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Beyond classical theories

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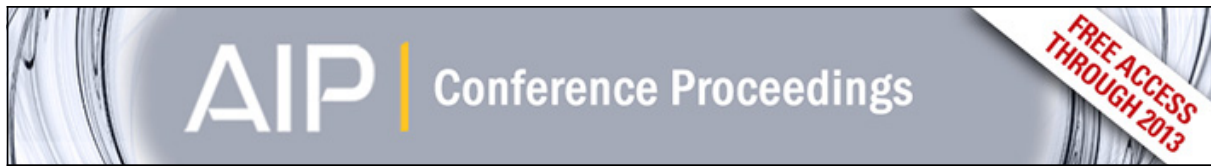
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Shawn M. Kathmann, Bernhard Sellner, Andrew J. Alexander, and Marat Valiev

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Abstract. Both Classical Nucleation Theory (CNT) and ground state adiabatic descriptions of matter have taught us a great deal about nucleation phenomena. However, recent experiments have confirmed the existence of luminescence, in both the deep UV and visible regions, during crystallization of NaCl from solution – referred to as crystalloluminescence (XTL). Given the difficulty in experimentally probing the underlying nucleation mechanisms in condensed phases, the emission of radiation is characteristic of the chemical processes giving rise to that emission. This opens the possibility of using XTL as an exquisite probe of nucleation mechanisms. The inclusion of electronically excited states in the nucleation mechanism lies beyond both CNT and ground state adiabatic interactions. Here we outline the chemical physics relevant to these findings and their consequences on how we understand and model nucleation.

INTRODUCTION AND BACKGROUND

Classical Nucleation Theory (CNT) has been the most successful and widely used description of nucleation. CNT treats nucleation as an activated rare event process whereby the critical cluster is treated as a well-defined embryo of the new phase and yields a steady state nucleation rate proportional to the condensation rate of monomers onto the critical cluster. The elegance and simplicity of CNT are further underscored in that the only ingredients needed are the bulk surface tension and density of the nucleating substance. The resulting nucleation rate $J = J_o \exp[-A\sigma^3]$, where σ is the surface tension and J_o and A are constants for a given temperature and supersaturation, clearly show the sensitivity of the rate on the surface tension i.e., that small variations in σ can give rise to very large variations (many orders of magnitude) in J. In fact, experimental measurements of nucleation have demonstrated an incredible sensitivity to a variety of sources (temperature and concentration gradients, sound, electric fields, light of different polarizations, trace contaminants, etc.). But, CNT has its limitations insofar as it is a phenomenological model; if agreement between CNT and experiment occurs, it is limited to certain substances and only within narrow ranges of temperature and supersaturation. Over the past 50 years or so researchers have gradually considered how the chemical physics or molecular nature of nucleation changes the

free energies and kinetics of cluster formation compared to CNT. These calculations have found large differences arising from the molecular nature of the clusters. Furthermore, the free energetics arising from a molecular description depend greatly on the approximations used to compute them e.g., using the rigid rotor harmonic single configuration treatment commonly employed in quantum chemistry codes versus exhaustive sampling of billions of configurations in the partition function using both classical and quantum interactions. This extreme sensitivity prompted further study into single and multicomponent nucleation sensitivity where it was found, not surprisingly, that extremely accurate potential energy surfaces and statistical mechanical sampling are essential to a quantitative molecular description of absolute nucleation rates and mechanisms. An interesting example, that illustrates the caution and care required when using atomistic point charge simulations, is the difference (10^6) in solubility between aqueous NaCl and AgCl – clearly point charge models cannot capture the subtle electronic effects in describing Na$^+$ versus Ag$^+$ in supersaturated solution.

## Beyond Classical Descriptions of Nucleation

As stated previously, observations some 200 years ago reported the emission of long-lived light resulting from the crystallization of certain salts (e.g., NaCl, KCl, etc.) – *crystalloluminescence*[1,2] (XTL – see FIG.1). It is commonly assumed that ions in the supersaturated solution simply transform into crystals, during which their charge state does not change. The formation of ionic solids from solution represents a special class of crystallization where ions attract each other to form a crystal lattice.
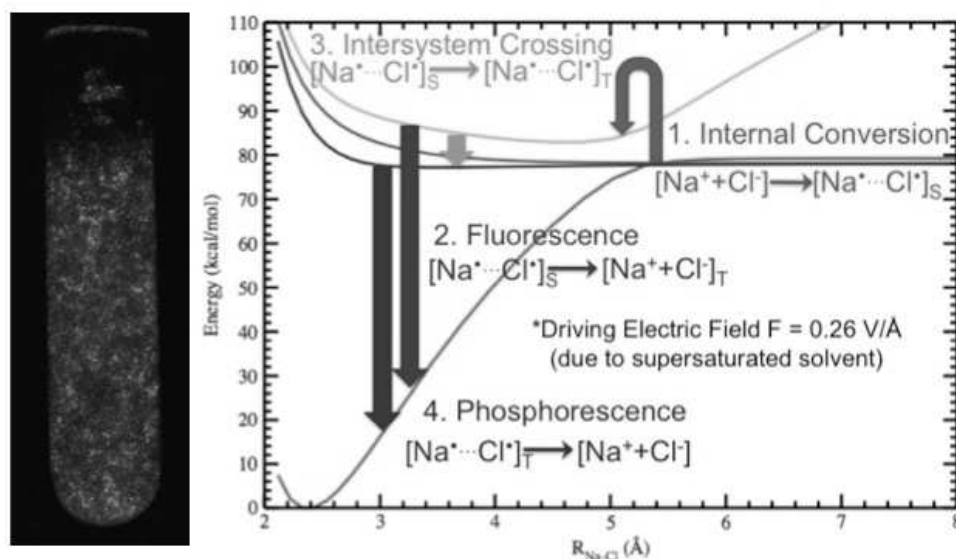
FIGURE 1. (Left) Photograph of NaCl XTL where 47 ppm Cu^{2+}/Na$^+$ was used as a trace dopant. (Right) MRCI/aug-cc-pvtz calculations of the ground and excited states of the NaCl dimer in an electric field as a portrayal of the kinds of states and transitions involved in the mechanism of XTL.

Luminescence is typically defined in terms of the conditions under which it is observed as opposed the exact underlying nuclear and electronic states that comprise

the entire mechanism. *We propose a mechanism where the ions, in the rapid rare event configurations sampled during crystallization, transform into radicals and then luminesce back into ions again while forming the crystal.* This can only happen if there exist "doorway states" which allow the relevant ions on the heterolytic electronic energy surface to pass through conical intersections and end up on the homolytic surfaces for some duration (via internal conversions and intersystem crossings) before radiatively (using fluorescent "fast" and phosphorescent "slow" pathways) and non-radiatively decaying. *Thus, the nucleating system may exploit its excited electronic degrees of freedom to find lower free energy pathways, compared to the ground state adiabatic picture, in order to relieve the electrical stresses in the supersaturated state.* Our objective is to uncover these doorway states via QM/MM condensed phase statistical mechanical simulations. As an example (see FIG. 1), MRCI/aug-cc-pvtz calculations on the gas-phase NaCl dimer with zero and non-zero applied electric fields show that the avoided crossing (~9 Å at zero field) moves inward (to ~5.4 Å) with an applied biasing field of 0.26 V/Å and the excited triplet state becomes stabilized with a vertical phosphorescence of ~2.8 eV (blue light). This is not to say the NaCl dimer is responsible for the luminescence during crystallization, but these high-level multireference calculations served as initial benchmark calculations for the electronic structure and excited state manifolds of larger clusters occurring in aqueous solution. Moreover, it provides a simple portrayal of the general concepts.
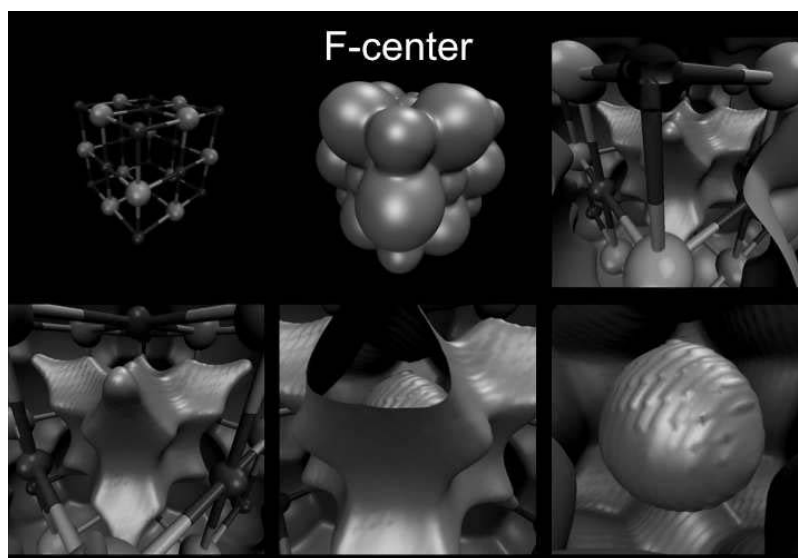
FIGURE 2. Quantum mechanical (B3LYP/aug-cc-pvdz) calculation of an F-center in a cube of NaCl (Na = blue, Cl = green). The grey surfaces show the electron density isocontours as one zooms into the central Cl vacancy where the electron density is peaked (non-nuclear attractor - NNA). Bader charge analysis shows that the NNA has a charge q(F-center) = -0.5 e.

Put differently, non-adiabatic dynamics play a role in the dynamic heterogeneities of cluster formation[3,4] underlying the thermodynamics and kinetics of crystallization. Moreover, there is experimental[5] and theoretical[6] evidence for low barrier hydrolysis reactions at NaCl defect sites - this further complicates the possible reaction channels to be investigated. The known visible luminescent centers in water and salt are the solvated electron and F-centers, respectively – see FIG. 2. These can be referred to as

non-nuclear attractors since the electron density is peaked in regions of space away from nuclei and these types of novel electronic structures can be optically active. Our calculations must include these non-nuclear attractors as possible condensed phase electronic states to elucidate the underlying mechanisms. Moreover, EPR measurements can be used to detect and characterize the radicals during the luminescence.

To understand and accurately quantify the mechanisms underlying nucleation[7,8] several challenging aspects of condensed phase chemical physics must be confronted: concentration effects, charge transfer, and electronic transitions. The central quantities underlying crystallization from solution are the cluster formation free energetics as well and the kinetic rates for association and dissociation. But, before these can be computed, the relevant electronic states must be determined and then appropriately evaluated in the configurational partition functions – aspects that lie well beyond the CNT and ground state adiabatic dynamics. Concentrated aqueous solutions have strong electric fields at the ion positions due to the water molecules and other ions in the first solvation shell. The cluster populations increase in size as the solution concentration increases such that the critical sized clusters become more probable. However, distributions of clusters exist even in undersaturated solutions as measured by dynamic light scattering. We have performed NWChem QM/MM calculations on aqueous NaCl electrolytes where the ion clusters were treated as QM (B3LYP/6-31+G*) and the rest of the water and ions treated as MM. These calculations showed cluster triplet-singlet energy gaps peaked in the UV with some minimal population bleeding into the visible. Moreover, as part of these calculations we also need to find the doorway states leading to the excited radical states and obtain the relevant spin-orbit oscillator strengths. In summary, XTL potentially offers a wealth of information concerning the details of the nucleation event that otherwise would be inaccessible to measurement. Going beyond the classical theories holds the promise of great reward toward a better quantitative and mechanistic description of nucleation.

ACKNOWLEDGMENTS

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