Pressure Effects on the Dynamics and Hydrogen Bond Properties of Aqueous Electrolyte Solutions: The Role of Ion Screening

Amalendu Chandra* and Snehasis Chowdhuri

Department of Chemistry, Indian Institute of Technology, Kanpur, India 208016

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We have performed a series of 56 sufficiently long molecular dynamics simulations of aqueous alkali halide solutions at infinite dilution and also at a higher concentration at 298 and 258 K and at 7 different pressures ranging from 0.1 to 875 MPa to investigate the role of ion screening in the pressure dependence of various dynamical and hydrogen bond properties of aqueous ionic solutions. We found that the orientational relaxation at both temperatures and the ion conductance and diffusion at the supercooled temperature show anomalous behavior with the application of pressure. The extent of the anomaly decreases somewhat in the concentrated solution because of ion screening effects. Correlations of these pressure-induced dynamical changes with the changes of hydrogen bond properties of the aqueous solutions are discussed.

1. Introduction

Liquid water shows many anomalous properties with changes of pressure and temperature, such as an increase of the rates of translational and rotational diffusion with the application of pressure at low temperature.[1−6] This behavior becomes more pronounced in the supercooled phase of water, and it is generally attributed to the changes of the hydrogen-bonded open network structure of water molecules at higher pressures. At low temperature and pressure, the majority of water molecules have four hydrogen-bonded nearest neighbors.[7,8] However, a small fraction of water molecules have more than four hydrogen-bonded nearest neighbors that provide low-energy pathways for the translational and orientational motion of water molecules.[9,10] With an increase of pressure, the number of water molecules with a fifth neighbor increases, which enhances the rates of diffusion and orientational relaxation at low temperatures. At very high pressures, the excluded volume effect becomes more important, and it leads to a decrease of the diffusion coefficient and an increase of the orientational relaxation times that one observes in normal nonassociated liquids.

In numerous experimental situations, one deals with a liquid medium of aqueous ionic solutions rather than pure water. In such systems, both the relaxation of the water molecules and the dynamics of the ions play crucial roles in determining the overall dynamical behavior of the medium.[11−15] In view of the dramatic variation of the dynamical properties of pure water at high pressure and low temperature, appreciable changes in the dynamics of ions in water are also expected with variations of the temperature and pressure, and these dynamical changes are likely to be correlated with the changes of the hydrogen-bonded structure of the aqueous medium. These structural and dynamical changes can vary with ion concentration because of ion screening effects.[16,17] In fact, the presence of ions has been shown to influence both the statistics and dynamics of hydrogen bonds at normal pressure and room temperature;[17−20] similar studies at higher pressures and lower temperatures have not yet been carried out.

There have been a few limited experimental studies on ion dynamics in aqueous solutions at high pressures. Nakahara et

al.[21,22] and Ueno et al.[23−25] measured the pressure dependence of the conductance of alkali halide solutions at very low concentrations at varying temperature. At low temperature, especially in supercooled water, the conductance was found to first increase and then decrease with increasing pressure. The results were analyzed in terms of Stokes and dielectric friction at the continuum level, but no molecular explanation could be given for the observed pressure dependence of ionic mobility and conductance. Also, these measurements were done at very low concentration, and more concentrated solutions, where ion screening effects can be significant in making structural changes, were not investigated. Speedy[26] measured the conductivity of 0.1 and 1 M KCl solutions at varying temperatures and at two different pressures—0.1 and 50 MPa. The conductivity was found to be higher at 50 MPa at low temperatures. However, no measurements were made at higher pressures. Also, none of the above experiments measured the pressure dependence of either diffusion or the orientational motion of water molecules in the presence of ions. To the best of our knowledge, no theoretical or simulation study has yet been carried out to investigate the pressure dependence of the microscopic dynamics of aqueous ionic solutions at ambient and supercooled conditions. Such studies are extremely important in understanding the role of ion screening in the modification of hydrogen-bonded structure and the dynamical properties of ions and water molecules with the application of pressure.

In this work, we have carried out molecular dynamics simulations of a series of solutions consisting of sodium, potassium, and chloride ions immersed in water at infinite dilution and also at a higher concentration (2.3 *m* NaCl) at varying temperature and pressure. Altogether, we have simulated 56 different systems to investigate the role of ion screening on the pressure dependence of various hydrogen bond and dynamical properties of the solutions at normal and supercooled temperatures. We found that the orientational relaxation at both normal and supercooled temperatures and the ion conductance and diffusion at supercooled temperature show anomalous behavior with the application of pressure and that these changes are correlated with the pressure-induced changes of the hydrogen bond properties of the aqueous solutions. The relative changes

* Corresponding author. E-mail: amalen@iitk.ernet.in.

of the hydrogen bond and dynamical properties with the application of pressure are found to be somewhat smaller in the concentrated solutions than in pure water because of ion screening effects.

The outline of the rest of the paper is as follows. In section 2, we discuss the models and the simulation details. In section 3, we present the hydrogen bond properties, and in section 4, we discuss the dynamical properties. Our conclusions are summarized in section 5.

2. Models and Simulation Details

In the present simulations, the water molecules are characterized by the extended simple point charge (SPC/E) potential,[27] and the ions are modeled as charged Lennard-Jones particles.[28,29] In these models, the interaction between atomic sites (or ions) is expressed as

$$u(r_i, r_j) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{r_{ij}} \qquad (1)$$

where q_i is the charge of the ith atom (or ion). The Lennard-Jones parameters σ_{ij} and ϵ_{ij} are obtained by using the combination rules $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$. The values of the Lennard-Jones and electrostatic interaction potential parameters are described in ref 30.

The simulations were carried out in a cubic box with a total of 256 particles (water plus ions). The simulations of various solutions were performed at two different temperatures (298 and 258 K) and at seven different pressures (0.1, 55, 125, 250, 475, 675, and 875 MPa). We employed the minimum image convention for the calculation of the short-range Lennard-Jones interactions. The long-range electrostatic interactions were treated using the Ewald method,[31] and the temperature and pressure were monitored by using the weak coupling scheme of Berendsen et al.[32] For the integration over time, we adapted the leapfrog algorithm with a time step of 1 fs. MD runs of 400−800 ps were used to equilibrate each system, and then each system was run for another 800−2400 ps depending on its temperature for the calculations of the various structural, energetic, and dynamical quantities.

3. Hydrogen Bond Properties

We first calculate the pressure effects on the hydrogen bond properties of the aqueous solutions. Following previous work,[17−19,32−34] we use a geometric criterion in which two water molecules are taken to be hydrogen bonded if their interoxygen distance is less than 3.5 Å, the hydrogen−oxygen distance is less than 2.45 Å, and the oxygen−oxygen−hydrogen angle is less than 30°. We have calculated the average number of hydrogen bonds per water molecule (n_{HB}), the average energy of a hydrogen bond (E_{HB}), and the percentage of water molecules having n hydrogen bonds (f_n). The variation of some of these quantities with pressure for both pure water and 2.3 m NaCl solution are shown in Figures 1 and 2. In these Figures (and also in the Figures shown later), the values of various quantities are normalized by the corresponding values at $P = 0.1$ MPa (= P_0) to show the relative changes of the equilibrium and dynamical quantities with the application of pressure. The actual (unnormalized) values of the various hydrogen bond properties at $P = 0.1$ MPa are included in Table 1. We observed that the average number of hydrogen bonds per water molecule slightly increases with pressure. At higher pressure, some of the water molecules are forced to occupy interstitial positions, which leads
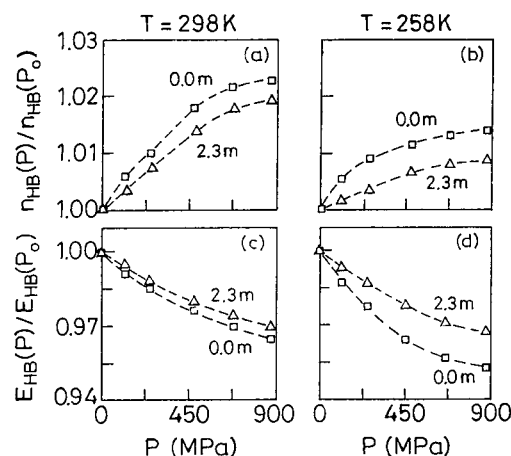
Figure 1. Pressure dependence of the average number of hydrogen bonds per water molecule and the average hydrogen bond energy in pure water and in 2.3 m aqueous NaCl solution. P_0 denotes 0.1 MPa.
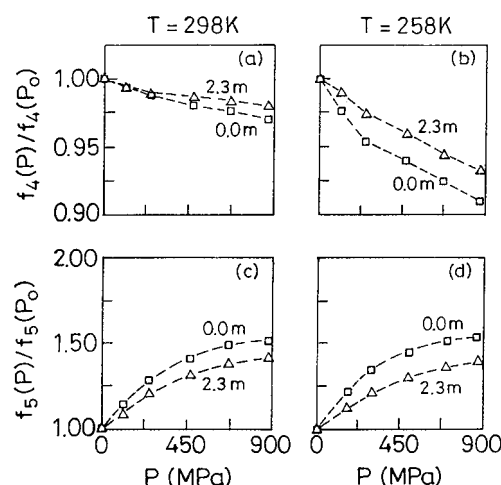
Figure 2. Pressure dependence of the percentage of water molecules with four and five hydrogen bonds in pure water and in 2.3 m aqueous NaCl solution. P_0 denotes 0.1 MPa.

TABLE 1: Average Number of Hydrogen Bonds Per Water Molecule, Average Hydrogen Bond Energy (in kJ/mol), and the Percentage of Water Molecules with Four and Five Hydrogen Bonds at $P = 0.1$ MPa[a]

quantity	258 K	298 K	258 K	298 K
n_{HB}	3.68	3.50	3.13	3.0
E_{HB}	−20.00	−19.15	−19.42	−18.80
f_4	62.50	49.5	36.40	31.20
f_5	6.50	6.20	4.10	4.2

[a] The first two columns are for pure water, and the last two columns are for 2.3 m NaCl in water.

to an increase of the number of molecules with five hydrogen bonds at the expense of more stable four-hydrogen-bonded water molecules and a decrease of the hydrogen bond strength, as can be seen from Figures 1 and 2. For 2.3 m NaCl solution, the results in Table 1 show that even at normal pressure many of the hydrogen bonds are broken and the strength of the hydrogen bonds is also weakened because of the effects of ion screening. Upon application of pressure, the strength of the hydrogen bonds is further weakened because of an increase in the number of five-coordinated water molecules and a decrease in the number of four-coordinated water molecules, but the relative changes of E_{HB}, f_4, and f_5 are somewhat smaller than those of pure water, which can again be attributed to ion screening effects.

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TABLE 2: Diffusion Coefficients ($\times 10^{-5} cm^2 s^{-1}$), Conductance Values ($cm^2 S mol^{-1}$), and Orientational Relaxation Times (ps) at $P = 0.1$ MPa[a]

quantity	258 K	298 K	258 K	298 K
D_{Na^+}	0.34	1.33	0.23	0.94
D_{K^+}	0.70	1.92		
D_{Cl^-}	0.56	1.64	0.32	1.22
Λ_{NaCl}	40.3	115.0	23.8	70.0
D_{H_2O}	0.86	2.65	0.58	2.0
τ_1^μ	10.70	3.95	14.10	5.1
τ_2^μ	3.95	1.35	5.15	1.80
τ_1^{OH}	11.00	3.90	13.15	4.7
τ_2^{OH}	4.55	1.55	5.70	2.0

[a] The first two columns are for a single ion in water, and the last two columns are for 2.3 *m* NaCl in water.

4. Dynamical Properties

The pressure effects on ion dynamics were studied by calculating the self-diffusion coefficients of individual ions and the conductance of a salt. The self-diffusion coefficient D_α of ionic species α is related to the time integral of the velocity—velocity autocorrelation function (VAF) by

$$D_\alpha = \frac{k_B T}{m_\alpha} \int_0^\infty C_{v,\alpha}(t)\, dt, \tag{2}$$

where k_B is Boltzmann's constant, m_α is the mass of an ion of species α, and $C_{v,\alpha}(t)$ is the velocity—velocity time correlation function

$$C_{v,\alpha}(t) = \frac{\langle v_i(t)\, v_i(0)\rangle}{\langle v_i(0)\, v_i(0)\rangle} \tag{3}$$

where $v_i(t)$ is the velocity of ion i of species α at time t and the average is carried out over all the ions of that species and over the initial time. The self-diffusion coefficient of an ion can also be calculated from the long-time limit of the mean square displacement (MSD) by

$$D_\alpha = \lim_{t \to \infty} \frac{\langle [r(t) - r(0)]^2\rangle_\alpha}{6t} \tag{4}$$

where $r(t)$ is the position of an ion of species α at time t and the average is carried out over all the ions of that species and over the initial time.

The diffusion coefficients calculated using these two different routes have been found to be quite close to each other, and we have taken the average of the values obtained from these two routes as the simulation result of the diffusion coefficient at a given temperature and pressure (see Table 2). The self-diffusion coefficient of water molecules is also calculated in a similar way. At ambient temperature and pressure, the values of the diffusion coefficients as calculated in the present study are in good agreement with the results of earlier simulations.[30,35] The conductance of a salt is calculated by integrating the total ionic current—current time correlation function.[13]

The single-particle orientational motion of water molecules is analyzed by calculating the orientational time correlation function, $C_l^\alpha(t)$, defined by

$$C_l^\alpha(t) = \frac{\langle P_l(e^\alpha(t) \cdot e^\alpha(0))\rangle}{\langle P_l(e^\alpha(0) \cdot e^\alpha(0))\rangle} \tag{5}$$

where P_l is the Legendre polynomial of rank l and e^α is the unit vector that points along the α axis in the molecular frame.
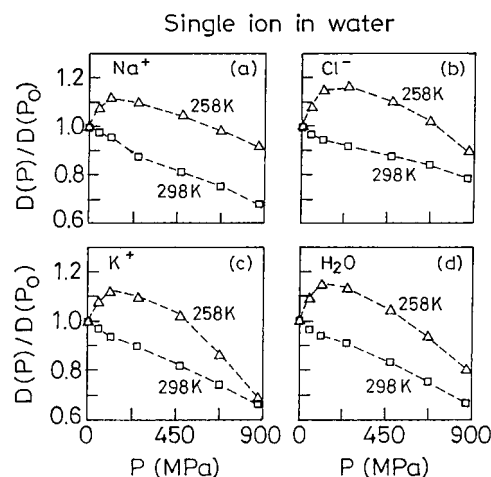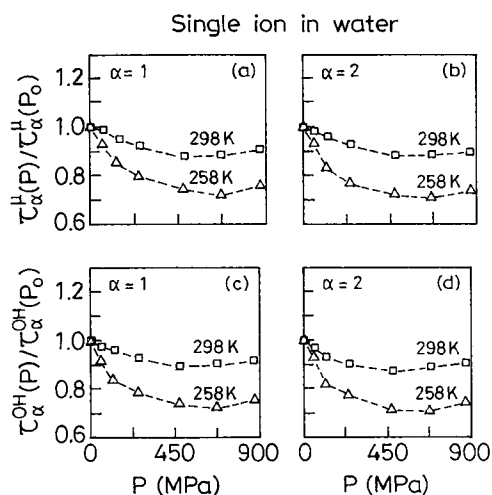

Figure 3. Pressure dependence of the diffusion coefficients of sodium, potassium, and chloride ions and water molecules in aqueous solutions at the infinite dilution limit.

The time dependence of $C_l^\alpha(t)$ for $l = 1, 2$ and for three different e^α values, the molecular dipole vector μ, the H—H vector, and the O—H vector is studied here. At short times, the decay of $C_l^\alpha(t)$ is generally nonexponential because of inertial and non-Markovian effects. At long times, when these effects are not important and the relaxation is diffusional, $C_l^\alpha(t)$ decays exponentially. The orientational correlation time, τ_l^α, is defined as the time integral of the orientational correlation function

$$\tau_l^\alpha = \int_0^\infty dt\, C_l^\alpha(t) \tag{6}$$

In the present study, we calculated τ_l^α by explicit integration of the $C_l^\alpha(t)$ function from simulation until 6 ps at 298 K and from simulation to 12 ps at 258 K and by calculating the integral for the tail from the fitted exponential functions.[36] Experimentally, the orientational relaxation of the H—H and O—H vectors can be measured by ^1H—^1H and ^1H—^{17}O dipolar relaxation NMR experiments, respectively. Such studies have been carried out to explore the pressure effects on orientational relaxation in pure water.[2,3] However, we are not aware of any experimental measurement of the effect of ion screening on the pressure dependence of orientational relaxation times.

We first discuss the results at infinite dilution. In Figure 3, we show the pressure dependence of the diffusion coefficients of ions and water molecules. It is found that at 298 K the diffusion coefficients of ions and water molecules decrease monotonically with increasing pressure. At the supercooled temperature, however, the diffusion coefficients first increase and then decrease with increasing pressure. The increase of D for the chloride ion is found to be somewhat larger than that for sodium and potassium ions, which can be attributed to the hydrogen-bonded coordination of negative ions in water.[37-39] In fact, the relative increases of D at its maximum for the chloride ion and water molecules are rather similar. The anomalous pressure dependence of the diffusion coefficients at the lower temperature can be attributed to an increase of the number of higher-energy, five-hydrogen-bonded water molecules and a decrease of the number of lower-energy, four-hydrogen-bonded water molecules with the application of pressure. A five-hydrogen-bonded water molecule participates in two bifurcated hydrogen bonds through one of its hydrogen atoms. These bifurcated hydrogen bonds, being of higher energy, are easier to break and help diffusion.[9,10] This diffusion process, which is aided by the breaking of bifurcated hydrogen bonds,
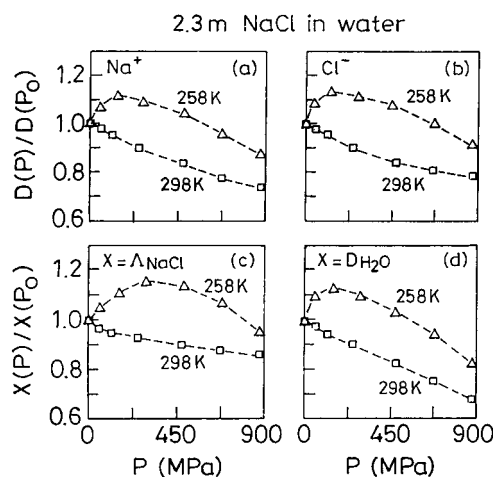
Single ion in water

Figure 4. Pressure dependence of the orientational relaxation times of the dipole and O—H vectors of water molecules in aqueous solutions at the infinite dilution limit.

becomes especially important at the supercooled temperature, where the thermal energy is not large enough to break the regular lower-energy hydrogen bonds easily. Hence, the anomalous behavior appears to be more pronounced at the supercooled temperature. At very high pressure, the excluded volume effect takes over, and the diffusion coefficients show a decreasing trend at both temperatures.

In Figure 4, we present the orientational relaxation times of the dipole and the O—H vectors of water molecules in the infinite dilution limit. The results of τ_l^{H-H} are very similar to those of τ_l^{O-H}; therefore, the H—H results are not shown here. As can be seen from Figure 4, the orientational relaxation times of water reveal a rather interesting pressure dependence at both temperatures. The pressure dependences decrease up to 675 MPa due to the higher flexibility or decreasing energy of the hydrogen bonds at increased pressure, and at very high pressure, the orientational relaxation times increase with pressure as one would expect from the excluded volume effects. We note that the minimum of τ_α^u is located at a higher pressure than the maximum of the diffusion coefficients observed at the lower temperature, which is due to the fact that excluded volume effects are more important for translational motion, in which a molecule has to move from one location to another location in space, whereas such effects are felt only at a higher pressure for rotational motion, in which a molecule can remain at the same location and can still change its orientation.

We next discuss the effects of ion screening on the pressure dependence of various dynamical properties. The results of diffusion and orientational relaxation times, including the results of conductance Λ, for 2.3 m NaCl solution are shown in Figures 5 and 6. Here also, at 298 K, the diffusion coefficients decrease monotonically with the application of pressure, and they pass through a maximum at 258 K. However, at the lower temperature, the relative increase of D at its maximum is found to be somewhat smaller than that at infinite dilution. The orientational relaxation times pass though a minimum at both temperatures. The somewhat smaller rise of the diffusion coefficients at 258 K and the lowering of the orientational relaxation times at both 258 and 298 K with pressure compared to that at infinite dilution can be attributed to the fewer number and decreased strength of the hydrogen bonds in the presence of ions at finite concentration. The application of pressure leads to a weakening of the already weakened hydrogen bonds in the presence of ions. Clearly, ion screening influences the pressure dependence of

2.3 m NaCl in water

Figure 5. Pressure dependence of the diffusion coefficients of sodium and chloride ions and water molecules and the ionic conductance in 2.3 m aqueous NaCl solution.

2.3 m NaCl in water
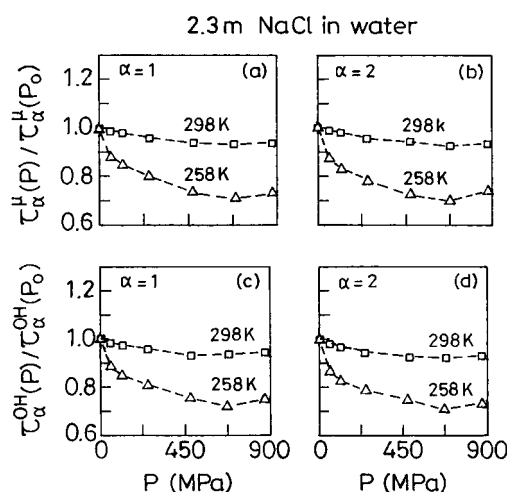
Figure 6. Pressure dependence of the orientational relaxation times of the dipole and O—H vectors of water molecules in 2.3 m aqueous NaCl solution.

diffusion and the orientational relaxation in aqueous solutions. Again, at very high pressures, both diffusion and orientational motion slow because of the excluded volume effects. It is also seen from Figure 5 that the pressure dependence of the conductance is somewhat different from that of the diffusion coefficients of sodium and chloride ions. The conductance is a collective ionic property that includes, apart from self correlations, the dynamic cross correlations between ionic velocities. Thus, the difference in the pressure dependence of the ionic conductance and the self-diffusion coefficients arises from the different pressure dependence of the dynamic cross correlations and self correlations of ionic velocities. We note that, at infinite dilution, conductance is determined solely by the ionic self-diffusion coefficients because there is no cross correlation in this limit, hence the pressure dependence of conductance and of the diffusion coefficients shows similar behavior in this limiting situation.

5. Summary and Conclusions

We have carried out molecular dynamics simulations of aqueous electrolyte solutions at infinite dilution and also at a higher concentration at varying pressure and temperature. Our main goal has been to investigate the effect of ion screening on the pressure dependence of various hydrogen bond and dynami-

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cal properties of the solutions at normal and supercooled temperatures. Among the hydrogen bond properties, we have calculated the average number of hydrogen bonds per water molecule, the average hydrogen bond energy, and the percentage of water molecules having *n* hydrogen bonds. The dynamical properties that we investigated include the diffusion coefficients of ions and water molecules and the conductance and orientational relaxation times of water molecules.

We found that with the application of pressure the average number of hydrogen bonds per water molecule increases and the average energy of a hydrogen bond decreases to some extent. These results can be attributed to the fact that at higher pressure some of the water molecules are forced to occupy interstitial positions, which leads to an increase of the number of molecules with five hydrogen bonds at the expense of the more stable four-hydrogen-bonded water molecules. The presence of ions in the concentrated solution reduces both the number and the strength of hydrogen bonds, which in turn leads to a relatively weaker change in the hydrogen bond properties with pressure. The orientational relaxation at both normal and supercooled temperatures and the ion conductance and diffusion at supercooled temperature show anomalous behavior with the application of pressure. These anomalous changes are correlated with the pressure-induced changes of the hydrogen bond properties discussed above. Again, because of the presence of ions, the relative changes of the dynamical properties with the application of pressure are found to be somewhat smaller in the concentrated solutions than in pure water. Finally, we note that the results of ion screening effects on the pressure dependence of hydrogen bond and dynamical properties of aqueous ionic solutions are presented here for the first time. We hope that the present contribution will encourage further experimental work in this area.

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