Dephasing Statistics of Triatomic Molecules at Mixed Quantum Classical Level: Beyond Conventional Analysis

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When a molecule is in isolation, its energy levels are the nonfluctuating eigenvalues of the time independent Schrödinger equation, and the spectroscopic measurements of the transition frequencies among these energy states yield sharp peaks. Such is the case in many high temperature, low density gas phase spectroscopic experiments. Thus, in the case of low density high temperature experiments, from the point of view of optical spectroscopy or control theory [1], there is no need to worry about the ever modulating energy levels. On the other hand, when a molecule is in contact with an environment, say an infinite heat bath, which is a more realistic and interesting situation compared to isolation, it suffers many collisions with the surrounding molecules, and the picture of well defined transition frequencies is lost. Energy eigenvalues constantly fluctuate and this in turn causes broadening and perhaps a shift in the observed spectroscopic peaks. The time scale of the collisions of course depends on the temperature and density, but an order of magnitude is roughly a pico second or a fraction thereof. An accurate modeling of dephasing of a molecule embedded in a solvent must go beyond the naïve assumption of Gauss-Markov processes and use some level of molecular mechanics. Although studies of dephasing that uses only classical mechanics exist and are used together with stochastic assumptions [2] we believe because of strong quantum mechanical nature of molecular vibrations any model which purely relies on classical mechanics, especially when the vibrations of light weight molecules are involved, is subject to criticism. In a previous study [3] we have explored the dephasing statistics of simple diatomic molecules like HCl, DCI, TCI, and ICI in dense Ar fluid at two different temperatures. Although our findings regarding the vibrational dephasing of a diatomic molecule in solvent are conclusive the system itself was too simple: a diatomic has only one vibrational degree of freedom. The contents of our talk and the questions we address is twofold: (1) As an extension to our previous study we intend to investigate the vibrational dephasing of triatomic molecules in dense solvents and observe how more than one vibrational degrees of freedom affect each other. Which vibrational mode is more susceptible to the collisions? Do their statistics differ at all? (2) As a major build up to the previous work we also want to address the issue of complexity of and causality in the real time modulations. In statistically quantifying the modulations one computes histograms, correlation functions, Fourier transforms, etc. While all these are fine, they do not get the most information out of data. We need to use a more informative tool [4] to ascertain the complexity of modulations and how it varies with temperature and density. Can we exploit our statistical findings in generating the “fake data”?

References: