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Analysis of atomic zinc luminescence in rare-gas solids A zinc–rare gas cluster approach

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Abstract

The luminescence spectroscopy of atomic zinc isolated in the solid rare gases (Zn/RG) is compared with theoretical predictions obtained with the use of diatomic Zn·RG potentials. In particular, the existence of pairs of emission bands, both of which are assigned to the same gas-phase electronic transition, is examined with the use of diatomic pair potentials to simulate the potential-energy surfaces of the Jahn–Teller active vibrational modes of Zn in the solid. The close agreement found between theory and experiment indicates the validity of the use of pair potentials in the analysis of matrix zinc spectroscopy. Thus, it allows identification of the high-energy emission bands in the Zn/RG systems as arising from motions of the rare-gas atoms surrounding the atomic zinc guest and the lower-energy bands as associated with the motion of the zinc atom into an octahedral interstitial site in the lattice.

Keywords: Matrix isolation; Luminescence; Zn; Jahn–Teller effect; Pair potentials

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1. Introduction

Samples of atomic zinc isolated in thin films (10–30 μm) of the solid rare gases Zn/RG were prepared by the codeposition of atomic Zn vapour, generated by electron bombardment, with the rare gases. Luminescence spectra were recorded at the HIGITI beamline at the synchrotron radiation facility HASYLAB/DESY, Hamburg, and fluorescence lifetime measurements were made using the time-correlated single-photon-counting technique. Table 1 gives the spectral positions and measured lifetimes of the emission bands recorded for atomic zinc isolated in solid Ar, Kr and Xe. From emission lifetime measurements and spectral positions, the pair of emission bands observed in the UV, at 218.7 and 238 nm in Ar and 239.5 and 258.7 nm in Kr matrices are assigned [1] to the singlet transition, while the bands in the near-UV in Kr and Xe are assigned as the triplet emission of atomic zinc.

2. Method and results

The key assumptions in the theoretical model [2] employed are: (a) all interactions are obtained by the sum of diatomic pair potentials; and (b) the atomic electronic angular momentum J_e at the molecular asymptote is conserved in the cluster. The diatomic (Zn·RG) interaction potentials used in the simulation of the optical spectroscopy of atomic Zn isolated in rare-gas clusters (Zn·RG$_n$) and matrices (Zn/RG) were either obtained from high-level ab initio calculations [3] for purely repulsive states or extracted from

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Table 1
Photophysical characteristics of the luminescence observed in the Zn/RG matrix systems at 6 K. For comparison the singlet ($4p\,^1P_1 \rightarrow 4s\,^1S_0$) and triplet ($4p\,^3P_1 \rightarrow 4s\,^1S_0$) resonance transitions of atomic zinc in the gas phase are also given. The predicted emission wavelengths are derived from the emission energies E_{em} as calculated in the text. The abbreviations s and t refer to singlet and triplet assignments of the observed emission bands while b and w refer to the body and waist modes, respectively, of Zn/RG

	λ_{abs} (nm)	λ_{em} (nm)	τ (ns)	λ_{calc} (nm)
Zn/gas phase	213.86	213.86 (s)	1.41	—
		307.59 (t)	30.4 μs	—
Zn/Ar	206.7	218.7 (s)	0.93	(w) 216.4
		238.0 (s)	1.42	(b) 245.6
Zn/Kr	212.4	239.5 (s)	1.26	(w) 239.9
		258.7 (s)	1.63	(b) 255.9
		315.6 (t)	> 10 μs[a]	
Zn/Xe	219.9	356.0 (t)	> 10 μs[a]	(w) 361.4
		399.0 (t)	> 10 μs[a]	(b) 387.7

[a] Lower-limit estimates of the decay time made using the TCSPC technique with an excitation repetition rate of 1.042 MHz.

experimental data derived from laser spectroscopy [4] of the bound molecular states in supersonic expansions.

The ground-state interaction potential $W_x(R)$ of Zn-RG$_n$ molecules is simple to evaluate due to the spherical symmetry of the atomic electronic angular momentum (EAM) $J_e = 0$ at the asymptotic limit, i.e., Zn ($^1S_0$). It is given by the sum of the diatomic Zn·RG and RG–RG X-states

$$W_x(R) = \sum_{k=1}^{n} V^{x}_{Zn\cdot RG}(R_k) + \sum_{i=1}^{m} V^{x}_{RG-RG}(r_i), \qquad (1)$$

where n is the number and R_k the length of zinc–rare-gas atom bonds in the cluster. The second term in Eq. (1) includes the energy of the m RG–RG bonds in the Zn·RG$_n$ cluster.

Obtaining the energy of the excited molecular states is considerably more complex due to the axial symmetry of $J_e = 1$, the atomic angular momentum of Zn($^1P_1$) at the molecular asymptote. Expressions for the particular cases of the triatomic (Zn·RG$_2$) and tetrameric (Zn·RG$_3$) clusters have already appeared in the literature [5]. The specific form of the excited-state energies of the Zn($^1P_1$)·RG$_4$ and Zn($^1P_1$)·RG$_5$ cluster will, however, be presented with the objective of obtaining the behaviour of this electronic state Zn($^1T_{1u}$)/RG in solid rare gases.

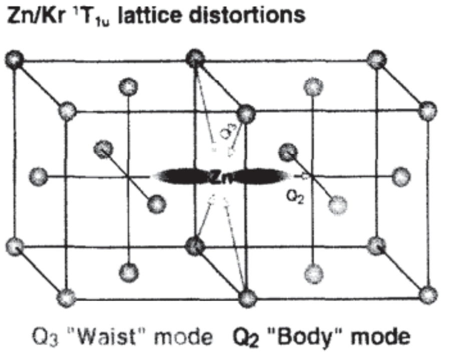

Fig. 1. A pair of unit cells of solid Kr indicating the possible lattice motions which allow the attainment of the stable Zn(p_z)·Kr$_4$ species for a Zn atom originally occupying a substitutional site in the Kr lattice. Q_2 involves motion of the Zn atom along the body of the pair of unit cells shown into an octahedral interstitial site $I_{Oh}(1)$. Q_3 involves a contraction of the four rare-gas atoms at the corners surrounding the Zn atom.

In the highest symmetry (C_{4v}) of the RG$_4$ cluster, approach of the Zn atom is restricted to a single axis, defined as the z-axis, chosen perpendicular to the plane of the four rare-gas atoms. For this complex the expressions

$$W_{A1}(R) = 4[\cos^2\theta\, V_\Sigma(R) + \sin^2\theta\, V_\Pi(R)], \qquad (2)$$

$$W_E(R) = 2[\sin^2\theta\, V_\Sigma(R) + [\cos^2\theta + 1]\, V_\Pi(R)] \qquad (3)$$

are appropriate for the $A(p_z)$ and the doubly degenerate $E(p_x, p_y)$ electronic state. Expressions corresponding to Eqs. (2) and (3) can be obtained [6] for this perpendicular C_{nv} approach of Zn($^1P_1$) to a planar cluster composed of any number n of rare-gas atoms. With Kr atoms separated by the equilibrium internuclear distance of the ground electronic state of Kr dimer, calculations show [6] that the Zn·Kr$_n$ species showing the largest stabilization energy is Zn·Kr$_4$.

In the calculation of the stabilization occurring on the excited $^1T_{1u}$ electronic surface of Zn in solid rare-gas matrices, particular attention was given to the vibronic modes which allowed the attainment of the Zn·RG$_4$ species. An examination of a pair of unit cells of an FCC solid, shown in Fig. 1, indicates two possible ways of achieving a dominant interaction of the zinc atom with four of its 12 nearest-neighbour atoms when isolated in a substitutional site. One method is simply the contraction of four of the nearest-neighbour atoms around the zinc, the other is the motion of the

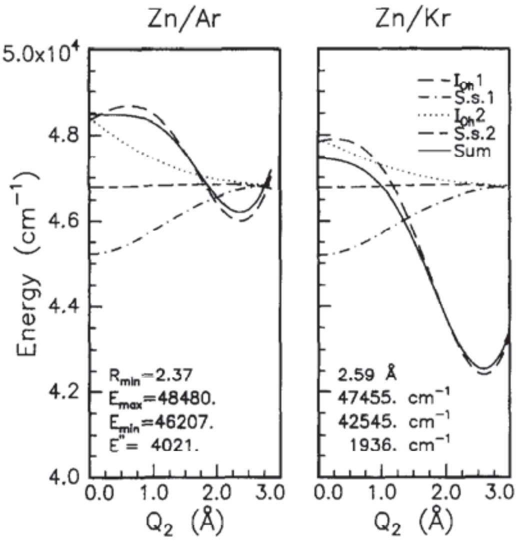

Fig. 2. The excited $^1T_{1u}$ state energies of Zn/Ar and Zn/Kr associated with the motion of the Zn atom along the body of a pair of "relaxed" unit cells of the rare-gas solid. The contributions to the four interactions considered between the Zn atom and its surroundings are indicated by the legend. Note that in both the Zn/Ar and Zn/Kr cases, destabilization associated with this body motion arises only from the four atoms originally surrounding the Zn atom in the substitutional site 1. All other interactions lead to a lowering of energy, especially $I_{Oh}(1)$ and $I_{Oh}(2)$ as occupancy of the Zn atom in the accepting octahedral interstitial site is approached. For the calculation of the emission energies the ground-state energy at the internuclear separation at the minimum energy of the excited state must be obtained. It is indicated as E'' in the figure.

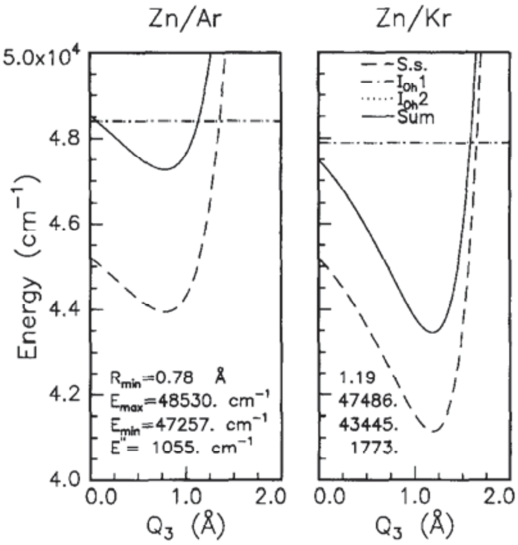

Fig. 3. Excited $^1T_{1u}$ state energy curves of Zn/Ar and Zn/Kr calculated for the waist mode.

zinc atom into one of the adjacent octahedral interstitial (I_{Oh}) sites.

Calculations of the stabilization energy of the latter motion, hereafter referred to as the "body" mode, can be made using Eq. (2) for an $M{\cdot}RG_5$ square pyramid cluster which represents motion into an I_{Oh} site of the solid. Summing up the 18 Zn–Kr interactions considered, a stabilization energy of 2703 cm^{-1} results from the motion of atomic zinc 2.21 Å away from the substitutional site it originally occupied in the ground state. The present calculation is for a rigid Kr lattice, fixed at the lattice parameter of solid krypton. A further lowering of energy will be achieved as the Zn atom gets closer to having a complexation number of 4, i.e., the centre of the I_{Oh} site at $R = 2.82$ Å. This can be pursued by minimizing the repulsive Σ interaction between $Zn(p_z)$ and the Kr atom at the apex of the square pyramid by moving the latter into its adjacent cell. The minimum energy on the body mode exists at $R = 2.59$ Å and is achieved by displacing the Kr atom 0.8565 Å thereby inducing a destabilization energy (E_{Kr-Kr}) of 1533 cm^{-1} in the neighbouring Kr unit cell. The energy of the emission originating from the calculated minimum on the body mode is obtained from the expression $E_{em} = E'(R'_{min}) - E''(R'_{min}) - E_{Kr-Kr}$. Using Morse function parameters of the X state of Zn·Kr, the ground-state energy E'' at $R = 2.59$ Å is calculated, from Eq. (1) to be 1936 cm^{-1}. Using the values quoted in Fig. 2, the emission energy of Zn/Kr is found to be 39 076 cm^{-1} a value which compares well with 38 655 cm^{-1}, the 258.7 nm band of Zn/Kr. Following the procedure outlined above for Zn/Kr, the emission energy resulting from the body mode in the Zn/Ar and Zn/Xe systems are collected in Table 1 for comparison with the observed bands.

Calculation of the stabilization energy associated with the "waist mode" of the rare-gas lattice can be obtained from (1) the sum of two I_{Oh} sites, i.e., two $M{\cdot}RG_5$ cluster calculations with the Zn–RG distance (R) set at the substitutional site size of the solid rare gas and (2) the sum of four diatomic Zn·RG $^1\Pi_1$ state potentials of variable R. The resulting potential energy curves for this waist mode are shown in Fig. 3 and as anticipated, contractions of 0.78, 1.19 and 1.50 Å from the substitutional site size are observed for the minima of this mode in Ar, Kr and Xe, respectively. For Ar and Kr the waist-mode results in emission energies of 46 202 and 41 672 cm^{-1}, values to be compared with 45 725 and 41 753 cm^{-1} for the 218.7 and the 239.5 nm emission bands observed in Zn/Ar and Zn/Kr, respectively.

3. Conclusions

The existence of the pair of singlet emission bands in the Zn/RG matrix systems are predicted accurately in the theoretical simulations. This agreement between experiment and theory indicates the validity of using diatomic interaction potentials to model the spectroscopy of matrix-isolated atoms and thereby indicates a dominant localized interaction of Zn in the solid rare gases. It thereby provides insight, on a microscopic level, into the atomic motions occurring in the solid during an optical cycle.

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