

## 2D IR: A new dimension to infrared spectroscopy

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A novel analytical technique, called two-dimensional infrared spectroscopy (2D IR)<sup>1</sup>, is based on principles similar to two-dimensional nuclear magnetic resonance spectroscopy (2D NMR)<sup>2</sup>. In 2D IR, vibrational spectroscopy is used to probe the reorientation of the electric dipole moments associated with the vibration of the bonded atoms in a perturbed system.

In conventional infrared spectroscopy, absorption of infrared radiation at different frequencies, by a sample, is recorded. The intensity of the absorption at a certain frequency, by a molecule (or part of a molecule), is dependent on, among other factors, its orientation with respect to the oscillating electric field of the exciting electromagnetic radiation. In general, molecules in a sample are randomly oriented giving an average intensity of absorption of radiation. However, the molecules can be oriented in a particular direction by applying perturbations such as external electric fields, strain (deformation), etc.

In the 2D IR experiment, reported by Noda, a sinusoidally oscillating tensile strain (of amplitude 0.1% and frequency 23 Hz) is applied to the solid sample as the perturbation. This makes the bonds in the molecules change their orientation (relax) continuously. Each bond relaxes at its own characteristic rate. The intensities of absorption at each frequency are recorded at two particular values of strain on the sample. This gives information about the rate at which the different parts of the molecules or the molecules themselves (i.e. the groups in the sample that are absorbing radiation of corresponding frequencies) in the sample change their orientations with the changing strain. So, from the rate of change in intensity of absorption, the rate of change in the orientation of bonds in the molecules can be obtained.

The principle and the experimental set-up of this technique are based on the technique used for dynamic infrared linear dichroism<sup>3</sup> (dependence of absorption intensity on the direction of orientation of molecules). However, the

most interesting part of the technique is processing of the recorded data by correlating the rates of change in the absorption intensity at different frequencies of radiation. If the absorption intensities at two particular frequencies change at the same rate, this indicates that the origin of the absorptions at the two frequencies is from the same part of a molecule or from two different parts that are bonded in such a manner that they relax at the same rate on changing the strain.

The intensities of absorption at different frequencies are connected quantitatively by using correlation functions. Synchronous 2D IR correlation intensity, a function of the absorption intensities at two frequencies measured at two different values of strain, is generated from the data. This quantity will have a higher value if the changes in the absorption intensities corresponding to the two frequencies are synchronized. This correlation intensity is plotted in a three-dimensional contour map over a spectral plane defined by two independent wave number (or frequency) axes. A typical spectrum is shown in Figure 1, which is a contour map representation of the synchronous 2D IR correlation spectrum for a mixture of polystyrene and polyethylene, the system used in Noda's experiment. A similar quantity known as the asynchronous correlation intensity can be generated and plotted to indicate the frequencies whose relaxation of absorption intensities are not synchronized.

From Figure 1 we can see that the synchronous correlation intensity corresponding to the frequencies 1495 and 1454  $\text{cm}^{-1}$  is high. This is expected as both the frequencies correspond to the phenyl rings of the polystyrene and so their absorption intensity relaxation is synchronized. On the other hand, the frequencies 1459 and 1454  $\text{cm}^{-1}$  give high values of the asynchronous correlation intensity. This is because the 1459  $\text{cm}^{-1}$  absorption is due to the  $\text{CH}_2$  groups of the polystyrene chain backbone, which reorient at a different rate compared to the phenyl rings on perturbation. The frequencies corres-

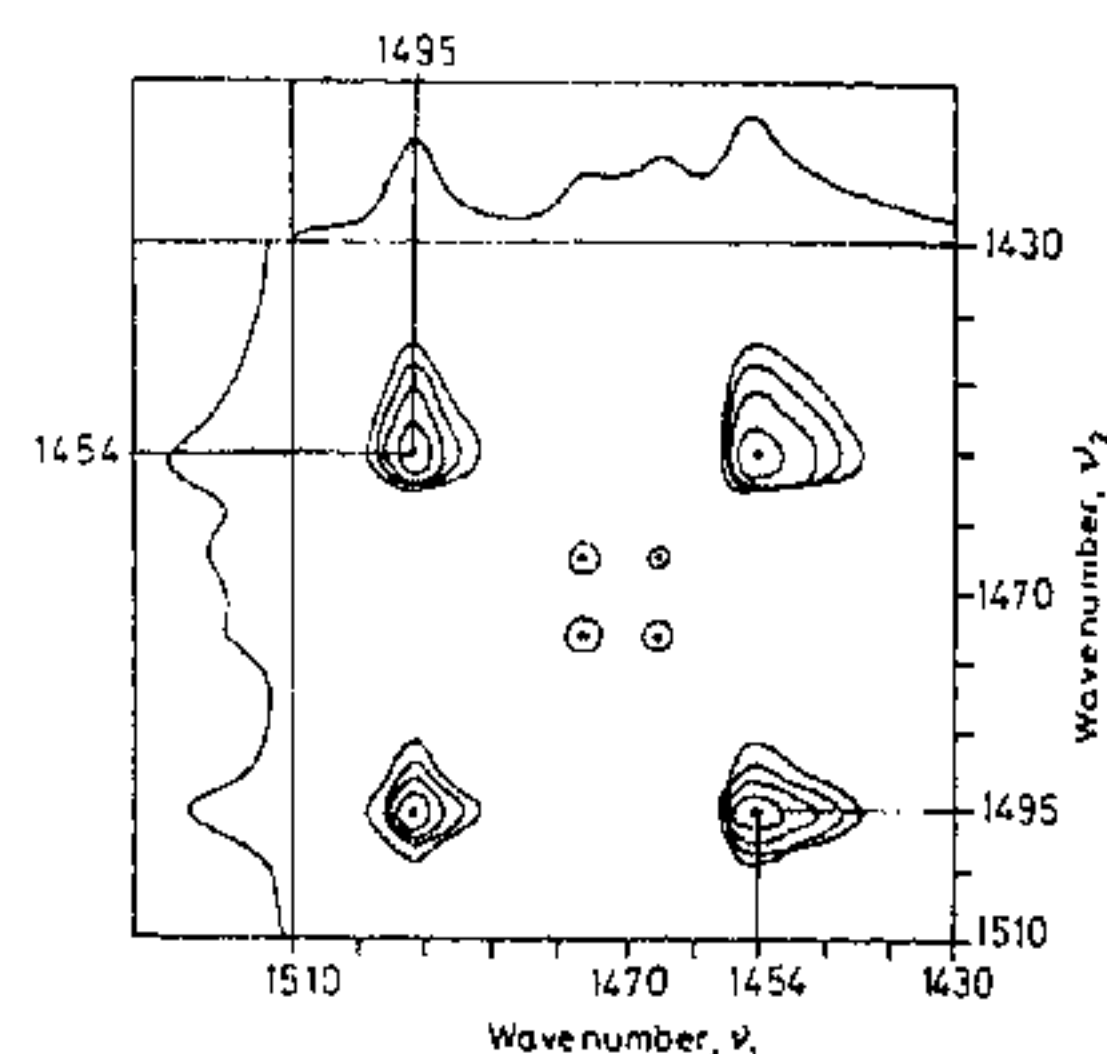


Figure 1. Contour map representation of the synchronous 2D IR spectrum of a mixture of polystyrene and polyethylene. The conventional absorption spectra are shown at the top and the side of the map. (Adapted from figure 3 of ref. 1.)

ponding to the polyethylene chain (1475 and 1466  $\text{cm}^{-1}$ ) have high asynchronous intensity when correlated with a frequency corresponding to the polystyrene (1495 or 1454  $\text{cm}^{-1}$ ), showing that the two polymers in the mixture are segregated at the molecular level.

Although, in this first report of the new concept of 2D IR, a comparatively simple system has been considered, with the availability of sophisticated technologies and computational facilities it is hoped that this novel concept will mature into a powerful analytical tool. It is expected to be useful for assignment of vibrational peaks of complicated systems, such as biological molecules, in studies of the interaction between the different components in solid solutions, and in determination of the structure and conformation of molecules.

1. Noda, I., *J. Am. Chem. Soc.*, 1989, **111**, 8116.
2. Turner, D. L., *Prog. Nucl. Magn. Reson. Spectrosc.*, 1985, **17**, 281.
3. Noda, I., Dowrey, A. E. and Marcott, C., *Appl. Spectrosc.*, 1989, **42**, 203; Noda, I., Dowrey, A. E., Marcott, C., *J. Polym. Sci. Polym. Lett. Ed.*, 1983, **21**, 99.

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