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Vibrational spectra and assignments of amino acid L-asparagine

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The infrared and Raman spectra of L-asparagine and its ND_3^+ , ND_2 deuterated derivative as solid samples were recorded and measured. In the basis of the isotopic shifts obtained a general assignment of the fundamental vibrations of this molecule was proposed. To support these assignments, a normal coordinate analysis was performed by using the MNDO semiempirical method.

1. INTRODUCTION

In the last few years the vibrational spectra of amino acids related with both glutamic and aspartic acids have been extensively studied [1-5]. These works involved infrared and Raman spectra, deuterium and 15-nitrogen substitutions, and normal coordinate calculations. Here we present some results concerning the amino acid asparagine, $\text{NH}_3^+\text{-CH}(\text{COO}^-)\text{-CH}_2\text{-CONH}_2$, a molecule that plays an important role in the metabolic control of cell functions in nerve and brain tissue [6]. In spite of its interest, this amino acid has received a relatively little attention from researchers up to this date, and we have not found previous works on the interpretation of the vibrational spectra of asparagine. Therefore it seemed useful to study it in depth from this point of view.

2. EXPERIMENTAL

The vibrational spectra were obtained by using untreated L-asparagine monohydrate (98+% of purity) furnished by Sigma. Asparagine- d_5 acid was prepared by lypholizing the natural derivative twice from D_2O (99.9 atom % D, Aldrich), obtaining a high degree of substitution checked by measuring the N-D and O-D stretching and bending vibrations.

Infrared spectra between 4000 and 400 cm^{-1} were obtained from potassium bromide pellets on a Perkin Elmer 1700X FTIR spectrophotometer purged with Ar gas, with a spectral resolution of 2 cm^{-1} . Raman spectra from microcrystalline powder were recorded on a Jobin Yvon Ramanor U1000 spectrometer, using excitation radiations at 514.5 nm generated by a Spectra

Physics Ar⁺ ion laser working at 300-500 mW. The best resolution obtained was 1 cm⁻¹.

3. CALCULATIONS

The semiempirical MNDO method was used as implemented in the MOPAC [7] package. The quadratic force constants were calculated by evaluating the first and second analytical derivatives of the energy respect to the cartesian coordinates. Previously we had to find the molecular structure corresponding to a minimum in the potential energy surface where the calculated frequencies were all positive. This point was obtained starting from the zwitterionic structure and allowing that all the geometrical parameters were optimized simultaneously.

The initial cartesian force field was transformed to a set of local symmetry

Table 1
Experimental^a and calculated structural parameters^b for asparagine.

Bond	Exper.	MNDO	Angle	Exper.	MNDO
C ₁ -C ₂	1.518	1.642	C ₂ -C ₁ -O ₅	115.7	115.1
C ₁ -O ₅	1.265	1.248	C ₂ -C ₁ -O ₆	118.2	114.3
C ₁ -O ₆	1.247	1.240	C ₁ -C ₂ -C ₃	115.7	116.0
C ₂ -C ₃	1.511	1.542	C ₁ -C ₂ -H ₇	104.4	106.0
C ₂ -H ₇	0.973	1.119	C ₁ -C ₂ -N ₈	110.8	108.5
C ₂ -N ₈	1.501	1.522	C ₃ -C ₂ -H ₇	110.9	107.9
C ₃ -C ₄	1.516	1.536	C ₂ -C ₃ -C ₄	112.5	115.7
C ₃ -H ₁₂	1.006	1.114	C ₂ -C ₃ -H ₁₂	105.3	106.9
C ₃ -H ₁₃	0.987	1.117	C ₂ -C ₃ -H ₁₃	106.7	110.3
C ₄ -O ₁₄	1.243	1.235	C ₃ -C ₄ -O ₁₄	120.6	121.7
C ₄ -N ₁₅	1.332	1.401	C ₃ -C ₄ -N ₁₅	116.5	118.4
N ₈ -H ₉	0.932	1.025	C ₂ -N ₈ -H ₉	109.5	112.1
N ₈ -H ₁₀	0.954	1.024	C ₂ -N ₈ -H ₁₀	109.2	110.2
N ₈ -H ₁₁	0.935	1.021	C ₂ -N ₈ -H ₁₁	112.2	112.9
N ₁₅ -H ₁₆	0.929	1.003	C ₄ -N ₁₅ -H ₁₆	119.8	116.7
N ₁₅ -H ₁₇	0.919	1.003	C ₄ -N ₁₅ -H ₁₇	122.1	116.5

^a Values from Reference 10.

^b Numerical values are bond lengths in angstroms and angles in degrees.

coordinates defined following the Pulay coordinate description [8]. In order to obtain a better set of calculated frequencies and descriptions the force constants were scaled by transferring a set of scaling factors from similar molecules. Frequencies and normal coordinates were determined by the Wilson FG matrix method [9]. All calculation were performed in a VAX 8530 computer.

4. RESULTS AND DISCUSSION

The structure of asparagine monohydrate was obtained with X-rays diffraction [10]. The molecules in the crystal appear as zwitterions which are stabilized by several hydrogen bonds involving the water molecules. A single asparagine molecule has 17 atoms, having 45 normal vibrations, all of these infrared and Raman actives. In order to describe easily the fundamentals, we have adopted a set of symmetrized local modes as reported elsewhere [4]. The assignments were based on the measured isotopic shifts and on correlations with previous studies about aspartic acid and glutamine [2,4]. The results concerning the optimized structural parameters are listed in the Table 1, where they are compared with the experimental values, while the Table 2 summarizes the observed and calculated frequencies for the hydrogen and deuterium stretching vibrations of asparagine-h₅ and asparagine-d₅ respectively, and the proposed assignments.

As can be observed in the Table 1, the optimized data compare favourably

Table 2

Hydrogen stretching frequencies (in cm⁻¹) of asparagine-h₅ and asparagine-d₅.

Assignment	Asparagine-h ₅		Asparagine-d ₅	
	Observed	Calculated	Observed	Calculated
$\nu_a(\text{NH}_2)$	3384	3383	2501	2452
$\nu_a(\text{NH}_3^+)$	3243	3238	2348	2370
$\nu_a(\text{NH}_3^+)$	-	3212	2319	2348
$\nu_s(\text{NH}_2)$	3112	3119	2303	2291
$\nu_s(\text{NH}_3^+)$	-	3037	2172	2191
$\nu_a(\text{CH}_2)$	2934	2936	2935	2936
$\nu(\text{CH})$	2958	2952	2960	2952
$\nu_s(\text{CH}_2)$	2967	2974	2968	2974

with those experimental, taking into account that the calculation was performed with an isolated asparagine molecule. As expected, the C-H and N-H bond distances were overestimated systematically; however the fitting for the bonds between the weighed atoms is satisfactory. An exception is the C₁-C₂ bond length; the calculated value, 1.642 Å, deviates appreciably from the observed data, 1.518 Å. This result were always obtained in the semiempirical calculations performed on other amino acids, and it gives rise to a carbon-carbon stretching force constant smaller that the rest of C-C coordinates. Concerning bond angles, the experimental values have been reproduced with minimal errors, even for those involving the polar groups.

The observed frequencies listed in the Table 2 compare well with those reported for and other similar molecules such as glutamine, specially for the three stretching vibrations, which were reported at 2963, 2952 and 2933 cm⁻¹ [2], being the rest of frequencies of near values. As was pointed above, the initial set of force constants was scaled by transferring the scaling factors from glutamine and aspartic acid [3,4]. For the hydrogen stretching force constants we have used the following scaling factors: 0.84 (C_α-H), 0.80 (C-H sym.), 0.86 (C-H antisym.), 0.75 (N-H sym.) and 0.89 (N-H antisym.). The MNDO method systematically evaluate the symmetrical stretching vibrations at higher frequency than the antisymmetrical one, therefore the scaling factors for the former have to be always smaller. As can be seen in the Table 2, the differences between the observed and calculated frequencies are negligible in both the natural and deuterated derivatives, except for the N-D antisymmetric stretching modes, and the proposed assignments were confirmed by the potential energy distribution in all the cases.

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