The trans/gauche conformational equilibrium and associated thermodynamic parameters of liquid 1,2-dibromoethane as studied by infrared electroabsorption spectroscopy

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ABSTRACT

Infrared electroabsorption spectroscopy is used to study the trans/gauche conformational equilibrium and associated thermodynamic parameters of the two conformers of liquid 1,2-dibromoethane at room temperature. Electric-field modulation induces an increase in the population of the gauche conformer that has the permanent dipole moment and a decrease in that of the trans conformer that has a center of inversion symmetry and hence no dipole moment. The Gibbs free energy difference ΔG and the entropy difference ΔS between the gauche and trans conformers are obtained as 4.5 kJ mol^{-1} and $-2.7 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively, using the reported enthalpy difference.

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1. Introduction

Internal rotation around a C–C single bond is the simplest example of molecular flexibility. Because the internal rotation can be restricted by the substituents attached to the C–C bond, it often gives rise to rotational isomerism. The internal rotation around the C–C single bond was first discovered by Mizushima and co-workers [1] through a series of infrared (IR) and Raman measurements of 1,2-dichloroethane (DCE). Since then, due to its significance in structural chemistry, molecules that show rotational isomerism have been studied intensively by both experimental [2–7] and theoretical [8–12] methods.

1,2-Dihaloethanes $CH_2X–CH_2X$, probably one of the most studied model systems for C–C single bond internal rotation, occur in three stable conformers, i.e., two gauche and one trans conformers. The trans conformer has a center of symmetry and is nonpolar, whereas the gauche conformer does not have inversion symmetry and has the dipole moment. The free energy difference associated with the trans/gauche conformational equilibrium governs the population ratio between these conformers and therefore knowledge on the free energy difference is highly important to understand the nature of the conformational equilibrium. Measurements of the temperature dependence of IR or Raman spectra are powerful for obtaining the enthalpy difference [4,13–15], but the free energy difference still cannot be obtained unless the entropy difference is correctly estimated. In many cases, the estimation of the entropy term is not straightforward; it might be calculated from the rotational and vibrational partition functions [4,16] or even simply neglected [17]. In previous papers [18,19], we successfully used IR electroabsorption spectroscopy as a new method for studying the trans/gauche equilibrium of liquid DCE and were able to determine germane thermodynamic parameters. In our method, the free energy difference is directly determined from the analysis of IR absorbance change (ΔA) spectra. Knowing the enthalpy difference from other measurements, it is also possible to obtain the entropy difference experimentally, which provides new insight into intermolecular interactions in the liquid state. In the present work, we extend our work on DCE [18,19] to 1,2-dibromoethane (DBE).

Replacing two chlorine atoms by bromine atoms will introduce at least two major effects on the properties of 1,2-dihaloethane. One is the overlap of the halogen atoms (imagine the Newman projections). Since the atomic radius of bromine (114 pm) is larger than that of chlorine (99 pm), there will be stronger electrostatic repulsion in the gauche conformer of DBE than in that of DCE. This effect makes the DBE gauche conformer less stable relative to the DCE gauche. The other effect originates from the fact that the dipole moment of the DBE gauche conformer (2.2 D in the gas phase [14]) is smaller than that of the DCE gauche (2.55 D [14]), as expected from electronegativities of chlorine and bromine. Such a change in the dipole moment contributes to the orientational polarization, where polar molecules tend to be oriented along an electric field via the dipolar interaction. On the other hand, the influence on the trans one appears to be minor.

In this Letter we present IR electroabsorption data on liquid DBE and discuss the trans/gauche conformational equilibrium and related thermodynamic parameters such as the free energy difference and the entropy difference between the two conformers. A comparison is made to the previous results on DCE.

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2. Molecular responses to an applied electric field

Absorbance changes ΔA in IR electroabsorption measurements arise from several distinct molecular responses to an external electric field. As in the previous works [19,20], we consider the conformational equilibrium change, orientational polarization, and electronic polarization.

Of our most interest in this study is the equilibrium change between the trans and gauche conformers of DBE. Due to an applied electric field, the population of the gauche conformer increases, and that of the trans conformer decreases accordingly. The equilibrium constant K^0 has the form [19]

$$K^0 = \frac{N_g^0}{N_t^0} = 2 \exp\left(-\frac{\Delta G}{RT}\right), \tag{1}$$

where N_g^0 and N_t^0 denote the numbers of the gauche and trans conformers, respectively, ΔG the free energy difference between the gauche and trans conformers (i.e., $\Delta G = G_g - G_t$), R the gas constant, and T temperature. Keep in mind that the quantities that appear in Eq. (1) are defined as those without an external electric field. It has been shown that as a result of applying an electric field E, absorbance change ratios for the gauche and trans conformers are given by [19]

$$\left(\frac{\Delta A}{A}\right)_g = \frac{1}{(1+K^0)^2}\frac{\gamma_{equ}^2}{6} + \frac{K^0}{1+K^0}\frac{(\gamma_{equ}+\gamma_{ori})^2}{6} \tag{2}$$

and

$$\left(\frac{\Delta A}{A}\right)_t = -K^0\left[\frac{1}{(1+K^0)^2}\frac{\gamma_{equ}^2}{6} + \frac{K^0}{1+K^0}\frac{(\gamma_{equ}+\gamma_{ori})^2}{6}\right], \tag{3}$$

respectively. Here, $\gamma_{equ} = \mu_g E/k_B T$ is the electrostatic interaction parameter for an isolated gauche molecule, relevant to stabilization in energy due to the electric field E, where μ_g is the permanent dipole moment of the gauche conformer, and k_B the Boltzmann constant. The other electrostatic interaction parameter γ_{ori} accounts for rotational orientation. To a first approximation, γ_{ori} is taken to be identical to γ_{equ}. In the liquid state, however, it comes as no surprise that those two parameters could be different because of considerable intermolecular interactions. Actually in the case of liquid DCE [19], γ_{ori} turned out to be about 10% smaller than γ_{equ}. From Eqs. (2) and (3), it can be seen that a ΔA spectrum due to the equilibrium change is proportional to the absorption band shape (i.e., zeroth derivative component of the band shape).

Electric-field-induced orientational anisotropy also gives rise to IR absorbance changes. When an external electric field is applied to a sample, rotational orientation of polar molecules that have the dipole moments takes place. For DBE, only the gauche bands show orientational polarization ΔA signals. The absorbance change ratio can be written as [19]

$$\frac{\Delta A}{A} = \frac{\gamma_{ori}^2}{12}(1 - 3\cos^2\eta). \tag{4}$$

Here, normal incidence of the IR light on the sample cell is assumed, which is the case in this study. For DBE, η is equal to 0° for symmetry species a and 90° for b. Like the equilibrium change, orientational polarization signals appear in the ΔA spectrum as zeroth derivative shapes.

Finally, the electronic polarization is considered. Electronic responses of a molecule to an applied electric field, known as the Stark effect, change the height, width, and peak position of the IR band, resulting in the zeroth, first, and second derivative shapes in the ΔA spectrum. The absorbance change in this case can be expressed as [19–21]

$$\Delta A(\tilde{v}) = E^2\left[c_1 A(\tilde{v}) + c_2 \tilde{v}\frac{d}{d\tilde{v}}\frac{A(\tilde{v})}{\tilde{v}} + c_3 \tilde{v}\frac{d^2}{d\tilde{v}^2}\frac{A(\tilde{v})}{\tilde{v}}\right], \tag{5}$$

where $\tilde{v}$ denotes the wavenumber, and c_1–c_3 the coefficients of the zeroth, first, and second derivative terms, respectively, which are functions of the Stark parameters such as the difference dipole moment and difference polarizability referring to the differences between the ground and excited states. It has been shown both experimentally [22] and theoretically [19], that the zeroth derivative component of the electronic polarization is considerably small compared with the present detection limit. We thus disregard the contribution of the electronic polarization signal to the zeroth derivative component.

In summary, the model function that we use in the analysis of the ΔA spectrum consists of the zeroth derivative component arising from the equilibrium change between the two conformers and from the orientational polarization of the gauche conformer, and first and second derivative components arising solely from electronic responses.

3. Experimental

The IR electroabsorption apparatus has been described previously [19]. The light source was a ceramic IR emitter. A pair of elliptical mirrors focused the mid-IR light on the sample cell. The sample cell was composed of a brass cell holder, two p-type boron doped Si windows that also act as electrodes, and a mylar film spacer. A 25 kHz sinusoidal electric-field modulation ($E_{ext} = 1.5 \times 10^7$ V m^{-1}) was applied across the two Si electrodes. The magnitude of the external electric field, E_{ext}, was estimated using the applied voltage (80 V$_{0-p}$) and the cell gap (5.2 μm) obtained from the interference fringe pattern. The transmitted light was analyzed by a grating *dispersive* monochromator and detected with a photoconductive HgCdTe (MCT) detector. The signal was then subject to AC-coupled amplification and phase-sensitive detection with a lock-in amplifier at 50 kHz (twice the frequency of the modulation), extracting the intensity change ΔI only that was caused by the applied electric field. ΔI was converted to an absorbance change ΔA, using the relation $\Delta A = -\log(1 + \Delta I/I)$, where I is the IR light intensity without the applied electric field. This apparatus has the ability to detect ΔA as small as $\sim 1 \times 10^{-7}$ [19], which might not be reached even by the latest FT-IR method [23,24]. The high potential of this technique has been best demonstrated in the study of dilute solutions (~ 30 mM) of p-nitroaniline [20].

Reagent-grade 1,2-dibromoethane was commercially obtained from Sigma Aldrich and used as received. The liquid sample was circulated through the cell so as to prevent possible heat accumulation. Six runs were averaged in order to obtain a decent ΔA spectrum, which required about 2 h for the spectral range of ~ 200 cm^{-1}.

4. Results

4.1. Infrared electroabsorption spectrum

Fig. 1 shows the IR electroabsorption and absorption spectra in the wavenumber region of 1350–1140 cm^{-1}, of liquid DBE at room temperature. The out-of-phase ΔA signals, which are presumably due to artificial retardation of the signal relative to the applied electric field [19], are negligibly small, so we focus on the in-phase ΔA signals. Three IR bands seen in the absorption spectrum (Fig. 1b) are assigned to the CH$_2$ wagging of the trans and gauche conformers [25]. The gauche conformer is responsible for the two higher-wavenumber bands, and the trans one for the lowest-wavenumber band. Table 1 summarizes assignments of the three bands
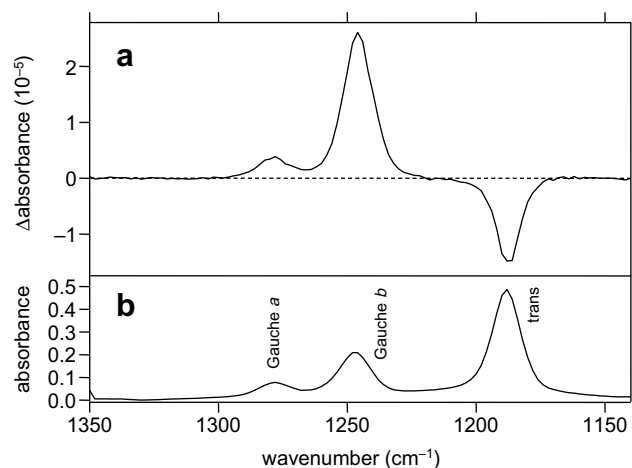
Fig. 1. Infrared electroabsorption (a) and absorption (b) spectra of liquid 1,2-dibromoethane. Backgrounds are corrected in these spectra.

Table 1
Assignments, frequencies, conformations, and symmetries of observed IR absorption bands of liquid 1,2-dibromoethane.

| Assignment[a]	Frequency (cm^{-1})	Conformation	Symmetry
CH$_2$ wag	1279	Gauche	a
CH$_2$ wag	1247	Gauche	b
CH$_2$ wag	1188	Trans	b_u

[a] Taken from [25].

and corresponding conformations, together with the peak positions obtained form the fitting (see below). The ΔA spectrum (Fig. 1a) looks rather different from the absorption spectrum. The gauche b band gives marked positive ΔA signals and the gauche a band a small structure, whereas the trans band shows up as large negative signals. These features are similar to those observed for DCE [19]. In order to separate the ΔA signals due to the equilibrium change from those emanating from other origins, we fit the ΔA spectrum based on the model for molecular responses to an applied electric field discussed in Section 2.

4.2. Decomposition of infrared electroabsorption spectrum

The absorption spectrum was first fit to the sum of three Lorentzian line shapes that represent the two gauche and one trans modes. The results are displayed in Fig. 2b, and the frequencies of the band peaks so obtained are listed in Table 1. Those frequencies are in good agreement with the literature [25]. Using the zeroth, first, and second derivatives of those Lorentzian line shapes with the model outlined above (Eqs. (2)–(5)), the ΔA spectrum was analyzed subsequently. Fig. 2a shows the best fit. Two adjustable parameters were used for generating the first and second derivative components of each band, and two global adjustable parameters (K^0 and $\gamma \equiv \gamma_{equ} = \gamma_{ori}$) for the zeroth derivative component. In contrast with the DCE case [18,19], assuming independent parameters of γ_{equ} and γ_{ori} does not improve much the quality of the fit, and in the spirit of trying to minimize the number of adjustable parameters in the fitting analysis, we used a single γ value as representing the electrostatic interaction parameter. K_0 and γ are determined to be 0.33 ($\pm$0.04) and 0.018, respectively. Fig. 3 shows how the fitting analysis decomposes the ΔA spectrum into the zeroth, first, and second derivative components. The zeroth derivative spectrum is further decomposed into the two contributions of the equilibrium change and orientational polarization. Small but
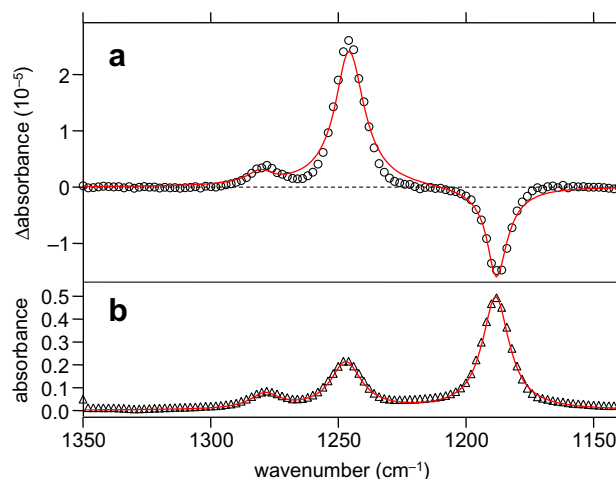
Fig. 2. (a) Observed ΔA spectrum (○) of liquid 1,2-dibromoethane and the best fit (solid curve) to the model functions outlined in Section 2. (b) Observed absorption spectrum (△) and the best fit (solid curve) to the sum of three Lorentzian line shapes (see text).
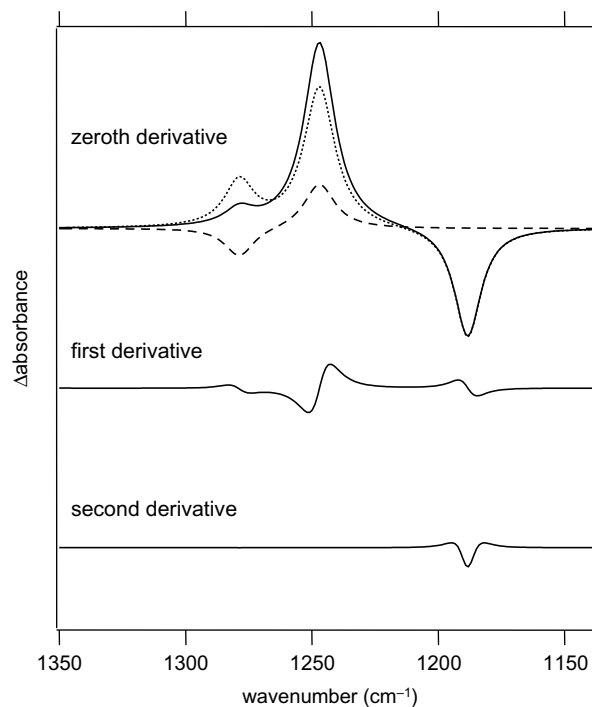
Fig. 3. Decomposition of the ΔA spectrum of liquid 1,2-dibromoethane into the zeroth (top trace), first (middle), and second (lower) derivative shapes. The dotted curve shows the contribution of the equilibrium change, and the dashed curve that of the orientational polarization.

meaningful first and second derivative components indicate that the electronic polarization does contribute somewhat to the IR electroabsorption of liquid DBE.

5. Discussion

The trans/gauche equilibrium change of liquid DBE is represented by the two parameters: the electrostatic interaction parameter $\gamma = 0.018$ and the equilibrium constant $K^0 = 0.33$. The dipole moment of DBE in the gas phase, $\mu_g = 2.2$ D [14], and the magnitude of the applied electric field $E = fE_{ext} = 1.5 \times 10^7$ V m^{-1} yield

Table 2
Thermodynamic parameters associated with the trans/gauche conformational equilibria of liquid 1,2-dichloroethane (DCE) and 1,2-dibromoethane (DBE).

	DCE[a]	DBE[b]
K^0	1.4 (±0.2)	0.33 (±0.04)
ΔG (kJ mol^{-1})	0.9 (±0.4)	4.5 (±0.3)
ΔS (J K^{-1} mol^{-1})	−3.0	−2.7
ΔH (kJ mol^{-1})	∼0.0[c]	3.7[d] (±1.1)

[a] Taken from [19].
[b] This work.
[c] Taken from [5,16].
[d] Average of the values reported in [2,14–17].

$\gamma = 0.026$. In the present study, we simply set the coefficient f to be unity. The coefficient f contains two major causes of the corrections, the voltage drop at electrical contacts [19] and the dielectric polarization of the sample. The discrepancy between the calculated value ($\gamma = 0.026$) and the experimental value ($\gamma = 0.018$) might be attributed to the second correction due to the local field effect and/or to the use of the dipole moment in the gas phase. Another point worth mentioning is that the observed ΔA spectrum of DBE is well reproduced by assuming a single electrostatic interaction parameter γ. This is not the case for DCE [19], where two independent parameters γ_{equ} and γ_{ori} are needed. The fact that the free energy difference and the rotational orientation are determined by the same parameter γ is indicative of weaker dipole–dipole interactions in liquid DBE than in DCE; DBE molecules respond to the external electric field more independently than DCE.

The smaller-than-unity value of K^0 indicates that DBE molecules exist in favor of the trans conformer (∼75% of the molecules). This contrasts with what is observed for liquid DCE; $K^0 = 1.4$, and the gauche conformer is more favored [19]. From Eq. (1), the free energy difference ΔG is calculated to be 4.5 (±0.3) kJ mol^{-1}. To the best of our knowledge, this is the first ΔG value for liquid DBE determined directly by experimental methods. There are several reports [2,14–17] on experimental determination of the enthalpy difference ΔH. The reported ΔH values range from 2.7 kJ mol^{-1} [14] to 5.4 kJ mol^{-1} [17]. Here we treat the scattered values evenly and obtain $\Delta H = 3.7$ (±1.1) kJ mol^{-1} as their average. The cited error bound in ΔH was determined by statistics of the five reported values. The large ΔH value compared with that of DCE ($\Delta H \sim 0.0$ kJ mol^{-1} [5,16]) nearly explains the ΔG value, but despite large uncertainty in the ΔH value, the discrepancy between ΔG and ΔH still appears meaningful. Using the thermodynamic equation $\Delta G = \Delta H - T\Delta S$ with $\Delta H = 3.7$ kJ mol^{-1}, we obtain the entropy difference $\Delta S = -2.7$ J K^{-1} mol^{-1}, which is close to the value for DCE (−3.0 J K^{-1} mol^{-1} [19]). These thermodynamic parameters associated with the conformational equilibrium of liquid DBE are summarized in Table 2, together with those for DCE [19]. The entropy difference ΔS is the sum of the translational entropy difference $\Delta S_{\mathrm{trans}}$ (note that the subscript 'trans' does not mean the trans conformer), rotational entropy difference ΔS_{rot}, and vibrational entropy difference ΔS_{vib}. Using $\Delta S_{\mathrm{rot}} = 1.34$ J K^{-1} mol^{-1} and $\Delta S_{\mathrm{vib}} = -2.78$ J K^{-1} mol^{-1} [17] evaluated from the moments of inertia and fundamental vibrational frequencies leaves $\Delta S_{\mathrm{trans}} = -1.3$ J K^{-1} mol^{-1}. Instead, if we use $\Delta S_{\mathrm{rot}} = 0.0$ J K^{-1} mol^{-1} on the assumption that in the liquid state the rotational motion is frozen, we have $\Delta S_{\mathrm{trans}} \sim 0$ J K^{-1} mol^{-1}.

According to statistical thermodynamics, the translational entropy difference between the gauche and trans conformers is related to the free volumes V_{g} and V_{t}, of those conformers as follows:

$$\Delta S_{\mathrm{trans}} = R \ln \frac{V_{\mathrm{g}}}{V_{\mathrm{t}}} = R \ln \frac{1 + \Delta V/V}{1 - \Delta V/V}, \tag{6}$$

with the volume change from the trans to gauche conformer and the total volume being $\Delta V = V_{\mathrm{g}} - V_{\mathrm{t}}$ and $V = V_{\mathrm{g}} + V_{\mathrm{t}}$, respectively. ΔV can be determined experimentally by such methods as the pressure dependence of IR band intensities [6] and ultrasonic relaxation [17]. Also, theoreticians can compute ΔV and use the value as a test of their theories [12]. In this study, we are able to estimate the $\Delta V/V$ values in the two limiting cases, that is, $\Delta V/V = -0.08$ for free rotation limit and $\Delta V/V \sim 0$ for frozen rotation limit. The actual volume change ratio is likely to lie in between these two limiting values. This result accords quantitatively with the $\Delta V/V$ value derived from an ultrasonic relaxation study on liquid DBE [17]. In the previous work on DCE [19], the free volume of the gauche conformer is estimated to be in between 73% (free rotation limit) and 84% (frozen rotation limit) of that of the trans conformer, and corresponding $\Delta V/V$ values are −0.16 and −0.09, respectively. The $\Delta V/V$ value for DBE is likely to be smaller than that for DCE, which seems consistent with the prediction based on the dipole–dipole interaction unique to the gauche conformer. This trend also appears to agree with the conclusion derived from the electrostatic interaction parameter γ.

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