J. Braz. Chem. Soc., Vol. 9, No. 5, 487-493, 1998.
Printed in Brazil.

0103 – 5053 $6.00 + 0.00

Article

Spectroscopic Study of the Interaction of Nd^{3+} with Amino Acids: Phenomenological 4f-4f Intensity Parameters

***Soraya Jericó*[a], *Célia R. Carubelli*[a], *Ana M.G. Massabni*[a], *Elizabeth B. Stucchi*[a], *Sergio R. de A. Leite*[a]*, *and Oscar Malta*[b]**

[a]*Instituto de Química, Universidade Estadual Paulista C.P. 355, 14801-970 Araraquara – SP, Brazil*

[b]*Departamento de Química Fundamental, Universidade Federal de Pernambuco, 50670-901 Recife – PE, Brazil*

Received: June 1, 1998

Estudamos o comportamento dos parâmetros fenomenológicos de intensidade das transições 4f-4f em compostos de Nd^{3+} com glicina, ácido L-aspártico, ácido L-glutâmico, L-histidina, ácido DL-málico e Aspartame® em solução aquosa como função dos valores de pK e das cargas parciais sobre os átomos de oxigênio dos grupos carboxilatos dessas moléculas. Os resultados são discutidos e interpretados qualitativamente em termos dos mecanismos das intensidades 4f-4f por dipolo elétrico forçado e acoplamento dinâmico, indicando como dominante o mecanismo de dipolo elétrico forçado.

We have studied the bevahior of the phenomenological 4f-4f intensity parameters in compounds of the Nd^{3+} ion with glycine, L-aspartic acid, L-glutamic acid, L-histidine, DL-malic acid and Aspartame^{TM} in aqueous solution, as a function of the pK values and partial charges on the oxygens of the carboxylate groups of these molecules. The results are discussed and qualitatively interpreted in terms of the forced electric dipole and dynamic coupling mechanisms of the 4f-4f intensities, thus indicating that the forced electric dipole mechanism is dominant.

Keywords: *neodymium, amino acids, transition intensity parameters*

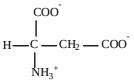
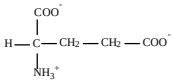
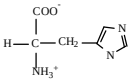
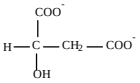
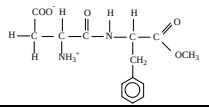
Introduction

The study of the chemical bonding between trivalent lanthanide ions (Ln^{3+}) and amino acids or peptides has its origin in the interest in using these ions as structural probes in biological systems, particularly in those systems which contain Ca^{2+} in their structure[1,2]. The Ca^{2+} ion is optically inactive and is, therefore, not suitable for providing information, through optical spectroscopic measurements, about the chemical environment in which it is embedded. On the other hand, almost all Ln^{3+} ions are know to exhibit rich optical spectra, either in absorption or emission, and it occurs that, due to the similarity between ionic radii, they may substitute Ca^{2+} ions in the chemical structures.

There is strong evidence that the bonding between Ln^{3+} ions and amino acids is made with the oxygens of the carboxylate group, and that the bonding via the nitrogen of the amino group is unlikely to occur at least in a range of pH values up to 5.6[3,4]. In this paper we examine the relation between the basicity of the carboxylate groups of glycine (Gly), L-aspartic acid (Asp), L-glutamic acid (Glu), L-histidine (His), DL-malic acid (Mal) and Aspartame^{TM} (APM) (Table 1), and the intensity parameters of 4f-4f transitions in their compounds with Nd^{3+} ion. The intensity parameters are qualitatively interpreted in terms of the forced electric dipole and dynamic coupling mechanisms of 4f-4f intensities[5-10]. Both mechanisms are dependent on the chemical environment around the Ln^{3+} ion. The basicity of the carboxylate groups is considered according to pK values and partial atomic charges on the oxygens which were calculated from molecular mechanics and the semi-empirical PM3 quantum chemical method.

* Correspondence should be addressed at: Instituto de Química - UNESP, C.P. 355, 14801-970 Araraquara – SP, Brazil.

Table 1. Covalent structures of the ligands.

Name	Structural formula[(a)]	pK_1 [(b)] (α-COOH)	pK_2	pK_R (side chain)
Glycine		2,34	9,60 (α-NH_3+)	
Aspartic acid		1,88	9,60 (α-NH_3+)	3,65 (β-COOH)
Glutamic acid		2,19	9,67 (α-NH_3+)	4,25 (γ-COOH)
Histidine		1,82	9,17 (α-NH_3+)	6,00 (imidazole)
Malic acid		3,40 (α-COOH)	---	5,11 (β-COOH)
Aspartame		2,40 [(c)]	---	---

(a) Ionic forms predominating at pH 7,0; (b) The pKa values from the *CRC Handbook of Chemistry and Physics*[21]; (c) Estimated value from titration curves in this work.

Experimental

The samples were prepared from aqueous solutions of $Nd(ClO_4)_3$ and the amino acids glycine, L-aspartic acid, L-glutamic acid and L-histidine, the dipeptide Aspartame™ or the DL-malic acid. The absorption spectra were measured in a Carl Zeiss M-40 UV-visible spectrophotometer between 11000 cm^{-1} and 30000 cm^{-1}. Solutions of $Nd(ClO_4)_3$ with pH 5.0-5.5 were prepared from Nd_2O_3 (Aldrich, 99.99%) and standardized by EDTA / xylenol orange titration. Solutions of the ligands were standardized by titration with NaOH / phenolphtalein or by potentiometric titration. The concentration of all solutions were around 5.00 x 10^{-2} mol L^{-1}.

We have firstly examined the behavior of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ hypersensitive transitions of Nd^{3+}, between 16600 cm^{-1} and 18200 cm^{-1}, as a function of the molar ratio Nd^{3+}: Ligand and the pH of the solution, which was varied from 1 to 5.5 for each ratio. The solutions of the $Nd(ClO_4)_3$ and the ligand were mixed in a quartz cell of 1.00 cm optical pathway which was coupled to a quartz bulb with 20 mL capacity. Volumes were measured with calibrated pipetes. The molar ratio Nd^{3+} / Ligand was varied from 1:1 to 1:10. The pH was adjusted by addition of acid or base and measured directly in the cell with a combined glass microelectrode. Concentrations were corrected for the volume. Wavenumber scan was made with variable slits and constant energy beam at the photodetector and the absorbance values were read to the fourth decimal place in a digital display. All the measurements were made at 25 ± 1 °C. Doubly destilated water was used as reference. The samples with the ratio Nd^{3+} / Ligand and pH that gave the highest absorption in the region of hypersensitivity were used to obtain the entire spectra from which the spectroscopic parameters were obtained. The best ratio Nd^{3+} / Ligand is 1/4 except for the Nd^{3+} / Aspartame, in which case the experimental oscilator strength always rises with increasing of the quantity of the ligand. Figure 1 shows the curves of P_{exp} *vs.* pH for several samples using histidine as ligand. As we see, P_{exp} decreases as the ratio goes to higher values than 1/4.

As we observed nine groups of transitions in the entire spectral region under investigation, we obtained nine equations for P (Eq. 2), where the following values were introduced for the calculation of τ_λ: experimental P values as obtained in the Eq. 1, experimental σ values as the baricenter of a group of transitions obtained from the area measurements under the absorption curve, $U^{(\lambda)}$ values as obtained of the medium value for the $U^{(\lambda)}$ of the transitions in each group[11]. A program in BASIC was developed to treat these nine equations by a least square method to obtain the τ_λ parameters. The least square method reduces a system of n equations with 3 unknown quantities to a system of 3 equations with 3 unknowns, which are the phenomenological τ_λ parameters.

Results and Discussion

The experimental oscillator strengths are obtained through the expression

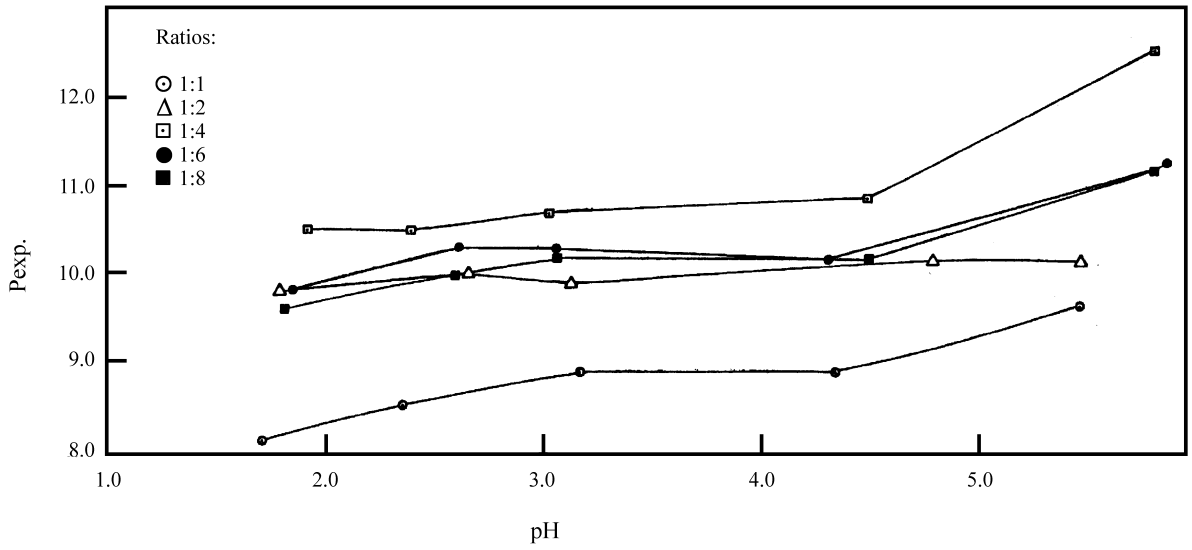


Figure 1. Oscillator strength *vs.* pH. Nd^{3+}: L-histidine system.

$$P_{exp} = 4.318 \times 10^{-9} \int \varepsilon(\sigma)\, d\sigma \quad (1)$$

were $\varepsilon(\sigma)$ is the molar extintion coefficient at wavenumber σ (cm^{-1}) and the integral in Eq. 1 is directly proportional to the area under the absorption curve.

According to the theory of 4f-4f intensities[5], the oscillator strength of a transition between two manifolds, with respective total angular momenta J and J', of a given $4f^N$ electronic configuration is given by:

$$P = \sum_{\lambda = 2,4,6} \frac{\sigma\, \tau_\lambda < (4f^N)\, \psi\, 'J' \,||\, U^{(\lambda)} \,||\, (4f^N)\, \psi\, J >^2}{(2J+1)} \quad (2)$$

where σ is the baricenter of the transition energy (in wavenumbers), $U^{(\lambda)}$ is a unit tensor operator of rank λ and the τ_λ are the so-called intensity parameters which depend on the chemical environment, radial integrals and interconfigurational energy differences in the lanthanide ion. The reduced matrix elements of $U^{(\lambda)}$ in Eq. 2 have been calculated, in the intermediate coupling scheme, for the whole series of the trivalent lanthanides[12].

An alternative way of expressing the theoretical oscillator strength has been of common use in the literature, in terms of the Ω_λ intensity parameters which are related to the τ_λ parameters by $\Omega_\lambda = \tau_\lambda / 1.085 \times 10^{11}\, \chi\ cm^{-1}$, where $\chi = (\eta^2 + 2)^2/9\eta$, η being the index of refraction of the medium[13]. For the sake of comparison with the results of previous studies on 4f-4f intensities in compounds of trivalent lanthanides with amino acids[14,15], the expression of the theoretical oscillator strength in terms of the τ_λ intensity parameters as in Eq. 2 is used in the present work.

In principle these parameters can be calculated from theoretical models provided structural data around the lanthanide ion are available[5,9]. However, a common procedure is to treat them as adjustable parameters to reproduce the observed oscillator strengths. The τ_λ thus obtained are refered to as phenomenological intensity parameters. In this procedure the least square method is commonly used in which the input data are the values of the measured oscillator strengths, the squared reduced matrix elements of $U^{(\lambda)}$ and the transition energies σ. Table 2 presents the values of the oscilator strengths and transition energies, corresponding to the transitions observed in the absorption spectrum of the complex with L-aspartic acid, as a function

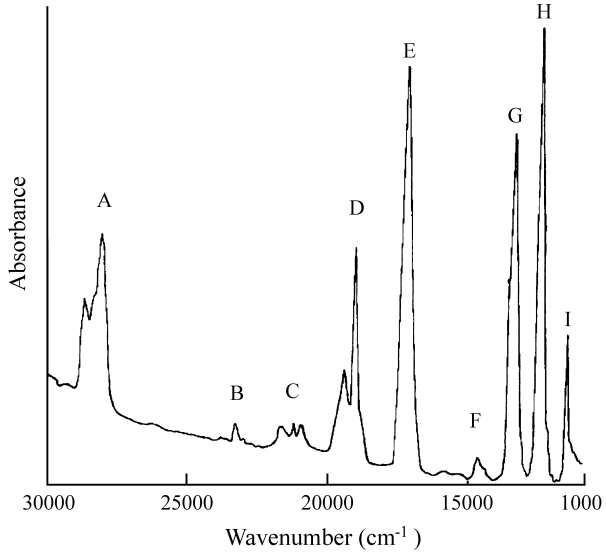


Figure 2. Absorption spectrum of $Nd(ClO_4)_3$: L-aspartic acid in aqueous solutions.
Transitions from the $^4I_{9/2}$ to: A) $^2L_{15/2}$, $^4D_{1/2}$, $^4D_{5/2}$, $^2I_{11/2}$, $^4D_{3/2}$ B) $^2P_{1/2}$ C) $^4G_{11/2}(^2D, ^2P)_{3/2}$, $^2G_{9/2}$, $^2K_{15/2}$ D) $^4G_{9/2}$,$4G_{7/2}$, $^2K_{13/2}$ E) $^4G_{5/2}$, $^2G_{7/2}$ F) $^4F_{9/2}$ G) $^4S_{3/2}$, $^4F_{7/2}$ H) $^2H_{9/2}$, $^4F_{5/2}$ I) $^4F_{3/2}$.

Table 2. Spectral transitions of Nd(III) complexed by L-aspartic acid: average wavenumber (spectral band baricenter), experimental and calculated oscillator strength at some pH values.

Transition from $^4I_{9/2}$ to:	pH	ν (cm^{-1})	Pexp (x 10^9)	Pcalc. (x 10^9)
$^2L_{15/2}$, $^4D_{1/2}$, $^4D_{5/2}$, $^2I_{11/2}$, $^4D_{3/2}$	1.6	28415	8.90	10.0
	2.4	28415	8.80	10.0
	3.5	28390	8.45	10.0
	4.2	28365	9.05	10.2
	5.4	28365	8.74	9.30
$^2P_{1/2}$	1.6	23360	0.40	0.400
	2.4	23355	0.400	0.400
	3.5	23345	0.400	0.400
	4.2	23355	0.300	0.400
	5.4	23340	0.300	0.200
$^4G_{11/2,}$ (^2D, $^2P)_{3/2,}$ $2G_{9/2}$, $^2K_{15/2}$	1.6	21350	1.70	1.50
	2.4	21320	1.70	1.50
	3.5	21355	1.60	1.50
	4.2	21350	1.66	1.50
	5.4	21345	1.51	1.40
$^4G_{9/2,}$ $4G_{7/2}$	1.6	19250	5.40	5.70
	2.4	19235	6.50	5.70
	3.5	19240	6.75	5.80
$^2K_{13/2}$	4.2	19240	6.90	5.90
	5.4	19240	6.44	5.70
$^4G_{5/2}$, $^2G_{7/2}$	1.6	17365	8.90	10.6
	2.4	17350	9.10	11.1
	3.5	17315	11.0	11.8
	4.2	17305	11.7	11.8
	5.4	17305	12.0	12.7
$^4F_{9/2}$	1.6	14700	0.500	0.900
	2.4	14685	0.500	0.900
	3.5	14690	0.495	0.900
	4.2	14710	0.565	0.900
	5.4	14700	0.528	0.900
$^4S_{3/2}$, $^4F_{7/2}$	1.6	13490	8.22	12.5
	2.4	13485	8.30	12.4
	3.5	13480	8.40	12.4
	4.2	13470	8.31	12.4
	5.4	13470	8.30	12.4
$^2H_{9/2}$, $^4F_{5/2}$	1.6	12540	8.60	10.6
	2.4	12548	8.10	10.6
	3.5	12560	8.10	10.3
	4.2	12532	8.10	10.4
	5.4	12533	8.10	10.6
$^4F_{3/2}$	1.6	11533	2.00	2.10
	2.4	11550	2.10	2.10
	3.5	11540	2.20	2.10
	4.2	11543	2.10	2.20
	5.4	11540	2.00	2.00

of the pH. It may be noted that the intensity of the hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2},2G_{7/2}$ transitions increases as the pH increases up to aproximately 5.4 value. For pH values above 5.5 the Nd^{3+} ion hydrolyses.

In the fitting procedure to obtain the phenomenological τ_λ parameters, the squared reduced matrix elements of $U^{(\lambda)}$ for the transitions separated by groups, as indicated in Table 2, were summed together. The results are presented in Table 3.

In the case of the glycine ligand, the τ_λ values presented in Table 3 in the range of pH above the pK_1 agree with the values obtained by Legendziewicz *et al.*[14,15] for the compounds in the crystalline phase. The same agreement is not observed when the ligand is glutamic acid, where τ_4 and τ_6 are discrepant from the solid state values. This fact can be explained if we consider that the two carboxylate groups of the glutamic acid may or may not be involved in the coordination at the pH value used in these measurements.

Among the τ_λ parameters, in general τ_2 is the most sensitive to the coordination geometry and the characteristics of the ligands[13]. We have examined the behavior of τ_2 with the ligand's pK; τ_2 has varied linearly with pK_1 provided the monocarboxylic and dicarboxylic species were considered separately (Fig. 3). We have also examined the behavior of τ_2 with the average value <pk> = (pK_1 + pK_2) / 2, since at pH ~5 both carboxylic groups are expected to be equally deprotonated. In this case, τ_2 has increased with <pk>, but not linearly (Fig. 4). Note that in this plot, <pk> = pK_1 for the monocarboxylic species.

An interesting correlation is also obtained between τ_2 and the average partial charges on the carboxylate oxygens. The molecular amino acid modelling was performed by empirical calculation methods. Firstly, the geometry optimization was made by a method of molecular mechanics, using a modified MM2 force field[16,17,18] named MM+, and the Polak-Ribiere minimum energy search procedure[19]. Secondly, a single point calculation was performed by the quantum mechanical semi-empirical PM3 method[20]. This

Table 3. Observed values of the τ_λ parameters (x 10^9 cm^{-1}).

Ligand	PH	τ_2	τ_4	τ_6
Glycine	5.08	3.22	4.63	10.8
	4.04	3.26	4.33	10.5
	3.02	3.27	4.36	10.5
	2.06	2.41	5.44	10.8
	1.07	2.10	5.35	10.7
L-Aspartic acid	5.43	3.60	4.82	9.50
	4.22	3.28	5.07	9.55
	3.50	3.05	4.74	9.69
	3.40	1.82	4.90	9.64
	1.62	1.70	4.85	9.65
L-Glutamic acid	5.42	4.06	7.17	5.59
L-Histidine	5.45	3.17	4.46	11.1
	4.17	2.83	4.52	11.1
	3.68	2.74	4.32	10.9
	2.84	2.30	5.12	10.6
	1.72	2.10	5.20	10.7
DL-Malic acid	5.45	4.92	7.38	13.3
Aspartame™	5.05	3.24	5.16	11.6
	4.10	2.91	3.73	11.1
	3.61	2.86	4.91	10.8
	2.88	2.56	4.92	10.8
	1.81	2.19	4.93	10.6

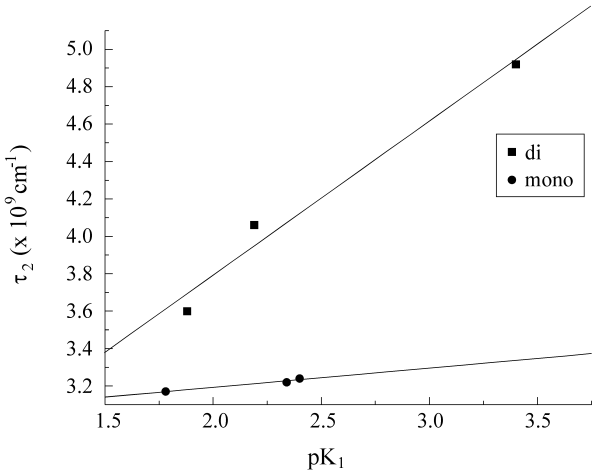


Figure 3. Judd-Ofelt parameter τ_2 versus first ionization acid constant pK_1. From left to right:
• monocarboxylic acids: His, Gly, APM
■ dicarboxylic acids: Asp, Glu, Mal.

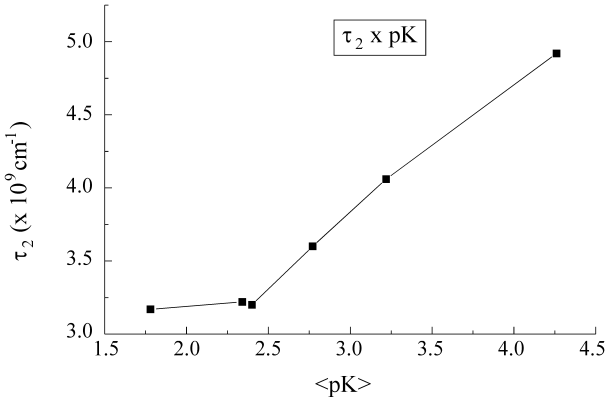


Figure 4. Judd-Ofelt τ_2 parameter versus the carboxylic acid average ionization constants <pK>= (pK_1 + pK_2)/2. For monocarboxylic species, <pK> values are merely the pK_1. From left to right: His, Gly, APM, Asp, Glu and Mal.

leads to the partial atomic charges in the ligands. The idea is not to get the most reliable set of partial atomic charges, but rather to follow the trends involving partial charges on the oxygens, the pK values, and consequently the basicity of the oxygens, and τ_2. The results are summarized in Table 4. Figure 5 shows a plot of τ_2 *vs.* the average charges on the carboxylate oxygens. As in the case of Fig. 4 an increasing behavior of τ_2 is also observed.

Figure 6 indicates the partial charges on the concerned atoms of the ligand molecules.

The oxygen charges in Table 4 and Fig. 5 correspond in each case to the average value between the charges on the oxygens of the carboxylate groups.

From the point of view of the ligand field theory, the larger the negative charge on the oxygens, the greater is the ionic interaction between the ligand and the lanthanide ion.

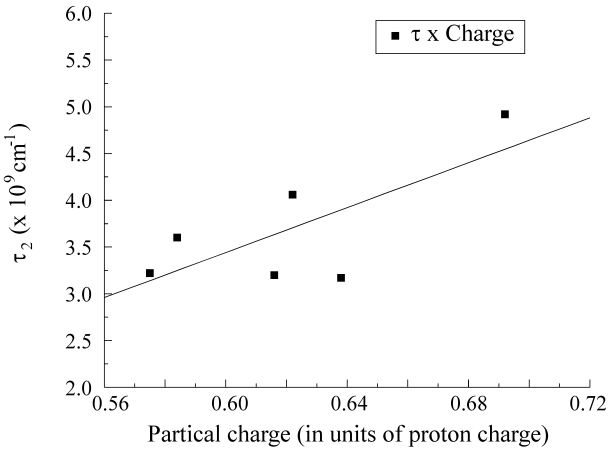


Figure 5. Judd-Ofelt parameter τ_2 *vs.* average carboxylic oxygen partial charges, in units of electron charge.

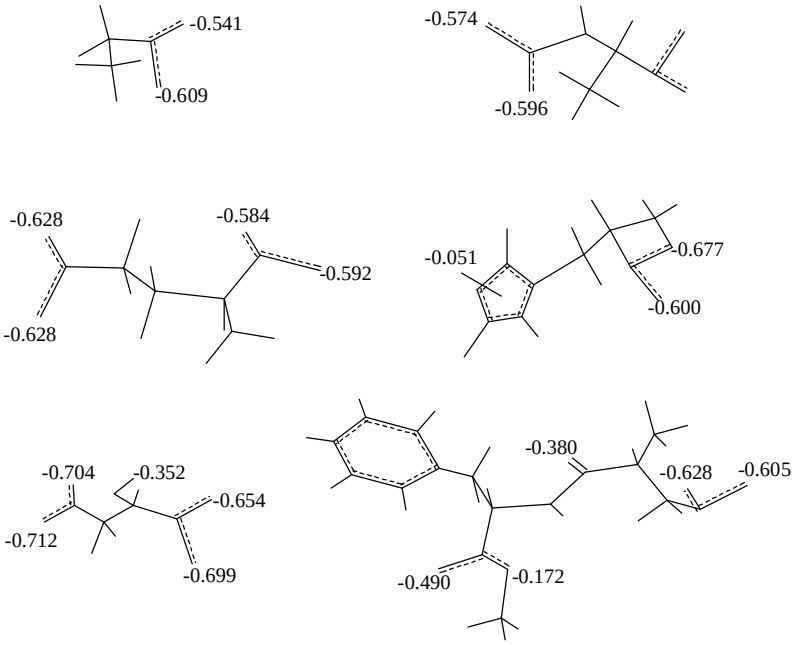


Figure 6. Optimized structures of ligand molecules with Mülliken partial atomic charges, calculated by a PM3 semiempirical quantum mechanical method. From top to bottom and left to right: glycine, L-aspartic acid, L-glutamic acid, L-histidine, DL-malic acid and Aspartame™.

Table 4. Average atomic charges on carboxylate oxygens, as obtained from a PM3 calculation. Comparison with τ_2 values and average pK.

Ligand	Average charge of carboxylate oxigens	τ_2 (x 10^9 cm^{-1})	$(pk_1+pK_2^*)/2$
Glycine	-0.575	3.22	2.34**
L-Aspartic Acid	-0.584	3.60	2.77
L-Glutamic Acid	-0.622	4.06	3.22
L-Histidine	-0.638	3.17	3.88
DL-Malic Acid	-0.692	4.92	4.26
Aspartame™	-0.616	3.20	5.0***

* For L-histidine and Aspartame™, pK_2 is the constant for the 2nd acid group ionized at the concerned pH, which in these cases is not a carboxylate group; ** Only pK_1; *** Estimate from a titration plot.

Theoretically, it has been accepted that there are two dominating mechanisms contributing to the τ_λ parameters. These are the forced electric dipole and dynamic coupling mechanisms[8,9]. The τ_λ can be expressed as:

$$\tau_\lambda = C \sum_{t,p} \frac{|B_{\lambda,t,p}|^2}{(2t+1)} \quad (3)$$

where C is a constant and the quantities $B_{\lambda,t,p}$ are the so-called intensity parameters for 4f-4f transitions between individual Stark levels. The $B_{\lambda,t,p}$ are expressed as a sum of the two contributions:

$$B_{\lambda,t,p} = B_{\lambda,t,p}\,(\text{forced electric dipole}) + B_{\lambda,t,p}\,(\text{dynamic coupling}) \quad (4)$$

It has been shown that these two contributions have opposite signs[10]. A strong ligand field tends to favor the forced electric dipole mechanism. Further, the dynamic coupling Hamiltonian is directly proportional to the oxygen polarizability, which decreases as the localized charge on the oxygens increases. Thus, the observed increasing behavior of τ_2 with the pK and with the partial charges on the carboxylate oxygens suggests that, in the present compounds with the Nd^{3+} ion, the forced electric dipole mechanism is dominant. On the other hand, it is not obvious why this increasing behavior of τ_2 is approximately linear. This is a point which deserves a more detailed theoretical analysis and is beyond the scope of this paper.

Finally, we notice that in the range of pH with acceptable τ_λ values, there is a predominant complex species that allows a comparative analysis of the results in the scope of this work.

Acknowledgments

The authors acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and the Fundação para o Desenvolvimento da UNESP (FUNDUNESP) for financial support. FUNDUNESP also helped in meeting the publication costs of this article.

We are also very grateful to Prof. Romeu Magnani (IQ-UNESP) for the development of the computational program to calculate the τ_λ parameters.

References

1. Nieboer, E. *Structure and Bonding*, **1975**.
2. Martin, R.B.; Richardson, F.S. *Quart. Rev. Biophys.* **1979**, *12*, 181.
3. Prados, R.; Stadtherr, L.G.; Donato Jr., H.; Martin, R.B. *J. Inorg. Nucl. Chem.* **1974**, *36*, 689.
4. Legendziewicz, J.; Huskowska, E.; Kozlowski, H.; Jezowska-Trzebiatowska, B. *Inorg. Nucl. Chem. Letters* **1979**, *15*, 349.
5. Judd, B.R. *Phys. Rev.* **1962**, *127*, 750.
6. Ofelt, G.S. *J. Chem. Phys.* **1962**, *37*, 511.
7. Mason, S.F.; Peacock, R.D.; Stewart, B. *Chem. Phys. Letters* **1974**, *29*, 149.
8. Judd, B.R. *J. Chem. Phys.* **1979**, *70*, 4830.
9. Malta, O.L.; Ribeiro, S.J.L.; Faucher, M.; Porcher, P. *J. Phys. Chem. Solids* **1991**, *52*, 587.
10. Xia, S.-D.; Reid, M.F. *J. Phys. Chem. Solids* **1993**, *54*, 777.
11. Carnall, W.T.; Fields, P.R.; Rajnak, K. *J. Chem. Phys.* **1968**, *49*, 4424.
12. Carnall, W.T.; Crosswhite, H.; Crosswhite, H.M. In *Energy Level Structure and Transition Probabilities of the Trivalent Lanthanides in LaF_3*, Argonne National Laboratory, Report, 1977.
13. Peacock, R.D. *Structure and Bonding* **1975**, *22*, 83.
14. Legendziewicz, J.; Huskowka, E.; Strek, W.; Jezowsk-Trzebiatowska, B. *J. Luminescence* **1981**, *24/25*, 819.
15. Legendziewicz, J.; Huskowska, E.; Argay, Gy.; Waskowska, A. *Inorg. Chim. Acta*. **1984**, *95*, 57.
16. Allinger, N.L. *J. Am. Chem. Chem. Soc.* **1977**, *99*, 8127.
17. Allinger, N.L.; Yuh, Y.H. In *Quantum Chemistry Program Exchange*, Bloomington, IN Program # 395.
18. Burkert, U.; Allinger, N.L. In *Molecular Mechanics*, ACS Monograph 177, 1982.
19. HyperChem™ In *Computational Chemistry*, Autodesk, Sausalito, CA, 1993.
20. Stewart, J.J.P. *J. Comp. Chem.* **1991**, *12*, 320.
21. Lide, D.R., editor; "CRC Handbook of Chemistry and Physics", 72nd ed., 1991-1992.

FAPESP helped in meeting the publication costs of this article