Discovery of a new effect: CFM effect

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A report on the discovery[1] of a new effect, named Continuous Frequency Modulation Effect (CFM effect) is reported here. The CFM effect occurs in the power spectrum of oscillators undergoing a continuous modulation of the vibrational frequency. Agrawal *et al.*[1] have shown that a single sharp line, normally characteristic of an oscillatory system, broadens and exhibits a wealth of fine structure components when the system undergoes a continuous frequency modulation. Then also gives the relationship between the fine structure and the frequency modulation rate. The fine structure so observed has been termed as the 'CFM fine structure'.

For an analytical justification of the CFM effect, the authors present a detailed mathematical treatment of a pulse, $Y = A \sin \omega t$, of duration T such that ω is continuously varying with time:

$$\omega = 2\pi\nu_0 (1 - kt).$$

If the pulse duration T and the frequency modulation rate constant k are such that $2kT < 1$, then it is shown that the power spectrum of such a pulse exhibits CFM effect – the existence of a wealth of fine structure components. Further, it is shown, numerically as well as analytically, that the position of the fine structure extrema depends linearly upon the initial oscillator frequency and the square root of the absolute value of the modulation rate. The peak-to-peak spacing is shown to be proportional to the square root of the absolute value of the modulation rate.

Such CFM effect has been experimentally observed by the authors while the resonant frequency in the NMR studies is continuously changed by varying the main magnetic field B with time. In this connection, the authors also suggest a method of identifying the electronic transients in an NMR spectrum by using the CFM effect. The authors write: 'This observation suggests a method for identification of such transients in a complex NMR spectrum. One simply removes the field lock and takes an NMR spectrum with B varying. All the NMR lines will broaden and split, but the electronic transients will be unaffected. Once identified they can be safely subtracted from the NMR spectrum.'

The CFM effect has also been verified by a computational study of different types of oscillators such as harmonic system with an exponentially modulated frequency with and without amplitude depression.

In several classical trajectory studies of chemical reactions, it has been observed in the past by different research groups that the power spectrum of a molecule transferring vibrational energy during a reaction contains unexplained fine structure. Agrawal *et al.* point out that with the help of the CFM effect not only is the fine structure explainable, but one can also deduce the rate of energy transfer by the molecule from the knowledge of the CFM fine structure.

Such a point has been presented in detail by correlating the rate of vibrational energy transfer with the rate of frequency modulation rate and the computed CFM fine structure for different diatomic molecules vibrating under the influence of the Morse potential.

For the application of the CFM effect to the molecular reaction dynamics, the authors discuss three examples: (1) Determination of vibrational relaxation rate coefficient from the knowledge of the CFM fine structure in a computational study of HONO in a cryogenic rare gas matrix, (2) The use of CFM effect to extract the rate of energy transfer from a diatomic molecule to a surrounding matrix cage of Ar atoms, (3) The instantaneous energy transfer rate from the knowledge of the CFM fine structure. However, the CFM effect may not be applicable in the molecular systems if the vibrational frequencies cannot be continuously modulated due to the constraints imposed by quantum mechanics.

Since the CFM effect is applicable whenever there is a continuous frequency modulation of a vibrating system, it becomes an effect of fundamental importance and its application cannot be limited to a few cases. It may be of importance in Physics, Chemistry, Electronic-engineering, Astrophysics, and many such disciplines where the vibrational frequencies are continuously modulated even for a short duration of time. Further, from the point of view of research in mathematics, the CFM effect widens the scope of research in the Fourier transform of different types of functions representing vibrations with continuous frequency modulation.

1. Agrawal, P. M., Sorescu, D. C., Kay, R. D., Thompson, D. L., Raff, L. M., Conrey, J. B. and Jameson, A. K., *J. Chem. Phys.*, 1996, **105**, 2086–2700.

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