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Publication Date
1972-02-01
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February 1972

AEC Contract No. W-7405-eng-48
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Temperature Dependence of Matrix Shifts

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Abstract

The observed temperature dependence of the Pb singlet in matrices is used to construct a simple model for the matrix shifts. This model is then applied to interpret the different temperature dependence of the triplet components of many other metals in matrices which cannot be accounted for by earlier theories. The proposed model is further shown to successfully predict the correlations observed between the triplet splittings and the matrices used for most of the metals studied.

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The absorption spectra of many metal atoms trapped in rare gas matrices show temperature dependent frequency shifts.¹⁻⁷ For most atoms with p ← s transitions a triplet is observed; the highest frequency component shifts reversibly to the blue while the other two components reversibly shift to the red when the matrices expand upon warming. Some work directed toward understanding these facts is reported in this paper.

Matrix Shifts of Pb Singlet in Xe, Kr and Ar

The Pb spectra in matrices are first discussed because of their simplicity. The observed blue shift compared to the gas of the Pb 6p7s ³P₁ ← 6p² ³P₀ singlet at 20°K 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. The McCarty-Robinson approximation was used to test whether the interaction between Pb and matrix atoms might be mainly responsible for these facts.

Using the observed shifts of the Pb singlet in Xe and Kr at 20°K, the calculated shift in Ar was 4017 cm⁻¹, compared with the observed 5553 cm⁻¹. The experimental work¹ further showed that the Pb singlet in Ar shifted only slightly to the red upon warming. This last fact is significant considering the huge blue shift observed in Ar compared to the much smaller blue shifts noted in Xe and Kr; yet the red shifts in these two matrices upon warming were rather large.

These facts can be interpreted on the basis of an increasingly unsymmetrical environment around the Pb atom from Xe to Ar. The much
larger blue shift than expected in Ar suggests that Pb is possibly
trapped in a site with considerable distortion from the symmetrical
substitutional site assumed in the above calculations. The relatively
small red shift observed upon warming indicates that the distortion
increases with some of the Ar neighbors coming closer to the Pb and
offsetting the withdrawal of the other Ar atoms due to matrix expansion.
The development of this asymmetry during the deposition process will
be discussed below.

Next, the spectral shifts of the Pb singlet in Xe and Kr with
increasing temperatures were calculated and compared with the observed
values, as shown in Table I. Qualitative agreement is seen for Pb in
Xe at all temperatures studied, while rapidly increasing deviations in
an opposite direction are noted for Kr. The quantitative agreement
might be improved by including finer interactions between Pb and the
matrix. However, such interactions must be of decreasing magnitudes
at increasing temperatures due to the matrix expansion which increases
the distance between the interaction species. Therefore, it is the
qualitative difference between the matrix shifts in Xe and Kr that
deserves more attention. A trend similar to that observed for Pb in
Ar is noted for Pb in Kr as the temperature is increased, i.e., the
asymmetry of Kr neighbors increases with increasing temperature.
Predicted Temperature Dependencies from the Earlier Theories

It is readily seen that to interpret the observed triplet for the p → s transitions in matrices one must also consider the different temperature dependencies for the triplet components. With this in mind, the earlier theories are individually checked to see if the correct temperature dependencies can be deduced.

The missing-neighbor or distortion model\textsuperscript{10} gives red shifts for all three components upon warming. The non-nearest metal-metal interaction model\textsuperscript{3} gives, according to the potentials used by these authors, no shift if the metal atoms stay the same distance apart, all blue shifts if they move closer toward one another, and all red shifts if they move farther from one another. The Stark splitting model\textsuperscript{2,5,11} can be readily shown\textsuperscript{12} to give the same direction of shifting for the two higher frequency components. The recent model for Hg\textsuperscript{13} gives either all red shifts or blue shifts for two of the components.

None of these theories can account for the observed temperature dependencies. The earlier model for the Pb spectra is now applied to the triplet case.

Proposed Interpretation for the Temperature Dependencies of the Triplet

For both the s → p and p → s transitions of metal atoms, the excited state orbital is much expanded compared to the ground state and interaction of the excited state with the rare gas neighbor is assumed to be the main source of the spectral shifts compared to the
free gas. Unsymmetrical environments will not produce splittings for Pb s→p transitions because of the symmetry of the s orbital. However, the triplet splitting for metal atoms with p→s transitions is attributed to directional sensitive of the excited p orbitals. Different distortions along different directions would certainly shift the triplet components differently. The Pb work implied that the metal atom is in an environment that is distorted from one direction compared to a symmetrical substitutional site. If the distortion along this same direction further increased upon warming, as implied by the Pb spectra, it would cause a blue shift for the component responsible for the interactions along this direction. Distortions along the other directions, however, decrease as the matrix expands upon warming, and therefore cause red shifts for the other components. According to this model, it is always the component highest in frequency that shifts to the blue upon warming while the other two components shift to the red. The shifting is expected to be reversible due to the reversible expansion of the matrix films. These are all in agreement with the observed spectra.

Next, we try to rationalize the model with the following possible mechanism involved. The qualitative agreement between the calculated and observed temperature dependence for the Pb singlet in Xe implies that Pb occupies a substitutional or nearly-substitutional site. The work on Pb/Kr and Pb/Ar further implies an off-center substitutional site. Considering the matrix formation during deposition, such off-centering is most likely along the normal-to-target direction due to
possible metal penetration toward the inner layer matrix atoms. This is not unexpected in view of the large difference in melting points generally encountered between the metal and the rare gas crystals. Such a large difference in melting points means: (1) a relatively much smaller mobility of the metal atoms at the cryogenic temperatures, usually 20°K or lower;\textsuperscript{15,16} and (2) larger attraction between the matrix and metal atoms than that between the two matrix atoms. Also, the thermal energy released by the metal atom upon condensing could soften the inner layer matrix and allow for slight penetration of the metal atom. These factors combined would make the metal atom stick more closely to the inner layer matrix atoms. The matrix should expand isotropically upon warming. However, since thermal energy is transferred from the target to the matrix film during the warm-up process, this would lead to an outward expansion of the matrix along the normal-to-target direction. The inner layer matrix is pushed outward and increases its distortion relative to the metal atom, again due to the rather large attractive force which keeps the metal atom from moving freely. The other two parallel-to-target directions, however, expand freely. Upon cooling the reverse takes place. The proposed mechanism might be tested by the X-ray diffraction studies of the temperature dependence of the matrix structure. It has already been demonstrated that small amounts of impurities can change the structure of solid rare gases.\textsuperscript{17}
Dependences of the Triplet Splittings on the Matrix Gases and Metals

Additional information about the matrix effects can be obtained by studying the variations of the triplet splittings with the matrices for metals of the same series.

According to the proposed model for the triplet, the p orbital, say \( p_z \), along the normal-to-target axis is responsible for the highest frequency component; let \( p_x \) and \( p_y \) be the orbitals for the second highest and lowest frequency components, respectively; and \( \Delta_{xy} \) denotes the energy difference between transitions to \( p_x \) and \( p_y \), etc. \( \Delta_{xy} \) is expected to increase and \( \Delta_{xz} \) to decrease with increasing orbital size of the metal atom, and \( (\Delta_{xy} - \Delta_{xz}) \) to decrease from Ar to Kr to Xe. It is emphasized that metals of the same series should be compared to eliminate complexities other than the orbital size change and the type of interactions involved. Table II shows the available experimental data in this respect.

The observed changes in \( \Delta_{xy} \) and \( \Delta_{xz} \) follow as expected with the exceptions of Ca in Kr and, in part, K. The successful prediction of the correlations observed for most of the atoms reported is considered as a further support to our proposed asymmetrical lattice site model for the triplet splitting in matrices.

Conclusions

The observed triplet in matrices for the metals with \( p \rightleftharpoons s \) transitions is believed to be caused by local asymmetric distortions. The observed temperature dependencies of the matrix shifts are explained...
using a simple model formulated from the observed Pb spectra. The possible mechanism involved is suggested and should be tested by structural determinations.

One problem remaining unanswered is the local symmetry of the trapped metal atom in the matrix plane parallel to the target. The symmetry must be low enough to split the two p orbitals in this plane. Again, an exact knowledge of the matrix structure is needed to answer it.

Acknowledgement

I wish to thank Professor Leo Brewer for his encouragement and helpful discussions. This work was supported by the U. S. Atomic Energy Commission.
Table I. Calculated and observed warm-up shifts of the Pb $^3P_1 \leftarrow ^3P_0$ singlet in Xe and Kr matrices.

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$d_{ab}$ (Å) *</th>
<th>$\Delta \nu_{calc}$ cm$^{-1}$</th>
<th>$\Delta \nu_{obs}$ cm$^{-1}$</th>
<th>$\Delta \nu_{calc} - \Delta \nu_{obs}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe 20</td>
<td>4.34</td>
<td>2483</td>
<td>2483</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>4.345</td>
<td>2451</td>
<td>2437</td>
<td>14</td>
</tr>
<tr>
<td>40</td>
<td>4.352</td>
<td>2408</td>
<td>2379</td>
<td>29</td>
</tr>
<tr>
<td>50</td>
<td>4.361</td>
<td>2355</td>
<td>2317</td>
<td>38</td>
</tr>
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<td>60</td>
<td>4.371</td>
<td>2296</td>
<td>2260</td>
<td>36</td>
</tr>
<tr>
<td>70</td>
<td>4.380</td>
<td>2245</td>
<td>2210</td>
<td>35</td>
</tr>
<tr>
<td>77</td>
<td>4.389</td>
<td>2196</td>
<td>2148</td>
<td>48</td>
</tr>
<tr>
<td>Kr 20</td>
<td>3.999</td>
<td>2974</td>
<td>2974</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>4.005</td>
<td>2930</td>
<td>2928</td>
<td>2</td>
</tr>
<tr>
<td>40</td>
<td>4.014</td>
<td>2860</td>
<td>2896</td>
<td>-36</td>
</tr>
<tr>
<td>50</td>
<td>4.025</td>
<td>2771</td>
<td>2858</td>
<td>-87</td>
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</table>

* Rare gas lattice constants from Reference 9.
Table II. Triplet splitting for atoms in matrices.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Observed differences between $\Delta_{xy}$ and $\Delta_{xz}$</th>
<th>Dependence of $(\Delta_{xy} - \Delta_{xz})$ on matrix gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li, Na, K*, Rb</td>
<td>$\Delta_{xy} &lt; \Delta_{xz}$</td>
<td>not reported</td>
</tr>
<tr>
<td>Cs</td>
<td>$\Delta_{xy} &gt; \Delta_{xz}$</td>
<td>Ar &gt; Kr &gt; Xe</td>
</tr>
<tr>
<td>Au</td>
<td>$\Delta_{xy} &gt; \Delta_{xz}$</td>
<td>Kr &gt; Xe</td>
</tr>
<tr>
<td>Ag</td>
<td>$\Delta_{xy} &gt; \Delta_{xz}$</td>
<td>Ar &gt; Kr &gt; Xe</td>
</tr>
<tr>
<td>Cu</td>
<td>$\Delta_{xy} &lt; \Delta_{xz}$ in Xe</td>
<td></td>
</tr>
<tr>
<td></td>
<td>but $\Delta_{xy} \sim \Delta_{xz}$ in Kr</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>$\Delta_{xy} &gt; \Delta_{xz}$</td>
<td>Kr &gt; Xe</td>
</tr>
<tr>
<td>Ca</td>
<td>$\Delta_{xy} &gt; \Delta_{xz}$ in Xe</td>
<td></td>
</tr>
<tr>
<td></td>
<td>but $\Delta_{xy} &lt; \Delta_{xz}$ in Kr</td>
<td></td>
</tr>
</tbody>
</table>

* K does not follow this trend very well.
References


