



# Intermolecular repulsive–dispersive potentials explain properties of impurity spectra in soft solids

Indrek Renge<sup>a,\*</sup>, Margus Rätsep<sup>a</sup>, Arvi Freiberg<sup>a,b</sup>

<sup>a</sup> Institute of Physics, University of Tartu, 142 Riia Street, EE51014 Tartu, Estonia

<sup>b</sup> Institute of Molecular and Cell Biology, University of Tartu, 23 Riia Street, EE51014 Tartu, Estonia

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## ABSTRACT

Behavior of optical impurity spectra in van der Waals glasses is rationalized with the aid of a two-particle Lennard–Jones model of intermolecular interactions. Simple mathematical manipulations with the 6–12 potential yield inhomogeneous distribution functions (IDFs) of zero phonon lines (ZPLs) at different compressions, and the expressions for wavelength dependent pressure shift coefficients of ZPLs (or holes), local phonon frequencies, and linear and quadratic coupling constants. Experimentally, the ZPL to phonon wing intensity ratios (Huang–Rhys or Debye–Waller factors) are measured for bacteriochlorophyll *a* in glass-forming triethylamine 5 K. Enhancement of coupling strength with increasing transition wavelength is observed, in qualitative agreement with the model.

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## 1. Introduction

Molecular crystals, polymers, and proteins belong to “soft” materials sustained predominately by van der Waals forces. Remarkable propensity to glass formation facilitates doping with chromophores for spectroscopic probing. Persistent spectral hole burning is a direct way to reveal frequency dependent behavior, including sensitivity to electric field [1], pressure [2,3], and temperature [4]. Resonant emission spectroscopy may be more difficult to apply, because of scattering, but can provide important additional information about phonon coupling as a function of wavelength [5–9]. Color effects refer to correlations of properties of zero phonon lines (ZPLs) with absolute solvent shifts within inhomogeneous distribution function (IDF). Universal bathochromic (red, negative) shifts of spectra by means of the dispersion interaction depend on the polarizability increase upon excitation, and are related linearly to the Lorenz–Lorentz function of refractive index. Although the role of repulsion remains hidden, it should be prominent, since at least 70% of the shift originates from the closest layer of solvent molecules [10]. A steep dependence of dispersive ( $-r^{-6}$ ) and repulsive potentials ( $r^{-12}$ ) on intermolecular distance  $r$  is responsible for the local origin of solvent shifts, in sharp contrast to long range Coulomb’s law ( $\pm r^{-1}$ ), valid in ionic systems. Thus, the solute–solvent interactions must be described as a superposition of attractive and

repulsive parts, for example in the form of a Lennard–Jones 6–12 function [11–17].

Another crucial and difficult issue, besides the repulsion, is the equilibrium geometry in the excited state. Reduction of benzene–argon distance upon excitation of the van der Waals complex [18] can be generalized to other  $\pi$ -electronic chromophores. It turns out that the ratio of the equilibrium distances in the excited and the ground state ( $\sigma^*/\sigma_g$ ) is a key parameter, controlling most spectral properties, in particular, the relative contributions of dispersion and repulsion to spectral shift [11–17].

Liner electron–phonon coupling (LEPC) strength, defined as a relative ZPL intensity (Debye–Waller factor,  $\alpha$ ), or as a number of phonons accompanying the electronic transition (Huang–Rhys factor,  $S$ ;  $S = -\ln \alpha$ ) was predicted to depend on spectral position within IDF [16,17]. Experimentally, it has been rather difficult to distinguish between the contributions of the ZPL and the wing in both hole-burning and site-selection spectra. Recently, a hybrid site-selective spectroscopic technique referred to as “difference fluorescence-line-narrowing” ( $\Delta$ FLN) spectroscopy has been applied for detailed characterization of electron–phonon coupling of chlorophylls in solvent glasses and native pigment–protein complexes [5–9]. Here, the dependence of LEPC on spectral position within the 0–0 band is measured for bacteriochlorophyll *a* in glassy triethylamine, a less polar compound of nearly spherical molecular shape. Approximate isotropy and reduced electrostatic interactions are favourable for comparison to simple Lennard–Jones model. The predicted increase of LEPC strength at longer wavelengths is indeed observed.

\* Corresponding author. Tel.: +3727 374716; fax: +3727 383033.  
E-mail address: [indrek.renge@ut.ee](mailto:indrek.renge@ut.ee) (I. Renge).

## 2. Experimental

Bacteriochlorophyll (BChl) *a* was purchased from Sigma and used without further purification. Solvent triethylamine (TEA) was passed through a column filled with aluminum oxide (Fluka) for drying. Plastic cells of 9 mm diameter (2 ml polypropylene tubes from Axygen<sup>®</sup>) and gelatin capsules of 4 mm diameter were used for absorption and fluorescence experiments, respectively. Concentrations of BChl *a* of  $3 \times 10^{-6}$  M or below were applied in fluorescence measurements, ensuring optical densities less than 0.1. Samples were cooled down from room temperature to 4.5 K during  $\sim 0.5$  h. Selective fluorescence excitation was carried out in resonance with the inhomogeneously broadened  $S_1(Q_y)$  absorption band using a Spectra Physics model 3900S Ti: sapphire laser of  $<0.5$  cm<sup>-1</sup> line width, pumped by an Ar-ion laser (Spectra Physics, model 171, USA). The spectra were recorded with a 0.3 m spectrograph equipped with a CCD camera (both Andor Technology, UK). Fluorescence spectra were corrected for the wavelength sensitivity of the detection system. Spatial filtering and a carefully designed sample holder could minimize the scattered laser light. Low-temperature measurements were performed in a He-bath cryostat (Utreks, Ukraine), where the samples were kept just above the level of liquid helium at  $4.5 \pm 0.2$  K. Temperature was measured with a calibrated silicon diode and a temperature monitor (model 211, Lakeshore Cryotronics, USA).

## 3. The model

As for the structure of molecular glasses, a box filled with identical balls will provide some insight. When rattling of the box stops, tight packed lattices, hexagonal or cubic, are not formed, because of friction. The number of closest neighbours is less than 12, varying, typically, between 8 and 11, although the pair wise distances remain the same as in the “crystal”. At variance to macroscopic balls, atoms and spherical ions are “slippery”, giving rise to crystalline phases of rare gases, metals, and salts. However, most organic solvents form glasses when plunged into liquid N<sub>2</sub>, since low symmetry and/or conformational flexibility of molecules provides sufficient “friction” to suppress crystallization. Glass formation cannot be regarded as a phase transition, because no phase boundary is created. Below glass temperature  $T_g$  the Boltzmann thermometer fails, and so does (equilibrium) thermodynamics [19]. Solid state physics basing on symmetry properties of lattices, obviously, does apply neither. Theories of continuous media remain valid, but are largely irrelevant to impurity spectroscopy.

However, the inapplicability of traditional branches of physics does not mean that the theory of amorphous state should necessarily be intricate. Conceptually, salient features of disordered solids at low temperatures may be easier to capture, as compared to liquid–glass transition itself [20]. Similar to a heap of balls, the density of the glassy phase is typically by  $\sim 10\%$  less than that of the tight packed structure. As a result of van der Waals attraction between the molecules (negligible in macroscopic scale), the incomplete solvation is equivalent to an increase of energy. Unfilled volume causes a huge amount of potential energy of about  $k_B T_g$  ( $k_B$  is Boltzmann constant) per particle to be deposited in a glass on cooling. We can define potential energy  $U_g$  per molecule that depends on density of its closest environment. The minimum of  $U_g$  belongs to a certain coordination number (perhaps, close to 10 or 11 in case of spheres), whereas a minority of centers with appressed or loose intermolecular contacts has elevated  $U_g$ . The overall fluctuation range of  $U_g$  is in the order of thermal energy at the glass point  $k_B T_g$ , obeying a distribution  $\Phi(r)$  of intermolecular

coordinates  $r$

$$\Phi(r) = \exp(-U_g/k_B T_g) \quad (1)$$

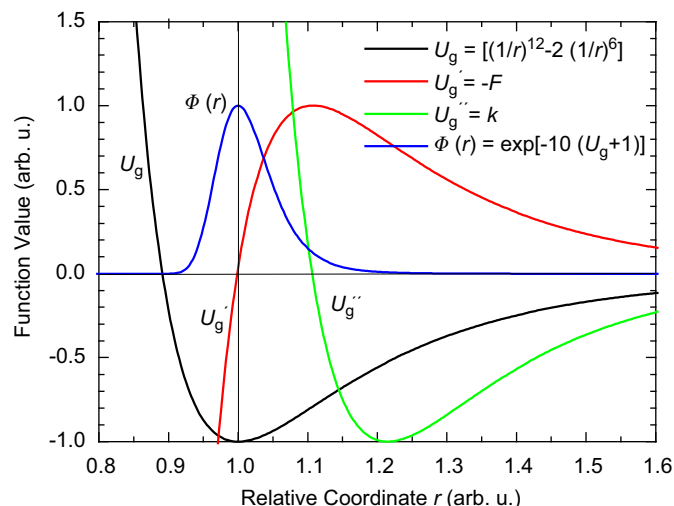
Instead of a harmonic potential, Lennard–Jones (L–J) 6–12 function would be a more natural choice for  $U_g$ , with the well depth  $-\varepsilon_g$  and minimum coordinate of the ground state  $\sigma_g$  (Fig. 1)

$$U_g = \varepsilon_g[(\sigma_g/r)^{12} - 2(\sigma_g/r)^6] \quad (2)$$

Thus, the distribution  $\Phi(r)$  is slightly asymmetrical, rather than Gaussian (Fig. 1). The first derivative of Eq. (2) corresponds to a hypothetical relaxation-driving force  $F (F = -U'_g)$ . Further, the second derivative yields the force constant  $k (k = U''_g)$  that has been applied for calculation of harmonic local phonon frequencies  $\omega_g$ , as  $\omega_g = (2\pi)^{-1}(k/\mu)^{1/2}$  ( $\mu$  is the reduced mass) [11–17]. The force constant vanishes at the inflexion of the potential curve (Fig. 1), giving rise to a zero frequency mode at distances  $r$  exceeding  $\sigma_g$  only by 10%. It is easy to imagine that the presence of voids can indeed lead to phonon softening and localization in glasses or defect crystals [21].

The solvent shift of optical transition energy  $\Delta v(r)$  is expressed as a difference between the potential function of excited state  $U^*$  that is up-shifted by the transition energy of free chromophore  $v_0$ , with well depth  $-\varepsilon^*$  and equilibrium distance  $\sigma^*$ , and  $U_g$ . The spectral distribution of transition energies (inhomogeneous distribution function, IDF) is obtained by plotting the ground state distribution  $\Phi(r)$  (Eq. (1)) versus the solvent shift  $\Delta v(r)$ . The shape and width of IDF are very sensitive with respect to the relative shift of potential minima  $\sigma^*/\sigma_g$ . One can also investigate the baric coefficients of line (hole) shifts using the first derivative of the solvent shift  $U^* - U'_g$ , taking into account linear isothermal compressibility  $\alpha_T$  equal to  $-(dr/dP)_T/r$  [11–17].

According to Franck–Condon principle, the displacement of potential minima is directly related to the strength of linear electron–phonon coupling (LEPC). Following Hook’s law, LEPC is expected to be proportional to an absolute difference of forces in the connected states. First derivative of our master potentials characterizes a hypothetical force that would drive the guest–host system towards equilibrium, if given such an opportunity. Thus, the



**Fig. 1.** Lennard–Jones potential  $U_g$  (Eq. (2),  $\varepsilon_g = \sigma_g = 1$ ) and the normalized derivatives  $U'_g$  and  $U''_g$  that are proportional to the force  $-F$  and the force constant  $k$ , respectively. Blue curve shows the Boltzmann distribution of centers, for thermal energy at the glass transition temperature equal to 10% of potential well depth ( $\varepsilon_g/k_B T_g = 10$ , Eq. (1)). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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