FORCE FIELD AND MEAN SQUARE AMPLITUDES IN PrF_3 MOLECULE — ORBITAL VALENCY FORCE FIELD APPROXIMATION

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Orbital valency force constants are fitted, internal and cartesian mean square amplitudes of molecular vibrations are calculated.

1. Introduction and results

In a previous paper [1], the infrared (IR) spectra of the matrix-isolated lanthanide trifluorides LnF_3 (Ln — $4f$ rare-earth atom) have been studied to provide information on the geometry and force constant trends for metal halide species. The results of these studies indicate that LaF_3, CeF_3, NdF_3, EuF_3, GdF_3, H_oF_3, LuF_3 are piramidal (C_{3v}) while PrF_3 is planar (D_{3h}). Fortunately, for one of these molecules, PrF_3, the Raman spectra were obtained by Lesiecki and co-workers [2]. Therefore, for this planar molecule we know a complete set of the four fundamental frequencies which are classified as [3] (symmetry D_{3h}),

$$\Gamma_{\text{vib}} = A_1'(\text{Raman, } 526\ \text{cm}^{-1}) + A_2''(\text{IR, } 86\ \text{cm}^{-1}) + 2E'(\text{IR, Raman, } 99 \text{ and } 458\ \text{cm}^{-1}). \tag{1}$$

Consequently, it is possible to try to perform the normal coordinate analysis for PrF_3, assuming a reasonable model of the intramolecular potential V. As a first approximation we propose the orbital valency force field model (OVFF) which was shown to be satisfactory for the XY_n type of molecules with n bonds to a central atom X [4, 5].

The assumed OVFF potential function for a planar (symmetry D_{3h}) molecule is [3]

$$2V = K \sum_{i=1}^{3} \Delta r_i^2 + 2r_0 K' \sum_{i=1}^{3} \Delta r_i + F \sum_{i,j=1}^{3} \Delta R_{ij}^2 + 2R_0 F' \sum_{i,j=1}^{3} \Delta R_{ij} + r_0^2 D \sum_{i=1}^{3} \beta_i^2,$$

$$K' = -3F'. \tag{2}$$

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The notation is fairly standard, similar to that used in most Urey-Bradley treatments; β_i is the angle between the actual position of the i-th ligand atom and the direction where the i-th orbital is centered when the orbital energy is minimized [5]. In order to obtain the four force constants K, F, F', D we ought to calculate them in agreement with Eqs. (9)—(12) of our previous paper [3]. The results of these calculations are given in Table I.

TABLE I

Calculated orbital valency force constants for PrF_3 matrix isolated in argon

Observed frequencies in cm^{-1}				Force constants in md/Å			
A_1'	A_2''	E'	E'	K	F	F'	D
526	86	99	458	1.927	0.39	0.51	1.60

Our next step is the calculation of the internal $\langle r^2_{Pr-F}\rangle^{1/2}$ $\langle R^2_{F...F}\rangle^{1/2}$ and cartesian $\langle x^2_{Pr}\rangle^{1/2}$, $\langle x^2_F\rangle^{1/2}$ mean square amplitudes of vibrations (the notation is standard [6]) in agreement with the procedure described by Cyvin [6]. Of course, in this calculation we have used the orbital valency force constants which are given in Table I. The results of these calculations are listed in Table II.

TABLE II

Calculated internal and cartesian mean square amplitudes of vibrations (in Å) for PrF_3 matrix isolated in argon

Temperature	$\langle r^2_{Pr-F}\rangle^{1/2}$	$\langle R^2_{F...F}\rangle^{1/2}$	$\langle x^2_{Pr}\rangle^{1/2}$	$\langle x^2_F\rangle^{1/2}$
0K	0.049	0.083	0.028	0.096
298K	0.051	0.085	0.029	0.098

At last, it is worth mentioning here that this is a first report on the force constants values and mean square amplitudes in PrF_3 molecule.

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