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ENERGY DISSIPATION IN CHEMICAL REACTIONS ON ULTRAFAST TIMESCALES

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Abstract

A series of picosecond experiments and computer simulations will be presented that test collisional and hydrodynamic models for vibrational relaxation in liquids. The relationships between isolated binary collision models (IBC) and stochastic dynamics will be presented. The appropriateness of IBC theory in describing vibrational relaxation in liquids will also be discussed.

A proper description of vibrational energy transfer is essential to the development of chemical reaction theory. In liquids, progress in this area is far behind that which has been made in other phases because of the complexity inherent to this phase. Generally, two approaches have been taken in attempting to model the vibrational relaxation of an excited oscillator in solution. One approach takes the perspective of the excited molecule being solvated in a continuous viscoelastic media which exerts a frictional force on the molecule. The most general form of this interaction is described by the generalized Langevin equation:

$$ma(t) = -\int_{t_0}^{t} dt' m\gamma(t') v(t-t') + R(t) \qquad (1)$$

where m is the mass of the particle, R(t) is the random force, and $\gamma(t)$ is the memory function which provides the friction. In this description, the noninstantaneous response of the media to the motions of the oscillator are included. The difficulty with this method has been in developing a model of determining the form of $\gamma(t)$ [the frequency dependence of the friction]. Very early during the theoretical development of vibrational relaxation in liquids, prior to use of the generalized Langevin model, a simpler form of this model known as the Langevin equation was used to describe vibrational relaxation in solution.[1] According to the Langevin equation,

$$ma(t) = -\gamma v(t) + R(t) \qquad (2)$$

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In the Langevin model, γ, the friction coefficient, is a constant and thus, the solvent is assumed to respond instantaneously to all oscillator motions. While this model has been successful in describing some phenomenon where the solute moves slowly in relation to the solvent molecules, it has failed in the modeling of vibrational relaxation where the oscillator motions can be quite fast in comparison to that of the solvent.[2]

An alternative perspective adapted to describing vibrational relaxation in solution is that based on the molecular nature of the solvent-solute interactions. In this framework, the interactions which are important to vibrational relaxation are assumed to be dominated by isolated binary collisions between the solvent molecules and the oscillator, just as they occur in the gas phase. This model known as the Isolated Binary Collision Model (IBC) states that $K_{i \to j}(\rho, T)$, the relaxation rate of vibrational level i to j, is:

$$K_{i-j}(\rho, T) = P_{i-j} \cdot Z(\rho, T) \tag{3}$$

where $P_{i \to j}(T)$ is the probability of i→j per collision, $Z(\rho, T)$ is the oscillator-solvent collision frequency, ρ is the solvent density, and T is the solvent temperature. Since $P_{i \to j}$ is independent of density, the difference between relaxation in the liquid and gas phases at constant T is solely given by $Z(\rho)$. Thus, multibody effects (i.e., correlations between collisions) are considered to be inconsequential in this model. The validity of this assumption has been the subject of a longstanding debate in the literature.

As a test system for IBC theory, we have examined its applicability to experimental measurements and computer simulations

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of the ground state vibrational relaxation of geminately recombined I_2 in liquid Xe. Following photodissociation and recombination on the ground state surface, the I_2 has an excess of 12500 cm^{-1} of vibrational energy which it then dissipates to the solvent. This relaxation process occurs over 100 I_2 vibrational levels with the vibrational spacing varying from 0 to 214 cm^{-1}. Since I_2 contains only one vibrational degree of freedom, the role of the solvent in dissipating the excess vibrational energy of the excited I_2 can be studied with this system without competition from intramolecular vibrational energy transfer. Furthermore, Xe is an ideal choice as the solvent because of its spherical geometry which makes computations on this system easier and eliminates all but the translational degrees of freedom as the solvent energy accepting modes.

IBC theory is not expected to be valid for this system for two reasons. First, the low vibrational frequencies involved are comparable to the expected collision frequencies. Thus, interference between collisions would be expected to occur. Second, IBC theory should not be applicable to a highly excited oscillator in solution as the collisions will be driven by the large amplitude motions of the oscillator rather than occurring at random intervals resulting from the solvent motion. In contrast, previous studies of the IBC theory's validity at liquid density have focussed on the density dependence of the v=1→0 time of high frequency oscillators such as H_2 and N_2 where the above conditions do not exist and IBC theory may be valid.[3]

Additionally, study of the multilevel relaxation process of I_2

offers a unique perspective on the validity of the IBC model as compared to these other experiments. The difficulty with interpreting the results of the $v=1 \rightarrow 0$ studies is that a calculation of $Z(\rho)$ is necessary in order to ascertain the validity of the IBC model since the relative change in relaxation rates between two densities ρ_1 and ρ_2 according to the IBC model is given by:

$$\frac{K_{i-j}(\rho_1)}{K_{i-j}(\rho_2)} = \frac{Z(\rho_1)}{Z(\rho_2)} \qquad (4)$$

In solution, a collision is a nebulous concept and calculations of Z vary widely in magnitude with model and are very sensitive to parameters such as molecular size. Thus, studies in which the relaxation rate between two levels is measured as a function of density do not test the underlying assumption of the density independence of P_{i-j} separately from the model of $Z(\rho)$ employed. In the experiments on I_2, the relaxation has been experimentally measured over approximately 30 vibrational levels (we could not directly observe the relaxation over the upper half of the ground state surface). Following the relaxation over a large number of vibrational levels as a function of solvent density eliminates the need of calculating Z in testing the density dependence of the P_{i-j}.

To understand this distinction, consider the relaxation process over many vibrational levels in the IBC framework. After $Z(\rho) \cdot t$ binary collisions, the vibrational population distribution vector, $N(t)$, would be

$$N(t) = P \cdot P \cdot P \ldots \cdot P \cdot N(t=0) = P^{Z \cdot t} \cdot N(t=0) \qquad (5)$$

where P is the matrix of relaxation probabilities per collision for

transitions between all levels of the system. The role of $Z(\rho)$ in this description of the relaxation is to control the timescale of the relaxation process. If the time were normalized by $Z(\rho)$, i.e., $t'=t/Z(\rho)$, then the resulting $N(t')$ would be identical for all ρ. Hence, plots of the average energy of the system as a function of time for different density should show the same functional form, differing only by a linear scaling of the time axis which accounts for the change in $Z(\rho)$. Provided $Z(\rho)$ does not vary with vibrational energy, any deviation from linear scaling would be an indication of nonbinary behavior. The timescaling factor S necessary to overlap the energy decay curve at ρ_2 to that of ρ_1 can be determined from

$$Z(\rho_1) \cdot t = S \cdot Z(\rho_2) \cdot t \quad . \tag{6}$$

which leads to

$$S = \frac{Z(\rho_1)}{Z(\rho_2)} \tag{7}$$

The I_2 vibrational energy as a function of time is determined experimentally through picosecond transient absorption spectroscopy. Due to the change of the Franck-Condon factors with vibrational energy, the transient absorption shifts from the near infrared at high vibrational energies to approximately 520 nm at $v=0$. With the transient absorptions in this wavelength region and by calculating the extinction coefficients for the ground state absorption, the vibrational population distribution can be determined as a function of time by applying Beer's law. This analysis has been performed for the lower 6000 cm^{-1} of the I_2 ground

state potential surface. The density range of Xe in which the experiment was performed was 1.8 to 3.4 g/cc at 280 K which corresponds to a Lennard-Jones reduced density ($\rho\sigma^3$) range of 0.57 to 1.07 at a Lennard-Jones reduced temperature (kT/ϵ) of 1.26. A sample plot of vibrational energy vs. time for the 1.8 g/cc and the time scaled 3.0 g/cc is shown in the figure 1. <u>The functional form of the relaxation at all densities is the same.</u> Thus, the $P_{i \to j}$ are density independent over the entire liquid density portion of the Xe phase diagram as is assumed in the IBC model.

Concurrent with the experiments, a theoretical model of the I_2/Xe system was constructed. In order to provide a reference system for comparison of IBC and continuum theories, a molecular dynamics simulation of I_2/Xe was performed. Comparisons of the predictions of these theories with the simulation results will therefore not depend upon differences in the potentials assumed (in contrast to comparisons with the experimental results).[4] The system was a classical molecular dynamics simulation using periodic boundary conditions. The potentials used were a Lennard-Jones potential between the iodine atoms and Xe atoms and a RKR potential for I_2. There were 255 xenon atoms and one iodine molecule in the system, these numbers were chosen because they minimized the effects of heating of the liquid after dissociation due to the small number of particles and was it still a small enough system to allow a reasonable number of trajectories to calculated on a Cray X-MP. The functional forms of the vibrational energy vs. time for all the densities performed were the same. This would seem to indicate as described above that the $P_{i \to j}$ are density independent.

Also, the functional form found from the molecular dynamics simulations was seemingly the same functional form found in the experiments. The only difference was that the molecular dynamics relaxed about 12.4 times faster than the experiment. This may be due in part to the finite volume of Xe heating up from the dissociation energy of the iodine. Also, the Lennard-Jones potential may be steeper than the real I_2-Xe potential. Qualitatively, the density dependence of the relaxation was the same for both the molecular dynamics and the experiment. There was some discrepancy in the actual numbers. Over the liquid range studied by the experiment, from 1.8 g/cc to 3.4 g/cc, the vibrational relaxation was 4 times faster. The molecular dynamics was also 4 times faster for the range of 1.8 g/cc to 3.0 g/cc. The molecular dynamics could not be run at 3.4 g/cc because that is a Lennard-Jones solid while real Xe is a fluid. This shows that the molecular dynamics seems to be a fairly realistic representation of the vibrational relaxation in the liquid and only fails mainly to lack of exact potentials.

Given the success of reproducing experimental results by the molecular dynamics and the evidence that IBC theory may provide a valid model for explaining the experimental results, an IBC calculation was performed. The calculation of $P_{i \rightarrow j}$ performed for I_2 and Xe is a one dimensional classical calculation of energy loss. Studies have shown that the one dimensional calculation is a reasonable substitute for three dimensions if the constraints described in a paper by McKenzie are realized.[5] The I-I potential used is the same RKR surface as used in the molecular dynamics

simulations. The potential between I and Xe is a Weeks Chandler Anderson (WCA) decomposition of the Lennard-Jones potential.[6] Note that the WCA decomposition was originally intended to explain liquid structures for reduced densities greater that 0.6 . Even though most of the comparisons to molecular dynamics will be in this range, WCA was not chosen for this reason.

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left[\left(\frac{\sigma}{r}\right)^6\right] + c \quad where \ r < r_c\right.$$

$$c = 4\varepsilon\left[\left(\frac{\sigma}{r_c}\right)^{12} - \left(\frac{\sigma}{r_c}\right)^6\right] \quad where \quad r_c = 2^{\left(\frac{1}{6}\right)}\sigma \tag{8}$$

$$V(r) = 0. \quad where \ r > r_c$$

The WCA decomposition was chosen for three reasons. When a gas liquifies, energy (the heat of vaporization) is released due to the solvent atoms spending most of their time in the bottom of the well where the potential is repulsive. The attractive part of the potential is defined as the part of the potential where the accelerations are negative. Note that in the Lennard-Jones potential, the potential energy may be negative for $r < \sigma\,2^{1/6}$, but the accelerations are not negative. Since the liquid rarely samples the attractive part of the potential, it was thought that the IBC simulation would be more realistic if it also did not sample that part of the potential. The turning point in the gas phase will also be on average at a smaller radius than in the liquid due to the heat of vaporization, however, the one dimensional model's turning point should be comparable to the molecular dynamics simulation due to the use of the WCA potential. Secondly, not having an attractive section of the potential makes the integration of the trajectory much quicker since there is less

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distance to integrate over and there is no possibility of forming a long lived complex. Thirdly, the molecular dynamics simulation that the one dimensional trajectories would be compared to used a Lennard-Jones potential and the WCA decomposition is the closest approximation to the Lennard-Jones potential within the above constraints.

The trajectories show qualitatively what you would expect keeping in mind I_2's anharmonicity. Vibrational energy transfer increases non linearly as a function of v, the vibrational quantum number. This at variance to Landau Teller theory, which predicts a linear increase with v. Of course, Landau Teller theory is based on a harmonic oscillator and I_2 is most definitely not a harmonic oscillator. A calculation of I_2's average vibrational energy vs. time was performed using data provided by the one dimensional calculations and it was found that the functional form of the energy loss was the same as both the molecular dynamics simulations and the experiments.

In order for IBC theory to be a useful theory it must also be able to make quantitative predictions of the relaxation for a particular density and predictions of the density dependence. The collision rate of 4.5 per ps., which was required to fit the molecular dynamics simulation, is a quite reasonable first order guess of what the collision rate should be for Xe at 1.8 g/cc. Since the trajectory calculations were one dimensional, there must be some steric weighting factor to take into account that some collisions are not collinear. It is not clear what that factor should be, the value for the steric factor could range from one to

less than $1/3$.[7,8]   Nevertheless, the fact that $P_{i \to j}$ seems to be constant as a function of density demonstrates that the steric factor is also a constant of density.   An estimate of the scale factor can be found using

$$\frac{K_1}{K_2} = (\frac{\rho_1}{\rho_2}) \frac{g_1(R^*)}{g_2(R^*)} \qquad (9)$$

K_1 is the rate for the liquid at density ρ_1, where the $i \to j$ subscript has been dropped, K_2 is rate at liquid density ρ_2, $g_1(R^*)$ is the radial distribution function for that liquid density evaluated at some R^*, and $g_2(R^*)$ is the radial distribution function evaluated at R^* for density 2. R^* is the turning point for the most effective collisions and it is assumed that this region is small.   In 1971, Davis and Oppenheim derived this equation, using a master equation approach to describe vibrational relaxation in the weak coupling limit in a liquid.[9,10]   Their theory was thought at the time to apply only to high frequency oscillators, although work by Chesnoy seems to indicate otherwise.[11]

This presents the problem of calculating the $g(R^*)$ for the oscillator. One approach to this problem was to use the attractive hard spheres pair distribution model by Delalande and Gale.[12] This model assumes that the collision rate should be calculated at the hard sphere radius.   One then assumes the radial distribution function at R^* can be approximated by the Carnahan and Starling approximation,[13]

$$g(R^*) \approx g_{HS}(sig) = \frac{(1-\frac{\eta}{2})}{(1-\eta)^3}; \qquad \eta = \frac{\pi}{6}\rho\sigma^3 \qquad (10)$$

where σ is the hard sphere contact distance and ρ is the number

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density. The problem with this approximation is that the hard sphere radius which provides the best model for the radial distribution is not necessarily the correct radius at which to evaluate R^*. A more sophisticated version of this theory was employed by Madden and van Swol.[14] They used WCA theory to calculate the cavity distribution function which was then related to the ratio of vibrational relaxation rates in a dilute gas to a dense liquid. This assumed that g(R) could be approximated by a properly chosen hard sphere fluid of the same density. They did not equate R^* with the hard sphere diameter used to calculate the radial distribution function. We calculated the radial distribution of an iodine atom in liquid Xe directly. Using the R^* calculated from the one dimensional trajectories, 3.7-3.8 Å, good agreement was found for the scale factors given by equation nine for the different densities.

The scale factors could also have been calculated using continuum theories. It has been shown that the vibrational relaxation rate is affected by[15,16]

$$F(t) = \langle \sum_b f(r_b(t)) \sum_c f(r_c(0)) \rangle \qquad (11)$$

$$F_b(t) = \langle \sum_b f(r_b(t)) f(r_b(0)) \rangle \qquad (12)$$

Where F(t) is the total force autocorrelation, $F_b(t)$ is the binary force autocorrelation and f(t) is the coupling from the liquid to the oscillator at time t. Oxtoby has also considered this type of division of the forces.[17] From these correlation functions and the Golden Rule, the relaxation rate is

$$\frac{1}{T_1} = \int dt e^{i\omega t} F(t)$$

Basically, the component of the force autocorrelation spectrum at the oscillator frequency determines the relaxation rate. Figures 2 and 3 show the force autocorrelations and the frequency spectrum for an I atom in liquid Xe at 1.8g/cc. It has been found that the binary force autocorrelation function frequency spectrum was very similar to the total force autocorrelation function frequency spectrum, down to frequencies of ≈ 50 cm^{-1}. This is evidence for the appropriateness for using IBC theory to model the vibrational relaxation even though I$_2$ has such a low vibrational frequency. This implies that the coupling to the bath is weak and could be treated as linear. Accordingly, stochastic theories should also be appropriate for this system. A stochastic approach should work due to the linearity of the system and its ability to take into account the many body forces through the total force autocorrelation. Smith and Harris have applied a generalized Langevin equation technique to this problem and also found results that agree with the molecular dynamics simulations.[18,19]

Both of the above approaches will fail if the coupling between the bath and oscillator is strong. IBC theory will also fail if the binary force autocorrelation function power spectrum at the appropriate frequency is not the same as the total force autocorrelation. The most probable reason for the two force autocorrelation functions not being the same is if many body effects become more important and provide damping at the oscillators frequency.

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Thus we have shown through experiments and calculations that IBC theory and continuum theories seem to model well the vibrational relaxation of I_2 in a simple liquid. This is somewhat surprising given that I_2 is such a low frequency oscillator and the I_2 vibrational amplitude is quite large in the upper part of the well. Further experiments in a simple Lennard-Jones fluid such as Ar are required to test the above theories in a more quantitative fashion.

ACKNOWLEDGMENTS

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Figure Captions

Figure 1.

The I_2's average vibrational energy as a function of time in 1.8 g/cc Xe (circles) and in 3.0 g/cc Xe (line) where the time base of the 3.0 g/cc data has been multiplied by 3.0. The functional form of the relaxation is identical for the two solvent densities. The error bars represent one standard deviation of the average energy for the 1.8 g/cc Xe solution.

Figure 2.

The total force autocorrelation and the binary force autocorrelation described in equation 11 and 12 are calculated for an I atom in 1.8 g/cc Xe. The early time components are very similar.
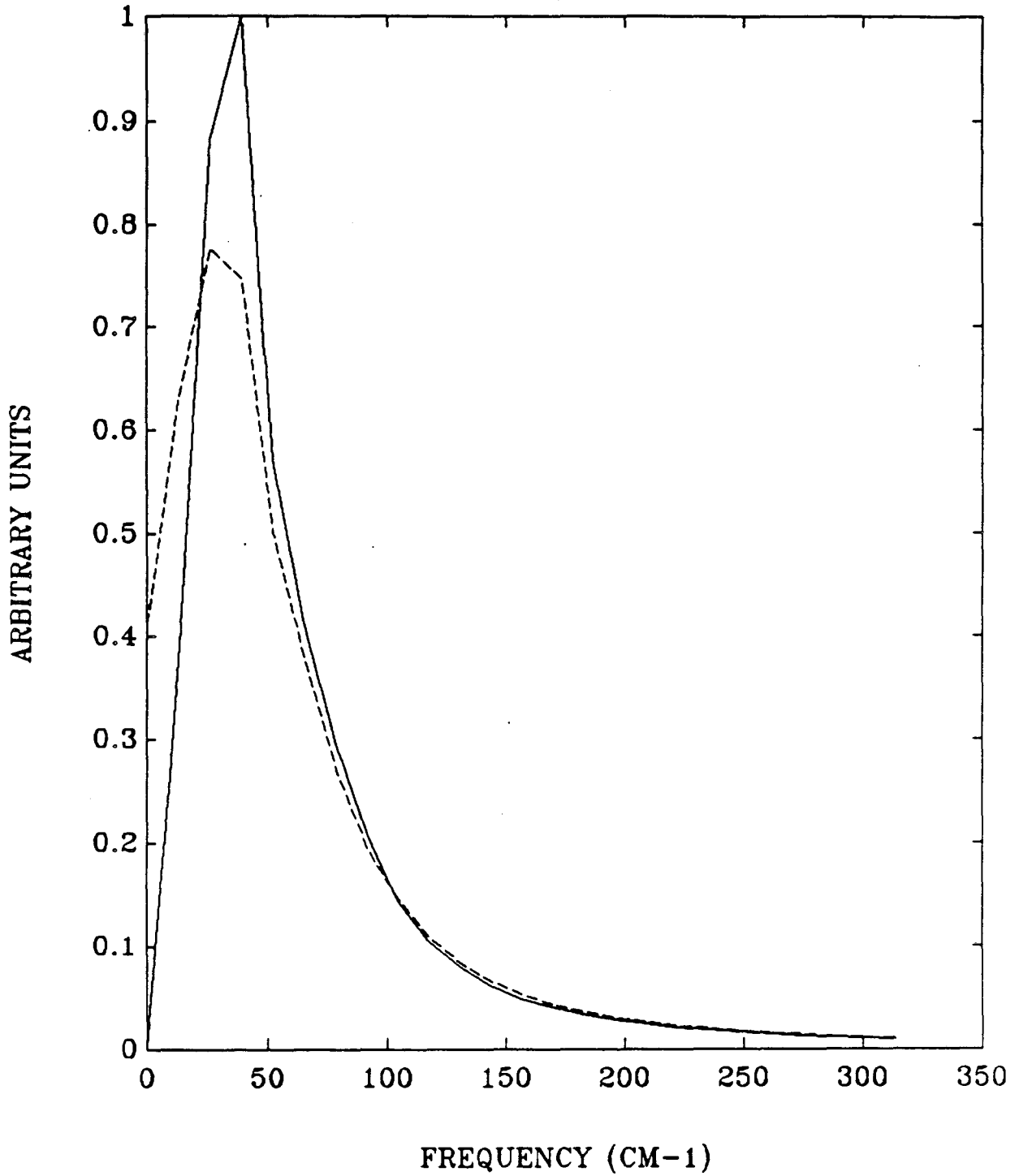
Figure 3.

The power spectrum of the total and binary force autocorrelation from figure 4. The magnitudes are about the same for vibrational frequencies above 50 cm^{-1}, which suggests that IBC theory may be appropriate for I_2 in Xe.

VIB. ENERGY (1000 CM-1)

TIME (PSEC)

o 1.8 G/ML

— 3.0 G/ML

(SCALED BY 3.0)

XBL 903-1155

16
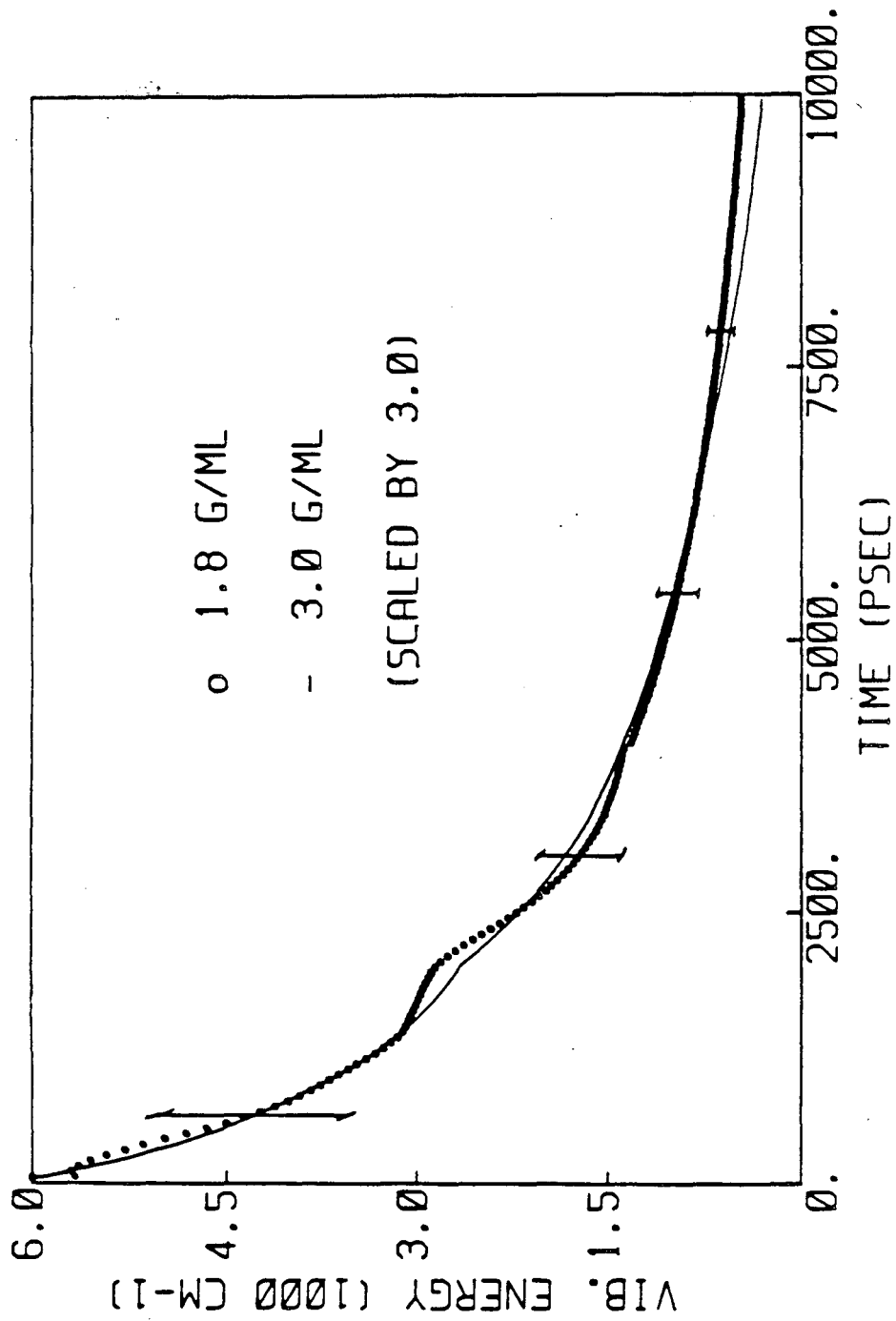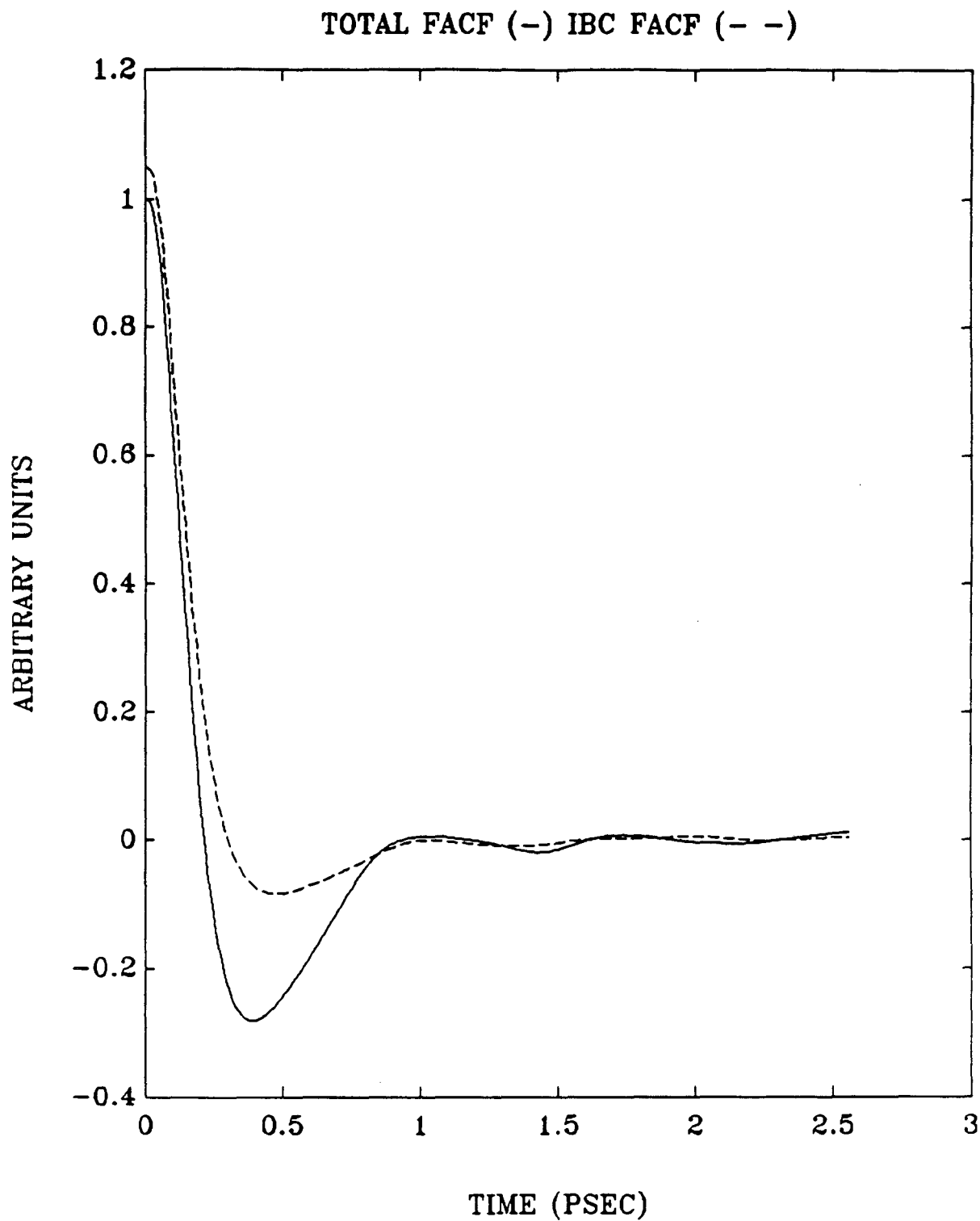
TOTAL FACF (−) IBC FACF (− −)

POWER SPECTRUM OF TOTAL FACF (−) AND IBC FACF (− −)

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