Chemical Exchange and Raman Line Broadening III. A Comment to [1]

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The question of whether the integrated intensities of vibrational spectra are changed due to fast chemical reactions [2] or whether they are not [1] is discussed theoretically and experimentally.

1. Theory

An earlier treatment of line broadening in vibrational bands due to chemical exchange [2] was based on a second order perturbation theory. It differs already for the case of non-exchanging systems from the density matrix procedure given by [1,3], although in this case the finite results are identical.

To clear the issue it may prove helpful to derive the relevant equations using a pure classical method [4].

We consider a linear harmonic oscillator as a simple model for a vibrating molecule. Without a damping force the oscillator will vibrate monochromatically for an infinite time. The equation of motion including a damping term reads

$$m\frac{d^2 x}{dt^2} = -\omega_0^2 \cdot x - 2\beta \frac{dx}{dt}. \tag{1}$$

The solution of Eq. (1) is

$$x = x_0 \exp(-\beta t) \exp(-i\omega_0 t). \tag{2}$$

The averaged energy of the oscillator is

$$W = m(\overline{\dot{x}^2} + \omega_0^2 \cdot \overline{x^2})/2 = W_0 \exp(-2\beta t). \tag{3}$$

Thus the energy decreases with a time-constant $1/2\beta$ which is the lifetime of the oscillator.

The electric field E associated with the vibrating oscillator dipole is proportional to the amplitude of vibration and decays with a rate constant β. Therefore, with $t > 0$

$$E(t) = E_0 \exp(-\beta t) \exp(-i\omega_0 t). \tag{4}$$

With a finite β E is no longer monochromatic but extends over a frequency range of the order of β. This is realized by Fourier transforming Eq. (4) into the frequency domain

$$E(\omega) = \frac{E_0/2\pi}{i(\omega_0 - \omega) + \beta}. \tag{5}$$

The intensity distribution then becomes ([5]; compare [6])

$$I(\omega) = \text{const} \cdot EE^* = \frac{I_0\beta/\pi}{(\omega_0 - \omega)^2 + \beta^2}. \tag{6}$$

The factor I_0 is equal to the total intensity $\int I(\omega)\,d\omega$. Eq. (6) is a Lorentzian with half line width 2β i.e. β is the equivalent

of $1/T_2$ in the Bloch equations. Eq. (6) refers to the stationary spectrum of many stochastically excited oscillators. Abbreviating

$$\alpha = i(\omega_0 - \omega) + \beta \tag{7}$$

Eq. (5) reads

$$\alpha E = E_0/2\pi \tag{5a}$$

which is equivalent to Eq. (7a) of our paper [2]. Eq. (6) (multiplyed with the concentration c of the oscillators) is the equivalent of Eq. (7a) in [2].

To calculate the line shape for an oscillator exchanging between two positions A and B with frequencies ω_A and ω_B and with average lifetimes τ_A and τ_B we write

$$\alpha_A E_A = E_0/2\pi + E_B/\tau_B - E_A/\tau_A \tag{8a}$$

and the corresponding Eq. (8b) with interchanged indices A and B. We solve Eqs. (8) for E_A and E_B and insert into Eq. (9)

$$I(\omega) = c_A\beta_A E_A E_A^* + c_B\beta_B E_B E_B^* \tag{9}$$

which is Eq. (6) for the case of exchanging oscillators A and B with concentrations c_A and c_B. Eq. (9) describes the line broadening of the spectrum due to rapid exchange. It predicts a decrease of the integrated intensity I_0 due to exchange processes as described in our earlier paper [2].

The parameter β is equivalent to the reciprocal of the spin-spin relaxation time T_2 in NMR spectroscopy. It depends on all mechanisms which lead to a depopulation of the excited state except chemical exchange. β can be experimentally determined provided that conditions can be chosen such that no chemical exchange is involved. In our work the constant β for the free nitrate ion was obtained from Raman spectra of $NaNO_3$ solutions.

The form of Eq. (9) (or rather its equivalent Eq. (13) in [2]) including the factors β_A and β_B has been derived quantum mechanically by Heitler [7]. It has been made plausible in our paper [2]. It must be realized that by omitting the factors β_A and β_B in Eq. (9), the kinetic depression effect on the spectral amplitudes is not removed.

An important issue has been discussed by Strauss and MacPhail [4] regarding the lower time range of reaction times accessible to line broadening techniques. The model of an instantaneous switching from state A to B and vice versa in a reaction $A \rightleftharpoons B$ is only an approximation. A finite

transition time τ_t is necessary for the proper reaction, during which all parameters such as vibration frequencies, damping constants β, polarizabilities (or dipole moments) change continuously from the values valid in state A to those valid in state B. This time will be of the order of a vibration period. Therefore, the inequality (10) must hold

$$\nu_i \tau_i \gg 1 \quad i = A \text{ or } B. \tag{10}$$

Whereas in NMR spectroscopy Eq. (10) is excellently fulfilled, this may not be the case with exchange broadened bands in vibrational spectroscopy. With typical values in our measurements on nitric acid $\tau = 10^{-12}$ s and a Raman wave number of 1000 cm^{-1} the product $\nu \tau$ is 30. Therefore, the assumption that reaction rate and β-relaxation are independent of each other, will not be too bad an approximation. However, chemical reaction times shorter than about 10^{-13} s are ill defined physical quantities.

Three approaches to the problem of chemical exchange and line broadening of vibrational spectra exist:

1) The formula of Kreevoy and Mead [6] which is claimed to be valid for the "slow case" ($\Delta\omega \cdot \tau \gg 1$). It is quite analogue to the Bloch equations of NMR.
2) The formula of Strauss et al. [1,3] and
3) The approach of Strehlow et al. [2,8].

Fortunately, the line shapes calculated are very similar with all three methods. Therefore older results which have been evaluated using the Kreevoy-Mead technique will not be obsolete. The important difference in the three formulas is the dependence of the integrated intensity of the spectrum on the kinetics. Method 1) and 2) predict only a small dependence whereas according to 3) strong kinetic amplitude damping effects may occur. What is the experimental evidence?

2. Experiments

Unfortunately, most of the earlier measurements of kinetically broadened vibrational spectra have only been discussed in terms of line shape, neglecting consideration of total intensity. One of the few exceptions is the measurement of the interconversion of rotamers of 1,2-dichloroethane at different temperatures by Cohen and Weiss [9]. Two series of infrared spectra, one in the neat liquid and one in a 4% v/v solution in Cs$_2$, are displayed in Fig. 1. The effect of the kinetics on the total intensity is clearly visible.

These authors in a later paper [10] presented kinetically broadened IR-spectra of acetylacetone where, unfortunately, "*for convenience of presentation all spectra were normalized to the same height*".

The most informative relevant measurements have been performed by Irish and Puzic [11] and by [2] with nitric acid. The Raman spectra show strong bands between 900 and 1100 cm^{-1}. The precision of the calibrated measurements is very good. It has been demonstrated in [2] that the depression of the total intensity at higher rates cannot be explained by assuming different Raman sensitivities of HNO$_3$ and of NO$_3^-$.

A further (not yet published), possibility to obtain rate constants for the nitric acid system from total intensity ratios alone will be presented now. As shown in [8] the ratio F of the Raman total intensity of the exchanging system (2 M HNO$_3$) to that of the non-exchanging system (2 M NaNO$_3$) is given by

$$F = \beta\tau/(1 + \beta\tau). \tag{11}$$

Eq. (11) holds strictly only for the slow case with a reaction of the type $A \rightleftharpoons B$. In nitric acid we have three species of nitrate: free NO$_3^-$, a solvent separated ion pair NO$_3^-$ H$_2$OH$^+$ and undissociated nitric acid HNO$_3$. However, in 2 M nitric acid the two latter species are at low concentrations and are not visible in the Raman spectrum. Thus we may apply Eq. (11) to the band of the free nitrate ion. $\beta = 3.9$ cm^{-1} = $7.35 \cdot 10^{11}$ rd s^{-1} was obtained from a NaNO$_3$ solution. The ratio of the total intensity F for 2 M HNO$_3$ and 2 M NaNO$_3$ was experimentally found to be 0.89. From these experimentally determined values we calculate an average lifetime for the nitrate ion of 11.0 ps in 2 M nitric acid which compares favourably with the value 11.8 ps calculated with the full fitting program. It should be realized that these two data are independent of each other. Their equality lends further support to the theory that fast kinetics is the reason for the observed amplitude depression.
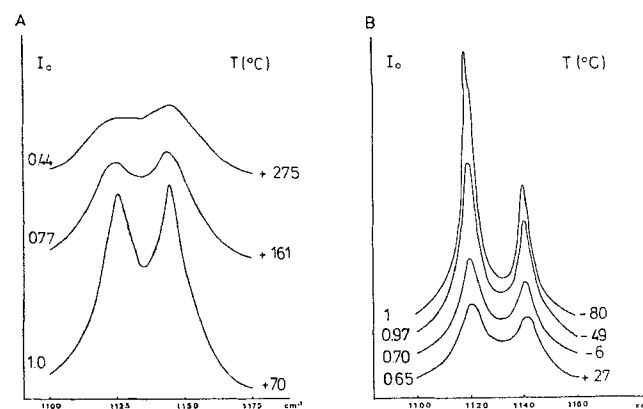

Fig. 1
A   Spectra of liquid 1,2-dichloroethane at different temperatures [9].
B   Spectra of 1,2-dichloroethane in CS$_2$ (4% v/v) at different temperatures [9].
The relative integrated intensities I_0 are precise to only about $\pm 5\%$ due to uncertainties in the base lines.
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Another argument in favor of this interpretation is the effect of HCl on F for the nitrate ion in 2 M nitric acid. For the concentrations of HCl 0, 4, and 5.82 M the ratio F was found to be 0.89, 0.75, and 0.62. The lowest value of F (= 0.47) was observed in 14.7 M HNO$_3$.

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