

## Systematics of the $4f$ energies in a series of rare-earth organic complexes determined by resonant photoemission

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(Received 7 May 2004; published 22 October 2004)

We report a photoemission study of the systematics of the  $4f$  electronic structure of a family of rare-earth organic compounds. Resonant photoemission has been used to determine the binding energies of the  $4f^{N-1}$  ground states, relative to those of the ligand orbitals, of a number of rare-earth tris-8-hydroxyquinolines (REQ<sub>3</sub>'s). Using an empirical model these results have been extrapolated to the full series (Ce-Lu) of REQ<sub>3</sub>'s. It is found that in all cases, with the possible exception of Ce, the energy of the  $4f^{N-1}$  ground state is less than that of the highest occupied molecular orbital, and therefore individual holes on lanthanide sites will not be stable.

DOI: 10.1103/PhysRevB.70.153104

PACS number(s): 79.60.Fr, 71.20.Rv, 78.66.Qn

Rare-earth organic compounds represent a class of materials whose electronic structure has not, to date, been widely studied, although the study of rare-earth metals and their inorganic compounds using photoemission is a flourishing field. Aside from fundamental interest in the electronic structure of rare-earth organics, their  $4f$  energies are of significant practical importance—the sharp emission lines from trivalent lanthanide ions (Ln<sup>3+</sup>) combined with the well-known processing advantages of organic compounds, have made luminescent lanthanide-organic chelates of great interest for electroluminescent devices such as light-emitting diodes (LEDs).<sup>1</sup>

For photoluminescence there are two principal routes to the formation of the emissive Ln<sup>3+</sup> excited states. Both proceed via the creation, via photoabsorption, of singlet states on the ligand, since the photoabsorption cross-sections of organic molecules are typically orders of magnitude higher than those of trivalent lanthanide ions.<sup>2</sup> Singlet transfer to the lanthanide is thought not to occur, as these states are too short-lived. Rather, intersystem crossing, greatly enhanced by the presence of the lanthanide, via the so-called “heavy ion effect,”<sup>3</sup> creates triplet states which can then transfer to the lanthanide.

For lanthanides with more than one stable oxidation state, such as Yb and Eu, singlet transfer via an intramolecular redox reaction is also possible.<sup>4</sup> Whether these processes are energetically favorable depends on the relative energies of the emissive Ln<sup>3+</sup> excited states and those of the ligand singlet and/or triplet excitons.<sup>5</sup>

In an electroluminescent device an alternative route exists, in that direct capture of isolated carriers into  $4f$  states represents an intermediate stage towards the formation of the Ln<sup>3+</sup> excited state. For this to occur the resulting  $4f^{N-1}$  (for hole capture) or  $4f^{N+1}$  (for electron capture) state must be stable. For hole capture, stability depends upon the relative energies of the occupied ligand orbitals and the  $4f^{N-1}$  ground state,<sup>6</sup> both of which can be simultaneously measured against the same reference level using photoemission spectroscopy.

The rare-earth tris-8-hydroxyquinolines, REQ<sub>3</sub>, have been

of particular recent interest<sup>7-9</sup> as they represent one of the few families of organic molecules which emit in the infra-red in the solid state. The emission wavelengths of YbQ<sub>3</sub>,<sup>7</sup> NdQ<sub>3</sub>,<sup>8</sup> and ErQ<sub>3</sub>,<sup>9</sup> are 980 nm, 1.3 μm and 1.5 μm, respectively, which makes them potentially very important materials as these are three of the most commonly used wavelengths for communications technology. Due to the low triplet energies in the REQ<sub>3</sub>'s, visible light emission from these materials via triplet transfer is not energetically favorable.<sup>5</sup> Previously we have studied the ligand orbital electronic structure of these materials using photoemission and x-ray absorption.<sup>10</sup> In this work we examine their  $4f$  energies, determining the energies of the  $4f^{N-1}$  states of a number of REQ<sub>3</sub>'s. The  $4f$  energies of the rare-earth metals themselves were first determined almost 25 years ago.<sup>11</sup> Thiel *et al.*<sup>12</sup> have recently developed an empirical method to determine the  $4f$  energies of a series of rare-earth compounds, relative to the host bands, from measurements of a few members of the series, and we employ this method to determine whether direct hole capture in the entire series of REQ<sub>3</sub>'s is possible.

The REQ<sub>3</sub> materials were synthesized as described in Ref. 7. Thin films were evaporated onto an Ag(100) substrate in ultra-high vacuum, and their composition checked using x-ray photoemission spectroscopy (XPS), as described in Ref. 13. Photoemission spectra, at room temperature, were taken using a Vacuum Generators CLAM 2 analyzer, using the PM1 beamline at the BESSY II synchrotron source, with an energy resolution of 0.8 eV. Photon energies were calibrated using the Fermi level of the clean Ag substrate, measured with the calibrated analyzer.

Photoemission spectra of the REQ<sub>3</sub>'s are shown in Fig. 1. The spectra consist of a superposition of the core-like  $4f$  levels with the molecular orbitals of the ligand. To isolate the  $4f$  spectrum from the organic ligand contribution we used resonant photoemission,<sup>14</sup> which has been shown to be highly effective at separating the  $4f$  component in rare-earth ionic compounds.<sup>12</sup> The two spectra for each REQ<sub>3</sub> in Fig. 1 were taken using the resonance photon energy, at which the

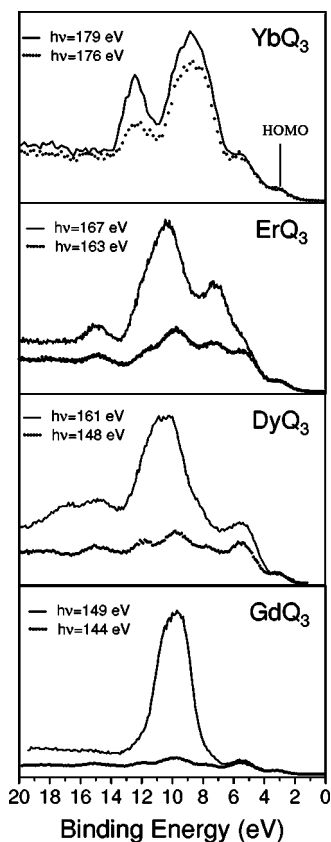


FIG. 1. Valence band photoemission spectra of  $REQ_3$ 's taken using resonant (lines) and anti-resonant (points) photon energies. Also shown is the energy of the upper edge of the HOMO.

$4f$  emission is enhanced, and the anti-resonance photon energy, at which the  $4f$  emission is suppressed, of the particular lanthanide. Difference spectra, after the subtraction of an inelastic background, are shown in Fig. 2.

The  $4f$  component is a complex lineshape consisting of the  $4f^{N-1}$  ground state, which is the lowest binding energy component, and a multiplet due to the fact that the photoemission process can leave the lanthanide ion in any of the possible  $4f^{N-1}$  excited states, reducing the kinetic energy of the outgoing electron. To estimate the energy of the  $4f^{N-1}$  ground state in a relatively objective manner, we employed curve fitting. We used the calculated multiplets of Gerken<sup>15</sup> with a 10–15% expansion to account for the different nuclear charge in the photoemission final state.<sup>15</sup> Each component was represented by a Gaussian. For Yb we allowed the intensity of the  $^1I_6$  peak to vary, as it is known to resonate unusually strongly,<sup>16</sup> while for Dy the  $^7F_6$  peak was allowed to vary as it is known that this peak resonates particularly weakly.<sup>17</sup> There is also an unusually strong resonance in the high binding energy region of the Er spectrum, but this was not compensated for in the fit, as it is a long way from the region of interest. Apart from the exceptions discussed above, the relative intensities and energies of the multiplets were kept fixed, thus each fit had only three free parameters, i.e., the peak width, assumed to be the same for each component of the multiplet, and the binding energy and overall intensity of the multiplet. The peak width was found to be

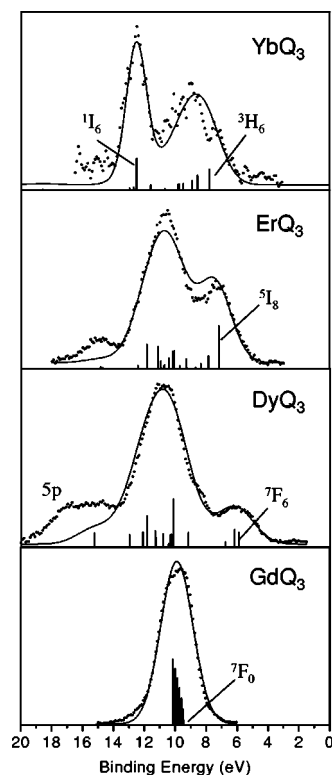


FIG. 2.  $4f$  spectra derived from the spectra of Fig. 1, with the calculated multiplet intensities<sup>15</sup> and curve-fitting results.

1.0–1.1 eV in all cases, i.e., slightly higher than the resolution, and comparable to that found for rare-earth ionic compounds by Thiel *et al.*,<sup>12</sup> whose experimental resolution was, at around 200–400 meV, rather better than ours. Note that this fitting procedure has its limitations in that the exact contribution of each multiplet component to the resonance can vary, as we explicitly recognized for Dy and Yb above. However, as can be seen in Fig. 2, the fit quality is reasonable, and certainly comparable to that obtained for other rare-earth compounds.<sup>12</sup> The poor fit to the high binding energy of the Dy spectrum is due to the presence of a  $5p$  component, which is not taken into account in the fit. The results of the peak fits give  $4f^{N-1}$  ground state energies of 9.5 eV (Gd), 5.9 eV (Dy), 7.2 eV (Er) and 7.8 eV (Yb). Given the values of the ionization energies of the  $Ln^{3+}$  ions,<sup>18</sup> these results can be used to predict the values for the other  $REQ_3$ 's using the empirical model of Thiel *et al.*<sup>12</sup> This assumes that the  $4f^{N-1}$  ground state binding energy  $E_{4f}$  is given by a rigid shift of the ionization energy, i.e.,

$$E_{4f} = I - E_L, \quad (1)$$

where  $E_L$  is a factor taking into account the shift from a vacuum level to a Fermi level reference, assuming a constant work function, and the electrostatic effect of the presence of the (negative) ligand ions. Taking  $E_L$  to be the average of the difference between the results of Fig. 2 and the ionization energy, 35.3 eV, we obtain the results plotted in Fig. 3. A correction for the change in the ionic radius across the series can be applied using<sup>12</sup>

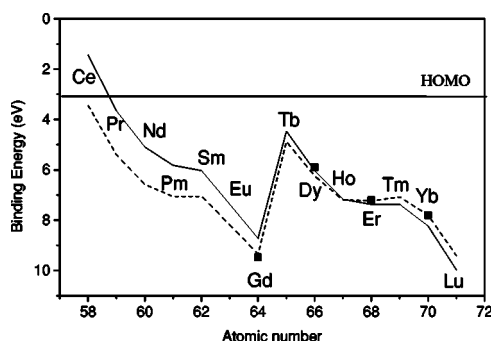


FIG. 3. Energy level diagram showing the measured binding energies of the  $4f^{N-1}$  ground state from Fig. 2 (squares), and the extrapolated results for the other rare earths using the one-parameter (solid line) and two-parameter (dashed line) models of Thiel *et al.* (Ref. 12.)

$$E_{4f} = I - E_L + \alpha_R(R - R_0), \quad (2)$$

where  $R$  is the ionic radius,  $R_0$  is the reference ionic radius, taken to be that of  $\text{Yb}^{3+}$ , and  $\alpha_R$  is the binding energy shift per unit change in the ionic radius. This gives a two-parameter model, for which a best fit was found for  $E_L = 35.44$  eV and  $\alpha_R = 11.48$  eV/Å. The resulting energies are also plotted in Fig. 3. These are compared to the binding energy of the ligand HOMO, for which we take the peak

energy of 3.15 eV,<sup>10</sup> rather than the leading edge of the peak, for consistency with the determination of the  $4f$  energies. Note that, with the exception of  $\text{CeQ}_3$ , both the one- and two-parameter models predict that the energy of the  $4f^{N-1}$  ground states is below that of the ligand HOMO. This implies that captured holes on the lanthanide sites will not be stable, as higher energy electrons from the ligands will rapidly relax into the lower energy  $4f$  state.<sup>6</sup> With the possible exception of Ce, these results imply that direct hole capture cannot represent an intermediate stage towards  $\text{Ln}^{3+}$  emission in the entire series of  $\text{REQ}_3$ 's.

We further suggest that, since the screening environment in most organic molecules is likely to be similar, the values for  $E_L$  and  $\alpha_R$  determined above can be used to predict  $4f^{N-1}$  energies for an entire series of lanthanide organometallic compounds based on the measurement of only one compound.

## ACKNOWLEDGMENTS

This work was financially supported by Agilent Technologies, and the German Bundesminister für Bildung und Forschung, Project 05 KS1WWA-5. One of us (E. U.) acknowledges financial support by the Fond der Chemischen Industrie. We wish to thank Torsten Kachel and David Batchelor for assistance at BESSY.

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