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Conformational Analysis

The Shape of Neutral Valine**

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Nowadays there is growing interest in the study of biomolecules under isolation conditions in the gas phase. Although the gas phase represents far from in situ conditions of the condensed medium in which biological reactions take place, important intramolecular properties of bare molecules are manipulated by the environment and it is difficult to distinguish in condensed phases which properties are intrinsically intramolecular.[1] Solid amino acids exhibit a bipolar zwitterionic structure[2] ($^{+}NH_3CH(R)COO^{-}$) far from that of the neutral structure present in the polypeptide chain as a result of intermolecular interactions. Therefore, the investigation of the neutral structure of amino acids must be conducted in the gas phase. The problem arises from the fact that most amino acids have high melting points and extremely low vapor pressures and quickly decompose under the classical heating methods of vaporization. Thus, only a limited number of studies on amino acids have been carried out in the gas phase.[1a–b] Relevant structural aspects concerning these building blocks of life are as yet unknown.

The amino acids have many possible degrees of freedom which result in a corrugated potential energy surface with many conformational minima, and the population can be spread over more than one minimum. Their conformational preferences are controlled by a delicate balance between the covalent forces and the noncovalent interactions, mainly intramolecular hydrogen bonding. The use of the collisionless environment of a supersonic jet expansion[3] constituted a major step forward in the isolation and detection of the existing conformers in the gas phase. The supersonic cooling quenches the population into the zero-point levels of each of the individual conformers if the potential-energy barriers separating them are sufficiently high. Thus, although the molecules are rotationally and vibrationally cooled, their conformational distribution is not necessarily so. Hence, conformers can be independently detected in the supersonic expansion and their individual structures can be obtained.

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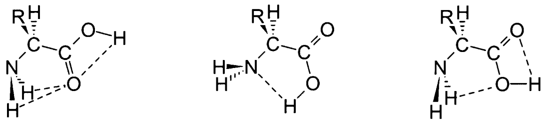
Two experimental approaches are mainly being used in the spectroscopic studies of amino acids and biological molecules in the gas phase.[1] Jet-cooled electronic spectroscopy (laser-induced fluorescence (LIF),[4,5] resonant two-photon ionization spectroscopy[6,7] (R2PI), and UV/UV or UV/IR "hole-burning"[8,9] double-resonance methods) has been applied to the three aromatic natural amino acids of phenylalanine,[4,8] tyrosine,[4,7] and tryptophan[5,6,9] since strong UV chromophoric absorptions facilitate the detection of the electronic spectrum corresponding to each conformer. Another experimental approach is based on microwave spectroscopy. Rotational studies of supersonically cooled amino acids provide detailed structural information for each of the individual conformations that are present in significant populations in the adiabatic expansion. Thermal heating has only enabled the study of the aliphatic natural amino acids glycine[10] (m.p. 240 °C) and alanine[11] (m.p. 315 °C), either in static samples[10a–c] or in supersonic jets.[10d–f,11] Laser-ablation and -desorption techniques[12] constitute an alternative way to overcome the problem caused by the low vapor pressures of the amino acids. Since the first experiment was carried out by Levy and co-workers,[13] this method of vaporization has been applied successfully in combination with laser spectroscopy techniques[14] for the study of neutral molecules of biological interest. Suenram and co-workers[10d] reported the first trial of the use of a laser ablation device in the analysis of the rotational spectrum of glycine in the microwave region. No improvement was observed over that obtained with the usual heating method. We have recently developed a new instrument based on a laser ablation system in combination with Fourier transform microwave spectroscopy in a supersonic jet (laser-ablation molecular-beam Fourier transform microwave, LA-MB-FTMW). This system has been successfully applied to the structural study of the natural amino acid proline (m.p. 228 °C), and two conformers were observed in the supersonic jet.[15]

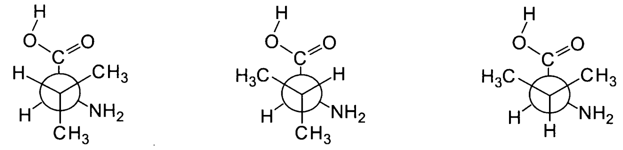
Valine (m.p. 295–300 °C) is an aliphatic natural α-amino acid ($NH_2CH(R)COOH$) with a lateral isopropyl chain ($R = CH(CH_3)_2$). Like glycine[10] (R = H) and alanine[11] ($R = CH_3$), the conformational behavior of valine should reflect the stabilizing effects from the *cis*-carboxylic functional group and the potential formation of the three intramolecular hydrogen bonds shown in Scheme 1. Configuration **I** is stabilized by a bifurcated amine-to-carbonyl (N–H···O=C) hydrogen bond, while configuration **II** exhibits an intramolecular hydrogen bond between the hydrogen atom of the hydroxy group and the lone pair of electrons on the nitrogen atom (N···H–O). A third plausible form **III** exhibits an intramolecular hydrogen bond between the amine group and the oxygen atom of the hydroxy group (N–H···O–H). Configurations **I** and **II** have been observed by rotational spectroscopy in glycine[10] and alanine,[11] with configuration **I** being the most stable one.



I (N-H···O=C and *cis*-COOH) **II** (N···H-O) **III** (N-H···O-H and *cis*-COOH)

Scheme 1. Intramolecular hydrogen bonds and α-amino acid backbone configurations.

Additionally, the presence of a bulky lateral isopropyl group in valine could generate much greater steric demands compared to the methyl group of alanine, which could affect the conformation of the amino acid backbone of the molecule. Three unstrained staggered orientations of the isopropyl side chain "a", "b", and "c" (Scheme 2) can be considered for each of the three configurations above. Ab initio molecular orbital calculations[16] predict different energies for for the side-chain orientations.



Conformer **Ia** Conformer **Ib** Conformer **Ic**

Scheme 2. Possible conformations for configuration **I** of valine.

No previous experimental studies of valine in the gas phase have been reported. The application of our LA-MB-FTMW technique to valine will provide the first information on the conformation and structure of the neutral form of this natural amino acid. The results will help to understand how the intramolecular interactions govern the conformational behavior.

The experimental spectroscopic searches were initially guided by simple structural models and theoretical predictions. We focused our attention on the previously predicted nine lowest energy conformers[16] (Figure 1) and ab initio calculations were conducted using second-order Møller–Plesset perturbation theory (MP2) with a standard 6-311++G(d,p) basis set[17] to predict values of relevant molecular properties such as rotational constants, the ^{14}N nuclear quadrupole coupling parameters, and the components of the electric dipole moment (Table 1). After long scans around the regions where the most intense transitions were predicted, a set of R-branch μ_a-type transitions of a near-prolate asymmetric rotamer were readily assigned. The experimental measurements were completed with R-branch μ_b-type transitions, but no μ_c-type transitions were observed. In addition to the Doppler splitting (see Experimental Section), all the transitions exhibited ^{14}N nuclear quadrupole hyperfine structure (Figure 2), thus confirming the presence of a single nitrogen atom. The measured rotational frequencies were fitted[18] to a Hamiltonian given by $H_{\mathrm{R}}^{(A)} + H_Q$, where $H_{\mathrm{R}}^{(A)}$ represents the Watson A-reduced semirigid rotor Hamiltonian[19] and H_Q is a nuclear quadrupole coupling interaction term,[20] to give the rotational parameters of Table 2. At first glance, the predicted rotational constants of Table 1 indicated the presence of conformer **IIa** in the supersonic expansion. However, a definitive argument came from the excellent

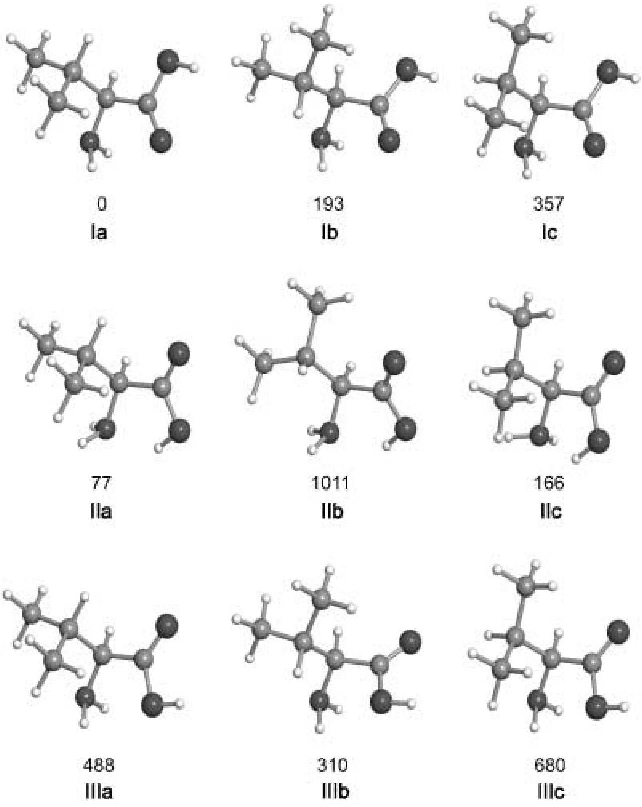


Figure 1. Conformers of valine and predicted relative energies in cm^{-1}.

agreement between the experimental and predicted values of the nuclear quadrupole coupling constants χ_{aa}, χ_{bb}, and χ_{cc} for conformer **IIa** in Tables 1 and 2. These parameters depend on the electronic environment around the amine nitrogen atom and are very sensitive to molecular conformation,[21] thus it is a precious tool for discriminating between the different conformers. The microwave power required for optimum polarization of the μ_a-and μ_b-type transitions is also consistent with the predicted values of the electric dipole moments for conformer **IIa**. The isotopic frequency shifts for the ^{15}N isotopomer were predicted on the basis of the assignment of the parent species. Transitions were found near the predicted values for an enriched sample, and they were readily recognized from the absence of nuclear quadrupole coupling hyperfine structure associated with a ^{15}N nucleus (see Figure 2). This is a further corroboration of the existence of conformer **IIa** in gaseous valine.

Wide frequency searches for transitions belonging to the other plausible conformers were carried out using the ^{15}N-enriched sample because the absence of hyperfine structure on the nuclear quadrupole coupling produces an enhancement in the spectrum signal. After rejecting the lines corresponding to conformer **IIa**, weak R-branch transitions of μ_a, μ_b, and μ_c types of a second rotamer were identified. After the rotational spectrum of the ^{15}N species had been analyzed, the weaker transitions of the ^{14}N species, split by nuclear quadrupole coupling effects (Figure 3), were also analyzed. Rotational parameters for the parent and ^{15}N species shown in Table 2 were obtained following the same procedure described for the conformer **IIa**. The notable agreement between the experimental rotational and quadrupole coupling constants in Table 2 and those predicted for the **Ia** conformer in Table 1 reveals that this newly detected conformer undoubtedly corresponds to the **Ia** conformer. The intensities of the different types of rotational transitions are in accordance with the predicted magnitudes of the electric dipole moment components. No transitions attributable to other plausible conformers remained in the spectrum. All the measured frequencies for conformers **Ia** and **IIa** are given in the Supporting Information.

Some information on the relative stability of the two observed conformers of neutral valine can be obtained from a comparison of the intensities of the rotational transitions.[22] The fact that the μ_b-type transitions are of comparable intensity in both conformers while the predicted μ_b values are about three times larger in conformer **IIa** clearly indicates that conformer **Ia** corresponds to the global minimum. The energy difference between conformers **Ia** and **IIa** can be estimated to be about 100 cm^{-1}.

Table 1: Ab initio molecular properties of valine.

	MP2/6-311++G(d,p)								
	Ia	**Ib**	**Ic**	**IIa**	**IIb**	**IIc**	**IIIa**	**IIIb**	**IIIc**
relative energy [kJ mol^{-1}]	0.0	2.3	4.3	0.9	12.1	2.0	5.8	3.7	8.1
[cm^{-1}]	(0.0)	(193)	(357)	(77)	(1011)	(166)	(488)	(310)	(680)
	rotational constants								
A [MHz]	2939	2800	2380	3026	3000	2454	2977	2828	2385
B [MHz]	1442	1586	1806	1488	1584	1811	1430	1562	1787
C [MHz]	1338	1240	1436	1274	1107	1450	1336	1260	1449
	^{14}N nuclear quadrupole coupling parameters								
χ_{aa} [MHz]	−4.58	−4.15	−2.99	−3.75	−3.97	0.17	−4.42	−4.03	−2.30
χ_{bb} [MHz]	2.89	2.55	2.55	2.10	2.40	2.62	2.76	2.35	1.86
χ_{cc} [MHz]	1.69	1.60	0.44	1.65	1.57	−2.78	1.66	1.68	0.44
	electric dipole moment								
μ_a [D][a]	0.4	0.5	0.5	4.3	3.6	2.4	0.6	0.2	0.5
μ_b [D]	1.0	0.7	1.1	3.2	3.5	4.2	1.0	0.3	0.8
μ_c [D]	0.6	0.8	0.5	0.0	0.5	1.9	0.8	1.4	1.0
μ_T [D]	1.3	1.2	1.3	5.3	5.1	5.2	1.5	1.5	1.4

[a] 1 D = ca. 3.3356×10^{-30} C m.

Table 2: Rotational parameters of valine.

	Conformer **IIa**		Conformer **Ia**	
	parent	[^{15}N]valine	parent	[^{15}N]valine
A [MHz][a]	3038.25151 (41)[f]	2983.53453 (65)	2944.58890 (42)	2892.03823 (19)
B [MHz]	1476.84596 (13)	1476.73942 (20)	1445.21281 (27)	1444.32066 (26)
C [MHz]	1261.22035 (13)	1251.74423 (19)	1326.37063 (22)	1315.45400 (20)
Δ_J [kHz][b]	0.2090 (20)	0.2132 (31)	0.2248 (42)	0.2185 (40)
Δ_{JK} [kHz]	0.408 (15)	0.387 (14)	0.562 (26)	0.5129 (72)
Δ_K [kHz]			−0.118 (30)	[−0.118]
δ_J [kHz]			0.0251 (42)	0.0182 (31)
δ_K [kHz]	0.533 (43)	[0.533][g]		
χ_{aa} [MHz][c]	−3.5387 (28)		−4.2053 (40)	
χ_{bb} [MHz]	1.9203 (46)		2.7421 (41)	
χ_{cc} [MHz]	1.6183 (46)		1.4632 (41)	
σ [kHz][d]	1.7	1.8	2.3	1.7
N[e]	63	17	59	28

[a] A, B, and C represent the rotational constants. [b] Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_K are the quartic centrifugal distortion constants. [c] χ_{aa}, χ_{bb}, and χ_{cc} are ^{14}N nuclear quadrupole coupling parameters. [d] rms deviation of the fit. [e] Number of fitted transitions. [f] Standard error in parenthesis in units of the last digit. [g] Parameters in square brackets were kept fixed in the fit.

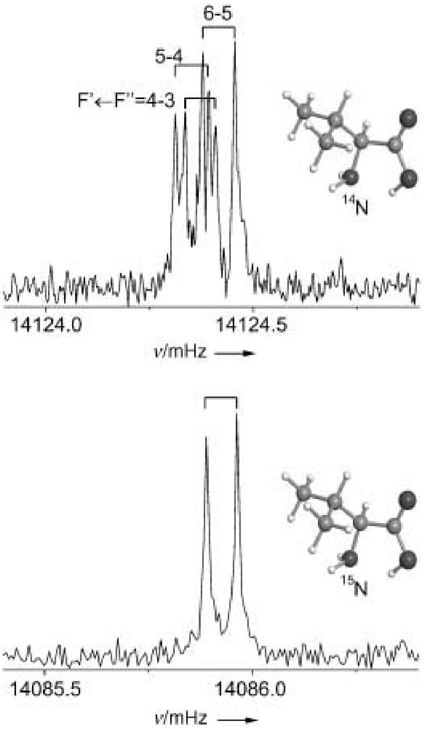


Figure 2. The $5_{1,4}$–$4_{1,3}$ rotational transition of conformer **IIa** for the parent ^{14}N (upper trace) and the ^{15}N isotopomer (lower trace) of valine. The hyperfine components of the ^{14}N isotopomer ($F'\leftarrow F''$) are labeled by the quantum numbers $F = I + J$. Each component appears as a doublet (⊓) as a result of the Doppler effect (see Experimental Section).

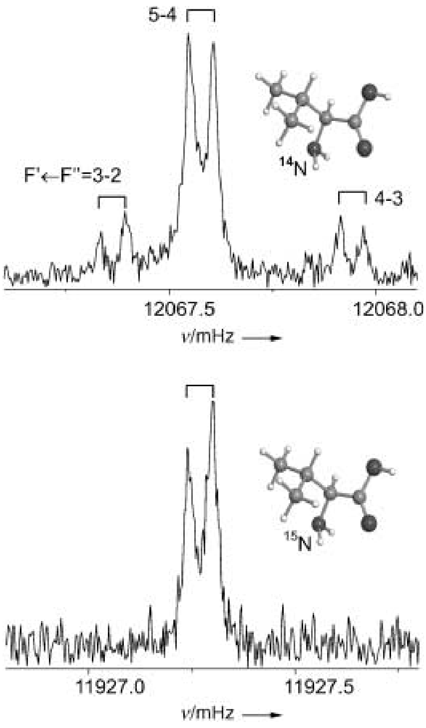


Figure 3. The $4_{1,4}$–$3_{0,3}$ rotational transition of conformer **Ia** for the parent ^{14}N (upper trace) and the ^{15}N isotopomer (lower trace) of valine. The hyperfine components of the ^{14}N isotopomer ($F'\leftarrow F''$) are labeled by the quantum numbers $F = I + J$. Each component appears as a doublet (⊓) as a result of the Doppler effect (see Experimental Section).

The conformational behavior of valine is in close agreement with that observed for the smaller aliphatic natural α-amino acids glycine[10] and alanine.[11] Affixing an isopropyl side chain to the α-amino acid backbone does not alter the relative energies of the lowest energy conformers. This observation indicates that the relative stabilities of the amino acid skeleton are controlled by intramolecular hydrogen bonding. The bifurcated amine-to-carbonyl hydrogen bond (N−H···O=C) gives rise to the most stable conformer in the three amino acids. This fact has been attributed to the cooperative stabilizing effect caused by the *cis* arrangement of the carboxylic acid.[23] Although the nitrogen-to-hydroxy (N···H−O) intramolecular hydrogen bond is predicted to have a larger stabilization effect,[23b] it gives rise to the second stable conformer since the carboxylic acid group is forced to adopt a *trans* arrangement. The preferred orientation for the isopropyl side chain is "a" in both conformers, which seems to minimize the steric strains in the molecule.

The absence of some of the conformational species shown in Figure 1 which are predicted to fall in the group of lowest energy deserves some comments. This problem of "missing conformers"[24] is associated with the fact that some conformers may relax to the most stable forms in the supersonic expansion if the barrier to interconversion is low enough. It is accepted that this event takes place by collisions with the noble carrier gas in the adiabatic expansion. This phenomenon has been observed in systems involving only one degree of freedom such as torsional isomerism[25] and axial/equatorial relaxation in hydrogen-bonded complexes[26] when energy barriers are less than about 400 cm^{-1}. Studies on systems with multiple degrees of freedom have proposed barrier heights below 1000 cm^{-1}.[27] In this context, Godfrey et al.[24] estimated barriers below 400 cm^{-1} for the interconversion between conformer **III** and conformer **I** in glycine[10] and alanine,[11] and proposed that conformational relaxation was the origin of the absence of conformer **III** in the supersonic expansion. The same can be argued for the absence of the type **III** conformations in valine. Relaxation of **Ib** or **Ic** to **Ia** and **IIb** or **IIc** to **IIa** by a rotation around the $^{\beta}$C–$^{\alpha}$C bond, which can also take place in the side chain of valine, may justify the observation of only the **Ia** and **IIa** forms. It must be taken into consideration that the observations in the expansion reflect both the relative energies of the conformers and the barriers hindering the interconversion between them.[27a] In any case, the two observed conformers of valine are the most stable forms, even if relaxation takes place.

The present work consolidates the use of the LA-MB-FTMW technique as a very important tool for the generation of isolated neutral amino acids, thus making possible the analysis of their rotational structure. The interpretation of the experimental data, coupled with high-level ab initio computations, is making it possible to begin the determination of the conformational landscapes of relevant biological molecules. Valine represents an intermediate step for the future studies of more complicated amino acids.

Experimental Section

Commercial samples of DL-valine (99%, Aldrich) and ^{15}N L-valine (98%, Cambridge Isotope Labs.) were used in this study. The laser-ablation molecular-beam Fourier transform microwave spectrometer, operating in the frequency region 6–18 GHz, has been briefly described previously.[15] Pressed sample rods of 6-mm diameter and 1–2-cm long were vaporized with the green line (532 nm) of a Nd:YAG laser, with energy pulses of ca. 50 mJ. Neon at stagnation pressures of about 5 bar was used as the carrier gas (gas pulses of 0.4–0.7 ms), with polarization pulses of 0.2–0.5 μs (1–300 mW). The delays between the gas, laser ablation, and microwave pulses were optimized for maximum signals. The free-induction decay in the time-domain signal was recorded in 40 ns intervals, which is equivalent to a frequency resolution of ca. 3 kHz. Frequency accuracy is better than 5 kHz. Each rotational transition is split by the Doppler effect because of the coaxial orientation of the supersonic jet and resonator axes, so the rotational frequencies are taken as the arithmetic mean of the two components of the Doppler doublet.

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