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Vibronic Spectra Analysis of Transition-Metal Ion Impurity Centers in II–VI Compounds

K. K. STAVREV AND K. D. KYNEV
Department of Chemistry, University of Sofia, Sofia 1126, Bulgaria

AND G. ST. NIKOLOV
Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria

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The paper presents a simple approach based on the single-coordinate model which could be used to analyze the vibronic spectra of impurity centers in crystals. The method is easy to apply to study the excited states of an activator and to assess the influence of its environment in different host lattices. It involves further a spectral analysis of the impurity center localized electron transitions by the angular overlap model. The AOM parameters extracted from such an analysis are found to correlate with the variation of ΔS (displacement of the potential energy minima) parameter.

I. Introduction

The divalent Mn, Fe, Co, and Ni embedded in the crystal lattices of II–VI compounds are known to form impurity centers which differ as to the electron transition localization at the activator ion (*1–3*). Mn^{2+} in ZnS, ZnSe, CdS, etc., absorbs and emits characteristically in the visible region, while Fe^{2+}, Co^{2+}, and Ni^{2+} do so mainly in the ir region (*1–3*).

Phonon-assisted vibrational spectral structures have been observed at low temperatures for most of the emission and absorption bands of these activators (*4–10*). To interpret the fine structure of the experimentally observed bands is of definite interest, since one can thus reveal the structure of the impurity center's excited states.

The aim of the present work is to interpret the vibronic spectra of Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} in ZnS, ZnSe, and CdTe using the single-coordinate model and the Franck–Condon (FC) principle (*11, 12, 17, 18*). Such an analysis could ultimately assess the validity of a simple approach in which the *M–L* bond strength is partitioned between the metal–ion activator and its nearest neighbors in the host crystal lattice.

II. Theoretical

The vibronic transition intensity depends strongly on the FC vibrational overlap integrals $R_{v'v''}$ (see, e.g., Ref. (*11*)),

$$R_{v'v''} = \int \Psi_{v'} \Psi_{v''} d\tau, \qquad (1)$$

where $\Psi_{v'}$ and $\Psi_{v''}$ are the vibrational wavefunctions, respectively, for the excited electronic state with quantum number v'

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and for the electronic ground state with quantum number v''.

At low temperatures (we interpret vibronic spectra observed at temperatures below 20 K as being low) it is reasonable to assume that the excited vibrational states of the electronic ground state are not populated and only *0–j* vibronic transitions are observed. In this approximation and by the procedure described in Ref. (*11*) we have calculated the relative (with respect to the zero-phonon line (ZPL) intensity) intensities of the vibronic *0–j* transitions. The required $R_{v'v''}$ values were obtained using recursion formulas published in Ref. (*12*).

The harmonic oscillator approximation is expected to give reliable results, because we deal with low values of the vibrational quantum number.

III. Strategy of Fitting

The model approximation for an absorption band structure with three vibrational frequencies (A, B, C) is illustrated in Fig. 1.

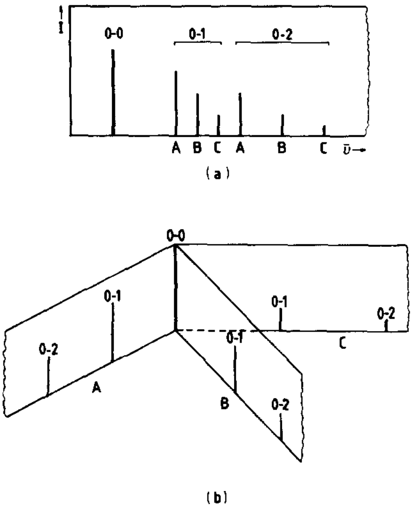

FIG. 1. (a) Vibrational structure for an absorption band with three vibrational modes (A, B, and C; $2\,\bar{\nu}_A > \bar{\nu}_C$). The vertical lines correspond to the maximum intensities of the vibronic transitions, the 0–3 line for A-mode being omitted. (b) Illustration of the approximation used in this paper—separation of the vibronic progressions with respect to the three modes.

We have applied the single-coordinate model to each progression in the band structure. This requires that the vibronically active vibrations are totally symmetric and that the harmonic approximation will hold. The validity of the harmonic factorization (no mixing between modes) is a rough approximation and it requires the vibronic effects to be small. The observed sharp equidistance of the vibrational satellites with respect to the ZPLs supports this assumption (*13, 16*). The nonsymmetric vibrations are completely left out since in the experimental spectra there are no even number sequences with the observed vibrational frequencies (*13*). Only bands that could be assigned to symmetry-allowed electron transitions were treated, because they are the ones that interact predominantly with the totally symmetric vibrations (*13, 20*).

The model presented in Fig. 1 is a serious oversimplification of real spectral patterns. The most frequently met complication is that the *0–j* sidebands overlap with neighboring progression sidebands, thus interfering with the exact determination of ΔS. In such cases we stopped using the sidebands when they start falling inside the next region. Of course, that is a restriction and it constitutes a loss of sidebands in the progressions and the resulting drop in accuracy of the spectral analysis. However, this is a practical way to solve the problem and we consider it as satisfactory at least for the treated spectral systems.

A look at Table I (vide infra) suggests that both ground and excited states of the studied system are subject to Jahn–Teller (JT) forces and spin–orbit (SO) coupling. If these two factors dominate the term splitting patterns, the FC analysis undertaken on the basis of simple T_d picture (neglecting JT and SO coupling) is found to fail. Conversely, if such an attempt is found to reproduce faithfully the observed intensity ratio, this is evidence per se that the JT and SO factors could be ignored as being of minor significance.

The FC analysis requires the knowledge of the vibrational components spacing and intensities. As a first approximation in getting these data from the observed experimental spectra we neglect the overlapping of the vibrational bands. To assess the error arising from this neglect we have carried out a deconvolution of the vibrational structures into Gaussian bands. It was shown that in most cases the error due to the neglect of the vibrational band overlap (VBO) is compatible with the error of fitting (*11*); therefore, VBO neglect is a good approximation and the vibronic transition intensities can be directly measured from the experimental spectra.

The ZPL energies and the vibrational frequencies for the ground and excited states were taken from the absorption and emission spectra of ZnS : Mn, ZnSe : Mn, ZnS : Fe, CdTe : Fe, ZnS : Co, ZnSe : Co, and ZnS : Ni (*4–10*). Since we consider only ML_4 clusters in breathing modes, the influence of the different cations constituting the second neighborhood in zinc chalcogenides and cadmium telluride could be ignored.

We have attempted to obtain the best fit by the least-squares method with a single variational parameter ΔS, the displacement of the excited state potential surface minimum relative to the ground state minimum, along the configuration coordinate. The ratio of the vibrational frequencies in excited and ground state was found to vary in the range 0.85–0.95 and to have a slight effect on the calculated intensities.

TABLE I

BANDS OF TRANSITION-METAL ION-DOPED II–VI COMPOUNDS INTERPRETED IN THIS WORK

Compound	Electron transition assignment	Reference
ZnS : Mn	${}^6A_1 \rightarrow {}^4T_2\,({}^4G)$	(*4*)
ZnSe : Mn	${}^6A_1 \rightarrow {}^4T_2\,({}^4G)$	(*5*)
ZnS : Fe	${}^5E \rightarrow {}^5T_2\,({}^5D)$	(*6*)
CdTe : Fe	${}^5E \rightarrow {}^5T_2\,({}^5D)$	(*6*)
ZnS : Co	${}^4A_2 \rightarrow {}^4T_1\,({}^4P)$	(*8*)
ZnSe : Co	${}^4A_2 \rightarrow {}^4T_1\,({}^4P)$	(*8*)
ZnS : Ni	${}^3T_1 \rightarrow {}^3T_2\,({}^3F)$	(*10*)

IV. Results and Discussion

Using the available experimental data (*4–10*) and keeping ΔS variable, we have analyzed the vibrational structure of 7 absorption bands corresponding to the electron transitions given in Table I. Good fitting patterns have been obtained for all the bands listed in Table I.

The calculated intensities are known to depend strongly on the ΔS values (*11, 12*). For complicated many-atom systems ΔS is theoretically inaccessible and its values could be obtained by semiempirical analyses of the experimental spectra (*17, 18*).

Figure 2 shows the dependence of the

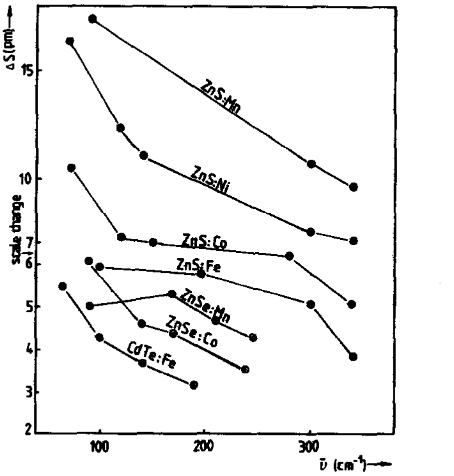

FIG. 2. Variation of the ΔS values obtained from the band structure analysis with the vibrational frequency. Only A_1-vibrational mode is taken into account. The symbol ⊙ indicates the cases where only one sideband is used in the analysis. Full circles denoted cases where more than one sideband is used in the analysis.

TABLE II

VALUES OF THE AOM PARAMETER e_σ (IN kK) EXTRACTED FROM THE IMPURITY CENTER'S ELECTRONIC SPECTRA

ZnS : Mn	ZnSe : Mn	ZnS : Fe	CdTe : Fe	ZnS : Co	ZnSe : Co	ZnS : Ni
6.6	6.2	2.7–2.9	2.1–2.3	3.5–3.8	3.4–3.7	4.5–4.9

best-fit ΔS values on the vibrational frequencies. A few points for ZnS centers and most of the points for the other centers correspond to a single sideband (0–1), the next bands overlying the subsequent progressions. These points are denoted in Fig. 2 (and also Fig. 3). Since the ΔS vs $\bar{\nu}$ curves are constructed with a small number of points and there are uncertainties as to the exact position of $\bar{\nu}$ when the number of sidebands used is small, the comments raised below should be viewed only as rough general trends.

It is seen from Figure 2 that:

(1) In most cases ΔS decreases or remains almost constant with increasing vibrational frequency. This trend is easy to explain by the increased force constants which are directly proportional to the vibrational frequency in the single-coordinate model. Since in the sequence ZnS, ZnSe, CdTe the vibrational frequencies decrease, the ΔS value changes should also decrease in the same sequence.

(2) It is seen from Fig. 2 that ΔS decreases appreciable in the ligand's sequence S, Se, Te. This trend could be due to (i) increased reduced mass effecting a decrease in the vibrational frequency and (ii) decreased σ-antibonding effect due to the increased M–L bond covalency (*11*, *19*).

We have recently investigated the central atom's covalency effect by applying the angular overlap model (AOM) to several Mn^{2+} centers in II–VI compounds (*21*). The AOM parameters are directly related to the bond properties and can be used to interpret the bond strength variations. The σ-antibonding e_σ parameters for the remaining impurity centers were obtained in this work by AOM analyses of the corresponding spectra, setting $e_\delta = 0$ and $e_\pi = (0.15–0.20)\ e_\sigma$ (*19*, *20*). The results are given in Table II.

The e_σ values are a measure of the σ-antibonding inherent in the M–L bond. It is seen that in the Mn–Ni series e_σ drops sharply from Mn to Fe and further increases slightly. The same trend is observed for ΔS with constant $\bar{\nu}$, thus revealing that the same factors may be operative in determining both e_σ and ΔS. It is therefore feasible that the ΔS variations could be due to bond strength variations only. The dependence ΔS vs e_σ (see Fig. 3) for the vibrational frequencies corresponding to the optical phonons is nearly linear, the slopes for both straight lines are almost the same.

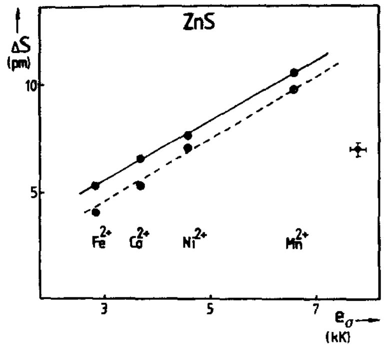

FIG. 3. Dependence of ΔS values obtained for two vibrational frequencies (~300 cm^{-1} (—) and ~350 cm^{-1} (– – –)) upon e_σ values extracted in AOM analyses from ZnS : M electronic spectra. The symbols ⊙ and ● have the same meaning as in Fig. 2.

The ΔS vs e_σ dependence should be considered as empirical. It is hard to rationalize, since the relative displacement of the minima is implicitly but not explicitly related to the bond strength. For further discussion, see Ref. (*11*).

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