Electronic Supplementary Material for PCCP

Supporting Online Material for

Thermal Effect on C-H Stretching Vibrations of the Imidazolium Ring in Ionic Liquids

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A Simple Oscillator Model. In order to understand the observed T-dependent behaviors of IR spectra, we consider here a forced damping oscillator model, with a mass m and a spring (or force) constant s under friction (resistance b: kg s^{-1} unit) with an external force $f\cos\omega t$, as illustrated in Figure 6. The external force would correspond to the applied IR light wave with an angular frequency (ω), and the oscillator to the C-H stretching vibrator with a drag force (F_d), which depends only on its velocity (for a given homogeneous medium):

$$F_d = -b\frac{dx}{dt}. \tag{1}$$

Then, the equation of motion can be written as:

$$\frac{d^2x}{dt^2} + \gamma\frac{dx}{dt} + \frac{s}{m}x = \frac{f}{m}\cos\omega t, \tag{2}$$

where γ is called the *damping coefficient* (or spectral *width*),

$$\gamma = b/m. \tag{3}$$

A physical model of the drag force (or b and γ) will be discussed in the next section.

The solution of eq 2 can be obtained by a standard mathematical method[S1,S2] and is given by:

$$x = a\exp\left(-\frac{\gamma}{2}t\right)\cos(\omega_f t + \theta) + A\cos(\omega t + \delta). \tag{4}$$

In the steady state (or after a sufficient time), the first term becomes zero and then the displacement x in eq 4 results in:

$$x = A\cos(\omega t + \delta), \tag{5}$$

where the amplitude A and the phase constant δ are not arbitrary and they are given by:

$$A = \frac{f}{m\sqrt{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}}, \tag{6}$$

$$\tan\delta = \frac{\gamma\omega}{\omega^2 - \omega_0^2}, \tag{7}$$

$$\omega_0 = \sqrt{s/m}\,. \tag{8}$$

Here, ω_0 is a harmonic oscillator (or normal mode) frequency of the stretching vibration. For a given amplitude f of the external force, the amplitude A of the oscillations is greatest at the following resonance frequency (from $dA/d\omega = 0$):

$$\omega_r = \sqrt{\omega_0^2 - \gamma^2/2} = \omega_0\left[1 - 2\left(\frac{\gamma}{2\omega_0}\right)^2\right]^{1/2}. \tag{9}$$

In the case of IR absorption spectra, where $\gamma << \omega_0$ (or so-called large resonance Q values: $Q \equiv \omega_0/\gamma >> 1$), ω_r differs from ω_0 only by a quantity of the second order of smallness and can be approximated by:

$$\omega_r/\omega_0 \approx 1 - \left(\frac{\gamma}{2\omega_0}\right)^2.$$

(10)

Now, we are interested in the power absorption (P) by the forced damping oscillator. Energy is continually absorbed by the system from the external force and dissipated by friction. The maintenance of the steady-state vibration requires a sustained supply of energy by the driving force. When the mass moves from x to Δx, the work done by the drag force (F_d) is $-F_d\Delta x$. If the movement takes time Δt, the rate at which energy is dissipated is $F_d(\Delta x/\Delta t)$. In the limit $\Delta t \to 0$, this becomes the instantaneous power absorption:

$$P = -F_d\frac{dx}{dt} = b\left(\frac{dx}{dt}\right)^2 = b\omega^2 A^2 \sin^2(\omega t + \delta),$$

(11)

where eq 1 is used for F_d and eq 5 for x.

The average power <*P*> (or denoted as $I(\omega)$) over many cycles is thus obtained, using eqs 3 and 6 as:

$$I(\omega) \equiv \langle P \rangle = \frac{b\omega^2 A^2}{2} = \frac{f^2}{2m\gamma} \frac{(\gamma\omega)^2}{\left(\omega_0^2 - \omega^2\right)^2 + (\gamma\omega)^2} .$$

(12)

When the driving force frequency ω is close to ω_0 and the damping is very light ($Q \equiv \omega_0 / \gamma$ >>1), we have:

$$\omega / \omega_0 \approx 1$$

(13)

$$\omega_0^2 - \omega^2 = (\omega_0 + \omega)(\omega_0 - \omega) \approx 2\omega_0 (\omega_0 - \omega)$$

(14)

Then, eq 12 is simplified as:

$$I(\omega) = \frac{f^2}{2m\gamma} \frac{(\gamma/2)^2}{(\omega_0 - \omega)^2 + (\gamma/2)^2} .$$

(15)

This power spectrum is known as a Lorentzian line shape. The height of the maximum is $I(\omega_0) = f^2 / 2m\gamma$, and inversely proportional to γ, which is the *full width* of the line shape at its *half* maximum (often called *half-width*). Thus, when the damping coefficient γ decreases, the line shape becomes more peaked. However, the area under the curve remains unchanged, being independent of γ and ω_0:

$$\int I(\omega) d\omega = \int_{-\infty}^{\infty} I(\xi) d\xi = \frac{\pi f^2}{4m} ,$$

(16)

where $\xi \equiv \omega_0 - \omega$.

In this section, using a forced damping oscillator model, we have shown that the IR spectra will possess a Lorentzian line shape characterized by a spectral (full) width of γ and that a small frequency shift (from the normal mode) is proportional to $-\gamma^2$; see eq 10. In the next section, we make a simple model for the friction force (or *b* and γ), in order to correlate the temperature dependence of γ.

Thermal Effects on Oscillators. In our forced damping oscillator model (Figure 6), the mass *m* (or a hydrogen atom in C-H stretching vibrations) would experience a frictional force (F_d), which may be modeled as collisional resistance due to surrounding (randomly moving) molecules in the liquid phase. Then, friction constant, *b* (unit: kg s^{-1}), may be given by a "hard friction" model[S3] for the hard sphere (diameter of σ) repulsion:

$$b = \frac{8}{3} n g(\sigma) \sigma^2 (\pi m k T)^{1/2},$$

(17)

where *n* is the number density, *m* the mass of the sphere, *g*(σ) the radial distribution (dimensionless) function at $r = \sigma$, and usual meanings for π and *k*. In the condensed phase, *n* will be proportional to $1/\sigma^3$. Then, this equation becomes:

$$b \propto \frac{g(\sigma)}{\sigma} (mkT)^{1/2}.$$

(18)

When the temperature dependence on $g(\sigma)/\sigma$ can be ignored, *b* or γ ($= b/m$; see eq 3) increases with temperature or is proportional to $\sqrt{T}$. The same result can be obtained by the use of Stokes law and the kinetic theory of gases. According to the Stokes law, the friction constant is proportional to a radius of particles and an ambient viscosity, which is proportional to $\sqrt{mT}$ based on the gas kinetic theory for thermal motions of particles. Thus, the spectral width γ is:

$$\gamma \propto \sqrt{T}\ , \tag{19}$$

and the resonance frequency (or peak frequency of the line shape) will decrease with T by a small amount when Q >> 1 according to eq 10:

$$\omega_r \propto -\gamma^2 \propto -T\ . \tag{20}$$

References:

(S1) Landau, L. D.; Lifshitz, E. M. *Mechanics*; 3rd ed. Permagon: New York, 1976, 74.

(S2) Main, I. G. *Vibrations and Waves in Physics*; Cambridge Univ. Press: Cambridge, 1978, 56.

(S3) Croxton, C. *Introduction to Liquid State Physics*; John Wiley & Sons: New York, 1975, 256.