Infrared Study of Reorientational Potential Barrier in Three Aliphatic Nitriles

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Several recent papers have emphasized the current interest in the study of infrared band shapes in condensed phases. The aim of this note is to report the temperature dependence of the half-widths of certain IR bands of succinonitrile, malononitrile and acetonitrile with primary interest in the elucidation of the mechanism influencing the half-width. Generally it is assumed that the main contributions are the vibrational or intrinsic (ΔW_v) and the reorientational (ΔW_r) relaxations. The separation of both contributions can be done by Raman spectroscopy [1, 2] but in our work we used the much simpler method due to Rakov [3]. The half-width is written as:

$$\Delta W = \Delta W_v + \Delta W_r \tag{1}$$

and only ΔW_r is a function of temperature $\Delta W_r \sim \exp(-\Delta E/k\,T)$ where ΔE is the activation energy.

All bands we have studied are free of overlap with others. The following bands were observed: succinonitrile [4]: CH_2 rocking (1002 cm^{-1}), C – CN stretching (917 cm^{-1}) and CH_2 rocking (960 cm^{-1}); malononitrile [5]: CH_2 rocking (936 cm^{-1}), C – N stretching (2270 cm^{-1}), C – C antisymmetric stretching (983 cm^{-1}) and C – C symmetric stretching (890 cm^{-1}); acetonitrile [6]: C – C stretching (919 cm^{-1}) and CH_3 rocking (1042 cm^{-1}).

The temperature dependence of the half-width was measured far below solidification of succinonitrile and acetonitrile because these two species have a plastic phase. The same was not possible for malononitrile because at the liquid-solid phase transition the bands split up.

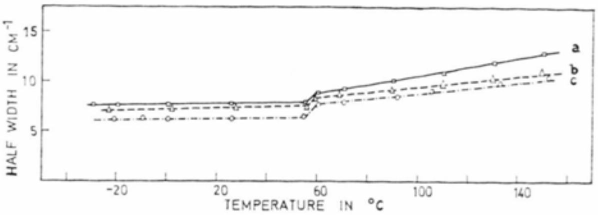

Fig. 1. Half-widths of succinonitrile: a (917 cm^{-1}), b (1002 cm^{-1}), c (960 cm^{-1}).

In Figs. 1 and 2 the measured half-widths are presented. In succinonitrile the activation energy has the same value (0.39 kcal/mol) for all three observed bands. The dipole correlation functions connected with the measured bands have a similar temperature dependence. From this one can conclude that the reorientations about two axes (perpendicular to C – CN stretching and CH_2 rocking) are isotropic. In malononitrile the activation energies for C – N stretching, C – C antisymmetric and symmetric stretching have a similar value (0.4 kcal/mol) while the activation energy for CH_2 rocking (0.98 kcal/mol) is much higher. If the above mentioned separation [Eq. (1)] is correct then the half-widths of the C – C symmetric stretching and the CH_2 rocking bands have to be of the same order. The reason why this is not so may be in the temperature dependence of ΔW_v. The results with acetonitrile are of particular interest. The separation of the vibrational modes into C – C stretching and CH_3 rocking is much more pronounced than in the previous two examples [6]. The dipole moment changes have better defined orientations. The dipole autocorrelation function of C – C stretching is influenced by the overall molecular reorientation. The dipole autocorrelation function of CH_3 rocking is influenced by two contributions from an overall reorientation and from the internal CH_3 group rotation. The separation into these two contributions can be done by supposing that both reorientations are independent. The measured dipole autocorrelation function C_m of CH_3 rocking is then given by

$$C_m = C_i \cdot C_0 \tag{2}$$

with C_i the autocorrelation function of the CH_3 group and C_0 the autocorrelation function of the overall molecular reorientation taken to be the autocorrelation function of C – C stretching. In accordance with Eq. (2) the measured bands were Fourier inverted to yield the dipole autocorrelation functions. The measurements done in CCl_4 solution were within experimental error

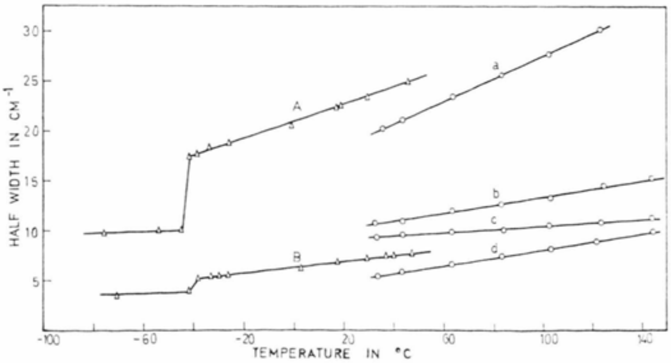

Fig. 2. Half-widths;
Malononitrile: a (936 cm^{-1}),
b (2270 cm^{-1}),
c (983 cm^{-1}),
d (890 cm^{-1});
Acetonitrile: A (1042 cm^{-1}),
B (919 cm^{-1}).

equal to that done on the pure sample. This is in accordance with the observation in Ref.[7] and therefore the cross correlation functions are neglected. The values of ΔE are 0.75 kcal/mol for C–C stretching and 1.20 kcal/mol for CH_3 rocking and the correction with Eq. (2) gives the value 0.54 kcal/mol. The dipole autocorrelation function of CH_3 rocking is changing with rotation of the CH_3 group around the C_3 axis. The value 0.54 kcal/mol represents then the potential barrier for the rotation of the CH_3 group.

Acknowledgement

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