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MATRIX EFFECTS ON TRAPPED ATOMIC LEVELS***

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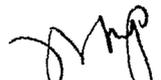
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ABSTRACT

We suggest a theoretical model for calculating the matrix perturbation on the spectra of atoms trapped in rare gas systems. The model requires the "potential curves" of the diatomic system consisting of the trapped atom interacting with one from the matrix and relies on the approximation that the total matrix perturbation is a scalar sum of the pairwise interactions with each of the lattice sites. Calculations are presented for the prototype systems Na in Ar. Attempts are made to obtain ab initio estimates of the Jahn-Teller effects for excited states. Comparison is made with our recent Matrix-Isolation Spectroscopic (MIS) data.

1. Introduction

As pointed out by Forstmann and Ossicini,¹ two different points of view have been taken in the literature in studying the perturbation of a Rare Gas (RG) matrix on the state of a trapped species. In the molecular approach,²⁻⁵ one constructs the pair-potential between the trapped atom and a RG atom. The energy levels and wavefunctions of the trapped atom are then obtained by solving a Schroedinger equation where the total potential consists of the atomic potential as well as the pair potentials coming from the matrix. The orthogonality requirement that the resulting orbitals are orthogonal to the

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host-matrix orbitals is ignored, since it is assumed that this is already accounted for while deriving the pairwise potentials. In the second approach⁶⁻⁹ advocated by Forstmann et al., one considers the matrix to act as a small perturbation and obtains the localized electronic levels of the trapped atom by solving a new wave equation in the presence of this perturbation with due inclusion of the orthogonality effects of the guest atom valence orbitals with respect to those on the Rg-atoms. In what follows, we shall present a model that in effect combines the pairwise potentials directly to yield the lineshifts. No new Schrodinger equation need be solved in the matrix environment; moreover, the nonadditivity corrections coming principally from the overlap effects are included.

2. Additivity of Pair Potentials in Rare Gas Matrices

The perturbation responsible for the levelshifts of an atom embedded in a RG matrix consists of three distinct components, one representing the electrostatic and exchange effects, another, the dispersive effects, and the third, the polarization effects.

Since the lattice constant of a typical RG matrix is quite large (7-8 a_0), it is reasonable to assume that the perturbations due to the atoms of the RG matrix are additive. We shall show below that this is indeed a good approximation. Expressions for the important nonadditive terms are also derived and discussed.

We shall consider, for simplicity, the case of a trapped alkali atom. Considering, as a zero-th approximation, the outermost electron on the alkali to be the only active electron, we can write the Hartree-Fock energy as:

$$E = E_{\text{core}} + \langle \phi | F^A + \sum_k V_k^{\text{RG}} | \phi \rangle \quad (1)$$

where F^A is the Fock operator of the isolated alkali atom A and V_k^{RG} the net interaction coming from the k-th RG atom. The orbital ϕ , the new orbital for

the alkali valence electron when the matrix effects are taken into account, can be written as:

$$\phi = \eta (\phi_0 - \sum_k \langle \phi_0 | n'p;k \rangle | n'p;k \rangle + \delta) \quad (2)$$

where the second term on the right-hand side arises by virtue of orthogonality to the n'p-electrons on the RG-atoms, δ , the polarization caused by the matrix perturbation and η is a normalization factor given by:

$$\eta^2 = 1 / (1 - \sum_k t_k^2 + \langle \delta | \delta \rangle^2), \quad (3)$$

with $t_k = \langle \phi_0 | n'p;k \rangle$.

Using (2) in (1),

$$\begin{aligned} \epsilon_0 + \Delta_{tot} &\equiv \langle \phi | F^A + \sum_k V_k^{RG} | \phi \rangle \\ &= \eta^2 [\epsilon_0 + \sum_k \{ \langle \phi_0 | V_k^{RG} | \phi_0 \rangle - 2 t_k^2 \epsilon_0 \\ &\quad + t_k^2 (\epsilon_{n'p} + V_{n'pk}^+) + \langle \delta | F^A | \delta \rangle \\ &\quad + 2 \langle \phi_0 | V_k^{RG} | \delta \rangle \}] \end{aligned} \quad (4)$$

where ϵ_0 , $\epsilon_{n'p}$ are the unperturbed valence orbital energies of the foreign and host atoms, respectively, and $V_{n'pk} = \langle n'p;k | V | n'p;k \rangle$, V being the alkali core potential.

Calling Δ_k as the correction due to the k-th RG atom, we have:

$$\Delta_{tot} = \frac{\sum_k (1 - t_k^2) \Delta_k}{1 - \sum_k t_k^2} \quad (5)$$

Thus Δ_{tot} deviates from perfect additivity by:

$$\Delta_{\text{tot}} - \sum_k \Delta_k = \frac{\sum_k \Delta_k \sum_l t_l^2 (1 - \delta_{kl})}{1 - \sum_l t_l^2} \quad (6)$$

For a substitutionally trapped atom in a regular lattice this reduces to:

$$\Delta_{\text{tot}} - N \Delta \approx N^2 t^2 \Delta \quad (6')$$

Note that for $t \sim .1$ and $N \sim 10$, the deviation from additivity can be appreciable. On the other hand, $t^2 \Delta$ by itself is not likely to be important. Hence, we shall work with the slightly simplified expression:

$$\Delta_{\text{tot}} = \frac{\sum_k \Delta_k}{1 - \sum_k t_k^2} \quad (5')$$

As an illustration, consider an alkali atom in the ground state. The polarization correction in a close-packed RG lattice can be written in the second-order perturbation approximation as:

$$\Delta E_{\text{pol}} = \frac{- \langle ns | V_k^{\text{RG}} | (n+1) p \sigma_k \rangle^2}{\epsilon_{(n+1)p} - \epsilon_0} \quad (7)$$

where $(n+1) p \sigma_k$ corresponds to the σ -component of the virtual alkali p-orbital with the molecular axis defined by the k -th RG atom. Obviously, ΔE_{pol} is identically zero for a symmetric undistorted lattice. Thus, the polarization corrections can be neglected for the present treatment.

The van der Waals terms, on the other hand, are additive to the same extent as the electrostatic and exchange effects are. In other words, they must follow the same formula indicated in Eq. (5').

3. General Formulation of the Matrix-Induced Level Shifts

We shall assume that the diatomic "potential curves" of the trapped atom in its ground and relevant excited states interacting with a RG atom are known. Let the leading terms of these wavefunctions $\Psi(i)$ in the matrix be:

$$\Psi(i)^{(0)} = \phi_i^A \phi_1^{RG} \phi_2^{RG} \dots \quad (8)$$

where ϕ_i^A and ϕ_k^{RG} are the free atomic wavefunctions of A and the k-th RG atom, respectively. Then the perturbation matrix over the set $\{\Psi(i)\}$ is given by:

$$\begin{aligned} H'_{ij} &\equiv \langle \Psi(i) | H' | \Psi(j) \rangle \\ &= \sum_k [t_{ik}^\sigma t_{jk}^\sigma \Delta E(\Sigma) + (u_{ik}^\pi u_{jk}^\pi + v_{ik}^\pi v_{jk}^\pi) \Delta E(\Pi)] \end{aligned} \quad (9)$$

where t_{ik}^σ , u_{ik}^π and v_{ik}^π are the geometric factors defined by:

$$\phi_i = t_{ik}^\sigma \phi_{\sigma,k} + u_{ik}^\pi \phi_{\pi x,k} + v_{ik}^\pi \phi_{\pi y,k} \quad (10)$$

$\phi_{\sigma,k}$, $\phi_{\pi,k}$ being the σ - and π -components of the atomic wavefunctions with the k-th RG-atom defining the molecular axis. Eq. (9) can easily be derived by writing down the full wavefunctions as:

$$\Psi(i) = A_0 \Psi(i)^0 + \sum_k \sum_{mn} A_{k,mn} \Psi(i)_{k,mn}^0 \quad (8')$$

where $\Psi_{(i),kmn}^D$ are the excitations such as $\phi_0 \phi_k^{RG} \rightarrow \phi_{0m} \phi_{kn}^{RG}$ leading to the pairwise van der Waals terms. A_0 and A_{kmn} are the expansion coefficients. In Eq. (9) $\Delta E(\Sigma)$ and $\Delta E(\Pi)$ are the interaction potential energies of the Σ and Π diatomic states. In order to get the total matrix perturbation energies, we have to solve the eigenvalue problem given by:

$$| H_{ij}^i - \lambda S_{ij} | = 0 \quad (11)$$

where

$$S_{ij} = \langle \Psi(i) | \Psi(j) \rangle$$

For an atom in the state s or s^2 , we have no degeneracy and the perturbed energy is simply:

$$\lambda_x = \frac{\sum_k \Delta E_{k,x}}{1 - \sum S_{k,x}^2} \quad (12)$$

where

$$S_{k,x}^2 = s_k^2 \text{ or } 2s_k^2; s_k = \langle ns | n'p\sigma; k \rangle \quad (13)$$

for s - or s^2 -type valence occupation respectively, s_k being the overlap of the ns -orbital of the guest atom with the $n'p$ -orbital of the RG atom. For an np - or $nsnp$ -type valence on the former, Eq. (11) is a 3×3 matrix eigenvalue problem, with:

$$S_{ij} = t \delta_{ij} - \Sigma [(S_k^\sigma \ t_{ik}^\sigma \ t_{jk}^\sigma + S_k^\pi (u_{ik}^\pi \ u_{jk}^\pi + v_{ik}^\pi \ v_{jk}^\pi))] \quad (14)$$

where

$$\begin{aligned} S_k^\sigma &= \langle np\sigma | n'p\sigma; k \rangle^2 \\ S_k^\pi &= \langle np\pi | n'p\pi; k \rangle^2 \end{aligned} \quad (15)$$

and

$$t = 1, \text{ or } 1 - \sum_k s_k \quad (16)$$

depending on whether it is an 'np' or 'nsnp'-atom. The geometric factors t^σ , u^π , and v^π are tabulated in Table I corresponding to a coordinate system in which the RG atom is situated at a point with polar coordinates (R, θ, ϕ) with respect to the trapped atom having a valence configuration np or $n_1s n_2p$.

4. Calculations, Results and Discussion

We shall consider only the case where the Na-atom is embedded substitutionally in an Argon matrix with a cubic closed-pack lattice structure. We shall use the accurate NaAr ab initio potential curves of Saxon et al.¹⁰ The overlap matrix is obtained by using the 3s- and 3p-atomic orbitals of Na and the 3p-orbitals of Ar. In Table II, we present the level shifts of the 3s and 3p levels for various nearest neighbor distances of the Ar cage, keeping the symmetry unchanged. Clearly, even though the atomic levels themselves change considerably with the change of separation, the lineshifts remain fairly unaffected. The calculated lineshift in absorption (a blue shift) at $R=7.26 a_0$ is in good agreement with experiment.

In Table III, we present the results of our study on the lineshifts in emission. Here the $3p_\sigma$ and $3p_\pi$ states of Na split because of Jahn-Teller distortion. To determine the exact nature of distortion, one will have to consider, in addition to the Na-Ar interaction, the details of the interaction within the matrix itself. We adopt here a simple model of distortion in which the Ar atoms in the xy-plane move nearer to the trapped atom while those lying outside the xy-plane move away from it by the same amount. In Table III, the first column indicates that we keep the median nearest neighbor distance (nnb) intact at $R=7.26 a_0$. Distortion of the order of 5.5% (of nnb) seem to reproduce the observed red-shift. The red-shifts seem particularly sensitive to distortion to the extent that one can confidently conclude that there results

a cage-distortion of the order of 5% as a result of a Jahn-Teller effect in the excited state.

In order to have an estimate of the nonadditivity effects, the lineshifts at $R=7.26$ are also calculated both in adsorption as well as emission with the overlap-matrix replaced by an identity matrix. The corresponding results are shown in Tables II and III in parentheses. The net additivity effects are less than 10% of the total lineshifts.

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Table I. $t_{ik}^\sigma, u_{ik}^\pi, v_{ik}^\pi$

$\langle x \sigma \rangle$	$\sin\theta \cos\phi$	$\langle x \pi_x \rangle$	$-\sin\phi$	$\langle x \pi_y \rangle$	$\cos\theta \cos\phi$
$\langle y \sigma \rangle$	$\sin\theta \sin\phi$	$\langle y \pi_x \rangle$	$\cos\phi$	$\langle y \pi_y \rangle$	$\cos\theta \sin\phi$
$\langle z \sigma \rangle$	$\cos\theta$	$\langle z \pi_x \rangle$	0	$\langle z \pi_y \rangle$	$-\sin\theta$

Table II. Lineshifts in absorption shown as function of changes in the nearest neighbor distances.

$R(a_0)$	$E_x(\text{cm}^{-1})$	$E_{A,B}(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$
7.0	2005.6	2667	662
7.26	1222 (1130)	2234 (2062)	1012 (930)
7.50	671.3	1858	1187
80	-101.8	1150	1252

Table III. Lineshifts in emission shown as function of Jahn-Teller distortion.

$R(a_0)$	$E_x(\text{cm}^{-1})$	$E_A^1(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	% Distortion
7.26	1397.6	1036.9	361	5
7.26	1435 (1324)	922.3 (850)	513 (474)	5.5
7.26	1476	808	686	6
7.26	1520	690	830	6.5
7.26	1619	467	1152	7.5
7.26	1930	-90	2120	10