Scaling relations in hyperfine shifts of impurity atoms in rare gas crystals

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When an impurity of atom A of ns^1 electron configuration is compressed by interatomic forces in a rare gas (Rg) matrix, the density of its unpaired s electron increases at its nucleus resulting in a larger hf constant a compared to the free atom value a_0 . Conversely, expansion of A dilutes the spin density at its nucleus which gives rise to a negative hf shift, $\Delta a = a - a_0 < 0$. The dependence of the hf constants a and a_0 on properties of the A nucleus cancels in the relative hf shift $\Delta a/a_0$, which therefore serves as a direct indicator for the state of compression or expansion of A .

The major compression/expansion effect on A can be considered in terms of space availability in the Rg host matrix. Compression occurs for oversized impurity atoms like Cu, Ag, Au, substituted on lattice sites, or for interstitial hydrogen, $H(i)$, leading to $\Delta a/a_0 > 0$ (see Table I). On the other hand, expansion occurs for the undersized hydrogen atom on a lattice site, $H(s)$, leading to $\Delta a/a_0 < 0$.

The effect from space availability on the state of compression (or expansion) of impurity atom A is modulated though by the subtle balance of van der Waals (vdW) attraction and short-range (sr) repulsion between A and Rg. Based on the dependence of interatomic forces on electron distribution, a useful measure for the balance between vdW attraction and sr repulsion of A and Rg is provided by the unitless ratio $q = \sqrt{R^{(2)}/\hat{r}}$ of orbital moments of free, closed-shell A^+ ions and Rg atoms.¹ Here $R^{(2)}$ is the total second moment of an ion's or atom's electron orbitals and $\hat{r}$ is the first orbital moment of its outermost electron shell. The vdW potential between impurity atom A and a Rg atom at distance r is $-C/r^6$ with an interaction coefficient C approximately proportional to the constituents' second orbital moments, $C \sim R_A^{(2)} R_{Rg}^{(2)}$. The potential of sr repulsion can be expressed as $B \exp(-r/\rho)$ with a hardness parameter ρ and an interaction coefficient B depending on the constituents' first orbital moments, $B \sim \exp[(\hat{r}_A + \hat{r}_{Rg})/\rho]$. Although not directly derived from interaction potentials, the ratios $q(A^+)$ and $q(Rg)$ of the orbital moments involved in vdW attraction and sr repulsion between A and Rg serve as a measure for each constituent's contribution to the net interaction energy when the forces between A and Rg balance. In particular, the larger a constituent's q value is, the more does the binding vdW energy dominate over the energy of sr repulsion.

It has been found empirically that the ratio q of orbital moments, obtained from first-principles calculations, correlates with crystal-structure preference of ionic crystals¹ and with diffusion activation enthalpies of closed-shell ions.² Here we investigate the dependence of hf interaction

of impurity atoms A in Rg crystals on the q values of Rg host atoms, $q(Rg)$, and of closed-shell impurity ion cores $q(A^+)$. The orbital-moments approach is in the spirit of the quantum mechanical Adrian model of impurity atom hf shifts,^{3,4} although on a simplified, more empirical level.

The left side of Fig. 1 shows measured relative hf shifts $\Delta a/a_0$ of impurity atoms in Rg matrices vs the calculated¹ $q(Ar) = 3.08$, $q(Kr) = 3.22$, $q(Xe) = 3.39$. The data for each impurity atom species in these hosts fall along straight lines with negative slopes.

Although space availability qualitatively explains the positive hf shift of impurity mint metal (Mm) atoms, $Mm = Cu, Ag, Au$, in Rg crystals, this argument is too crude to account for the observed sequence of $\Delta a/a_0(Au) < \Delta a/a_0(Cu) < \Delta a/a_0(Ag)$ in a given Rg host, which disagrees with the sequence of atomic radii, $r(Cu) < r(Ag) < r(Au)$. The $\Delta a/a_0$ sequence of Mm atoms scales, however, with the orbital-moments ratio of their closed-shell ion cores,¹ $q(Cu^+) = 4.41$, $q(Ag^+) = 4.31$, $q(Au^+) = 4.49$, as shown on the right side of Fig. 1.

FIG. 1. Relative hf shifts $\Delta a/a_0$ of impurity atoms A at substitutional (s) and interstitial (i) sites in rare gas crystals vs orbital-moments ratio $q(Rg)$ of free host atoms (left side) and $q(A^+)$ of free closed-shell ions (right side). The straight lines connect data of the same impurity A in different hosts (left side) and of different impurities in the same host (right side).

TABLE I. Measured relative hf shifts $\Delta a/a_0$ (in %) of hydrogen^a and mint metal^b impurity atoms at substitutional (*s*) and octahedral interstitial (*i*) sites in rare gas host crystals.

Host	H(<i>s</i>)	H(<i>i</i>)	Cu(<i>s</i>)	Ag(<i>s</i>)	Au(<i>s</i>)
Ar	-0.46	1.15	4.8	5.7	2.8
Kr	-0.59	0.47	3.0	3.8	1.4
Xe	-1.09	-1.04	0.5	1.0	-0.9

^aS. N. Foner, E. L. Cochran, A. V. Bowers, and C. K. Jen, *J. Chem. Phys.* **32**, 963 (1960).

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Combining these findings, we see from the bilinear scaling (with negative slopes) of $\Delta a/a_0$ vs $q(\text{Rg})$ and $q(\text{Mm}^+)$ on the left and right sides of Fig. 1 the cumulative contributions from the Rg host atoms and the Mm impurity atoms, respectively, to hf shifts through increasing dominance of vdW attraction over sr repulsion.

A qualitative understanding of the size expansion of an impurity atom *A* from increased vdW interaction is provided by the classical interpretation of vdW interaction in terms of mutually inducing dynamical dipoles from synchronously oscillating electron clouds of *A* and neighboring Rg atoms. Such oscillations give rise (on time average)⁵ to electron charge accumulations in the interatomic *A*-Rg regions and, consequently, to spin density depletion at the nucleus of *A*. Increasing dominance of vdW attraction over sr repulsion between *A* and Rg atoms, indicated by correspondingly increasing *q* values, enhances the effect which, in turn, causes the negative slopes, $s = \partial(\Delta a/a_0)/\partial q < 0$, on both the left and right sides of Fig. 1.

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