# Anharmonic Effects and Vibrational Dynamics in H-Bonded Liquids by Attenuated Total Reflectance FT-IR Spectroscopy

**V. Crupi, G. Maisano, D. Majolino, P. Migliardo,* and V. Venuti**

*Dipartimento di Fisica dell'Università and INFM Sezione di Messina, C.da Papardo, S.ta Sperone 31, P.O. Box 55, 98166 S. Agata, Messina, Italy*

*Received: November 4, 1999*

In the present work IR measurements as a function of temperature, performed, in the (2500−3700) cm$^{-1}$ region, on ethylene glycol (EG) and its homologous systems, namely ethylene glycol monomethyl ether (EGmE) and ethylene glycol dimethyl ether (EGdE), are presented and discussed. The goal is to analyze the evolution of the O−H stretching fundamental band in a wide range of temperature for systems having identical chemical structure except for the number of hydroxyl end groups, clarifying in this way the processes characterizing the vibrational dynamics of these H-bonded liquids. In particular, the O−H stretching band shape, through a quantitative study performed with FT-IR in the attenuated total reflectance geometry, has been connected to the different transient local environments of hydrogen-bonded molecular groups, and the role played by inter- and intramolecular interactions discussed within the framework of current theories for associated liquids. In addition, temperature-induced isosbestic points observed in the IR spectra for liquid EG and EGmE are analyzed in terms of a simple two-state model.

## Introduction

Because of its noticeable importance, linked to its possibility to show H-bonded inter- and intramolecular interactions, and to the fact that it constitutes the monomeric entity of the poly(ethylene oxide) (PEO) polymer, the ethylene glycol [EG, H(O−CH$_2$−CH$_2$)OH] molecule has been, in recent years, the focus of much interest in scientific research, from a theoretical and experimental point of view.[1,2] Its equilibrium configurations, both in the gas phase and in the liquid phase, have been intensively studied previously, also by our group from a dynamical point of view.[3]

As far as EG's structure is concerned, each molecule can generate many conformations (whose probability of existence depends on the corresponding potential energy minimum) by the rotation of the two CH$_2$−OH groups around the C−C axis.[1] In particular, in the "eclipsed" conformation the two groups of CH$_2$−OH atoms are so close that strong intramolecular repulsive forces arise. When, instead, the two sets of atoms are placed as far from one other as possible, the system is in the "staggered" conformation, which is repeated for every 120° of rotation. In this way we can distinguish three such structures, not energetically equivalent: the trans form, where the OH groups are as far apart from one other as possible, and the gauche form. In the absence of any other intramolecular bond, the staggered-trans configuration is the most energetically favored, but from a computer simulation performed in the case of an isolated EG molecule,[4] it turned out that a gauche form stabilized by an intramolecular H-bond (see Figure 1), which is unusual for small molecules, has the highest probability of existence. In addition, the OH interacting groups promote, via hydrogen bonding, a set of transient cross-links between neighboring molecules, giving relevant transient structures such as branched associated species and/or chains.[3]

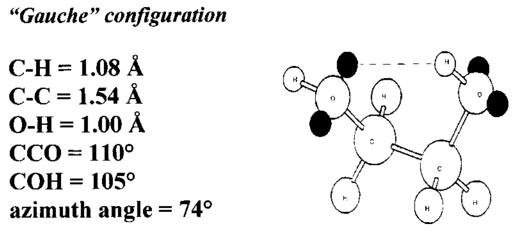

**Figure 1.** Gauche conformation for an isolated ethylene glycol molecule, stabilized by an intramolecular H-bond.

This work has the purpose of clarifying the role played by the H-bond in the structural environments of a class of H-bonded liquids having identical chemical structure except for the number of the hydroxyl end groups: EG, EG methyl ether (EGmE), and EG dimethyl ether (EGdE) (*two* OH groups for EG, *one* for EGmE, and *zero* for EGdE). This class of H-bonded liquids has recently been the object of dynamical studies by our group too. In particular,[5] Rayleigh wing, Raman scattering, and FT-IR absorption data in the bulk and confined state within nanoporous glasses, 25 Å sized, revealed the following relevant results: (i) In the bulk EG, characterized, as above stressed, by inter- and intramolecular links among OH groups, a distribution of relaxation times, described through the well-known Havriliak−Negami[6] relaxation function, characterizes the Rayleigh wing spectrum. In the confined state we observed a slowing of the reorientational diffusive dynamics with respect to the bulk one. (ii) In the EG monomethyl ether and EG dimethyl ether cases, we observed different kinds of interaction marking the liquid−surface coupling, chemical and physical trap effects. In addition, the fundamental O−H stretching vibration analysis allowed us to identify various transient species characterized by mean lifetimes imposed by intra- and intermolecular H-bonding.

To better understand the physical origin and meaning of the various contributions to the O−H band in these liquids, a vibrational dynamics analysis vs temperature is performed in

---

* Corresponding author. Phone: +39 090 391478. Fax: +39 090 395004. E-mail: migliard@dsme01.messina.infm.it.

10.1021/jp993900e CCC: $19.00

this paper, by means of infrared (IR) absorption. In fact, the investigation, in some detail, of the vibrational properties of the active sites for the interactions, i.e., the OH stretching region (3000−3800 cm$^{-1}$), gives almost direct evidence of the presence, in associated liquids, of various, H-bond imposed, intra- and intermolecular conformations.[7,8] As we will show in the following, several factors are hypothesized to contribute to the distribution of the spectra over a large frequency range (∼1000 cm$^{-1}$), to the intensity, and to the shape of the stretching band in such systems. The original narrow O−H band, centered at ∼3600 cm$^{-1}$, as observed by IR and Raman scattering in the gas phase at high temperature, undergoes in fact strong changes[9] in the liquid phase, marked by: (i) low wavenumber shift, (ii) broadening and extended spectral structure appearance, and (iii) variation with the temperature of the shape, intensity, and depolarization ratio in a light scattering experiment.

Although these changes represent almost direct evidence of intermolecular O···H bonding effects, they are difficult to explain by the unique theoretical model. As an example, the factors that should be considered to explain the band shift effects and the potential surface shapes can be derived by quantum mechanical computation and/or anharmonic coupling of the O−H fundamental vibration with low-frequency intermolecular modes due to intermolecular interactions. In addition, band-broadening effects[9,10] have been explained in the past in terms of anharmonic effects more or less coupled with the polarization and structural phenomena.

The obtained IR spectra, deconvoluted in symmetrical bands (Voigt profiles), whose parameters (center frequency, half-width at half-maximum, HWHM, and intensity) variations allow the evolution, on the time scale, of the different conformational arrangements to be clarified, confirm that a strong correlation between IR OH-bands and local structures, H-bond-imposed, exists.

## Experimental Section

We examined, by means of ATR FT-IR spectroscopy, high-purity samples (certified grade quality products) of ethylene glycol [$H(O-CH_2-CH_2)OH$], EG monomethyl ether [$CH_3(O-CH_2-CH_2)OH$], and EG dimethyl ether [$CH_3(O-CH_2-CH_2)-OCH_3$], as purchased from Aldrich Chemical Co., at different temperatures varying in a range between −10 and +170 °C.

Infrared absorption spectra were collected with a BOMEM DA8 Fourier transform infrared (FT-IR) spectrometer working with a globar lamp source, a KBr beam splitter, and a DTGS/KBr detector. The IR data measurements were performed by using the attenuated total reflectance (ATR) technique: as is well-known, when infrared radiation, under certain conditions, passes through a prism made of a high refractive index infrared transmitting material (ATR crystal), it will be totally internally reflected. When a sample is brought into contact with the totally reflecting surface of the ATR crystal, the evanescent wave will be attenuated in regions of the IR spectrum where the samples absorb energy. A property of the evanescent wave that makes ATR a powerful technique is that the intensity of the wave decays exponentially with the distance from the surface of the ATR crystal. The distance, on the order of micrometers, makes ATR generally insensitive to sample thickness, allowing for the analysis of thick or strongly absorbing samples, as our systems are in the O−H stretching region. In particular, we used a P/N 11875 Graseby Specac Inc. Squarecol liquid ATR accessory, which enabled highly reproducible spectra of strongly absorbing liquid media from ambient temperatures up to 200 °C. It is accessorized by a square rod of polished ZnSe with 45° faces at the end. The rod is contained in a stainless steel tube through which it is mounted onto the baseplate using two locating pins. The sample surrounds the ATR element completely. A cover plate is provided for preventing evaporation at elevated temperatures. The Squarecol liquid ATR system, having high absorbance linearity and a well-defined optical path length, is particularly suitable for accurate quantitative analysis.

The FT-IR spectrometer operated, in the O−H stretching region, from 2500 to 3800 cm$^{-1}$, at a resolution of 4 cm$^{-1}$, automatically adding 32 repetitive scans to obtain a good signal-to-noise ratio. All the IR spectra were normalized to take into account the effective number of adsorbers.

As is well-known, the O−H stretching mode, in particular, reveals a spread contribution, usually expected for H-bonded liquids, indicative of the cooperative character of this vibration[11] and a marked shift of the first moment of the distribution toward higher frequencies at the increase of the temperature. As far as the C−H stretching mode is concerned, the shape of the bands centered in the 2500−3000 cm$^{-1}$ frequency range is, as expected, temperature independent, confirming, in this way, the molecular character of this vibration.

Experimental IR data were deconvoluted into symmetrical Voigt profiles, $V(\omega)$, having a frequency shift with respect to the fundamental free O−H stretching vibration strictly correlated with the variation of the potential surface minimum, which occurs with the change in the $R_{O\cdots O}$ distances.[8]

## Results and Discussion

It has been well established[7,12−14] that the presence, in H-bond liquids, of the highly anisotropic and directional hydrogen bond, whose energy value ranges between 2 and 6 kcal/mol, leads to several kinds of intermolecular arrangements. Taking into account the several contributions[15] composing the potential energy surface of the hydrogen bond (electrostatic, polarization, charge transfer, dispersion), a strict correlation between the degree of association and the relative population of the local structures is expected, generating, in turn, a different dynamic response: this explains the appearance of peculiar bands according to the number of possible associative species. These aggregates are dynamically stable, and can be considered as *transient structures*, owing to the continuous breaking and re-forming process of the H-bond, whose mean lifetime is on the picosecond scale. On the basis of the cross-links among the inherent structures, corresponding to the various local minima in the system potential energy, it is possible to explain the spectral variations, for H-bonded liquids, of the O−H stretching vibration, which spreads out over a large $\omega$-range and changes dramatically in frequency (red shift), shape, and intensity with respect to the original narrow O−H band centered at ∼3630 cm$^{-1}$. It is a consequence of the existence, for these systems, of an electrical *anharmonicity* in the dipole moment function, other than a mechanical one that enters in the potential energy evaluation, that contributes to all nonlinear terms in the dipole moment calculation. It has been well established,[16] in fact, that H-bonded systems hold an exceptional position in vibrational spectroscopy, since the first derivatives of the dipole moment $\underline{\mu}$ with respect to the coordinates of motion $\partial\underline{\mu}/\partial q_i$ are improper for the prediction of intensities $I$. This means that the familiar relationship

$$I = K(\partial\underline{\mu}/\partial q_i)^2 \tag{1}$$

that usually expresses the intensity of an absorption band in the infrared due to the normal mode $q_i$, in which $K$ is a constant

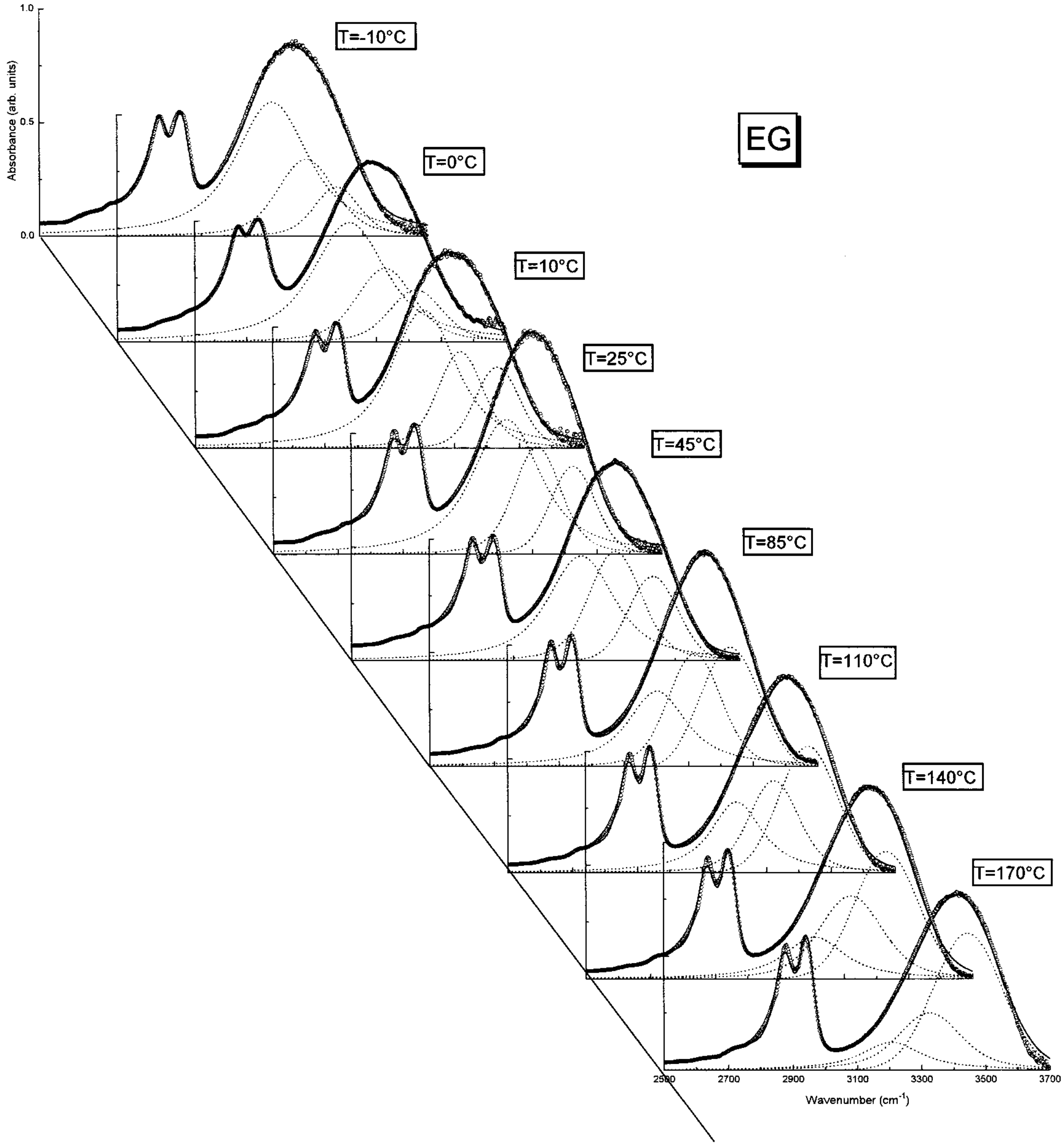

**Figure 2.** Experimental IR absorbance spectra for EG (circles) as a function of temperature, together with the theoretical fit (continuous line) and the deconvolution components (dashed lines) of the O−H stretching band.

that takes into account the number $n_i$ of oscillators involved in it, is no longer valid for a strong H-bond, but can be retained true for weak H-bonded systems, as ours are.

Supposing that the time-dependent electrical field is weak (so that its interaction with the stretching mode may be treated perturbatively to first order, and thus in a linear way with respect to the electrical field), theoretical studies of the shape of the high-frequency stretching vibration of hydrogen bonds are performed within the framework of the linear response theory.[17] According to it, the spectral density $I(\omega)$ of this stretching mode may be obtained by the Fourier transform of the autocorrelation function $G(t)$ of the dipole moment operator $\underline{\mu}$:

$$I(\omega) = 1(2\pi)^{1/2}\int G(t)\,\exp\{-i\omega t\}\,\mathrm{d}t \tag{2}$$

with

$$G(t) = \langle \mu^{+}(t)\,\mu(0)\rangle \tag{3}$$

What is required to find this spectral density is the knowledge of the autocorrelation function of the dipole moment operator of the fast mode averaged on some thermal properties. This autocorrelation function will differ according to the fact that the system is considered classically or quantum mechanically, and according to the hypothesis performed on the origin of the relaxation. Two main mechanisms have been considered: in the first one the fast mode, after excitation, relaxes directly toward the medium, whereas in the last one, it is relaxing via the slow mode to which it is anharmonically coupled.

Several approaches have been used to formulate a complete theory of band shapes of hydrogen-bonded systems: one of the most famous, from a historical point of view, formulated by Hadzi and Bratos,[9] related the spectral variations to intra- and intermolecular O−H bonding effects, as well as to quantum mechanical and anharmonic effects more or less coupled with the polarization. However, recently, the various theoretical models of IR spectra for H-bonded systems have been critically reviewed by Olivier Henri-Rousseau and Paul Blaise,[17] taking into account the anharmonic coupling effects between slow and fast vibrational modes in a well-finished quantum-mechanical approach.

**TABLE 1: IR Subbands Deconvolution Fit Parameters of the O−H Stretching Region for EG at the Analyzed Temperatures**

| temp (°C) | $\omega_\epsilon$(cm$^{-1}$) | $\Gamma_\epsilon$ (cm$^{-1}$) | $I_\epsilon$ (%) | $\omega_\delta$ (cm$^{-1}$) | $\Gamma_\delta$ (cm$^{-1}$) | $I_\delta$ (%) | $\omega_\gamma$ (cm$^{-1}$) | $\Gamma_\gamma$ (cm$^{-1}$) | $I_\gamma$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| −10 ± 0.1 | 3210 ± 6 | 231.6 | 62.1 | 3321 ± 3 | 196.1 | 25.4 | 3430 ± 7 | 197.3 | 12.5 |
| 0 ± 0.1 | 3210 ± 6 | 231.6 | 58.2 | 3321 ± 3 | 196.1 | 25.6 | 3430 ± 7 | 197.3 | 16.2 |
| 10 ± 0.1 | 3210 ± 6 | 231.6 | 56.1 | 3321 ± 3 | 196.1 | 24.9 | 3430 ± 7 | 197.3 | 19 |
| 25 ± 0.1 | 3210 ± 6 | 231.6 | 53.9 | 3321 ± 3 | 196.1 | 26.8 | 3430 ± 7 | 197.3 | 19.3 |
| 45 ± 0.1 | 3210 ± 6 | 231.6 | 45.2 | 3321 ± 3 | 196.1 | 33 | 3430 ± 7 | 197.3 | 21.8 |
| 65 ± 0.1 | 3210 ± 6 | 231.6 | 35.8 | 3321 ± 3 | 196.1 | 33.5 | 3430 ± 7 | 197.3 | 30.7 |
| 85 ± 0.1 | 3210 ± 6 | 231.6 | 30.9 | 3321 ± 3 | 196.1 | 33.9 | 3430 ± 7 | 197.3 | 35.2 |
| 110 ± 0.1 | 3210 ± 6 | 231.6 | 27.8 | 3321 ± 3 | 196.1 | 29.5 | 3430 ± 7 | 197.3 | 42.7 |
| 140 ± 0.1 | 3210 ± 6 | 231.6 | 19 | 3321 ± 3 | 196.1 | 34 | 3430 ± 7 | 197.3 | 47 |
| 170 ± 0.1 | 3210 ± 6 | 231.6 | 13.9 | 3321 ± 3 | 196.1 | 26.5 | 3430 ± 7 | 197.3 | 59.3 |

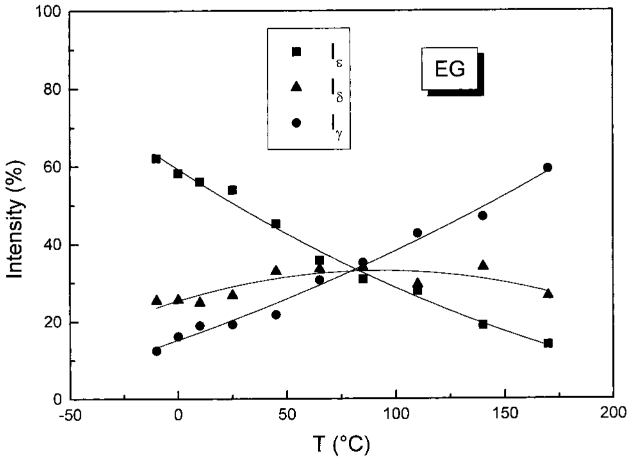

**Figure 3.** Temperature dependence of the percentage intensity for the $\epsilon$th (squares), $\delta$th (triangles) and $\gamma$th (circles) subbands of the EG O−H stretching band.

An authoritative time-resolved infrared spectroscopy study on the connection between the local environments of H-bonded molecular groups and the O−H stretching shape has been performed by Laubereau and co-workers.[14,15,18] In agreement with this formalism, we defined $\omega_\alpha$ as the fundamental O−H stretching mode of free and/or end groups and $\omega_\beta$ ($\omega_\gamma$) as the O−H stretching of proton-acceptor (donor) end groups corresponding to dimeric structures. Going on, $\omega_\delta$ indicates the O−H stretching of fully bonded hydroxyl O−H groups, generating trimers, and finally, $\omega_\epsilon$ is the vibration of OH groups involved in intramolecular H-bonds of monomeric closed structures.

Making reference to previous results obtained by our group in the case of bulk EG[5] and its oligomers poly(ethylene glycol)s,[3] as well as in the case of propylene glycol and poly(propylene glycol)s,[19,20] we deconvoluted the O−H stretching band into symmetrical Voigt profiles, and adopted the generally accepted rule[8,9,14,18,21] that the frequency shift in the O−H stretching vibration increases by decreasing the $R_{\mathrm{O}\cdots\mathrm{O}}$ distance. As far as the EG results are concerned, adopting the rule above-described, we assigned the band centered at ~3200 cm$^{-1}$ to the $\omega_\epsilon$ O−H vibration, the one centered at ~3350 cm$^{-1}$ to the $\omega_\delta$ O−H vibration, and, finally, the band centered at ~3500 cm$^{-1}$ to the $\omega_\gamma$ O−H vibration.

The results of the O−H stretching deconvolution into subbands (Voigt profiles) for the analyzed temperatures, in the case of EG are represented in Figure 2 and summarized in Table 1, where all the assigned subbands, center frequencies, line widths, and percentage intensities are reported.

First of all, it has to be noticed that, for all the investigated samples, the absence of $\omega_\alpha$ and/or $\omega_\beta$ indicates that there are not end and/or open monomers, almost all the OH groups being involved in inter- and intramolecular interactions via hydrogen bonding.

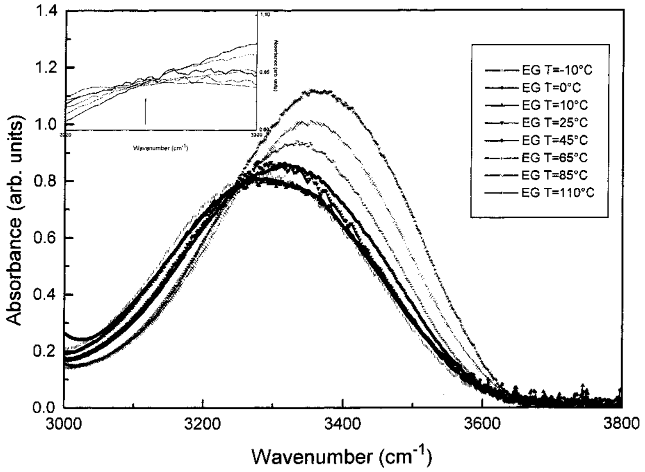

**Figure 4.** Experimental IR absorbance data for EG, in the O−H stretching region, plotted vs wavenumber for $T$ varying between −10 and +110 °C. The inset shows an isosbestic point centered at ~3262 cm$^{-1}$.

The obtained subbands suggest the existence of a large variety of aggregates (closed monomeric structures, together with dimers and trimers), as a consequence of the molecular dimension and the presence, in the chemical structure, of two terminal hydroxyl groups. Furthermore, an inspection of Figure 2 reveals that there is a large temperature variation of the intensity of the various bands in the O−H stretching region (dashed lines in the figure), whereas the molecular C−H bands are almost, as expected, $T$-invariant.

The study of this spectral evolution furnishes further information about the behavior of the different aggregative forms of intermolecular arrangements and, by means of an evaluation of the percentage areas (see Table 1), about their relative population.

First, directing attention to the intramolecular $\omega_\epsilon$ peak, its intensity decreases when $T$ increases, and the relative integrated area changes from 62.1% at −10 °C to 13.9% at 170 °C. This evidence shows that in the EG molecule the intramolecular H-bond population is strongly temperature dependent, supporting the existence of a "kinetic" of transition, previously revealed by means of Rayleigh wing spectroscopy,[3] between two configurational states: gauche in the presence of the intramolecular H-bond ("on" state) and gauche without such a bond ("off" state). On the other side, we observe, in going to higher and higher temperature values, an increase of the dimer population, as is pointed out by the increase of the relative intensity of the $\omega_\gamma$ vibration, showing that the "end-to-end" bonds are the most favorite in the case of high $T$. The relative percentage area of the $\omega_\delta$ subband does not reveal appreciable variations, indicating that the density of trimeric structures keeps almost constant in the entire temperature range explored.

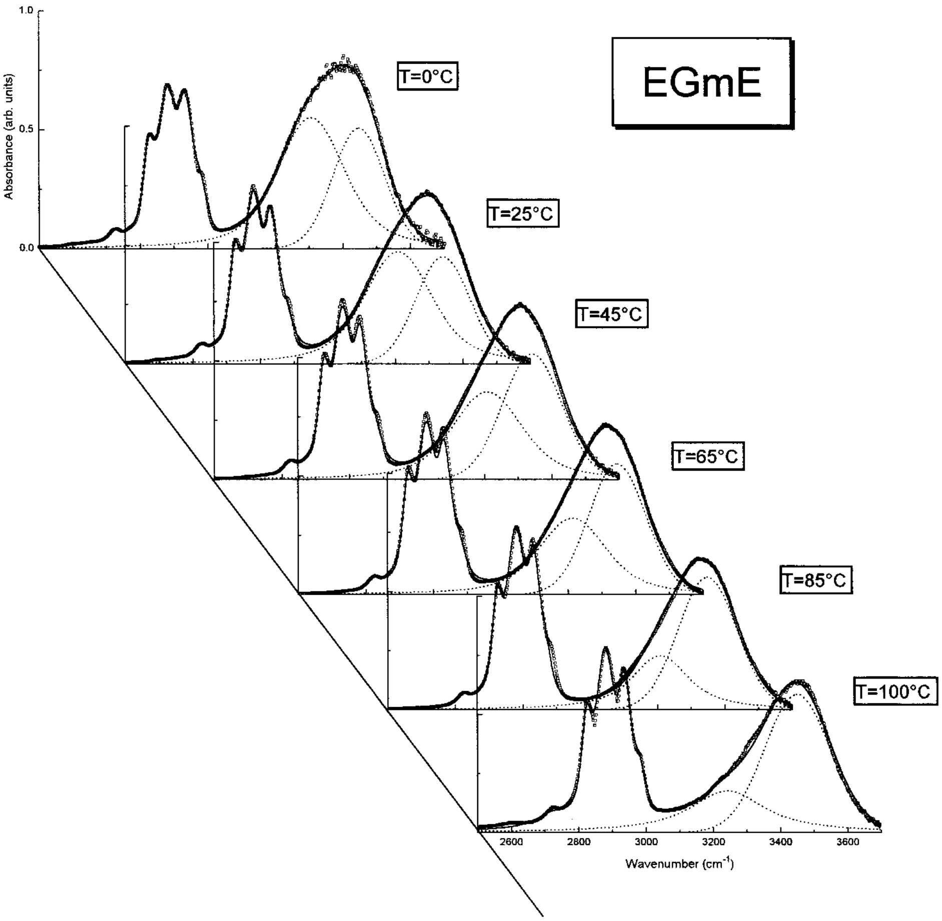

**Figure 5.** Experimental IR absorbance spectra for EGmE (squares) as a function of temperature, together with the theoretical fit (continuous line) and the deconvolution components (dashed lines) of the O−H stretching band.

Returning now to eq 1, it is to be noticed that the intensity of each O−H stretching band is related to $K$ (and hence to the relative population factor $n$) times the $(\partial \underline{\mu}/\partial q_i)^2$ factor. As a consequence, obviously, the temperature variation of each band relative intensity is not only related to the relative population variation. In our system, contrary to what is observed in the alcohol case,[7,22] because, for each $i$th subband, the center frequency $\omega_i$ and the line width $\Gamma_i$ do not change, with $T$, so that the binding potential well remains substantially the same as temperature varies, the relative variation with $T$ of each $i$th subband can be directly connected with the relative variation of the population factor $n_i$ of the $i$th oscillator. In Figure 3 the percentage intensities of the $\epsilon$th, $\delta$th, and $\gamma$th subbands are plotted vs $T$. From an inspection of the figure we can hypothesize that the increase, with $T$, of the dimeric $\gamma$th aggregative species occurs at the expense of the intramolecular $\epsilon$th structure, whereas the relative population of the $\delta$th species remains substantially constant with $T$.

An almost natural way to rationalize this concept is to verify whether an isosbestic point exists for the entire O−H stretching band. In Figure 4 the IR absorption bands vs wavenumber are plotted for all the investigated temperatures. Surprisingly, as is well shown in the inset of the same figure, we observe a very well-defined isosbestic point centered at $\sim$3262 $\text{cm}^{-1}$ wavenumber for the spectra ranging from $-10$ to $+110$ °C, whereas the bands relative to the extreme temperatures 140 and 170 °C do not obey this experimentally observed phenomenon.

Generally speaking,[23] an isosbestic point indicates a reversible chemical reaction, in our case spectroscopically tested, among two states. If two chemical species or two structural environments, for which the lifetime is so short (in our case the lifetime is estimated to be on the order of a few picoseconds) that it is not possible to define the existence of two species from a genuine chemical point of view, suffer a kinetic process under a temperature change and the respective spectral features are different but *overlap*, there *must* be a critical single point (isosbestic point) where all the spectra cross. In this case every spectrum of the system under examination may be explained in terms of a sum of two independent contributions. This occurrence was discovered some years ago by our group too[24] for the case of water and recently confirmed.[23] Even if such an experimental behavior should support a mixture model for water and for other H-bonded liquids (as the liquids actually under study), and this model may be, in our opinion, not totally acceptable, it indicates, *at least on the picosecond time scale*, the existence of a kinetic process for which, when an intramolecular H-bond is broken, another intermolecular one is reformed, and vice versa.

Finally, the occurrence that, at high temperature, this behavior seems to break down is, in our opinion, a manifestation of the disordering effects of the thermal energy $k_BT$. The latter plays a relevant role when its value exceeds the hydrogen bond energy, so the breakup process of intramolecular bonds contributes to both an increase of the intermolecular H-bond number and a dispersion of the potential energy into the thermal bath of our systems, populating, for example, the diffusive irreversible process.

As far as EGmE is concerned, Figure 5 shows the temperature variation of the OH-bands and the deconvolution results in two subbands (dashed lines in the figures), whose relevant param-

**TABLE 2. IR Subbands Deconvolution Fit Parameters of the O−H Stretching Region for EGmE at the Analyzed Temperatures**

| temp (°C) | $\omega_\delta$ (cm$^{-1}$) | $\Gamma_\delta$ (cm$^{-1}$) | $I_\delta$ (%) | $\omega_\gamma$ (cm$^{-1}$) | $\Gamma_\gamma$ (cm$^{-1}$) | $I_\gamma$ (%) |
|---|---|---|---|---|---|---|
| 0 | 3297 | 238 | 62 | 3446 | 202.4 | 38 |
| 25 | 3297 | 238 | 60.2 | 3446 | 202.4 | 39.8 |
| 45 | 3297 | 238 | 48.4 | 3446 | 202.4 | 51.6 |
| 65 | 3297 | 238 | 44.4 | 3446 | 202.4 | 55.6 |
| 85 | 3297 | 238 | 32.7 | 3446 | 202.4 | 67.3 |
| 100 | 3297 | 238 | 30.8 | 3446 | 202.4 | 69.1 |

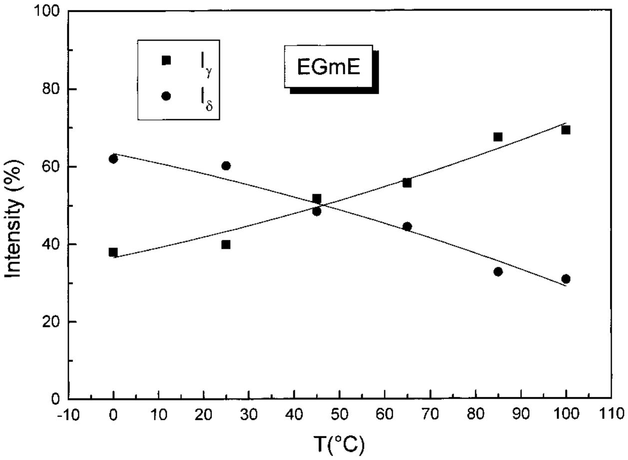

**Figure 6.** Temperature dependence of the percentage intensity for the $\delta$th (circles) and $\gamma$th (squares) subbands of the EGmE O−H stretching band.

eters are reported in Table 2. As can be noticed from an inspection of Table 2, $\omega_\epsilon$ disappears. This system is in fact characterized by the presence of only one OH end group in its structure, and this occurrence prevents it from arranging intramolecular H-bond interactions. Nevertheless, also in this case, the $\omega_\delta$ and $\omega_\gamma$ O−H stretching peaks, corresponding to dimers and trimers, have been clearly identified in the spectra, indicating that the steric hindrance due to the different molecular structure is not great to avoid polymeric aggregates of coordination number 2 or 3 existing in the liquid phase.[5]

Furthermore, as a matter of fact, we notice that the $\omega_\delta$ and $\omega_\gamma$ subbands have almost the same center frequencies with respect to the ones observed in the EG case.

In particular, we observe an increase, with *T*, of the percentage intensity of the $\omega_\gamma$ subband from 38% at $T = 0$ °C to 69.1% at $T = 100$ °C, indicating that the dimeric species relative population is more favored, at high *T*, with respect to the more collective $\omega_\delta$ band associated with the presence of three-bonded structures.

In Figure 6 we plot the *T* dependence of the $\omega_\delta$ and $\omega_\gamma$ subband integrated area (%).

The evolution of the two existing subbands in the EGmE case calls for a further verification of a probable existence also in this case of an isosbestic point. In Figure 7 the IR absorption OH-bands vs wavenumber are represented for all the investigated temperatures. The inset shows a definite isosbestic spectral point centered at ~3380 cm$^{-1}$ wavenumber for the spectra ranging between 25 and 65 °C, whereas the O−H stretching bands relative to the extreme temperatures (0, 85, and 100 °C) violate this trend.

The isosbestic point is related, in this case, to the transfer process involving the relative population factors of the trimers (which decrease with *T*) and the dimers (which increase with *T*).

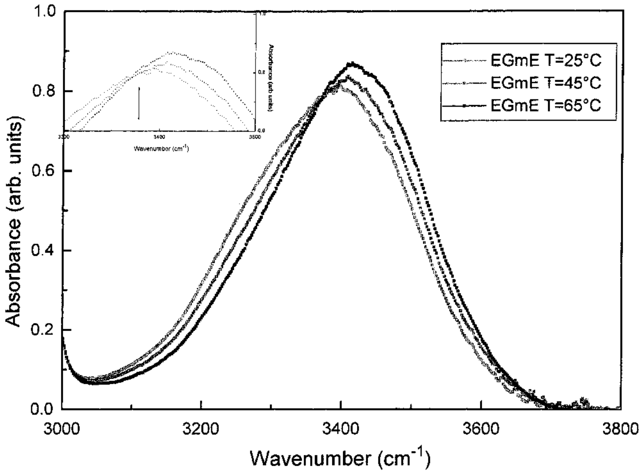

**Figure 7.** Experimental IR absorbance data for EGmE, in the O−H stretching region, plotted vs wavenumber for T varying between 25 and 65 °C. The inset shows an isosbestic point centered at ~3380 cm$^{-1}$.

Finally, as far as the EGde IR response is concerned, because this system does not belong to the class of H-bonded liquids, no peaks have been revealed in the O−H stretching region.

## Conclusions

In this paper we have presented an analysis of the high-frequency vibrational dynamics of ethylene glycol and its homologous ethylene glycol monomethyl ether and ethylene glycol dimethyl ether. The O−H stretching region was investigated in a very large temperature range by the use of the ATR FT-IR technique. The results allow us also to draw the following conclusions.

(i) The IR spectra unambiguously show the H-bonding effects through the strong influence of the symmetric subband parameters by the temperature. The connection between the local structure (i.e., association phenomenon) and vibrational bands is discussed in terms of a cooperative model[14,18] for associated liquids. The existence of intramolecular, H-bond-imposed, monomeric structures, and *n*-meric (dimeric and trimeric units) intermolecular species, also triggered by the hydrogen bond, is postulated for the EG case. Furthermore, the relative intensity of the subbands is strongly *T*-dependent. This circumstance was connected to the existence of a hierarchy of structures with relative population varying with *T* by means of a microscopic fast dynamic process.

In the case of EGmE we observe a dynamical process similar to that revealed for EG, together with a disappearance, as expected, of the intramolecular H-bond centered at ~3210 cm$^{-1}$. This occurrence, on the other hand, confirms in our opinion the validity of our assignment.

(ii) An isosbestic spectral point is observed for the two conformers EG and EGmE, explained in terms of a kinetic process occurring on the picosecond time scale, confirming that dissociation and reassociation of the various oligomers, measured for ethanol by Laubereau and co-workers with time-resolved infrared spectroscopy,[14] play a noticeable role in these H-bonded liquids.

Our results globally confirm that the O−H fundamental vibration in ethylene glycol and its homologous ethylene glycol monomethyl ether can be understood in terms of H-bond-imposed anharmonic effects.

## References and Notes

(1) Mandelker, L. *An Introduction to Macromolecules;* Heidelberg Science Library: Heidelberg, 1972.

(2) Buckley, P.; Giguerre, P. A. *Can. J. Chem.* **1966**, *45*, 397 and references therein.

(3) Crupi, V.; Jannelli, M. P.; Magazù, S.; Maisano, G.; Majolino, D.; Migliardo, P.; Sirna, D. *Mol. Phys.* **1995**, *84*, 645.

(4) We used a standard routine, "Alchemy II", Tripos Associates, Inc., 1988.

(5) Crupi, V.; Maisano, G.; Majolino, D.; Migliardo, P.; Venuti, V. *J. Chem. Phys.*, **1998**, *109* (17), 7394.

(6) Alvarez, F.; Alegria, A.; Colmenero, J. *Phys. Rev. B* **1991**, *44*, 7306.

(7) Crupi, V.; Magazù, S.; Maisano, G.; Majolino, D.; Migliardo, P.; Venuto, S. *Phys. Chem. Liq.* **1994**, *26*, 263.

(8) Olovsson, I.; Jonsson, P. G. In *The Hydrogen Bond II*; Shuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; p 393.

(9) Hadzi, D.; Bratos, S. In *The Hydrogen Bond II*; Shuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; p 565.

(10) Bratos, S. In *Vibrational Spectroscopy of Molecular Liquids and Solids;* Bratos, S., Pick, F., Eds.; Plenum: New York, 1980; Vol. 56-B, p 43.

(11) Volino, F. In *Microscopic Structure and Dynamics of Liquids*; Dupuy, J., Dianoux, A. J., Eds.; Plenum: New York, 1977.

(12) Crupi, V.; Jannelli, M. P.; Magazù, S.; Maisano, G.; Majolino, D.; Migliardo, P. *Phys. Chem. Liq.* **1994**, *28*, 117.

(13) Crupi, V.; Maisano, G.; Majolino, D.; Migliardo, P.; Musolino, A. M. *Il Nuovo Cimento* **1998**, *20D* (12 bis), 2191.

(14) Graener, H.; Je, T. Q.; Laubereau, A. *J. Chem. Phys.***1989**, *90*, 3413.

(15) Kollman, P. A.; Allen, L. C. *Chem. Rev.* **1972**, *72*, 283.

(16) Janoschek, R. In *The Hydrogen Bond I*; Shuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; p 166.

(17) Henri-Rousseau, O.; Blaise, P. In *Theoretical Treatments od Hydrogen Bonding*; Hadzi, D., Eds.; Wiley: New York, 1997; p 165.

(18) Graener, H.; Je, T. Q.; Laubereau, A. *J. Chem. Phys*. **1989**, *91*, 1043.

(19) Crupi, V.; Majolino, D.; Migliardo, P.; Venuti, V. *Il Nuovo Cimento* **1998**, *20D* (12 bis), 2163.

(20) Crupi, V.; Majolino, D.; Migliardo, P.; Venuti, V. *Atti dell'Accademia Peloritana dei Pericolanti,* in press.

(21) Jorgensen, M. L. *J. Am. Chem. Soc*. **1981**, *104*, 335 and references therein.

(22) D'Aprano, A.; Donato, D. I.; Migliardo, P.; Aliotta, F.; Vasi, C. *Phys. Chem. Liq*. **1988**, *17*, 279.

(23) Wilse Robinson, G.; Cho, C. H.; Urquidi, J.; Xiao, B. Submitted to *J. Chem. Phys*. **1998**.

(24) D'Arrigo, G.; Maisano, G.; Mallamace, F.; Migliardo, P.; Wanderlingh, F. *J. Chem. Phys.* **1981**, *75*, 4264.