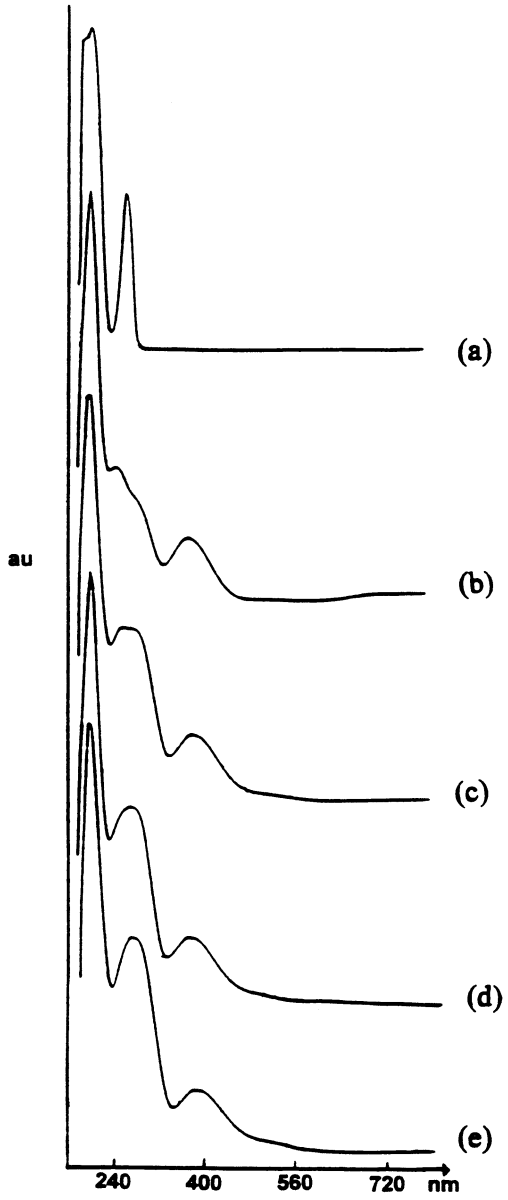

Fig. 5. (a) UV-Vis spectrum of 1×10^{-4} M dopamine solution prepared in 30% HCl. (b–e) UV-Vis spectra of the *ortho*-aminoquinone generation at time by the oxidation with excess of MnO_2 dust added to the solution (a).

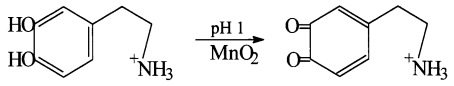

Fig. 6. The proposed mechanism of the dopamine oxidation with MnO_2 at pH 0–1.

The band around 1680 cm^{-1} for the three compounds is assigned to a ν(C=O) stretching vibration. This band is obviously absent before the oxidation with the Mn^{3+} ion in the dopamine for exemple (Fig. 8(b)), but is observed in this same region in the *ortho*-aminoquinone spectrum (Fig. 8(a)). The evidence for *ortho*-quinone formation is the absence of the intense Raman band at ca. 1290 cm^{-1} assigned to ν(C–OH) stretching. An intense band is observable at ca. 1630 cm^{-1}, and is assigned to the ν(C=C) stretching vibration of the benzene ring. In the *ortho*-aminoquinone this band is also observable in the oxidized as well as in the unoxidazed form. The bending mode of water, at ca. 1640 cm^{-1}, also lies between these two bands and is the origin of the broad feature in this region.

The spectral range 1400–1500 cm^{-1} causes greater difficulties for assignments. In dopachrome, aminochrome and adrenochrome, two bands are present at 1427, 1438 cm^{-1}, 1423, 1439 cm^{-1} and 1456, 1475 cm^{-1} respectively, and seem to arise from similar vibrations. In tryptophan there can be observed three bands in this region denominated W_4, W_5 and W_6 (in Takeuchi notation [18]) at 1487, 1458 and 1424 cm^{-1} respectively. The vibrations W_5 and W_6 are basi-

Table 1
Raman shift (ν (cm^{-1})) of adrenochrome, dopachrome and aminochrome principal bands and a tentative assignment

Mode	Adreno-chrome	Dopa-chrome	Amino-chrome
τ Ring	349		387
τ Ring	416	431	404
τ Ring	457	526	427
τ Ring	465	533	462
τ Ring	598		
τ Ring	621		
τ Ring	660		624
ν(CC)	669	665	658
W_{12} or ν(CH)	1178	1175	1178
W_7 or ν(CH):ν(CC)	1385	1343	1345
W_6.or.ν(C=N$^+$):ν(C–H)	1456	1427	1423
W_5 or ν(C=N$^+$):ν(C–H)	1475	1438	1439
W_1 or ν(CC)	1627	1632	1632
ν(C=O)	1686	1679	1680

Obervations: τ are ring or CH out-of-plane modes [19,20], W nomenclature from Maruyama and Takeuchi [18] and Rahaman and Korenkiewicz [19].

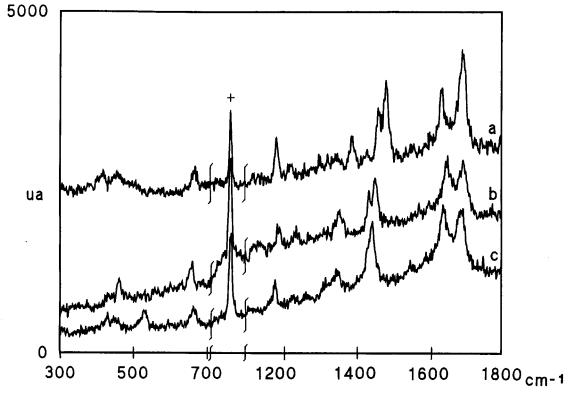

Fig. 7. The resonance Raman spectra of: (a) adrenaline (b) dopamine (c) L-dopa, 5×10^{-4} M in phosphate buffer pH 7.2 using $\lambda = 514.5$ nm laser radiation and 30mW of power laser on the sample. The band indicated with a plus (+) is the ca. 990 cm^{-1} sulphate internal standard.

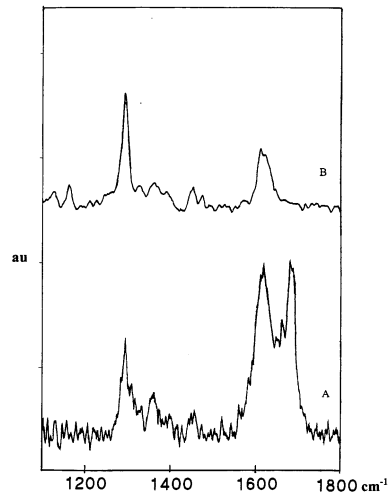

Fig. 8. Raman spectra using capillary and the laser radiation of $\lambda = 514.5$ nm for: (a) *ortho*-aminoquinone in 30% HCl solution with 70 mW laser power, (b) saturated dopamine solution in phosphate buffer pH 7.2 with 30 mW laser power.

cally ring skeleton displacements and involve hydrogen motions together with a substantial NH bending contribution. The W_4 band due to a CH bending vibration disappears from the 1490 cm^{-1} region under deuteration and appears around 820 cm^{-1} [18].This observation supports the assignment of the two aminochrome bands in this region as W_6 and W_5 vibrations. Morris [5] assigned these two bands to a $\nu(C{=}N^+)$ or a $\nu(C{=}N^+{-}C)$ vibration. In the adrenochrome molecule these frequencies show a shift to higher wavenumbers not observable in the other two chromes. This shift is due to the interaction of the methyl group motions with the ν(CN) mode when it is attached to the nitrogen atom.

This effect is also observed in the adrenalin-copper complex [19]. The Raman spectrum of this compound shows three bands in this region at 1480, 1460 and 1435 cm^{-1} assigned to the ν(CN), $\nu(H_3C{-}N)_{as}$ and $\nu(H_3C{-}N)_s$ modes respectively. The band at 1480 cm^{-1} assigned to a ν(CN) stretching, appears at 1435 cm^{-1} in the copper noradrenaline complex where no such interaction can take place since the complex has no methyl group. This frequency shift is also observed for the amide II' mode at 1450 cm^{-1} in deuterated *N*-methylacetamide and at a much lower frequency (1338 cm^{-1}) for diformylhydrazine which has no methyl groups [20].

The bands in the 1300–1380 cm^{-1} region are difficult to assign. In indole and tryptophan [21] only one fundamental, ν_{14} [22] (or W_7 in Takeuchi notation) is expected in this range and is described as a β(CH) mode with little ν(CC) contribution from the pyrrole ring. The bands present at 1385, 1343 and 1345 cm^{-1}, in adrenochrome, dopachrome and aminochrome respectively, seem to have the same origin.

For the three compounds the band at ca. 1170 cm^{-1} is probably the ν_{18} mode at 1203 cm^{-1} in the indole molecule, described as a benzene ring deformation and pyrrole-benzene ν(CC) stretching. The predominance of the benzene ring deformation in the mode composition may explain the small frequency shift between the compounds and the lack of dependence under the pyrrole ring substitutions.

It is a very interesting fact that in the 700–1100 cm^{-1} region, enhanced Raman bands are not present. In this range one expects there to appear the more intense Raman band at 789 cm^{-1}, (dopamine in aqueous solution) and 800 cm^{-1} (adrenaline in acid aqueous solution). This band is also observable as the most intense line of the indole Raman spectrum at 758 cm^{-1} (liquid). In tryptophan this band appears strongly enhanced at 762 cm^{-1} in the resonance Raman spectrum which is excited in the $B_{a,b}$ transition (218 nm).

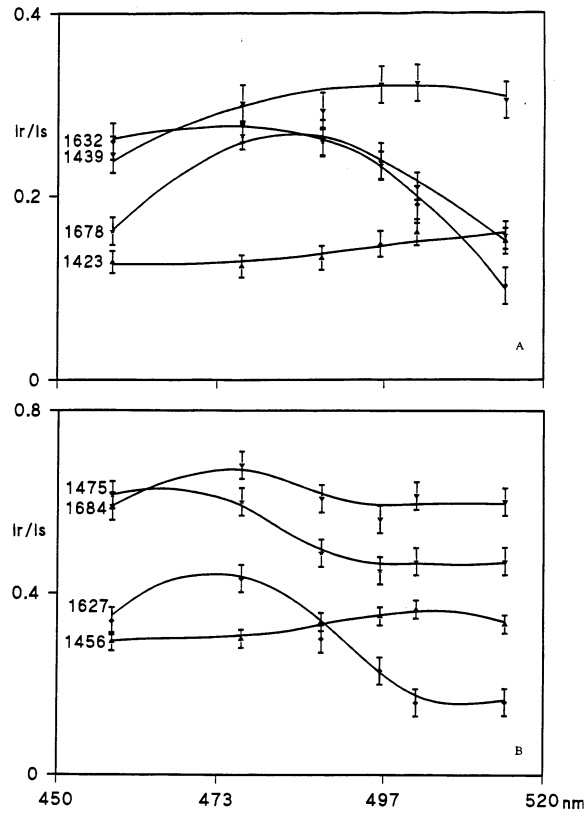

Fig. 9. Resonance Raman profile of 5×10^{-4} M of: aminochrome (A) and adrenochrome (B) in 0.01 M phosphate buffer pH 7.2 solution using the exciting radiation, 514.5, 501.7, 496.5, 488.0, 476.0 and 457.9 nm. To avoid the decomposition 30 mW laser power was used, and each value is the average of two measurements. The band resolution was ca. 7 cm^{-1}. The sulphate band at ca. 990 cm^{-1} was used as internal standard (I_r/I_s).

This band is assigned to the benzene and pyrrole ring-breathing in-phase mode [13].

In the 300–600 cm^{-1} range bands are observed that are assigned in the indole molecule, via a normal coordinate analysis, to ring out-of-plane bending modes [22].

The CO^- stretching mode, falling around 1260 cm^{-1} in anionic adrenaline, is observed in adrenochrome as a very weak band at 1215 cm^{-1}.

3.2.2. The excitation profiles

The excitation profiles for the most intense bands of aminochrome and adrenochrome are displayed in Fig. 9(a, b). The profiles obtained for dopachrome are not sufficiently reproducible. For the two compounds the bands assigned to ν(C=O) and ν(C=C) modes show the same profile pattern, with a maximum at ca. 470 nm. The band assigned to the $\nu(C{=}N^+)$ mode at 1456 cm^{-1} in adrenochrome and at 1423 cm^{-1} aminochrome present a red shift with respect to the visible band peak; however the band in adrenochrome at 1475 cm^{-1} shows a profile similar to ν(C=O) and ν(CC) modes.

This differences can be understood as the result of a usual Franck–Condon mechanism where, in this case, the modes with a strong ν(CN) contribution have a B term (B = Franck–Condon displacement) higher as compared with the other modes, and exhibit an expected red shift. The profile of the vibration at 1475 cm^{-1} in adrenochrome probably reflects the methyl group effect on mixing this mode more effectively with the ν(CC) ring mode.

The absence of the enhanced bands in the 700–1100 cm^{-1} range, where the intense breathing ring vibrations present in tryptophan are expected, indicates a different origin for this chromophore. This mode in tryptophan can be expected to exhibit a strong Franck–Condon activity in the allowed π–π^* transition. It is evident that in the n–π^* transition the same activity is not allowed and the molecule in the dipolar ion form presents a more localized chromophore, possibly between the carbonyl group (ν(CO) enhanced) and the pyrrole ring ($\nu(CN^+)$ enhanced).

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References

[1] D.G. Graham, Mol. Pharmacol. 14 (1978) 633.
[2] R.A. Heacock, Advan. Heterocycl. Chem. 5 (1965) 205.
[3] E. Herlinger, R. F. Jameson, W. Linert, J. Chem. Soc. Perkin Trans. 2 (1995) 259.
[4] F.S. Archibald, C. Tyree, Arch. Biochem. Biophys. 256 (2) (1987) 638.
[5] M.D. Morris, Anal. Chem. 47 (14) (1975) 2453.
[6] M.S. Rahaman, M.D. Morris, Talanta 23 (1976) 65.
[7] C.-Y Chen, M.D. Morris, J. Chromatogr. 540 (1991) 355.
[8] W.K. Kowalchyk, K.L. Davis, M.D. Morris, Spectrochim. Acta Part A 51A (1) (1995) 145.
[9] K. Kneipp, Y. Wang, R.R. Dasari, M.S. Feld, Spectrochim. Acta Part A 51A (3) (1995) 481.
[10] W.J. Barreto, D.A.M. Zaia, L.F.C. de Oliveira, Spectrochim. Acta Part A 50A (6) (1994) 1031.
[11] M.C.C. Ribeiro, W.J. Barreto, P.S. Santos, J. Raman Spectrosc. 25 (1994) 923.
[12] P. Sassi, M.L. Ceccarini, R.S. Cataliotti, Ber. Bunsen. Phys. Chem. 99 (1995) 779.
[13] R.P. Rava, T.G. Spiro, J. Phys. Chem. 89 (1985) 1856.
[14] R.T. Borchardt, E.E. Smissman, D. Nerland, J R. Reid, J. Med. Chem. 19 (1976) 30.
[15] B. Albinsson, B. Nordén, J. Phys. Chem. 96 (1992) 6204.
[16] F. Zhang, G. Dryhurst, Bioorganic Chem. 21 (1993) 392.
[17] J.D. Bu'Lock, J. Harley-Mason, J. Chem. Soc. (1951) 712.
[18] T. Maruyama, H. Takeuchi, J. Raman Spectrosc. 26 (1995) 319.
[19] M.S. Rahaman, S.M. Korenkiewicz, Can. J. Chem. 54 (24) (1976) 3815.
[20] T. Miyazawa, T. Shimanouchi, S.-I. Mizushima, J. Chem. Phys. 29 (3) (1958) 611.
[21] I. Harada, H. Takeuchi, in: R.J.H. Clark, R.E. Hester (Eds.), Spectroscopy of Biological Systems: Chapter 3, Wiley, Chichester, 1982, p. 117.
[22] M. Majoube, G. Vergoten, J. Raman Spectrosc. 23 (1992) 431.