The carbon–hydrogen stretching region of the Raman spectra of 1,6-hexanediame: N-deuteration, ionisation and temperature effects

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Abstract

The Fermi resonance interaction between the methylene symmetric C–H stretching mode and appropriate binary combinations involving the methylene bending mode in the Raman spectra of polyamines, namely in 1,6-hexanediame derivatives, under different conditions of deuteration and ionisation of the head amino groups and varying temperature has been analysed. The tentative assignment of the observed bands in the C–H stretching region of the registered Raman spectra is reported and the ratio of the Raman intensities of the symmetric stretching to the antisymmetric fundamentals is considered in its possible relation to the order/disorder of the skeletal hydrocarbon chains, from the \textit{all-trans} prevailing geometry in the solid state at lower temperatures to the increasing amount of \textit{gauche} arrangements on heating and melting. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polyamines are found in millimolar concentrations in most living cells, resulting from the carboxylation of basic aminoacids. They form intrinsic polycations essential for cell growth and differentiation. Due to their polycationic character, they are widely used as chelating agents for some metal ions and as agents for introducing direct cross-linking sites in polymers, namely in the blending of ionomers [1–3].

In the aliphatic diamines series, 1,6-hexanediame typically represents the diamines used for that purpose because the flexibility of its chain conformational structure and its strong basicity [2]. These physical properties are influenced by different factors, from steric, dipolar and hyperconjugative effects to hydrogen-bonding which greatly determine either its rotational isomerism or its intra- and intermolecular interactions involving the pairs of free electrons.

As it has been shown in the past decades, the Raman and infrared vibrational spectra in the C–H stretching region can be used for probing such an influence in the conformation environment and dynamics of complex hydrocarbon-chain assembling, especially those of model and real membranes [4,5].

In the present work, we report results for the C–H stretching region of N-protonated 1,6-hexanediame and its N-deuterated, N-diprotonated and N-dideuter-
ated derivatives studied at different temperatures and compared with results obtained from similar vibrational analysis of other diamines.

2. Experimental

The Raman spectra performed at room temperature were obtained on a Spex Ramalog 1403 double monochromater spectrometer (focal distance 0.85 m, aperture f/7.8) equipped with holographic gratings of 1800 grooves mm\(^{-1}\), and a detector assembly containing a thermoelectrically cooled Hamamatsu R928 photomultiplier tube. The spectrometer operated with slits of 320 µm, a wavenumber increment of 1 cm\(^{-1}\) and an integration time of 1 s.

The Raman experiments carried out at other temperatures were performed on a triple monochromator Jobin Yvon T64000 system (focal distance 0.640 m, aperture f/7.5) with holographic gratings of 1800 grooves mm\(^{-1}\). The premonochromator stage was used in subtractive mode and the entrance slit was set to 300 µm. The detection system was a non-intensified CCD (Jobin Yvon Spectraview 2D) detector.

The samples were illuminated by the 514.5 nm line of an argon ion laser (Coherent, model Innova), providing 100–120 mW at the sample position.

Temperature variation was carried out using a home-made Miller–Harney cell type assembly, monitored by the resistivity of a calibrated thermocouple.

Samples were sealed in Kimax glass capillary tubes of 0.8 mm inner diameter. Raman data were stored on disk, with the possibility of further processing. The error in wavenumbers is estimated to be within ca. 1 cm\(^{-1}\), while the error in temperatures is less than 1 K.

3. Results and discussion

3.1. The methylene C–H stretchings for N-hydrogenated and N-deuterated 1,6-hexanediame

The C–H stretching region (2800–3000 cm\(^{-1}\)) of the experimental Raman spectrum for N-hydrogenated and N-deuterated 1,6-hexanediame in the solid state, are presented in Fig. 1, together with the Raman spectra of the same region of N-hydrogenated 1,2-ethanediame and 1,4-butanediame, for comparison.

The analysis of this spectral region of our registered Raman spectra for diamines, in the solid state, encompassing alkyl hydrocarbon chains with 2–7 CH\(_2\) groups shows that the deuteration of the –NH\(_2\) amino groups has no significant effects on the frequencies and number of bands associated with the methylene C–H stretchings, as it is the case of N-hydrogenated and N-deuterated 1,6-hexanediame. Only some small changes in the relative band intensity are observed.

The frequency and the relative intensity changes in the observed bands in the same spectral region as the number of CH\(_2\) groups in the alkyl hydrocarbon chain increases is noticeable and complex.

Several FT-IR and Raman studies have already been reported for the simplest linear diamine, the 1,2-ethanediame, and its N-deuterated derivatives [6–9]. In the solid state, this molecule has an all-trans geometry. As expected, in the gaseous state its predominant species are the gauche conformers relative
to the central C–C bond, and in the neat liquid distinct conformers have been detected. In this case, from ab initio calculations it was found that the most stable conformers are the conformers where intramolecular
\(-\text{NH} \cdots \text{N} \) hydrogen bonds can occur [10].

Starting with the methylene C–H stretching region for solid N-hydrogenated 1,2-ethanediame, there is a main strong and sharp peak at ca. 2853 cm\(^{-1}\) and three other peaks at ca. 2896, 2908 and 2930 cm\(^{-1}\). The generally accepted assignment is as follows [6]: the peaks at 2853, 2908 and 2930 cm\(^{-1}\) are, respectively, the fundamental symmetric CH\(_2\) stretch and overtones of A\(_g\) species determined by intramolecular Fermi resonance interaction between the symmetric C–H stretching and the \(\rangle\) HCH scissors modes. The band at 2908 cm\(^{-1}\) is the B\(_{1g}\) antisymmetric CH\(_2\) stretching floating on top of a broad background of A\(_g\) species [11].

It is known that when gauche structures are generated the overtone trans levels around 2900 cm\(^{-1}\) are removed, giving back intensity to the overtone band around 2930 wavenumbers [5,12,13]. The observed frequency shifts and relative intensity changes as the alkyl hydrocarbon chain length increases are the result of the increasing in the gauche conformations due to more flexibility of the chain. The pattern of the C–H stretching region of the studied Raman spectra for the N-hydrogenated studied diamines having three or more methylene groups can easily be associated with such gauche content with increasing number of structural non-equivalent methylene groups.

Two distinct peaks in the 2845–2859 cm\(^{-1}\) range will correspond to the fundamental symmetric CH\(_2\) stretch of the methylene groups bonded to the head groups and the other methylene groups of the chain, respectively. The bands in the 2878–2890 cm\(^{-1}\) range will correspond to the antisymmetric CH\(_2\) stretching of the same groups. Going from the methylene groups adjoining the amino groups to the other methylene groups in the chain, a decrease in the strength of the C–H stretchings is expected.

3.2. The methylene C–H stretchings for N-hydrogenated and N-deuterated 1,6-hexanediamine dihydrochlorides

Long ago, it has been noted that the ionisation of the amino group has a marked influence on the C–H stretching frequencies of the adjoining methylene groups. In certain amino acids, namely in glycine and \(\beta\)-alanine, these frequencies were observed to increase by 40–60 cm\(^{-1}\) on protonation of a neighbouring amino group [14]. Although in a smaller extent, such an ionisation affects also the other methylene groups.

The ionic interactions resulting from the protonation of the amine groups and the formation of bonds of the type \(-\text{N}^+–\text{H} \cdots \text{Cl}^-\) with a greater strength than the normal hydrogen bonds lead to a closer molecular packing of the amine hydrocarbon chains as compared with the molecular packing in the non-ionised amines. In the closer packing, the interactions between the carbon and hydrogen atoms are stronger leading to a general upward displacement of the methylene C–H stretching frequencies, as it is the general pattern of the registered spectra for the studied alkylamines dihydrochlorides shown in Fig. 2.

The strength of the molecular packing changes with the size of the hydrocarbon chain. The increase in chain length allows for some releasing in the aggregate. As expected, due to this kind of releasing, the frequencies of the C–H stretches are observed to decrease as the hydrocarbon chain length increases, corresponding to more flexibility.

There are no significant changes in the general band pattern in this region of the registered Raman spectra of solid N-hydrogenated and N-deuterated 1,6-hexanediame dihydrochlorides (Fig. 2D and E); the same was observed for the other studied N-ionised alkylamines dihydrochlorides as compared with the corresponding N-deuterated diamines. As in the non-ionised alkylamines, the methylene frequencies are not at all affected by a change in mass of the hydrogen atoms attached to the adjoining \(-\text{NH}_3^+\) or \(\text{ND}_3^+\).

However, the general band pattern of this spectral region shows marked differences upon the increasing alkyl chain length of the studied N-ionised dihydrochlorides. As the number of CH\(_2\) groups increase such differences become smaller, but they are still clear in the spectrum of 1,6-hexanediame dihydrochloride as compared with the spectrum of 1,5-pentanediame dihydrochloride. This means that the effect of the chain length increase upon the closer packing of the CH\(_2\) groups in the N-ionised alkylamines dihydrochlorides is much stronger than in the corresponding non-ionic species.
Aside the changes in frequency and in relative intensity of the bands in the 2840–2950 cm\(^{-1}\) range, it is worthwhile to note the band at 2977 cm\(^{-1}\) in 1,2-ethanediame dihydrochloride, a band which is not at all observed in the non-ionised compounds. This band appears to split into two peaks as the chain length increases with the lower frequency peak gaining intensity at the expenses of the higher frequency peak and both shifting to higher frequencies along the series of increasing chain length diamine dihydrochlorides. Studying the Raman spectrum of ethylenediamine dihydrochloride, Mureinik and Scheuermann [15] have assigned this band to the N–H symmetric stretching of the ionised NH\(_3^+\) group. As the two peaks do not disappear upon deuteration of the NH\(_3^+\) group of the diamine dihydrochlorides (Fig. 2D versus E), such an assignment cannot be supported. The Raman spectra for solid N-hydrogenated and N-deuterated 1,6-hexamidine dihydrochlorides shown in Fig. 3, indicate that the N–H stretchings for NH\(_2\) and NH\(_3^+\) lie in the 3100–3400 and 3020–3150 cm\(^{-1}\) ranges, respectively; and the N–D stretchings for ND\(_2\) and ND\(_3^+\), in the ranges 2300–2550 and 2000–2400 cm\(^{-1}\), respectively.

Since in the Raman spectrum, C–H stretching modes are known to be among the most intense bands
[16], it seems to us, from the Raman spectrum of 1,2-ethanediamine dihydrochloride where there is only two intense bands, that the bands at 2912 and 2977 cm\(^{-1}\) must be assigned to the fundamentals C–H symmetric and antisymmetric stretchings. If so, the band at 2977 cm\(^{-1}\) in the spectra of the other studied alkyldiamine dihydrochlorides would also correspond to the C–H antisymmetric stretching of CH\(_2\) groups existing in the chain. Crystal field effects and the presence of more than one type of molecular packing could be responsible for this methylene C–H asymmetric stretching frequency. However, this interpretation will need further support, namely from ab initio MO calculations and inelastic neutron scattering which are being performed within our group [21].

3.3. Temperature effects on the 1,6-hexanediamine and its derivatives

The immediate effects of temperature changes in hydrocarbon systems involve changes in the conformation, mobility and packing of the molecular chains. In solid state the hydrocarbon chains of these systems exist mostly in trans-conformation, hosting small conformational distortions made up of different possible gauche conformations. For most hydrocarbon systems, the amount of these conformational distortions becomes dominant in the melt and in liquid solutions, approaching the 100\% in the gas phase.

As mentioned above, experimental observations show that in the Raman spectrum of trans-crystalline

![Fig. 4. The order/disorder parameter \(S = (r - 0.7)/1.5\) as a function of temperature for: (■) \(\text{H}_2\text{N(CH}_2)_6\text{NH}_2\); (▼) \(\text{D}_2\text{N(CH}_2)_6\text{ND}_2\); and (♦) \(\text{H}_2\text{N(CH}_2)_6\text{NH}_2\text{Cl}_2\).]
polyethylene chains, the bands corresponding to the methylene C–H symmetric (near 2850 cm$^{-1}$) and antisymmetric (near 2890 cm$^{-1}$) are the two main peaks, the former strong and broad and the latter strong and sharp, with other much less intense bands in the 2900–2930 cm$^{-1}$ range due to the fundamental symmetric CH$_2$ stretch and overtones of A$_g$ species in Fermi resonance. Upon melting, the band corresponding to the C–H symmetric stretching becomes the strongest feature in this spectral region, and the band corresponding to the antisymmetric mode collapses and shifts upward with increasing temperature becoming, seemingly, a very broad feature [12].

The reason of why the C–H stretching fundamentals in hydrocarbon systems should exhibit a profound sensitivity to the detailed molecular structure is complex and has been widely analysed. In this kind of analysis, experimental frequency-phase difference curves for the methylene C–H symmetric and antisymmetric stretchings show that the Raman line corresponding to the antisymmetric stretching floats on top of a broad background due to Fermi resonance interaction between the methylene in-phase C–H stretching fundamental and the overtone of the $\gt$HCH scissors modes which has maxima in the referred 2900–2930 cm$^{-1}$ range [11,17–19]. Thus, small changes in frequency of the methylene scissoring fundamental upon the formation of gauche isomers would remove the resonance condition, resulting in an intensity decrease of the C–H antisymmetric mode, not affecting the intensity of the C–H symmetric stretching mode. On this basis, it is possible to use the changes in the intensity ratio of the C–H symmetric and antisymmetric stretching modes as a measure of the conformational changes when gauche structures are introduced in hydrocarbon systems. Using simple C–H antisymmetric versus symmetric stretching peak heights ratio ($r$), Gaber and Petiolas have proposed as a quantitative parameter for measuring such conformational changes, the value of $S$ defined by the equation $S = (r - 0.7)/1.5$ so that $S = 1$ for a chain in all-trans and $S = 0$ for a chain in an all-gauche conformation [20].

Using this parameter, Fig. 4 shows the effects of temperature in conformational changes of N-hydrogenated and N-deuterated 1,6-hexanediame and 1,6-hexanediame dihydrochloride. At corresponding temperatures, the extent of trans conformations in the three 1,6-hexanediame derivatives is greater for the $\approx$N–H$^+$···Cl$^-$ intermolecular forces as compared with the N–H···N and N–D···N hydrogen bonds the most responsible for the molecular packing in each case. As expected, in the three solids, the most flexible hydrocarbon chains are the D$_2$N(CH$_3$)$_2$ND$_2$ chains whereas the most rigid are the chains in H$_2$N(CH$_2$)$_6$-NH$_2$Cl$_2$. On heating, the content of all-trans conformations in solid 1,6-hexanediame dihydrochloride changes from ca. 100% at 213 K to ca.78% at 310 K, i.e. less than 25%, whereas in the same temperature range, N-hydrogenated 1,6-hexanediame varies from $\approx$77 to $\approx$6% (still in the solid state) and N-deuterated 1,6-hexanediame from $\approx$72 to less than 2% (already in the liquid state).

The drastic changes in the C–H stretching region upon melting are shown in Fig. 5 for the case of N-hydrogenated and N-deuterated 1,6-hexanediame.

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**Fig. 5.** The C–H stretching Raman region for: (A) solid H$_2$N(CH$_3$)$_2$NH$_2$ at 243 K; (B) liquid H$_2$N(CH$_3$)$_2$NH$_2$ at 333 K; (C) solid D$_2$N(CH$_3$)$_2$ND$_2$ at 243 K; and (D) liquid D$_2$N(CH$_3$)$_2$ND$_2$ at 251 K.
4. Conclusion

The analysis of the C–H stretching region of the Raman spectra of 1,6-hexanediamine compounds shows that the deuteration of the amino groups does not greatly affect the intermolecular forces and hydrocarbon chain flexibility existing in the N-hydrogenated 1,6-hexanediamine species, whereas the ionisation of the same groups leads to much stronger intermolecular forces with a marked effect on that flexibility increasing very much its rigidity.

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