

Internal field correction of the far-infrared spectra of acetonitrile at different temperatures

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A dispersive local field method has been applied for the correction of the far-infrared spectra of acetonitrile at different temperatures. The influence of this effect on different band parameters such as peak position, peak intensity and band contour is demonstrated. This analysis leads to the conclusion that the relative population of monomer molecules in this highly associated liquid increases with an increase in temperature.

1 Introduction

It has been recognised that when infrared absorption spectra are measured in condensed phases, the observed spectra can be corrected for the internal local field effect¹⁻⁵. This correction results from the fact that the microscopic or the internal field acting directly on molecules is different from the applied macroscopic electric field⁶⁻⁸. The spectra obtained after this procedure provide information on a molecular level. Depending on the structure of the compound that has been used, either of two main models is used to take account of this effect. For isotropic homogeneous media the Lorentz model⁹ has been widely used while for the non-homogeneous systems the basic model used to take account of the internal field is the Onsager model¹⁰. The correction procedure of the experimentally observed spectra (the so called dispersive local field method) developed on the basis of the Lorentz model by Bakhshiev et al.¹¹ will be described below. The main advantage of this model is that it allows one to take into account simultaneously the influence of the local field on all parameters of the vibrational

band (peak position, intensity and band contour). Here this model has been applied to correct the far-infrared absorption spectra of acetonitrile obtained by Ohba and Ikawa¹² at different temperatures.

2 Dispersive Local Field Method

The local field method is based on the theory of the polarisation of dielectrics^{10,13}, which established a relation between the effective (E_{eff}) and average (E_{av}) optical frequency fields in a condensed medium. In condensed media, E_{eff} and E_{av} differ due to the polarising influence of the molecules on each other. This difference for isotropic media in form of the Lorentz model leads to the well-known Lorentz-Lorenz formula^{10,13}

$$\frac{\hat{n}^2 - 1}{\hat{n}^2 + 2} = \frac{4}{3} \pi N \hat{\alpha} \quad (1)$$

where \hat{n} is the complex refractive index of the medium, $\hat{\alpha}$ is the molecular polarisability and N is the number of molecules per unit volume.

Similar relations have been obtained for spectroscopic characteristics of the molecule and the condensed medium¹⁻⁴. Indeed, the analysis of the formula for the square of the refractive index, expressed in terms of Eq. (1), shows that the absorption integral is related to the oscillator strength of the molecule by a factor, $L = (n_{\infty}^2 + 2)^2 / 9$ (the Polo-Wilson effective field factor¹⁴), and that the position of the spectra assigned to the isolated molecule and to the molecules in condensed medium should differ. The difference will depend on the oscillator strength of the optical transition. The method based on the dispersion of the effective field constitutes an important and qualitative development of the concept of the local field in IR spectroscopy¹⁻⁵. This semiempirical approach allows one to take into account the spectroscopic difference between the local and average optical frequency fields within the limits of the bands under consideration. Thus the spectrum of molecules in the static field of the condensed-medium can be obtained, i.e. one can account for the influence of the local field effect on all the fundamental characteristics of the vibrational band. The method is based on the dispersion of the effective optical frequency field^{1,2,11,15} and the essential feature of this

method is that the local field strength varies with frequency within the limits of the optical transition (like molecular polarisability or the refractive index of the medium).

The relation between the spectrum of the molecule in the static field of the condensed medium, expressed in terms of Einstein coefficients, and the spectrum of this medium, can be obtained by considering the general expressions for the probabilities of quantum transitions involving the absorption of light and have the following form^{1,3,4,11}

$$B(\nu) = \frac{c\alpha(\nu)}{h\nu n(\nu)N} [L(\nu)]^{-1}, \quad (2)$$

where $L(\nu)$ is the effective field factor for the absorption of light

$$L(\nu) = \frac{|E_{\text{eff}}(\nu)|^2}{|E_{\text{av}}(\nu)|^2}. \quad (3)$$

Here $B(\nu)$ is the spectrum of Einstein coefficient; $\alpha(\nu)$ is the Bouguer absorption coefficient; N is the number of molecules per unit volume; $n(\nu)$ is the refractive index of the medium, h is Planck's constant and c is the velocity of light. Eq. (2) shows that spectra of the molecule in a static field $B(\nu)$ can differ in all its characteristics from the spectrum of the condensed medium $\alpha(\nu)$, because the effective field factor can vary substantially with the frequency within the band.

In order to calculate the spectrum of molecule $B(\nu)$ using Eq. (2), one should know the spectrum of the condensed medium and be able to find the effective field factor. The latter can be expressed in terms of the experimental optical characteristics, the refractive index $n(\nu)$ and absorption index $k(\nu) = \alpha(\nu)/4\pi\nu$ based on one of the models (Lorentz or Onsager) from the theory of the polarisation of dielectrics (see Ref.1,2,4 for details). According to the Lorentz model, the expression for the effective field factor is

$$L(\nu) = \left| \frac{\hat{n}^2 + 2}{3} \right|^2, \quad (4)$$

where $\hat{n} = n(\nu) - ik(\nu)$ is the complex refractive index of the medium in the region of the absorption band^{1,11}. Therefore, the spectrum $B(\nu)$ can be expressed via the optical characteristics of the medium in the following way:

$$B(\nu) = \frac{4\pi n(\nu)k(\nu)}{Nh} \times \left(\frac{9}{(n^2(\nu) - k^2(\nu) + 2)^2 + 4n^2(\nu)k^2(\nu)} \right). \quad (5)$$

The oscillator strength (or the square of the transition dipole moment derivative $(\partial\mu/\partial\theta)_0^2$ of an absorbing molecule) can be found when the integration of $B(\nu)$ is carried out over the entire absorption band

$$A_{cor} = h\nu c \int B(\nu) d\nu = \frac{\pi}{3c} \left(\frac{\partial\mu}{\partial\theta} \right)_0^2, \quad (6)$$

where A_{cor} is the absolute band intensity corrected for the internal field effect^{1,3,4,11}.

It should be noted that this method was successfully applied to the characterisation of different condensed media (solids, liquids and solutions) and to different types of spectra (IR, Raman and UV)^{1,2,4,16-19}. Here we are demonstrating the possibility of applying this method to the investigation of the far-infrared spectra of acetonitrile at different temperatures.

3 Results and Discussion

It should be pointed out that the acquisition of both optical characteristics (the refractive index and the absorption index) in the far-infrared region is a much more complicated task compared to the medium IR region. This is due to the technical problems that exist in the far-infrared region and, in particular, mainly due to the absence of conventional powerful light sources. Thus it is very difficult to obtain reliable data on optical constants of organic liquids in the far-infrared region, which are necessary for the application of the dispersive local field method. Nevertheless, quite precise measurements of the optical constants of acetonitrile in the temperature range 238-343 K have been carried out recently by

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Ohba and Ikawa¹². The authors used a synchrotron orbital radiation (SOR) source in order to obtain continuous spectra of the optical constants from transmission measurements in the region 20-250 cm^{-1} .

The spectra of the absorption and refractive indexes of acetonitrile at different temperatures have been scanned and tabulated, using specially developed software^{*)}, from Figs. 6 and 7 of Ref.12. Using these data the spectra of Einstein coefficients $B(\nu)$ of acetonitrile have been calculated with Eq. (5). Results for different temperatures are shown in Fig. 1. Experimentally observed absorption spectra $\alpha(\nu)$ are plotted in Fig. 2 using the tabulated data reproduced from Ref.12.

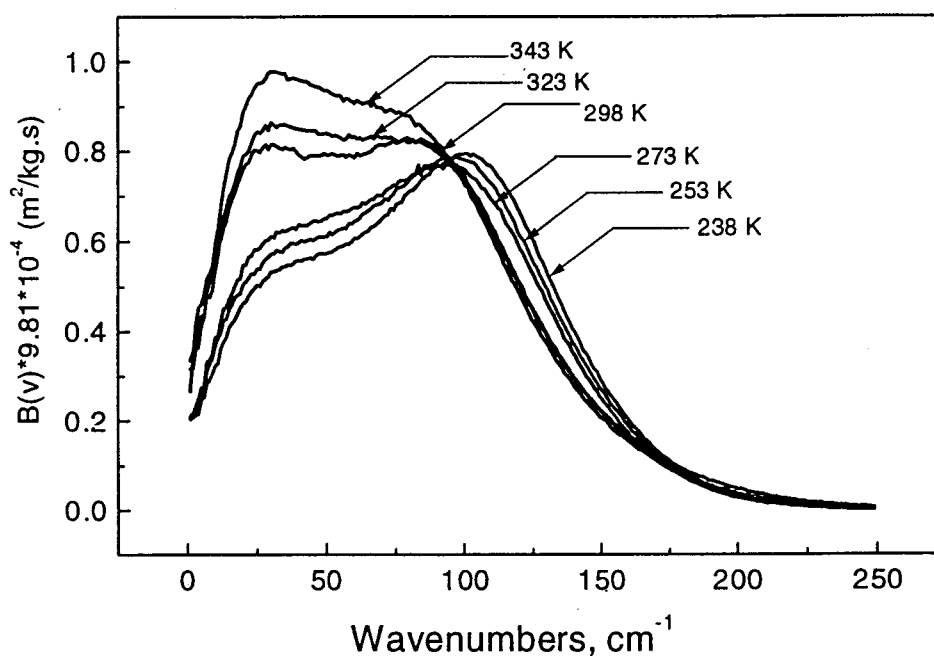


Fig 1: The far-infrared spectra of the Einstein coefficient, $B(\nu)$, of acetonitrile at different temperatures calculated using Eq. (5).

^{*)} All questions regarding this software should be forwarded to P.A. Perov (e-mail: peterpan256@yahoo.com).

As one can see from a comparison of these two types of spectra, the difference between $B(\nu)$ spectra at various temperatures is more pronounced in the low-frequency side of the spectrum and in particular at higher temperatures. However, at low temperatures (238 K, 253 K and 273 K) the band contours of $B(\nu)$ spectra are rather similar and show a pronounced peak around $\sim 40 \text{ cm}^{-1}$. As can be seen from Fig. 2 this peak in the $\alpha(\nu)$ spectra appears more pronounced at higher temperatures (298 K, 323 K and 343 K).

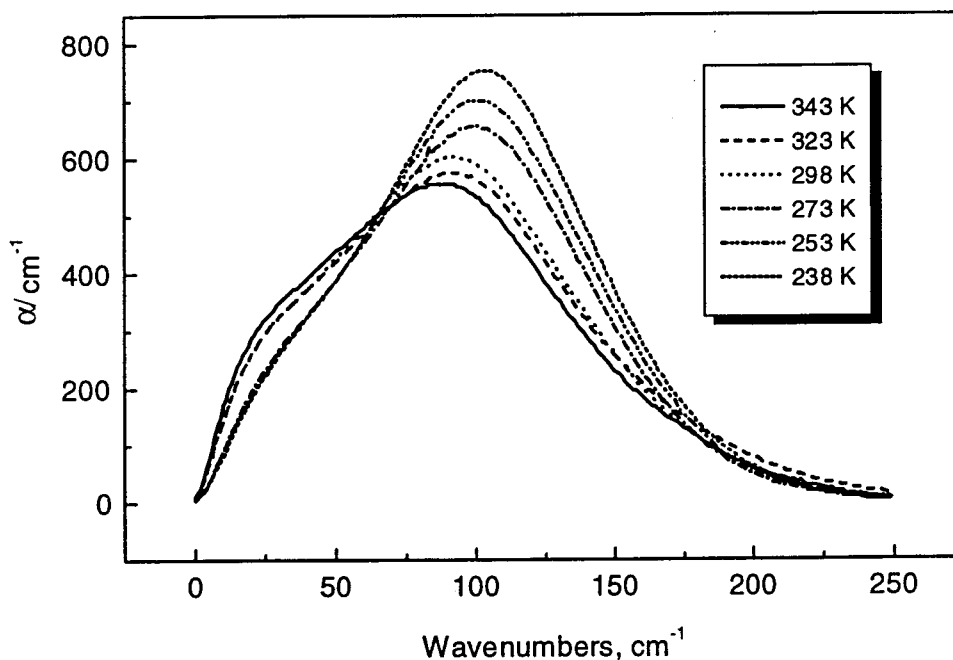


Fig 2: The far-infrared absorption spectra, $\alpha(\nu)$, of acetonitrile at different temperatures. (Reproduced with permission from *Molecular Physics*, 73 (1991) 985).

All $B(\nu)$ spectra are slightly shifted to the lower frequency side with a peak position located in the range $78\text{-}100 \text{ cm}^{-1}$. This behaviour of $B(\nu)$ spectra is different from one observed for various systems in the medium IR region¹⁶⁻¹⁹, where the peak position of $B(\nu)$ spectra is usually shifting to the higher frequency side from the position of the experimental absorption spectra. This can be explained by two factors: i) a unique behaviour of the frequency dependence of the refractive index in this spectral range in general and ii) the

complexity of the absorption band that we are dealing with. As seen from Fig. 1 the absorption of acetonitrile in this region is not due to one single band. The presence of a second band in the region of 30-40 cm^{-1} (and possibly a third one with a maximum of 60 cm^{-1} , which is seen in the $B(\nu)$ spectrum at 298 K) can influence the behaviour of the peak position around 90 cm^{-1} . In fact, the peak at approximately 60 cm^{-1} appeared in absorption spectra of a solution of acetonitrile in carbon tetrachloride. This band has been assigned to Poley absorption of monomer molecules²⁰. The low-frequency Raman spectra²¹ (in the $R(\nu)$ representation) of dilute solutions of acetonitrile in CCl_4 show the peak with maximum at $\sim 45 \text{ cm}^{-1}$. Knozinger et al.^{22,23} propose that the far-infrared band of acetonitrile is composite in nature and arises from three main absorptions. An absorption at 90 cm^{-1} is attributed to the orientational motions of molecules within certain clusters; an absorption at 75 cm^{-1} is assigned to the intermolecular vibrations of antiparallel dimer molecules and an absorption at 65 cm^{-1} arising from the absorption of the monomer molecules (the so called "Poley absorption"). The relative absorbance of the different species depends on the temperature. We believe that the increasing intensity of the $B(\nu)$ -band in the low-frequency side at high temperatures shows (Fig 1) that the population of monomers is increased when the temperature rises. However, this effect is masked in the $\alpha(\nu)$ spectra due to the frequency dependence of the local field factor.

Table 1: The oscillator strength of acetonitrile at different temperatures

T/K	$(\partial\mu/\partial\theta)^2$, [this work], cm^3/s^2	$(\partial\mu/\partial\theta)^2$, [Ref. 12], cm^3/s^2	n_∞ ^{*)}	$N/10^{23}$, ^{*)} molec. cm^{-3}
343	4632	4014	1.322	0.1066
323	4563	3831	1.333	0.1100
298	4461	3717	1.347	0.1137
273	4332	4002	1.360	0.1179
253	4398	3996	1.370	0.1210
238	4533	3951	1.378	0.1233

^{*)} (Reproduced with permission from *Molecular Physics*, 73 (1991) 985).

In Table 1 is shown the calculated value of $(\partial\mu/\partial\theta)_0^2$ obtained using two different methods. One value has been obtained as an integral of $B(\nu)$ according to Eq. (6) (see the

second column in Table 1) and the second one has been defined as an integral of the $\alpha(\nu)$ spectra with the simple Polo-Wilson internal field correction factor $L = (n_{\infty}^2 + 2)^2 / 9$ from Ref. 12 (see the third column in Table 1). The parameters N and n_{∞} (the refractive index at high frequency) are taken from Ref. 12. As one can see from Table 1 the oscillator strength obtained from the dispersive local field method is $\sim 8\%$ higher than the one obtained with the Polo-Wilson correction factor.

4 Conclusion

The dispersive local field method has been applied to the correction of far-infrared spectra of acetonitrile at different temperatures. The results obtained show that this method has wider applications as compared to the non dispersive one, because the dispersive local field method allows one to define simultaneously the influence of the local field effect on all parameters (peak position, oscillator strength and band contour). However, it should be pointed out that in this preliminary study the dispersive local field method has been used for the first time for an analysis of far-infrared spectra of liquids. Further work is required for obtaining a better understanding of this method to account for the local field effect in the far-infrared region of the vibrational spectra.

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