

Impurity spectroscopy in glasses and disordered crystals: Inhomogeneous broadening and electron phonon coupling

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Abstract

Parameters of optical impurity spectra in disordered solids were calculated using the potential energy distribution of the ground state and the guest–host interaction potentials of the lower and upper states. The model can yield inhomogeneous band shapes, pressure shift coefficients of zero phonon lines, (pseudo)local phonon frequencies, and linear and quadratic coupling constants to phonons. Results are compared to properties of Shpol'skii multiplets and zero phonon holes burned over the broad spectra in glasses. Crystal spectra contain discrete lines, but the overall width of multiplets and the bands in weakly polar solvent glasses is similar, and so are the pressure shift coefficients. A decrease of zero phonon transition probability (Debye–Waller factor) with increasing (negative) solvent shift was predicted and confirmed for crystal spectra. In general, no correlation exists between the strength of the first- and second-order couplings, and the vibrational modes involved can be different. Moreover, no relationship was established between the line shift and broadening in a temperature interval from 5 to 100 K.

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1. Introduction

Impurity spectroscopy has a long history as a traditional branch of condensed-phase physics [1,2]. Nevertheless, the influence of local and bulk properties of the guest and the host matrix on spectra remains incompletely understood, hampering many potential applications of impurity spectra as local probes to the structure and dynamics of solids. Sometimes it is difficult to rationalize dramatic spectral changes occurring in solids, such as the huge broadening of atomic spectra in rare gas crystals [3,4]. On the other hand, large π -conjugated porphyrin molecules dissolved in glassy polymers can have 95% of the first singlet transition intensity as resonant, zero phonon lines (ZPLs) [5]. The complexity of spectral transformations in the condensed phase is a result of interplay between static displacements

of electronic energy levels, giving rise to solvent shifts and inhomogeneous broadening, and, on the other hand, the linear and quadratic electron–phonon coupling (EPC) processes. The theories of these phenomena have reached a reasonably high level of sophistication [6–12], but unifying concepts still seem to be missing.

A qualitative approach to impurity spectra has been proposed recently in terms of isotropic intermolecular guest–host interactions. Based on two Lennard–Jones (L–J) 6–12 potentials with different parameters in the ground and excited state, expressions were derived for inhomogeneous spectral energy distributions, pressure-induced line shifts, and coupling strength to local phonons [13–15]. The non-equilibrium potential energy of individual centers has been assigned to a non-relaxing configurational coordinate that is, however, tunable by pressure. The solvent shifts and the degree of phonon localisation and softening were correlated with free volume in the vicinity of a chromophore. This way, a connection was established

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between the static and dynamic properties of spectra. A review of the model will be given in the first two sections of this paper, with the emphasis on elucidation of the concept.

The predictions of the model have already been compared to baric [16,17] and thermal shifts of spectral holes for pigments embedded in polymer or solvent glasses [13]. Opposite frequency dependencies of line shifts induced by temperature (T) and pressure (P) agree with the model, provided that the potential minimum of the excited state is shifted to a shorter distance. This conclusion is supported by high-resolution spectroscopy of an argon–benzene van der Waals complex, prepared in supersonic jet, revealing a decrease of equilibrium distance in the excited state by 1.65% [18].

The goal of the present work is to extend the L–J model to doped molecular crystals, including n -alkanes and other crystallizing solvents, referred to as Shpol'skii matrices in the broad sense, as well as aromatic hosts that are solid at ambient T [19]. The multiplicity of lines in these matrices means that the system is not in equilibrium at 0 K. Empty space and compressed atomic contacts occur in impurity-doped crystals as a result of mismatch in the size and shape of solute and matrix molecules. Pressure shift data for a large number of Shpol'skii absorption and fluorescence lines have already been reported [20]. Here we focus mainly on temperature shift and broadening of ZPLs that can be more conveniently investigated in crystals up to high T (100 K). Similar measurements on spectral holes in polymers are limited to T of 30–50 K [13–15].

Temperature effects on organic crystal spectra have been studied for a long time [21–26], sometimes in conjunction with thorough theoretical analysis [23,25,26]. However, the T shifts are rarely reported [21,25,26], and are usually treated without correction for the solvent shift caused by thermal expansion of matrix. Actually, the shift can be determined more accurately and in a wider T range than broadening. The shift, due to a volume change, is often comparable to or greater than the phonon-induced part, and must be subtracted in order to obtain the component of theoretical relevance [13,27]. A consideration of a sufficiently large and varied data set will lead to a conclusion that, in general, the strength of linear and quadratic EPC is not correlated, and, moreover, the shift and broadening cannot be characterized with a common quadratic coupling constant.

2. Experimental

Aromatic hydrocarbons, porphyrins and n -alkanes were obtained from Fluka or Aldrich and used as received. The samples were cooled as fast as possible by immersion into liquid N_2 and loaded to precooled CF204 or CF1204 continuous flow cryostats (Oxford). The pressure cell was made of a stainless steel cylinder of 20 mm in diameter, housing a 4 mm wide and 2 mm thick rectangular sample room [16,17,20]. Pressure shift measurements were performed either in fluorescence or in transmission spectra.

Fluorescence spectra were recorded on a computer-controlled total luminescence spectrometer, built on the basis of two Spex1402, 0.85 m double-grating monochromators (dispersion 0.5 nm per 1 mm slit width), an Osram XBO 2.5 kW high-pressure Xe lamp, a Peltier-cooled Hamamatsu R2949 photomultiplier, and a Stanford SR400 two-channel gated photon counter [20]. Transmission was measured in 0.5 or 1 mm thick polycrystalline layers with a LPD 3002E dye laser (line width 2.5 GHz, frequency 40 Hz) pumped with a LPX 100 excimer laser (both Lambda Physik). A two-channel JD2000 Joulemeter Ratiometer (Moletron) was applied for detection, with a sensitive J3S-10 (10^9 V/J) probe in the sample channel and a less sensitive one, J3-09 (10^3 V/J), as a reference.

3. Results and discussion

3.1. Potential energy of disordered solids

In a glass cooled to 0 K, the potential energy per particle is in the order of thermal energy at glass transition temperature $k_B T_g$ (k_B is Boltzmann constant). Incomplete solvation or free volume frozen in at T_g is mainly responsible for the huge amount of potential energy locked in a glassy phase, having typically a density less by $\sim 10\%$ than that of the crystal [28]. Depending on the amount of voids and compressed intermolecular contacts located nearby, the ground-state energies U_g of the impurities are different, and the respective coordinates r are distributed after Boltzmann as

$$\Phi(r) = \exp\{-[U_g(\varepsilon_g, r) + \varepsilon_g]/k_B T_g\}. \quad (1)$$

The distribution is normalized at the potential well minimum $-\varepsilon_g$, and its width depends on the ε_g to $k_B T_g$ ratio. The well depth, estimated from the enthalpy of sublimation, is about 50 kJ/mol [29], and organic solvents have glass points at several hundred K. Therefore, in molecular glasses ε_g exceeds $k_B T_g$ by a factor of ~ 20 .

As for the shape of potential U_g , it must possess a steep repulsive branch at close distances and a more shallow attractive part with dissociation limit. We have approximated the guest–host interactions to a L–J 6–12 potential, with equilibrium coordinate of the ground state σ_g [13–15]:

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

Each particle has a unique environment, characterized by a different configurational coordinate r , obeying the distribution $\Phi(r)$ (Eq. (1)). The interactions are considered isotropic, although ignoring the shape and size of particles is undoubtedly a drastic simplification. Steep potentials of r^{-12} or even r^{-6} hardly extend beyond the closest coordination layer, if the guest and host particles are of identical size. Each chromophore contains 12 neighbors in the case of an equilibrium tight packing of spheres. Thus, the average distance of the first coordination layer can be chosen as a configurational coordinate. From a local point of view, r characterizes the size of vacancies or compressed

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