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Citation: [The Journal of Chemical Physics](#) **85**, 4194 (1986); doi: 10.1063/1.450892

View online: <http://dx.doi.org/10.1063/1.450892>

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COMMUNICATIONS

Photoinduced ionization of bovine serum albumin by holographic relaxation methods^{a)}

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(Received 9 June 1986; accepted 24 July 1986)

Photochromic labels for polymers are sometimes responsible for laser induced conformational changes and aggregation/disaggregation reactions. Here we report evidence that bovine serum albumin (BSA) labeled with isothiocyanatoazobenzene (ABITC) undergoes a change in net charge when subjected to a pulse of 488 nm light. The dynamics of this system at low ionic strengths, as observed by holographic relaxation spectroscopy (HRS),^{1,2} are greatly influenced by the resulting transient gratings of ions.

Below 25 mM NaCl, two relaxation rates are evident, one of which corresponds to the expected tracer diffusion coefficient for BSA (6×10^{-7} cm²/s) while the other is described by an apparent diffusion coefficient which increases as the concentration of salt is decreased. Also, two components can be resolved by means of HRS combined with electrophoresis (EHRS).³ Four-pulse EHRS shows that the two components have charges approximately equal to $-9e$ and $-11e$, and that their diffusion coefficients are approximately equal. These results are consistent with a model in which absorption of light by the azobenzene moiety produces a change in net charge on the BSA molecule, and the dynamics are adequately described by a simple theory based on the model of Lee and Schurr.^{4,5} The coupled relaxation problem, which involves bleached and unbleached BSA as well as the small counterions and coions, yields both an observable tracer diffusion mode (D_t) and a collective diffusion mode (D_m).

Figure 1(a) shows the decay curve for BSA at 1.11 mM ionic strength obtained in a heterodyne HRS experiment.^{6,7} The solid curve was calculated with $D_m = 13 \times 10^{-7}$ cm²/s, $D_t = 6 \times 10^{-7}$ cm²/s, and with amplitudes having different signs, i.e., with gratings which are out of phase. Figure 1(b) shows the EHRS transient decay for the same sample. The mobilities for the two components are $\mu = 2.59 \times 10^{-4}$ cm²/(V s) and $\mu = 2.21 \times 10^{-4}$ cm²/(V s), and the associated diffusion coefficients are both equal to $D = 6.4 \times 10^{-7}$ cm²/s. The relationship between D and the pair D_m and D_t can be

understood as follows. The Fourier amplitudes of the laser induced concentration gratings are described by a set of four coupled differential equations. The solutions for the observable amplitudes, $\tilde{c}_1(\mathbf{K}, t)$ and $\tilde{c}_2(\mathbf{K}, t)$, associated with bleached and unbleached BSA, respectively, each have the form:

$$\tilde{c}_i(\mathbf{K}, t) = A_i \exp(-D_c K^2 t) + B_i \exp(-D_m K^2 t) + C_i \exp(-D_t K^2 t). \quad (1)$$

Here D_c is associated with the "charged" diffusion mode, which decays too rapidly to be observed, and $C_i \gg B_i$ for $i = 1, 2$. In the heterodyne HRS experiment the signal is pro-

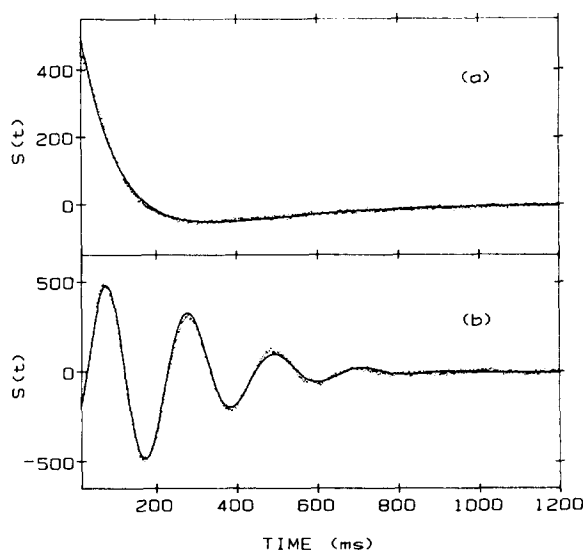


FIG. 1. (a) Typical HRS decay curve obtained for BSA-ABITC in 1.11 mM NaCl solution with the "phase shift with subtraction" experiment ($K^2 = 6.92 \times 10^6$ cm⁻²). (b) Typical four pulse EHRS curve for the same sample with the dc electric field equal to 39.4 V/cm ($K^2 = 7.16 \times 10^6$ cm⁻²).

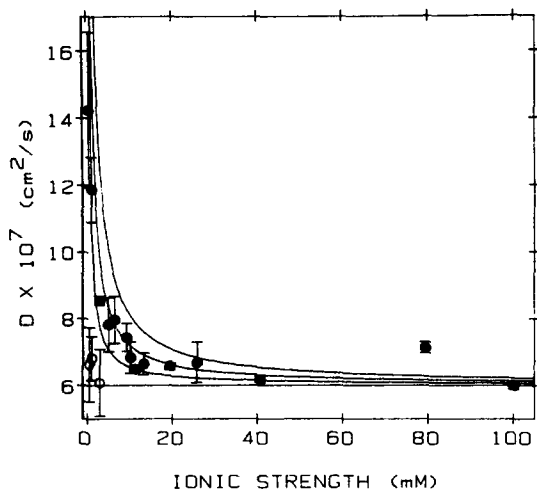


FIG. 2. A plot of the diffusion coefficients of BSA-ABITC vs the ionic strength (see the text). The solid curves were calculated by means of Eq. (2) with average molecular charges (z_2) of $-4e$, $-6e$, and $-8e$ for the lower, middle, and upper curves, respectively, and with $c_1/c_2 \ll 1$.

portional to $\sigma_1 \tilde{c}_1(K, t) + \sigma_2 \tilde{c}_2(K, t)$, and the decay rates associated with D_m and D_i have amplitudes proportional to $(\sigma_1 B_1 + \sigma_2 B_2)$ and $(\sigma_1 C_1 + \sigma_2 C_2)$, respectively, where σ_i is the scattering factor for the i th species.⁷ These amplitudes are similar in magnitude because C_1 and C_2 have different signs. In contrast to this, in EHRS $\tilde{c}_1(K, t)$ and $\tilde{c}_2(K, t)$ are resolved according to velocity, and in both cases the tracer diffusion mode dominates.

According to this model D_i is constant and in the limit of small K :

$$D_m = \left[\frac{D_i D_s (q_1^2 + q_2^2 + q_3^2 + q_4^2)}{D_i (q_1^2 + q_2^2) + D_s (q_3^2 + q_4^2)} \right], \quad (2)$$

where $q_i = (4\pi c_i z_i^2)/(\epsilon k_B T)$, c_i and z_i are the average concentration and charge of the i th species, respectively, and ϵ is the dielectric constant. The subscripts 3 and 4 refer to the counterions and coions, respectively, i.e., the salt; and we assume that $D_3 = D_4 = D_s$. Plots of D_m (●) and D_i (○) vs

the ionic strength are shown in Fig. 2. The data points were obtained by a fitting procedure based on Marquandt's algorithm. At ionic strengths below 5 mM, both D_m and D_i were optimized to obtain the best fit, and above 50 mM the data were described by a single exponential decay. However, at intermediate salt concentrations where D_m and D_i differ by less than a factor of 2, we resorted to holding D_i constant at the high ionic strength value while determining D_m and the amplitudes. The solid curves were calculated with z_2 equal to $-4e$, $-6e$, and $-8e$ and $c_1/c_2 \ll 1$ in Eq. (2). We estimate the best charge to be approximately $-5e$, a value lower than that estimated from the electrophoretic mobility. Similar discrepancies have been found with this type of theory in the analysis of quasielastic light scattering data.⁸⁻¹⁰ However, the model successfully explains (1) the presence of two decay rates and the ionic strength dependence of these rates in HRS, (2) the equality of the two decay rates in EHRS, and (3) different electrophoretic mobilities for the two components.

We wish to thank Professor J. M. Schurr for suggesting the photo ionization model and for advice concerning the calculations.

^{a)} This research was supported in part under the National Science Foundation Grant No. CHE-8317243.

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Rotationally resolved hot atom collisional excitation of CO₂(00⁰1) by time-resolved diode laser spectroscopy^{a)}

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(Received 25 June 1986; accepted 29 July 1986)

The transfer of energy between translational and internal degrees of freedom is an important topic in the study of chemically energetic systems. Theoretical models of inelastic collisional scattering processes which involve quasiclassi-

cal and quantum mechanical arguments have been refined to a high degree of sophistication,¹⁻⁶ but state specific experimental information which can be used to test these existing theories is scarce and usually limited to diatomic molecules.⁷