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Temperature Dependence of the Matrix Shifts

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It has been observed that many metal atoms when trapped in rare gas matrices showed temperature dependent frequency shifts.[1-7] For most atoms with $p \leftarrow s$ transitions, the component highest in frequency of the triplet shifted reversibly to the blue while the two lower frequency components reversibly shifted to the red upon warming the matrices. Some work was done toward understanding these facts:

A. The observed blue shift at 20°K of the Pb $6p7s\ ^3P_1 \leftarrow 6p^2\ ^3P_0$ transition was 2483, 2974, and 5553 cm^{-1} in Xe, Kr and Ar matrices, respectively.[1] Upon warming the matrix a reversible red shift was observed. This suggested that the interaction between Pb and matrix atoms might be mainly responsible for these facts. The McCarty-Robinson approximation[8] was used to test it.

Using the observed shifts in Xe and Kr at 20°K, the calculated shift in Ar was 4017 cm^{-1}, and the calculated shifts in Xe and Kr at higher temperatures are shown in Table I. The observed blue shift

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in Xe was "relaxed" faster than the calculated values while the reverse was noted in Kr in which the deviation increased with increasing temperatures. This indicated that the Pb/Xe case was better treated with the McCarty-Robinson approximation at increasing temperatures. In addition, the Pb/Ar line was observed[1] to "relax" to the least proportionality considering the huge blue shift observed at 20°K. All these results suggested that Pb atom might occupy a best substitutional site in Xe, and a least perfect one in Ar among the three matrices. The extent of such imperfection appeared to increase with increasing temperatures.

B. The earlier mentioned different temperature dependence of the triplet components are readily seen to be essential to the origin of the triplets observed. The present theories are checked in this respect.

The missing neighbor or distortion model[10] would predict red shifts for all three components upon warming. The non-nearest metal-metal interaction model[3] would predict no shift, all blue shift or all red shift if the metal atoms stayed same distance apart, moved closer or moved farther, respectively, from one another. The Stark splitting model[2,5,11] could be readily shown[12] to predict same direction of shifting for the two higher frequency components. The recent model on Hg[13] would predict either all red shift or blue shift for two of the components.

None of these theories could account for the observed temperature dependence. One possible way out would be the following: The triplet is due to removal of the three fold degeneracy by an asymmetric

environment which added the largest distortion to the p orbital responsible for the highest frequency component. If such distortion was further increased upon warming the matrix, due to possible blocking effect of the target, while distortions along the other two directions were relieved, this could explain the different temperature dependences of these matrix shifts.

C. It is worth noting the observed hexagonal close-packed structure for the impurity-containing Ar thin films.[14] And it would be interesting to see what correlation one obtained by assuming a hcp trapping site in the matrices.

The axis, say z, suffering largest distortion mentioned above could very possibly be the normal-to-target one, and let x and y be the long and short axes, respectively, of the hexagon formed by the matrix atoms; Δ_{xy} be the energy difference between transitions to p_x and p_y, etc. Δ_{xy} is expected to increase and Δ_{xz} to decrease with increasing orbital size of the metal atom, and $(\Delta_{xy} - \Delta_{xz})$ to decrease from Ar to Kr to Xe. Table II shows the available experimental data in this respect.

Except for Ca and partly K, the observed changes in Δ_{xy} and Δ_{xz} followed exactly as were expected. It is therefore urgent to know the exact trapping site geometry to fully understand those observed matrix effects.

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Table I. Calculated and observed warm-up shifts of the Pb $^3P_1 \leftarrow {}^3P_0$ line in Xe and Kr matrices.

	Temperature (°K)	d_{ab} (Å) *	$\Delta\nu^{calc}$ cm^{-1}	$\Delta\nu^{obs}$ cm^{-1}
Xe	20	4.34	2483	2483
	30	4.345	2451	2437
	40	4.352	2408	2379
	50	4.361	2355	2317
	60	4.371	2296	2260
	70	4.380	2245	2210
	77	4.389	2196	2148
Kr	20	3.999	2974	2974
	30	4.005	2930	2928
	40	4.014	2860	2896
	50	4.025	2771	2858

* Reference 9

Table II. Triplet splitting for atoms in matrices.

Metal[†]	Observed differences between Δ_{xy} and Δ_{xz}	Dependence of $(\Delta_{xy} - \Delta_{xz})$ on matrix gas
Li,Na,K*,Rb	$\Delta_{xy} < \Delta_{xz}$	not reported
Cs	$\Delta_{xy} > \Delta_{xz}$	in Ar > in Kr > in Xe
Au	$\Delta_{xy} > \Delta_{xz}$	in Kr > in Xe
Ag	$\Delta_{xy} > \Delta_{xz}$	in Ar > in Kr > in Xe
Cu	$\Delta_{xy} < \Delta_{xz}$ in Xe but $\Delta_{xy} \sim \Delta_{xz}$ in Kr	
Mg[‡]	$\Delta_{xy} > \Delta_{xz}$	in Kr > in Xe

† Metals in the same series should be compared to eliminate complexities other than the orbital size change and interactions involved.

* K does not follow this trend too well.

‡ Ca shows just the opposite with $\Delta_{xy} < \Delta_{xz}$ in Kr and $\Delta_{xy} > \Delta_{xz}$ in Xe.

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