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Conformational and Infrared Spectral Studies of L-Methionine and Its N-Deuterated Isotopomer as Isolated Zwitterions

Xiaolin Cao[†] and Gad Fischer*

Department of Chemistry, The Faculties, The Australian National University, Canberra, ACT 0200, Australia

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The mid-IR spectra of L-methionine and its N−D_3 deuterated isotopomer as isolated zwitterions in a KBr solid solvent have been obtained by means of a newly developed infrared sampling technique, which involves the production of thin films. Ab initio calculations of the nonaqueous self-consistent reaction field type, using the Onsager dipole-sphere model have been carried out at both the Hartree−Fock and density functional levels of theory for the prediction of the vibrational spectra and molecular structures of Met zwitterions isolated in KBr matrixes. Seven stable conformers of Met zwitterion were located, of which three were shown to be characterized by strong intramolecular H-bonding. Another conformer was found to have the same conformation, and similar molecular structure, as one of the two forms of Met crystals. The calculated structural data supplement the limited crystal data obtained by X-ray diffraction studies. Comparison of the calculated spectra of the seven conformers with the measured spectra favors the presence of zwitterions of conformer GtG in the KBr solid solvent. However, the evidence against a number of the other conformers, in particular, gtt and tGG, is not overwhelming.

Introduction

Three-dimensional models of protein structures depend largely on knowledge of accurate geometries of the component amino acids.[1] L-Methionine (Met) is one of the essential amino acids. It must be present in the diet of mammals to ensure normal growth.[2] As one of the two sulfur-containing amino acids, Met has attracted growing interest recently since it is thought to play an important role in the severe nephrotoxicity of cisplatin, inactivation of Pt complexes, and tumor resistance to treatment with Pt drugs.[3] Met has a bulky hydrophobic and nonpolar aliphatic side chain, and it has proven very difficult to grow the high-quality crystals required for high-precision neutron diffraction studies.[4] The geometric data of Met in the crystal reported in the literature are incomplete.[4,5] The locations of the hydrogen atoms have not been determined.

In conformity with the other amino acids, Met also has two possible structural forms, depending on its local environment: neutral zwitterions in the crystalline state or in aqueous solutions, and the un-ionized form for the isolated molecule. Literature reports on spectroscopic studies and ab initio calculations of Met are very limited. A small number of spectroscopic studies on its analogues and metal complexes have been reported,[6−11] but even fewer for Met itself.[12−15] None of these studies on Met zwitterions have involved the combined approach of infrared spectroscopy and targeted ab initio molecular orbital calculations.

For Met in the crystal, two crystallographically independent forms have been identified in X-ray studies.[4,5] Infrared spectra have been reported for Met in KBr pellets and adsorbed on surfaces.[14,15] Met adsorbed on a thick, evaporated gold surface has been studied by reflection absorption infrared spectroscopy.[14] In the multilayer regime, the spectrum indicated that Met is present as the zwitterion and is involved in strong intermolecular H-bonding. The spectrum has much in common with that of Met in a KBr pellet. At low surface coverage, the carboxyl group is protonated, and the spectrum is markedly altered. The electronic absorption, circular dichroism, and magnetic circular dichrosim spectra of Met in acidic solutions have been recorded between 210 and 350 nm.[13] Two novel low-lying singlet−triplet transitions of the C−S−C chromophore in Met were identified.

The formation energies of 27 conformers were determined by MNDO semiempirical calculations.[15] The calculations were carried out for isolated molecules for which all intermolecular interactions were neglected. These results should be viewed against the more recent ab initio calculations on other amino acids, which have shown that the isolated zwitterions are unstable and that they revert to the un-ionized molecules.[16−20] The vibrational spectrum of Met in the region from about 600 to 1600 cm^{-1} has been studied by surface-enhanced Raman scattering from electrochemically prepared silver surfaces,[12] but the correlation between the observed spectrum and the Met conformation(s) is difficult to establish.

There are no reports of ab initio calculations on Met zwitterions for which the purpose has been the determination of possible conformations and structures, as well as prediction of the vibrational spectra. Calculations for the zwitterions must take into account the local environment, since the isolated zwitterions are not stable.

In this paper, we report the mid-IR spectra of zwitterionic (ZW) Met and its deuterated isotopomer, Met-ND_3, isolated in a dielectric medium. The infrared spectra have been measured using a newly developed dissolution, spray, and deposition (DSD) sampling technique. Ab initio molecular orbital calculations which take into account the molecule-medium interactions have also been undertaken for the prediction of structures and vibrational spectra. The calculations are of the nonaqueous self-consistent reaction field (SCRF) type, using the Onsager dipole-

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* Author to whom correspondence should be addressed. E-mail: Gad.Fischer@anu.edu.au. Tel.: +61 2 6125 3043. Fax: +61 2 6125 0760.

[†] Present address: Department of Chemistry, 1-014 CST, Syracuse University, Syracuse, New York, 13244-4100.

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sphere model. It should be recalled that for aqueous solutions SCRF calculations are not ideal since the strong and specific interactions between water and solute molecules are not adequately accounted for by a uniform reaction field.[21] This problem has been partly overcome by the inclusion of a small number of specific water molecules.[22] However, such an inclusion of specific interactions should not be necessary for an alkali halide solid solvent such as KBr, since its dielectric constant is very small compared to that of water.

SCRF calculations were undertaken to determine all the stable conformers. For all the predicted conformers, their conformations, relative energies, and vibrational spectra are presented. Comparisons between the calculated and observed spectra are examined in detail, and the possible Met conformer(s) present in the KBr continuum is determined accordingly. One conformer is found to have the same conformation as that of one of the two forms of Met in the crystal. The detailed structural parameters of this specific conformer are presented and are compared to the parameters obtained from the crystal structure analysis.

Experimental Section

Details of the preparation of DSD samples of zwitterions of Met and its N-D$_3$ deuterated isotopomer (Met-ND$_3$) are similar to those described elsewhere for other amino acids.[20] Met was purchased from ICN and used without further purification. Met-ND$_3$ was prepared by exchange of Met with D_2O in mildly warmed deuterated water for about 2 h, and the process was repeated. For the preparation of aqueous solutions, Met was dissolved together with potassium bromide (KBr) in deionized water (Milli-Q plus) and stirred to homogenization. For Met-ND$_3$ aqueous solutions, D_2O was used as the solvent instead of H_2O. Mass ratios of KBr (FT-IR grade, Aldrich) to both Met and Met-ND$_3$ were chosen to be about 100. The quantity of H_2O or D_2O was controlled so that KBr was close to saturation in the aqueous solution ensuring rapid solvent evaporation. The solutions of the sample and KBr matrix were then deposited on IR windows, which were pure KBr pellets made by a standard KBr disk press. The deposition was accomplished by a series of intermittent fine sprays using a commercial airbrush (VL double action, Paasche Airbrush Co.). The IR window was attached to a hot plate (80 °C) to facilitate evaporation of water during and after each spray. Upon completion, the window with its deposition was heated to a higher temperature (∼100 °C) for the purpose of removing any residual water to ensure that only KBr and trapped Met or Met-ND$_3$ molecules remained in the deposition. During the course of spray and deposition, the DSD film on the window was monitored by measurements of its IR spectra. No detectable decomposition was found following sample preparation and solvent evaporation.

All the infrared spectra were measured by an FT-IR spectrometer (IFS66, Bruker) in the range of 400−4000 cm^{-1} and at a resolution of 4 cm^{-1}. The IFS66 spectrometer was equipped with a DTGS detector and a KBr beam splitter and was purged continuously by dry nitrogen. For comparison, the normal KBr pellet spectra of Met and Met-ND$_3$ were also recorded in the same spectral range and at the same resolution.

In some of the DSD spectra, intense interference fringes were observed. These were apparently a consequence of the thin films produced in the DSD sampling technique and were usually most pronounced in the high-frequency spectral region, from about 2500 to 4000 cm^{-1}. These fringes partly obscured some of the sample absorption bands. To remove them, spectral subtractions of background from DSD spectra were performed.[20] The background spectra were measured following the evaporation of sample molecules from the DSD disk that was used in the measurement of the DSD spectra.

Calculations

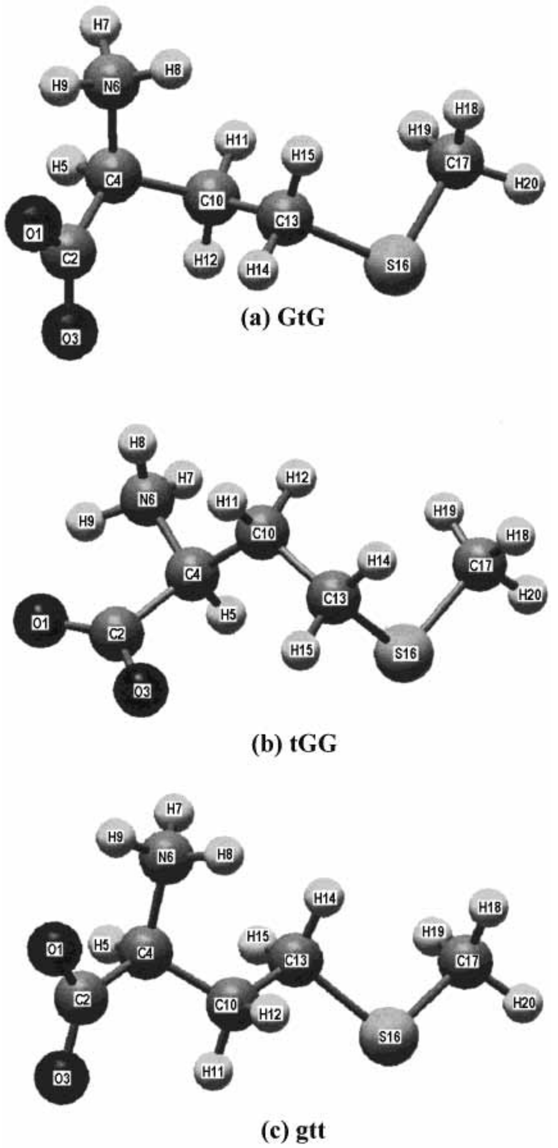
SCRF ab initio molecular orbital calculations[21] on zwitterionic Met and Met-ND$_3$ were performed at the Hartree−Fock HF/6-311++G(d,p) and density functional B3LYP/6-31G(d) levels, using the GAUSSIAN 98 version of the program.[23] For the SCRF calculations the Onsager dipole-sphere model[21,24] was used because it permits full structural optimizations and vibrational frequency calculations at a relatively low cost of computational resources. In this model, the solute occupies a spherical cavity within the solvent field. In more sophisticated models such as the PCM and self-consistent isodensity (SCIPCM), the shape of the cavity is represented by the combination of atomic spheres for the former and by an isodensity surface for the latter.[21] Despite the simplicity of the Onsager model, frequency calculations using it have been shown in a number of cases to be superior to those using the SCIPCM model.[21]

In the Onsager model, the sample molecules are viewed as solutes in a solvent (here KBr continuum) with a uniform dielectric constant. Two parameters, the cavity radius (a_0) of the solutes and the dielectric constant (ϵ) of the continuum, are needed for the SCRF calculations. In this study, the cavity radius was used as an adjustable parameter in both the HF and DFT calculations in order to reach the best agreement between the predicted and observed spectra. It should be noted that the cavity radii for ZW amino acids cannot be directly estimated by self-consistent field (SCF) optimizations with the “volume” keyword.[21] This is because the isolated ZW amino acids are not stable and need to be stabilized by intermolecular interactions, such as those present in solvents, the solid state, or, as in this study, the KBr matrix. Consequently, SCF optimizations on ZW amino acids usually revert to the un-ionized neutral structures.[16−20] This was also found to be the case in our calculations on Met ZW conformers. Starting from the structures of the zwitterions, un-ionized neutral Met conformers were obtained as the energy minima in the absence of the dielectric medium with B3LYP/6-31G(d) calculations.

For the HF calculations reported here, a large basis set was used. Similar calculations were also performed at the density-functional theory (DFT) level, but because of larger computational times, the smaller basis was used. The DFT calculations were undertaken to confirm the conclusions reached from the HF calculations regarding the relative energies of the various conformers and the identity of the conformer(s) present in the DSD sample.

The optimizations were carried out without imposing any geometrical constraints and starting from the structures of all possible conformers. A total of seven conformers was determined. Figure 1 displays the optimized structures of the three stable conformers whose infrared absorption spectra have been determined below to be most representative of the DSD spectra.

The results reported for the HF calculations refer to an optimum cavity radius of 3.26 Å (1 Å = 0.1 nm). It is in the range of values determined for a number of amino acids.[25] With this cavity radius, the main features of the calculated spectra for the majority of Met conformers display satisfactory agreement with the measured DSD spectra. Similarly, an optimum cavity radius of 2.90 Å was found for the DFT calculations. This is in agreement with the results for other amino acids where it was noted that the optimum DFT cavity radius was smaller than the HF value.[20]



(a) GtG

(b) tGG

(c) gtt

Figure 1. SCRF/HF optimized structures of three Met zwitterionic conformers: (a) GtG, (b) tGG, and (c) gtt.

The dielectric constant for the KBr continuum was taken as 4.88.[26] For such a small dielectric constant, in contrast to aqueous solutions, it is argued that specific K^+ and Br^- ions need not be included in the calculations.

Harmonic vibrational frequencies were calculated following the structure optimization by analytic second differentiation of the energy with respect to nuclear displacements. The raw predicted frequencies were all scaled using a single factor of 0.9 for the correction of the well-known 10−12% frequency overestimation.[21,27] The scaled vibrational spectra were then simulated and displayed using Mathcad©. Lorentzian bands with half width of 8 cm^{-1} were used to simulate all the fundamental vibrations. The integral area, or approximately the peak height of each Lorentzian band, is proportional to the vibrational intensities. For the convenience of spectral comparisons, relative band intensities are used for calculated spectra. The relative intensity of each band in a spectrum was scaled with respect to its strongest band, which was arbitrarily set to be 100. The band intensities for the observed spectra have been qualitatively described as vs, very strong; s, strong; m, medium; w, weak; etc. For some specific and prominent bands in the observed spectra, their intensities were also quantitatively described for the purpose of quantitative spectral comparisons. In Figures 2 and 3, the simulated spectra for all seven conformers of Met and Met-ND_3 are displayed respectively, together with the observed spectra of Met and Met-ND_3, obtained by DSD and KBr techniques, respectively.

Results and Discussions

Conformers. The seven optimized conformers of Met identified in the computations correspond to different local energy minima on the potential energy surface. These conformers are characterized by three key dihedral angles, χ^1, χ^2, and χ^3.[15] The definitions of these angles and the labeling of the seven conformers, as well as their relative energies at the HF and DFT levels, and some specific structural parameters obtained at the HF level are listed in Table 1. The labels used to assign these conformers adhere to those used in the previous MNDO studies,[15] where G, g, t notations denote gauche I (∼60°), gauche II (∼−60°), and *trans* (∼180°) configurations, respectively. For example, the three key dihedral angles for conformer gGt are about −60° (gauche), 60° (gauche), and 180° (trans), respectively. In an earlier conformational study, 27 conformers (3 × 3 × 3) and their relative energies were determined by MNDO calculations.[15] The results of this earlier study are in conflict with the seven stable conformers determined by ab initio calculations in the current work. The reduction in the number of stable conformers determined in our work is not surprising since ab initio calculations impose stricter convergence criteria, and consequently, fewer conformers are found to converge to energy minima in their structural optimizations.

For all conformers, the use of cavity radii larger than about 3.00 and 3.40 Å for the DFT and HF calculations, respectively, gave $O_1\cdots H_{amino}$ and/or $S\cdots H_{amino}$ separations that are relatively small, less than 2.0 Å, and are indicative of significant H-bonding. One consequence of the significant H-bonding is reflected in the prediction of strong bands in regions of the spectrum that are clear of absorption bands in the observed spectra (see below). For cavity radii less than 3.00 Å in the DFT calculations conformers, ttG, gGt, and ggt are not stable. They optimize to the other conformers, and hence, their stability depends on the existence of significant intramolecular H-bonding.

Close inspection of the measured spectra, detailed below, indicates that the conformer(s) present in the DSD sample are not marked by strong intramolecular hydrogen bonding. As a consequence, it follows that the ttG, gGt, and ggt conformers can be excluded from further consideration. Also, it can be concluded that valid cavity radii for the remaining conformers must lie in a range where H-bonding is not particularly marked, that is, for a_0, less than about 3.0 and 3.3 Å for the DFT and HF calculations, respectively.

At both HF and DFT levels and for the range of cavity radii for which all seven conformers exist, the gGt and ggt conformers were calculated to have the lowest energies (Table 1). However, the lowest energy conformers determined at the HF and DFT levels for the optimum cavity radii of 3.26 and 2.90 Å, respectively, are GtG, tGG, and gtt since conformers gGt and ggt do not exist or are marked by strong H-bonding at these "optimum" cavity radii. The three conformers are separated by less than 2000 cm^{-1} (Table 1).

In X-ray diffraction studies, Met was determined to have two crystallographical forms in the crystal, namely, Met A and Met B.[4,5] The dihedral angles for the two crystal forms are also included in Table 1 for comparison. It is seen that Met A and B have a similar angle, χ^1, but differ in the values of χ^2 and χ^3.

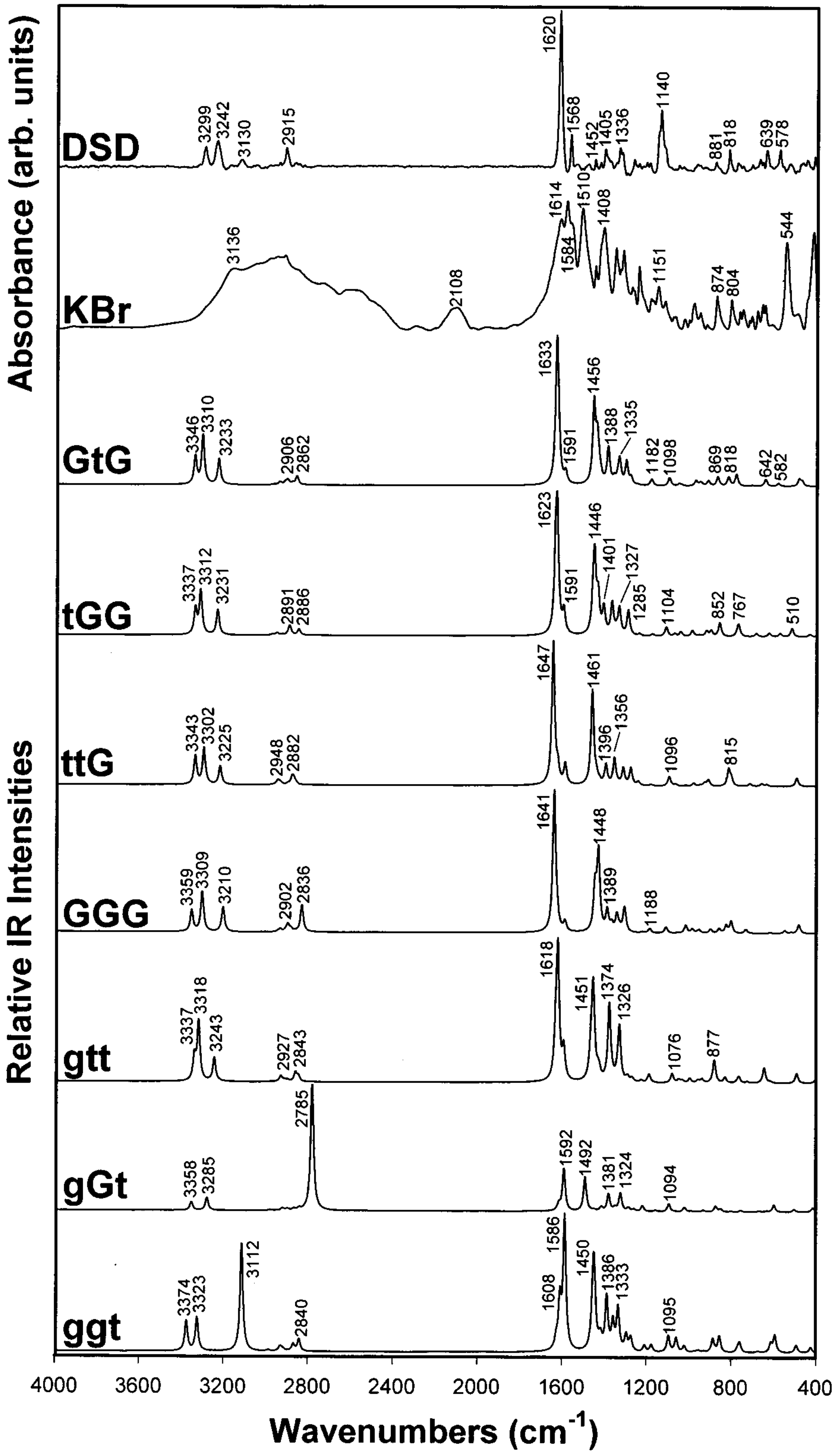


Figure 2. Observed (DSD and KBr pellet) and calculated (SCRF/HF/6-311++G(d,p)) vibrational spectra of zwitterionic Met, for seven conformers: GtG, tGG, ttG, GGG, gtt, gGt, and ggt.

Comparison with the structures of the seven SCRF/HF predicted conformers reveals that Met B has most in common with the conformer tGG, whereas Met A does not have a clear counterpart among the predicted conformers. The closest one to Met A is ttG, but it differs substantially in the torsion angle, χ^3.

Spectra. The nature of the amino acid species present in the DSD sample deserves some comment. It has been shown in this and earlier studies[20] that there is no difference between the spectra of amino acid−KBr mixtures directly dried from their aqueous solutions and those obtained by the normal KBr pellet method. This suggests that the DSD method only differs in the production of a far greater proportion of smaller clusters/monomers. For both samples, the amino acid is present as the ZW. The spectra, discussed in the following, confirm this.

Analyses of the DSD spectra are achieved through comparison with calculated spectra and, to a lesser extent, by comparison

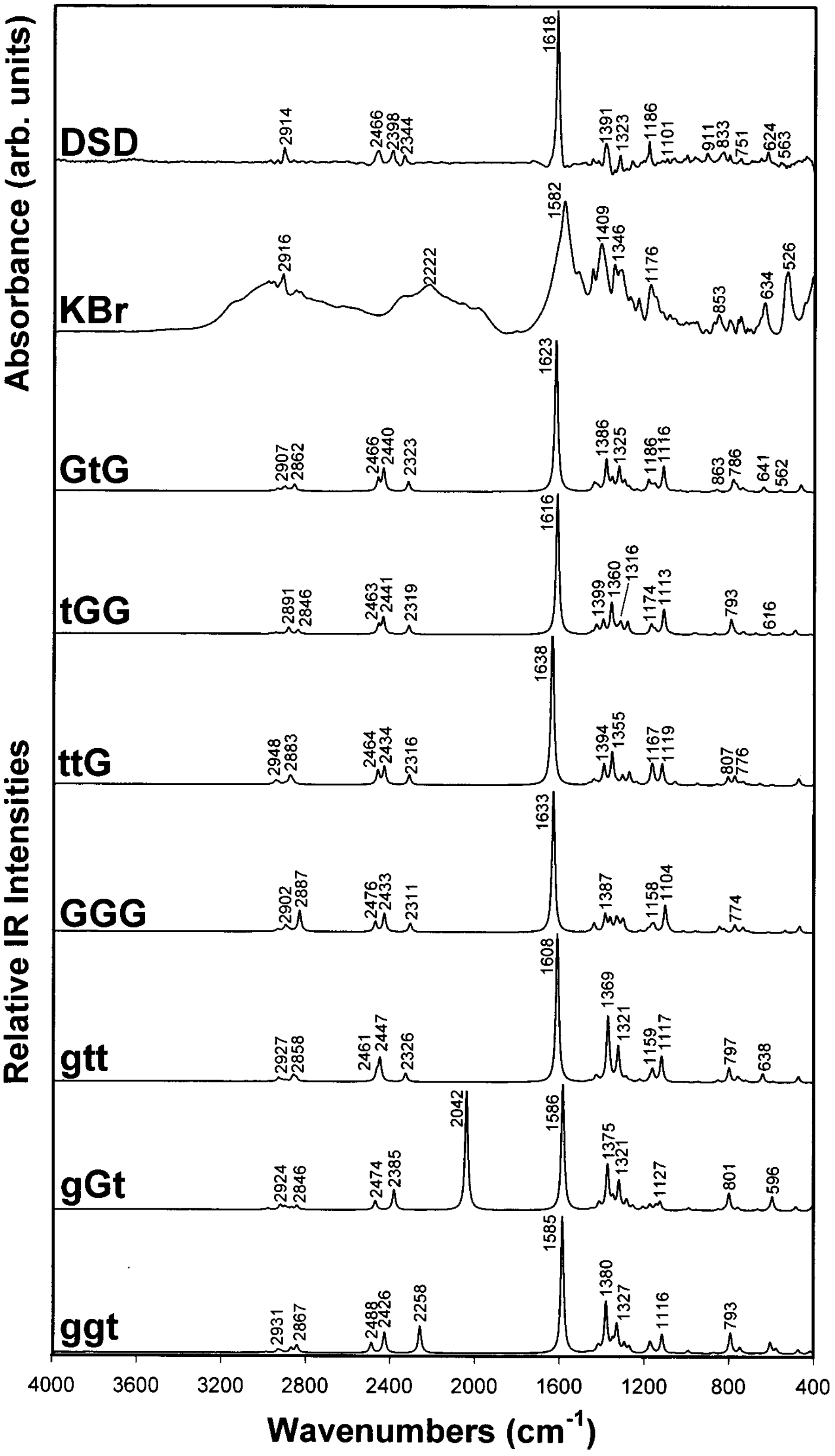


Figure 3. Observed (DSD and KBr pellet) and calculated (SCRF/HF/6-311++G(d,p)) vibrational spectra of zwitterionic Met-ND$_3$, for seven conformers: GtG, tGG, ttG, GGG, gtt, gGt, and ggt.

with the measured spectra of related ZW amino acids such as alanine.[20,28] For the former comparison to be meaningful the calculated and measured spectra should refer to the same molecular species. It is argued that the DSD sampling technique produces largely ZW monomers isolated in a dielectric medium and that the SCRF calculations undertaken to determine the optimized structures and the vibrational spectra do in fact match the measurements. The SCRF calculations are for the isolated ZW in a medium of KBr. However, before an appropriate comparison can be carried out, the structure of the ZW must be determined since it has been shown that there are seven stable conformers. The approach adopted here has been to compare the calculated spectra of all seven conformers for best agreement with the observed spectra. The details of this comparison are discussed in the following and refer to the HF calculations.

TABLE 1: Energy and Selected Structural Data (SCRF/HF/6-311++G(d,p), $a_0 = 3.26$ Å) for the Seven Predicted Zwitterionic Met Conformers, Including X-ray[4] Crystal Structure Data for Met A and Met B[a]

conformer	gtt	gGt	ggt	GtG	GGG	ttG	tGG	A	B
$\chi^1 = \tau$[N6−C4−C10−C13]	−58.27	−53.21	−41.69	67.62	58.54	159.25	−162.24	−166.1	−165.4
$\chi^2 = \tau$[C4−C10−C13−S16]	−172.35	81.98	−44.34	169.13	64.44	162.07	60.02	171.6	71.5
$\chi^3 = \tau$[C10−C13−S16−C17]	−167.65	−170.02	177.55	78.91	59.50	45.27	73.96	178.5	72.4
$\psi^1 = \tau$[O1−C2−C4−N6]	4.98	−7.49	8.72	5.47	7.79	−25.35	13.50	−16.3	−32.4
$\psi^2 = \tau$[O3−C2−C4−N6]	−176.86	172.10	−174.44	−176.48	−176.46	155.77	−169.27	−	−
O1···H (amino group)	2.075	2.080	2.263	2.064	1.997	2.121	2.026	−	−
S16···H (amino group)	4.514	2.152	2.484	4.430	3.694	5.257	4.550	−	−
relative energies (cm^{-1})									
HF (3.26 Å)	1992	0	605	3036	6051	5480	3338	−	−
DFT (3.26 Å)	2389	0	1336	3018	4789	4789	2841	−	−
DFT (2.90 Å)	0	−	−	1783	4114	−	1971	−	−

[a] SCRF calculated relative energies at HF/6-311++G(d,p), and B3LYP/6-31G(d) levels. O···H and S···H mark the closest separations of amino group hydrogens to the O and S atoms.

TABLE 2: Comparison of DSD Measurements with Predicted Data (SCRF/HF/6-311++G(d,p)) for Those Met Vibrations of the Seven Conformers Most Sensitive to Conformational Changes[a]

	gtt	gGt	ggt	GtG	GGG	ttG	tGG	DSD	assignment
Met	642 (12)	597 (5)	611 (6)	642 (5)	617 (1)	658 (2)	617 (3)	639 (16)	νSC
	770 (1)	668 (1)	673 (1)	742 (<1)	709 (<1)	746 (<1)	679 (3)	752 (5)	νSC
	1374 (60)	1381 (13)	1386 (40)	1388 (28)	1389 (15)	1396 (14)	1401 (24)	1405 (16)	$\nu_s CO_2^-$
						1356 (18)	1362 (29)		
	1451 (61)	1492 (26)	1450 (40)	1456 (61)	1448 (30)	1461 (65)	1446 (69)	1452 (10)	$\beta_s NH_3^+$
	1590 (25)	1616 (5)	1608 (37)	1591 (9)	1590 (7)	1590 (14)	1591 (21)	1568 (25)	$\beta_{as} NH_3^+$
	1628 (32)	1626 (<1)	1626 (7)	1625 (29)	1628 (8)	1625 (10)	1631 (62)		$\beta_{as} NH_3^+$
	1618 (100)	1592 (32)	1586 (100)	1633 (100)	1641 (100)	1647 (100)	1623 (100)	1620 (100)	$\nu_{as} CO_2^-$
	3243 (18)	2785 (100)	3112 (81)	3233 (20)	3210 (18)	3225 (13)	3231 (24)	3130 (10)	$\nu_s NH_3^+$
	3318 (47)	3285 (10)	3323 (25)	3310 (38)	3309 (29)	3302 (26)	3312 (41)	3242 (21)	$\nu_{as} NH_3^+$
	3337 (19)	3358 (7)	3374 (23)	3346 (22)	3359 (15)	3343 (20)	3337 (24)	3299 (17)	$\nu_{as} NH_3^+$
Met ND_3	638 (6)	596 (11)	605 (8)	641 (3)	616 (1)	657 (1)	616 (2)	624 (15)	νSC
	756 (3)	665 (1)	668 (<1)	728 (1)	706 (<1)	751 (1)	677 (1)		νSC
	1117 (18)	1127 (7)	1116 (14)	1116 (16)	1104 (19)	1119 (13)	1113 (18)		$\beta_s ND_3^+$
	1159 (7)	1147 (4)	1168 (3)	1156 (4)	1158 (5)	1163 (6)	1156 (3)	1186 (21)	$\beta_{as} ND_3^+$
	1171 (2)	1175 (4)	1174 (7)	1186 (9)	1169 (4)	1167 (4)	1174 (4)		$\beta_{as} ND_3^+$
	1369 (43)	1375 (34)	1380 (37)	1386 (20)	1387 (12)	1394 (12)	1399 (10)	1391 (20)	$\nu_s CO_2^-$
						1355 (20)	1360 (22)		
	1608 (100)	1586 (100)	1585 (100)	1623 (100)	1633 (100)	1638 (100)	1616 (100)	1618 (100)	$\nu_{as} CO_2^-$
	2326 (6)	2041 (92)	2258 (20)	2322 (6)	2311 (6)	2316 (6)	2319 (6)	2344 (12)	$\nu_s ND_3^+$
	2447 (15)	2385 (16)	2426 (15)	2440 (14)	2433 (13)	2434 (11)	2441 (12)	2398 (15)	$\nu_{as} ND_3^+$
	2461 (6)	2474 (7)	2488 (7)	2466 (8)	2476 (7)	2464 (9)	2463 (6)	2466 (15)	$\nu_{as} ND_3^+$

[a] Calculated frequencies (cm^{-1}) are all scaled by 0.9, and intensities (in parentheses) are arbitrarily scaled to the strongest at 100.

Met consists of 20 atoms and has 54 fundamental vibrational modes, all of which are formally IR and Raman active in the applicable C_1 point group. The ab initio vibrational frequency calculations predict that some 43 modes fall in the range of 400 to 4000 cm^{-1}, the range measurable by the FT-IR spectrometer and covered in the simulated spectra displayed in Figures 2 and 3. The calculated spectra are labeled according to the corresponding conformers; while the observed spectra are identified by the infrared techniques (DSD and KBr pellet) used to measure them. Direct visual comparisons of these spectra show that the majority of the calculated fundamental vibration frequencies and intensities are similar for all seven Met and Met-ND_3 conformers, respectively. However, there are several bands that show distinct variability and that clearly display sensitivity to the conformational changes. By examination of their normal coordinates, it is seen that these bands are associated with vibrations involving large contributions from the $-NH_3^+$ ($-ND_3^+$ for Met-ND_3) and $-CO_2^-$ groups. The frequencies and transition intensities of these vibrations in the calculated spectra for the seven conformers have been compiled in Table 2, together with the observed DSD bands. Comparisons of the calculated and observed DSD spectra are carried out to ascertain if any one or more of the calculated conformers can be assigned to the DSD spectra.

The shifts in the frequencies of bands upon deuteration of the amino group are very useful in identifying those bands having a large contribution from NH motion. In the DSD spectra, three medium-strong bands assigned to the $-NH_3^+$ ($-ND_3^+$) stretching vibrations are located at 3299, 3242, and 3130 cm^{-1} for Met and at 2466, 2398, and 2344 cm^{-1} for Met-ND_3 (Figures 2 and 3 and Table 2). The observation of three bands supports their assignment to NH_3^+ of the ZW.

SCRF calculations satisfactorily predicted these large shifts (ca. 800 cm^{-1}) upon deuteration of NH_3^+ for all the conformers. For both Met and Met-ND_3 the SCRF calculated frequencies for conformers GtG, tGG, ttG, GGG, and gtt are within about 3% of the observed DSD frequencies. Furthermore, the calculated patterns of relative intensities for the three bands of these five conformers faithfully reproduce the observed spectra. This is not the case for conformers gGt and ggt, where there are some large discrepancies in both frequencies and intensities. In particular, for the gGt conformer, the frequency of one $-NH_3^+$ stretching mode is substantially reduced by specific H-bonding (NH···S) to 2785 cm^{-1} (2042 cm^{-1} for ND_3^+), and the band is attributed the largest intensity in the calculated spectrum. A similar phenomenon is noted for the ggt conformer. These observations provide support for the exclusion of the conformers gGt and ggt from consideration in assignment of the DSD spectra.

It should be noted that only in the DSD spectra can the shifts of the three NH stretches of the amino group upon deuteration be clearly identified. This contrasts the traditional KBr pellet spectra where individual bands corresponding to the three NH stretches are not seen, and only a general broad shift of about 800 to 900 cm^{-1} is apparent.

The CO_2^- asymmetric stretch ($\nu_{as}CO_2^-$) vibrations of Met and Met-ND_3 are assigned to the bands at 1620 and 1618 cm^{-1}, respectively. They are the strongest in the DSD spectra (Figures 2 and 3 and Table 2). The small frequency shift for this band upon deuteration is in conformity with results for other amino acids[20] and reflects the small effect deuteration of the amino group has on the CO_2^- stretch frequencies.

The SCRF predictions for this vibration for conformers GtG, tGG, ttG, GGG, and gtt are in agreement with the observed bands in the DSD spectra. For the five conformers, the predicted frequencies are 1633, 1623, 1647, 1641, and 1618 cm^{-1}, respectively, for Met and 1623, 1616, 1638, 1633, and 1608 cm^{-1}, respectively, for Met-ND_3. All are predicted to be the most intense bands in the spectra. However, the agreement is less satisfactory for the remaining two conformers, gGt and ggt. The predicted CO_2^- asymmetric stretch frequencies for gGt and ggt are a little low, presumably an indirect consequence of the relatively strong intramolecular S···H bonding. For both gGt and ggt of Met, the CO_2^- asymmetric stretch is heavily mixed with NH_3^+ bending vibrations of similar but slightly higher frequencies. Comparison with the calculated spectra of these two conformers for Met-ND_3 is illuminating. For Met-ND_3, mixing of the CO_2^- asymmetric stretch with the ND_3^+ bending modes is unimportant because of the large frequency differences between the two modes. As a result the frequencies, relative intensities and band contours of the CO_2^- asymmetric stretch are similar for all the Met-ND_3 conformers, including gGt and ggt. This analysis of the spectral region about the CO_2^- asymmetric stretch thus supports the suggestion that conformers gGt and ggt do not contribute to the measured DSD spectra.

The calculated frequencies of the CO_2^- symmetric stretch ($\nu_sCO_2^-$) fall in a narrow range from 1374 to 1401 and 1369 to 1399 cm^{-1} for all seven conformers of Met and Met-ND_3, respectively (Table 2), compared to the respective DSD values of 1405 and 1391 cm^{-1}. Calculated intensities are all similar and moderate relative to the strongest bands in the spectra, in agreement with the observed bands in the DSD spectra. The subtle differences in frequencies, intensities, and composition for the calculated CO_2^- symmetric stretch vibrations of the seven conformers are hence not sufficient to allow differentiation among the conformers and hence assignment of a particular conformer to the observed DSD spectra.

A similar conclusion is reached from consideration of the NH_3^+ bending modes. From observation of the frequency shifts upon deuteration of the amino group, one of the three NH_3^+ bending modes has been securely assigned in the DSD spectrum. A strong band is seen at 1568 cm^{-1}, which is shifted to 1186 cm^{-1} for ND_3^+. These observations are in good agreement with the calculations, which place the bands at about 1590 and 1170 cm^{-1} for Met and Met-ND_3, respectively. However, the calculations predict a different pattern of relative intensities for the three bends. For both Met and Met-ND_3, the most intense of the three NH_3^+ bends are predicted to be the lowest frequency ones, at about 1450 and 1120 cm^{-1}, respectively. For Met, only a weak band is seen in the DSD spectrum at 1452 cm^{-1}, which has been tentatively assigned to the lowest frequency bend. The frequency of the third bend is calculated to be near 1620 cm^{-1}, the frequency of the CO_2^- asymmetric stretch. In the DSD spectrum, the third bend is assumed to be overlapped by the intense band of the CO_2^- asymmetric stretch and therefore not identified. It should be pointed out that the calculations predict one of the CH_2 bends is close in frequency to the lowest NH_3^+ bend and that substantial mixing of the character of the vibrations is possible and predicted. This may in part explain the poor agreement between the predicted and observed relative intensities. Because of their lower frequencies the ND_3^+ bends fall in a region of many other vibrations, mixing is predicted to be extensive. In summary, the differences in the calculated NH_3^+ bends among the conformers are not sufficiently marked to allow positive identification of the conformer(s) responsible for the DSD spectra.

Comparison of the bands predicted by the calculations for the SC stretches (νSC) of the seven conformers with the DSD observed spectra is revealing. The band of moderate intensity in the DSD spectrum of Met at 639 cm^{-1} appears to be shifted to 624 cm^{-1} for Met-ND_3. It is assigned to the SC stretch. The other SC stretch band must be one of the weak bands observed near 750 cm^{-1}, here assigned to the weak band at 752 cm^{-1} (not identified for Met-ND_3). For the conformers GGG, ttG, and tGG, both SC stretch bands are predicted to be weak/very weak, not in agreement with the observed moderate intensity of the lower frequency νSC. For conformers gGt and ggt, the intensities of the two SC stretch bands match the DSD spectra, but the frequencies are a little low. For the conformers gtt and GtG, good agreement is obtained for the intensities and frequencies between the calculated and observed νSC bands.

Two other bands in the range 1100 to 500 cm^{-1} that are prominent in the DSD spectrum on account of their moderate intensity are located at 818 and 578 cm^{-1}. They do not appear to have readily identifiable counterparts in the Met-ND_3 spectrum, although the weak bands seen at 804 and 563 cm^{-1} in the DSD spectrum of Met-ND_3 may be the corresponding ones. Comparison with the calculated spectra suggests that both bands contain significant contributions from a number of different internal coordinates, including the deformation mode of the $-NH_3^+$ group. As such, they are not good candidates for determining which conformer(s) is represented in the DSD spectra because of the variability of the composition calculated for the different conformers. Nevertheless, it should be noted that conformer GtG is apparently in best agreement in having bands of moderate/weak intensity at 818 and 582 cm^{-1} for Met and 786 and 562 cm^{-1} for Met-ND_3.

Consideration of the calculated spectra of the CH_n stretch region near 3000 cm^{-1} shows that they are similar for all the conformers and in agreement with the DSD spectra. Likewise, the prominent band of moderate intensity at 1336 cm^{-1} (1323 cm^{-1} Met-ND_3) in the DSD spectrum and assigned to the CH bend has corresponding bands of similar intensities ranging about 1336 cm^{-1} for all the conformers.

The observed DSD bands at 1620 (1618 for Met-ND_3) and 1405 (1391) cm^{-1} are in agreement with assignments to ν_{as} and ν_s, respectively, of CO_2^- (ZW) rather than to the corresponding bands of the CO_2H group (neutral molecule), for which a larger frequency separation would be expected. This is illustrated by the measurements for alanine.[28] In the crystal, corresponding to the ZW, bands are seen at 1623 and 1354 cm^{-1}, whereas for the low-temperature isolated matrix, bands are seen at 1780 and 1153 cm^{-1}. The calculated spectra confirm this interpretation. For the neutral molecule deriving from the GtG conformer, frequencies of 1813 and 1186 cm^{-1} were calculated. Further

TABLE 3: Comparison of Calculated (SCRF/HF/6-311++G(d,p)) Vibrational Frequencies (scaled) and Intensities for Conformer GtG with the Observed DSD Spectrum for Met (cm^{-1})[a]

no.	GtG (0.9)	DSD	assignment	no.	GtG (0.9)	DSD	assignment
12	470 (3)	413 (w)	βOCC	34	1360 (5)	1379 (vw)	$\rho CH_2/\rho CH$
13	484 (5)	449 (w)	$\beta NCC/\beta OCC$	35	1388 (28)	1405 (m)	$\nu_s CO_2^-$
14	582 (2)	578 (m)	$\beta CCC/\beta OCC$	36	1425 (4)	n.o.	βCH_3
15	642 (5)	639 (m)	νSC	37	1431 (1)	n.o.	βCH_2
16	704 (<1)	672 (w)	ρCH_2	38	1434 (7)	1426 (w)	βCH_3
17	742 (<1)	752 (w)	νSC	39	1441 (30)	1452 (w)	βCH_2
18	781 (9)	777 (w)	βCO_2^-	40	1456 (61)	1475 (w)	$\beta_s NH_3^+$
19	818 (7)	818 (m)	$\rho NH_3^+/\nu CC$	41	1591 (9)	1568 (s)	$\beta_{as} NH_3^+$
20	869 (7)	881 (w)	$\nu CC/\beta CO_2^-$	42	1625 (29)	1620 (o)	$\beta_{as} NH_3^+$
21	914 (4)	n.o.	ρNH_3^+	43	1633 (100)	1620 (vs)	$\nu_{as} CO_2^-$
22	946 (2)	n.o.	ρCH_3	44	2862 (7)	2828 (w)	$\nu_s CH_2$
23	954 (2)	n.o.	ρCH_3	45	2879 (<1)	2855 (vw)	$\nu_s CH_2$
24	972 (4)	969 (w)	ρNH_3^+	46	2887 (1)	2872 (vw)	$\nu_s CH_3$
25	1041 (1)	1033 (vw)	νCC	47	2906 (4)	2915 (m)	$\nu_{as} CH_2$
26	1053 (1)	1056 (w)	$\nu CC/\rho NH_3^+$	48	2917 (2)	n.o.	νCH
27	1098 (6)	1140 (s)	$\beta CH/\nu CN$	49	2943 (2)	2945 (vw)	$\nu_{as} CH_2$
28	1182 (5)	1193 (w)	βCH_2	50	2972 (<1)	n.o.	$\nu_{as} CH_3$
29	1249 (<1)	1208 (w)	βCH_2	51	2978 (<1)	n.o.	$\nu_{as} CH_3$
30	1281 (6)	1268 (w)	βCH	52	3233 (20)	3130 (w)	$\nu_s NH_3^+$
31	1302 (18)	1326 (m)	βCH_2	53	3310 (38)	3242 (m)	$\nu_{as} NH_3^+$
32	1335 (18)	1336 (m)	βCH	54	3346 (22)	3299 (m)	$\nu_{as} NH_3^+$
33	1342 (5)	1352 (sh)	βCH_3				

[a] ν, stretching; β, bending; ρ, all other deformations. vs, very strong; m, medium; w, weak; vw, very weak; n.o., not observed.; as, asymmetric; s, symmetric.

TABLE 4: Comparison of SCRF Calculated (HF/6-311++G(d,p)) Vibrational Frequencies (scaled) and Intensities for Conformer GtG with the Observed DSD Spectrum for Met-ND_3 (cm^{-1})

no.	GtG (0.9)	DSD	assignment	no.	GtG (0.9)	DSD	assignment
12	451 (<1)	n.o.	βCCC	34	1299 (6)	1294 (w)	βCH_2
13	464 (5)	442 (w)	$\beta CO_2^-/\beta OCC$	35	1325 (15)	1323 (m)	βCH
14	562 (2)	563 (w)	$\beta OCC/\beta CCC$	36	1341 (<1)	n.o.	$\beta_s CH_3$
15	641 (3)	624 (m)	νSC	37	1358 (7)	1352 (vw)	$\beta CH_2/\beta CH$
16	698 (<1)	n.o.	ρCH_2	38	1386 (20)	1391 (s)	$\nu_s CO_2^-$
17	728 (<1)	n.o.	νSC	39	1425 (2)	n.o.	βCH_3
18	741 (2)	n.o.	βNCC	40	1431 (<1)	n.o.	βCH_2
19	771 (4)	751 (w)	βCO_2^-	41	1434 (2)	1428 (w)	βCH_3
20	786 (7)	804 (w)	ρND_3^+	42	1444 (4)	1452 (w)	βCH_2
21	863 (2)	833 (m)	νCC	43	1623 (100)	1618 (vs)	$\nu_{as} CO_2^-$
22	885 (<1)	n.o.	νCC	44	2323 (6)	2344 (m)	$\nu_s ND_3^+$
23	946 (<1)	911 (w)	ρCH_3	45	2440 (14)	2398 (m)	$\nu_{as} ND_3^+$
24	954 (<1)	969 (w)	ρCH_3	46	2466 (8)	2466 (m)	$\nu_{as} ND_3^+$
25	982 (<1)	970 (w)	νCC	47	2862 (4)	n.o.	$\nu_s CH_2$
26	1036 (<1)	1007 (w)	νCC	48	2879 (<1)	n.o.	$\nu_{as} CH_2$
27	1067 (<1)	1067 (w)	$\beta CH/\nu CC$	49	2887 (<1)	2868 (w)	$\nu_s CH_3$
28	1115 (16)	1101 (w)?	βND_3^+	50	2907 (2)	2914 (m)	$\nu_{as} CH_2$
29	1156 (4)	1149 (vw)	βND_3^+	51	2917 (1)	n.o.	νCH
30	1170 (3)	1186 (s)	βND_3^+	52	2943 (2)	2946 (w)	νCH_2
31	1186 (7)	1186 (s)	βCH_2	53	2972 (<1)	n.o.	$\nu_{as} CH_3$
32	1242 (1)	n.o.	βCH_2	54	2978 (<1)	2980 (vw)	$\nu_{as} CH_3$
33	1278 (2)	1266 (w)	βCH				

confirmation that it is the zwitterion that is obtained in the DSD sample comes form the absence of an OH stretch band near 3600 cm^{-1}, (alanine, matrix isolation[28] 3555 cm^{-1}).

In summary, comparison of calculated and measured spectra of the seven conformers favors the presence of conformer GtG in the DSD samples. Nevertheless, the evidence against a number of the other conformers, in particular gtt and tGG, is not overwhelming. However, conformers ggt and gGt can be excluded, largely on the grounds of poor agreement in the NH_3^+ stretch region. The DFT calculations suggest that in addition, conformer ttG can also be excluded on similar grounds. In terms of their relative energies conformer, gtt is the most favored, although GtG and tGG are close.

On the basis of the conclusion reached regarding the most likely identity of the conformer present in the DSD samples, the SCRF calculated spectra of conformer GtG can be considered to be most representative of the measured DSD spectra of Met and Met-ND_3. Assignments other than those common to, and characteristic of, the amino acids such as νCO_2^-, νNH_3^+, and νCH_3 have been determined from comparison with the calculated spectrum of the GtG conformer. The spectral assignments proposed for the observed bands in the DSD spectra of Met and Met-ND_3, as well as the assignments for the calculated spectra of conformer GtG are presented in Tables 3 and 4. The assignments in the calculated spectra are qualitative and have been established by consideration of the normal coordinates and by visual scrutiny of the vibrational motions. It is noted that, particularly for the lower frequency vibrations, the normal coordinates cannot be equated to individual internal coordinates (group vibrations) but have substantial contributions from a number of group vibrations. In Tables 3 and 4, only the largest contribution, qualitatively identified, has been specified. Designations of assignments have been restricted to stretching (ν), bending (β), and deformation (ρ).

TABLE 5: Comparison of the Predicted Geometry (SCRF/HF/6-311++G(d,p)) of Conformer tGG with the Crystal Structure of Met B Obtained by X-ray Diffraction[4]

bond lengths (Å)			in-plane angles (deg)			dihedral angles (deg)		
bonds	tGG	Met B	atoms involved	tGG	Met B	atoms involved	tGG	Met B
C2−O1	1.233	1.264	O1−C2−O3	128.69	125.9	C4−C2−O1−O3	176.82	
O3−C2	1.228	1.246	C4−C2−O1	114.94	116.1	H5−C4−C2−O1	−99.39	
C4−C2	1.563	1.535	C4−C2−O3	116.30	118.0	N6−C4−O1−O3	−168.52	
H5−C4	1.082		H5−C4−C2	106.83		N6−C4−C2−O1 (Ψ^1)	13.50	−32.4
N6−C4	1.513	1.483	N6−C4−C2	107.78	109.8	N6−C4−C2−O3 (Ψ^2)	−169.27	
H7−N6	1.010		H7−N6−C4	112.97		H7−N6−C4−C2 (Φ^1)	−147.82	
H8−N6	1.019		H8−N6−C4	112.03		H8−N6−C4−C2 (Φ^2)	91.69	
H9−N6	1.013		H9−N6−C4	107.17		H9−N6−C4−C2 (Φ^3)	−25.71	
C10−C4	1.531	1.538	C10−C4−C2	118.22	111.2	C10−C4−C2−O1	136.85	
H11−C10	1.089		H11−C10−C4	109.40		H11−C10−C4−N6	75.43	
H12−C10	1.089		H12−C10−C4	108.50		H12−C10−C4−N6	−40.26	
C13−C10	1.531	1.516	C13−C10−C4	115.29	114.4	C13−C10−C4−N6 (X^1)	−162.24	−165.4
H14−C13	1.084		H14−C13−C10	108.30		S16−C13−C10−C4 (X^2)	60.02	71.5
H15−C13	1.080		H15−C13−C10	109.61		C17−S16−C13−C10 (X^3)	73.96	72.4
S16−C13	1.820	1.810	S16−C13−C10	116.15	114.9	H18−C17−S16−C13	56.50	
C17−S16	1.825	1.796	C17−S16−C13	102.93	100.1	H19−C17−S16−C13	−66.61	
H18−C17	1.081		H18−C17−S16	110.51		H20−C17−S16−C13	175.05	
H19−C17	1.080		H19C17−S16	111.76				
H20−C17	1.081		H20−C17−S16	106.71				

In contrast to the spectrum of Met in KBr obtained by the traditional pellet method, in the DSD spectrum, no bands are apparent in the region between about 1620 and 2900 cm^{-1}. Furthermore, instead of the broad envelope obtained extending over the region of the NH_3^+ and CH_n stretches, which is common to the KBr pellet spectra of amino acids, well-resolved bands are seen in this region of the DSD spectrum that can be assigned with confidence. The same observations apply to the Met-ND_3 spectra.

Most regions of the DSD spectra have been discussed in the context of comparisons with the calculated spectra of the seven conformers. However, one prominent band in the DSD spectrum which has no obvious corresponding band in the GtG calculated spectrum deserves comment. It is the strong band in the Met spectrum at 1140 cm^{-1}. It has been observed in repeated DSD spectra and hence is not an artifact encountered in one measurement. For the calculated spectra of all the conformers, only weak bands are predicted in the vicinity of 1140 cm^{-1}, and even in the KBr pellet spectrum, no strong band is evident at that frequency. Also, in the Met-ND_3 spectrum, no band of corresponding strength is evident. We have no explanation for this band other than it may be derived from the overlap of a number of near-lying bands or is an experimental artifact.

Structures. A comparison, Table 1, of the three torsion angles, χ^1, χ^2, and χ^3, calculated for the seven conformers with the corresponding torsion angles measured for the two forms of Met in the crystal by X-ray diffraction,[4,5] shows a match between conformer tGG and Met B. For Met B, the three torsion angles are, respectively, −165.4°, 71.5°, and 72.4°, while for conformer tGG, they are −162.2°, 60.0°, and 74.0°. However, a complete structural comparison cannot be undertaken. The Met structural parameters reported in the literature[4,5] are incomplete due to the difficulty of determining the hydrogen positions from low quality Met crystals by X-ray diffraction. On the other hand, the SCRF calculations do provide a full description of the molecular structures of the conformers. These are listed in Table 5 for conformer tGG together with the available data for Met B. Despite the reasonable agreement apparent between the tGG and Met B structures, it should be noted that Met zwitterions in a KBr matrix and in the crystal have different local environments. For the SCRF calculations conducted on Met in a KBr continuum, it is assumed that the intermolecular interactions are neither strong nor specific and can be adequately described by a uniform reaction field. In contrast, for Met in the crystal, relatively strong and specific intermolecular interactions (H-bonding) exist extensively between ionized amino and carboxyl groups. Therefore, structural parameters associated with the amino and carboxyl groups may differ appreciably between tGG in the KBr matrix and Met B in the crystal. For the remaining structural parameters, close similarity is expected.

This may explain the relatively large difference (ca. 10°) for χ^2 (S16−C13−C10−C4) between tGG and Met B, although it is nevertheless suggested that they have the same conformations. Similarly, other differences may have the same explanation. In particular, ψ^1 (N6−C4−C2−O1) is 13.5° for tGG while −32.4° for Met B. Differences are also evident in some bond lengths. For conformer tGG, the lengths of the two CO bonds, C2−O1 and C2−O3, and the CN bond, C4−N6, are predicted to be 1.233, 1.228, and 1.513 Å, respectively, while for Met B, these bond lengths are from X-ray diffraction measurements 1.264, 1.246, and 1.483 Å, respectively. It is noteworthy that the two CO bond lengths are more similar in the KBr matrix than in the crystal, an indication of the occurrence of H-bonding in the crystal leading to elongation of one of the CO bonds. The differences between "in-plane" angles of tGG and Met B are not significant, and the largest one is that of angle C10−C4−C2, about 7°, all others are less than 3°.

Conclusions

The mid-IR spectra of Met and its N−D_3 deuterated isotopomer as isolated zwitterions in a KBr matrix have been obtained for the first time by means of a dissolution, spray and deposition sampling technique. The vibrational spectra and molecular structures of zwitterionic Met have been predicted by SCRF ab initio molecular orbital calculations using the Onsager dipole sphere model. Seven Met conformers were identified by the SCRF calculations at the levels HF/6-311++G(d,p) and B3LYP/6-31G(d). The observed spectra correspond to the zwitterion and not the neutral molecule. Although conformers gGt and ggt have the lowest energies at all levels of calculation studied, their calculated spectra display important differences to the observed spectra. Comparison of calculated and measured spectra of the seven conformers of Met and Met-ND_3 favors the presence of conformer GtG in the DSD samples.

Nevertheless, the evidence against a number of the other conformers, in particular, gtt and tGG, is not overwhelming. The calculations show that the three conformers GtG, gtt, and tGG are of similar stabilities, with energies more negative than the remaining two conformers, ttG and GGG. Of the seven conformers, it is found that conformer tGG has a similar conformation to the Met B crystal form. The calculated structural parameters for tGG supplement the incomplete structural data determined for Met B from X-ray crystal data.

Apart from one band of moderate intensity observed for Met but not for Met-ND_3, good agreement has been established between the calculated spectra for the GtG conformer and the measured spectra of Met and Met-ND_3 in a KBr matrix prepared by the DSD method. The overall spectral agreement shows that Met in the KBr continuum (solid solvent) is present largely as individual zwitterions, stabilized by the surrounding continuum through the reaction field.

The sampling technique of dissolution, spray, and deposition (DSD) has provided a way to measure IR spectra of these zwitterionic species in a less perturbed local environment than in aqueous solutions or in the crystal. Instead of the broad envelope obtained extending over the region of the NH_3^+ and CH_n stretches, which is common to the standard KBr pellet spectra of amino acids, well-resolved bands are seen in this region of the DSD spectrum that can be assigned with confidence. It is this feature in particular that demonstrates most clearly the power of the DSD sampling technique.

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References and Notes

(1) Gould, R. O.; Gray, A. M.; Taylor, P.; Walkinshaw, M. D. *J. Am. Chem. Soc*. **1985**, *107*, 5921.

(2) Brown, T. L.; Lemay, H. E., Jr.; Bursten, B. E. *Chemistry the Central Science*, 6th ed.; Prentice-Hall: Englewood Cliffs, NJ, 1994; Chapter 26, p 982.

(3) Barnham, K. J.; Djuran, M. I.; Murdoch, P. D. S.; Ranford, J. D.; Sadler, P. J. *J. Chem. Soc., Dalton Trans.* **1995**, 3721.

(4) Dalhus, B.; Görbitz, C. H. *Acta Chem. Scand*. **1996**, *50*, 544.

(5) Torii, K.; Iitaka, Y. *Acta Cryst*. **1973**, *B29*, 2799.

(6) Onoa, B.; Moreno, V. *Trans. Met. Chem*. **1998**, *23*, 485.

(7) Tandon, P.; Gupta, V. D.; Prasad, O.; Rastogi, S.; Gupta, V. D. *J. Polym. Sci. B: Polym. Phys*. **1997**, *35*, 2281.

(8) Gatlin, C. L.; Turecek, F.; Vaisar, T. *J. Mass Spectrom*. **1995**, *30*, 1617.

(9) Grochowski, T.; Samochocka, K. *J. Chem. Soc., Dalton Trans.* **1992**, 1145.

(10) Isab, A. A. *Inorg. Chim. Acta* **1988**, *153*, 209.

(11) Kowalik, T.; Kozlowski, H. *Inorg. Chim. Acta* **1982**, *67*, L39.

(12) Stewart, S.; Fredericks, P. M. *Spectrochimica Acta* **1999**, *55A*, 1641.

(13) Faller, P.; Vašák, M. *Inorg. Chim. Acta* **1998**, *272*, 150.

(14) Cooper, E.; Krebs, F.; Smith, McD.; Raval, R. *J. Electron Spectrosc. Relat. Phenom*. **1993**, *64/65*, 469.

(15) Grunenberg, A.; Bougeard, D. *J. Mol. Struct*. **1987**, *160*, 27.

(16) Yu, D.; Armstrong, D. A.; Rauk, A. *Can. J. Chem*. **1992**, *70*, 1762.

(17) Ding, Y.; Krogh-Jespersen, K. *Chem. Phys. Lett*. **1992**, *199*, 261.

(18) Bonaccorsi, R.; Palla, P.; Tomasi, J. *J. Am. Chem. Soc*. **1984**, *106*, 1945.

(19) Tse, Y. C.; Newton, M. D.; Vishveshwara, S.; Pople, J. A. *J. Am. Chem. Soc*. **1978**, *100*, 4329.

(20) Cao, X.; Fischer, G. *Chem. Phys.* **2000**, *255*, 195.

(21) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Stucture Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996; p 237.

(22) Frimand, K.; Bohr, H.; Jalkanen, K. J.; Suhai, S. *Chem. Phys.* **2000**, *255*, 165.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(24) Frisch, Æ.; Frisch, M. J. *Gaussian 98 User's Reference*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1999; p 171.

(25) Cao, X.; Fischer, G. *J. Mol. Struct.* **2000**, *519*, 153.

(26) In *Handbook of Chemistry and Physics*, 78th ed.; R. C. Lide, D. R., Eds.; CRC Press LLC: Boca Raton, FL, 1997; pp 12−51.

(27) Scott, A. P.; Radom, L. *J. Phys. Chem*. **1996**, *100*, 16502.

(28) Rosado, M. T. S.; Duarte, M. L. R. S.; Fausto, R. *J. Mol. Struct*. **1997**, *410*−*411*, 343.