

# Static and Dynamic Structure of Molecular Monomers and Dimers of the Rare-earth Fluorides

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We determine a model of the ionic interactions in  $\text{RF}_3$  compounds, where R is a rare-earth element in the series from La to Lu, by an analysis of data on the bond length and the vibrational mode frequencies of the  $\text{PrF}_3$ ,  $\text{GdF}_3$  and  $\text{HoF}_3$  molecular monomers. All  $\text{RF}_3$  monomers are predicted to have a pyramidal shape, displaying a progressive flattening of the molecular shape in parallel with the lanthanide contraction of the bond length. The vibrational frequencies of all monomers are calculated, the results being in good agreement with the data from infrared studies of matrix-isolated molecules. We also evaluate the geometrical structure and the vibrational spectrum of the  $\text{La}_2\text{F}_6$  and  $\text{Ce}_2\text{F}_6$  dimers, as a further test of the proposed model. – PACS 36.40.Wa (Charged clusters)

**Key words:** Ionic Clusters; Molten Salts.

## 1. Introduction

A number of industrial and technical applications of the rare-earth halides have drawn continued interest to the study of the chemical and physical properties of these materials. The extraction and processing of rare-earth metals are based on molten salt technologies, motivating an intense effort at determining the thermodynamic and structural properties of these liquids by both experimental and simulational methods [1]. Intensive studies have also been made for a number of years of their vapours and of the volatile complexes that they form with alkali or aluminium halides [2, 3], in view of potential applications related to new energy sources, energy conservation, and recycling or separation processes.

Among the rare-earth halides, trifluorides are the most extensively studied systems with respect to the thermochemical properties of the vapour phase, the main attention being on the vapour pressure and the vaporization thermodynamics. In this connection the questions of the equilibrium shape of these molecules and of their vibrational frequencies are of great importance for the purpose of calculating entropy and free energy functions [4]. In contrast to the planar  $\text{D}_{3h}$  symmetry exhibited by the Group-IIIa (Al, Ga, In)

and Fe trihalides, most experimental work on rare-earth trifluorides indicates  $\text{C}_{3v}$  equilibrium geometries.

The strongest evidence comes from the infrared spectra of matrix-isolated  $\text{RF}_3$  molecules and from electric dipole deflection experiments. The symmetric stretch  $\nu_1$  mode is infrared-active in addition to the other fundamental frequencies only in the  $\text{C}_{3v}$  configuration and has been observed in most  $\text{RF}_3$  species from  $\text{LaF}_3$  to  $\text{LuF}_3$  [4, 5]. The electric deflection studies of most  $\text{RF}_3$  species have given evidence for a non-zero molecular dipole moment, as is appropriate for a pyramidal shape, or at least for small distortions from a planar geometry [6].

The experimental results mentioned above are supported by extended Hückel calculations carried out by Myers et al. [7]. These predicted values in the narrow range  $91^\circ$  –  $92^\circ$  for the apical F-R-F angle in trifluorides. A number of subsequent quantum-chemical calculations, as listed in the review of Hargittai [8], have shown that especially for the heavier members of the rare-earth series the result is sensitive to the theoretical approach: Hartree-Fock calculations tend to yield a planar structure, whereas computations including correlation effects lead to pyramidal geometries. Electron diffraction data seem to be available

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only for  $\text{PrF}_3$ ,  $\text{GdF}_3$ , and  $\text{HoF}_3$  among the rare-earth trifluorides [9]. The assignment of the vibrational frequencies on the basis of the  $C_{3v}$  symmetry [3] yields rather low values for the  $\nu_2$  mode, implying a small barrier to shape inversion and large thermal fluctuations in the molecular shape. It still seems, however, that the thermal-average structures from the electron diffraction experiments on rare-earth trihalides are mostly non-planar [8].

In the present work we propose and evaluate an ionic model for the potential energy function of rare-earth trifluoride compounds. As in earlier work on the other rare-earth trihalides [10, 11], a crucial element of the model is the inclusion of the electronic polarizability of the trivalent metal ions to permit an energy gain to be obtained from distortion of the molecule away from the planar shape. The model needs to be evaluated anew for fluorides, since from earlier work on aluminium trifluorides [12] we expect these compounds to be appreciably more ionic than the corresponding chlorides, bromides and iodides. Electron-shell deformability of the fluorines is allowed in the model through (i) effective valences and (ii) electrical and overlap polarizabilities. In related work on Al chloride clusters [13] such a description of the ionic interactions has been shown to yield good agreement with data on the molecular structure, the vibrational frequencies and the energetics of dissociation and ionization reactions from experiment and from quantum chemical and density functional calculations.

After a brief reminder of the essential aspects of the model as developed in earlier studies of trivalent metal halides [11 - 13], we determine the overall trends of the model parameters for the rare-earth metal ions in their trifluorides, i.e. their effective valence, ionic radius and electronic polarizability. To this end we analyze the available evidence on the  $\text{PrF}_3$ ,  $\text{GdF}_3$  and  $\text{HoF}_3$  monomers, which as already mentioned includes data on the bond length from electron diffraction on the gaseous phase [9] together with infrared spectra on matrix-isolated states [3]. The results are tested by evaluating the molecular shapes and vibrational frequencies for the other rare-earth trifluoride monomers as well as for the  $\text{La}_2\text{F}_6$  and  $\text{Ce}_2\text{F}_6$  dimers, on which spectral data are available from the work of Hastie *et al.* [4].

## 2. The Model and its Parameters

The potential energy  $U$  of a molecular cluster in an arbitrary configuration is taken to be a function of the

interionic bond vectors  $\mathbf{r}_{ij}$  and of the dipole moments  $\mathbf{p}_i$  carried by the ions. The form that we adopt for the function  $U(\{\mathbf{r}_{ij}\}, \{\mathbf{p}_i\})$  is

$$U(\{\mathbf{r}_{ij}\}, \{\mathbf{p}_i\}) = \sum_{i < j} \left[ \frac{z_i z_j e^2}{r_{ij}} + \Phi_{ij}(r_{ij}) - \frac{C_i C_j}{r_{ij}^6} \right] \quad (1) \\ + U_{\text{pol}}^{\text{cl}}(\{\mathbf{r}_{ij}\}, \{\mathbf{p}_i\}) + U_{\text{shell}}(\{\mathbf{r}_{ij}\}, \{\mathbf{p}_i\}).$$

We handle this function by a computer programme which (i) optimizes the structure of the molecule by searching for zero-force configurations corresponding to extrema in the total energy, and (ii) evaluates deformations of each zero-force structure in order to assess its mechanical stability and its vibrational frequencies.

The sum over ion pairs on the RHS of (1) includes (i) the Coulomb interactions of ionic charges with effective valences  $z_i$ , subject to charge compensation ( $\sum_i z_i = 0$ ); (ii) the overlap repulsive interactions described by a central pair potential  $\Phi_{ij}(r_{ij})$  of the Busing form [14]

$$\Phi_{ij}(r_{ij}) = f(\rho_i + \rho_j) \exp [(R_i + R_j - r)/(\rho_i + \rho_j)], \quad (2)$$

where  $R_i$  and  $\rho_i$  are characteristic radii and hardness parameters for the ions and  $f$  has the standard value  $f = 0.05 \text{ e}^2/\text{\AA}^2$ ; and (iii) the van der Waals interactions with a strength  $C_i$  being attributed to each ion (in practice this term is of some importance only for the fluorines). These rigid-ion terms are supplemented by the classical polarization energy  $U_{\text{pol}}^{\text{cl}}$  of the induced dipoles on the fluorine and rare-earth ions and by the shell deformation energy  $U_{\text{shell}}$  of the fluorines. The electrically induced dipoles are described by the electronic polarizabilities  $\alpha_{\text{F}}$  and  $\alpha_{\text{R}}$ , whereas a short-range  $\alpha_{\text{s}}$  polarizability accounts for changes in the state of overlap between the electron shells of near neighbours, which arise from their relative displacements [13].

As in earlier work [11 - 13] we assume transferability of potential-energy parameters for halogens between different compounds. Adopting, therefore, from an earlier study of fluorides [12] the parameters for the fluorine ion ( $R_{\text{F}} = 1.32 \text{ \AA}$ ,  $\rho_{\text{F}} = 0.215 \text{ \AA}$ ,  $C_{\text{F}} = 2.08 \text{ e}\text{\AA}^5/2$ ,  $\alpha_{\text{F}} = 0.88 \text{ \AA}^3$  and  $\alpha_{\text{s}} = 0.48 \text{ \AA}^3/\text{e}$ ) as well as simple proportionality between  $R_{\text{R}}$  and  $\rho_{\text{R}}$  for metal ions ( $R_{\text{R}}/\rho_{\text{R}} = 18.6$ ), the model involves for each rare-earth trifluoride three disposable parameters. These are the effective valence  $z_{\text{R}}$ , the radius

$R_R$  and the electronic polarizability  $\alpha_R$  of the rare-earth ion. Only the trends across the rare-earth series are, however, of present interest. The number of free parameters is thus greatly reduced, as is shown immediately below.

We have assessed the trends of these metal-ion parameters across the rare-earth series from  $\text{LaF}_3$  to  $\text{LuF}_3$  from the data on the  $\text{PrF}_3$ ,  $\text{GdF}_3$  and  $\text{HoF}_3$  monomers, with the following results:

(i) a constant value can be taken for the effective valence of the metal ions across the series, that is  $z_R = 2.8$ ;

(ii) the ionic radii can be chosen to obey the lanthanide contraction by relating them to the number  $n_{4f}$  of 4f electrons in the metal ion according to  $R_R = (1.42 - 0.01 n_{4f})\text{\AA}$ ; and

(iii) the metal-ion polarizability can be taken as proportional to the cube of the ionic radius according to  $\alpha_R = 0.6 R_R^3$ . Precisely, the above expression for the rare-earth ionic radius is obtained by fitting the measured values of the three bond lengths, while a constant value for the effective valence (within  $\pm 0.1$ ) and a constant value for the ratio  $\alpha_R/R_R^3$  (within a few percent) account for the measured infrared frequencies of the three chosen monomers (see Table 1).

As anticipated, the effective valence  $z_R = 2.8$  for the rare-earth ions in their trifluorides is quite close to the nominal valence. A similar reduction by only 7% was found for the fluorine ion in NaF crystals from dielectric constant studies [15]. The corresponding reduction in the other rare-earth halides has been found in [11] to be down to  $z_R = 2.6$ .

### 3. Static and Dynamic Structure of the Trifluoride Monomers

The second and third column in Table 1 report our results for the geometrical structure of the  $\text{RF}_3$  monomers. The molecular shape is found to be a trigonal pyramid with a slowly decreasing bond length across the series (second column) and an accompanying flattening through a slow increase of the F-R-F apical angle (third column). The experimental data for the bond length in  $\text{PrF}_3$ ,  $\text{GdF}_3$ , and  $\text{HoF}_3$ , which have been fitted in assessing the model parameters, are also shown in Table 1 and marked by underlining.

Our results for the shape of these molecules can be compared with those from a number of quantum chemical calculations, as reported in the review of Hargittai [8]. The quantum chemical values of the

Table 1. Equilibrium structure and vibrational frequencies of the  $\text{RF}_3$  monomers (bond lengths in  $\text{\AA}$ , bond angles in degrees and frequencies in  $\text{cm}^{-1}$ ). For each monomer our calculated values in the first row are compared with experimental data (or with estimates, given in parentheses) in the second row. The underlined data have been fitted in determining the model.

|                  | $r_{\text{R-F}}$     | $\angle \text{F-R-F}$ | $\nu_1$      | $\nu_2$     | $\nu_3$      | $\nu_4$      |
|------------------|----------------------|-----------------------|--------------|-------------|--------------|--------------|
| $\text{LaF}_3$ : | 2.12                 | 107.8                 | 547<br>540   | 84<br>82    | 527<br>510   | 121<br>125   |
| $\text{CeF}_3$ : | 2.11                 | 107.9                 | 550<br>549   | 85<br>80    | 530<br>519   | 121<br>115   |
| $\text{PrF}_3$ : | 2.10<br><u>2.091</u> | 108.0                 | 554<br>542   | 85<br>86    | 532<br>458   | 122<br>99    |
| $\text{NdF}_3$ : | <u>2.09</u>          | 108.1                 | 557<br>557   | 85<br>80    | 534<br>535   | 123<br>115   |
| $\text{PmF}_3$ : | 2.08                 | 108.2                 | 560<br>(560) | 85<br>(90)  | 537<br>(535) | 124<br>(124) |
| $\text{SmF}_3$ : | 2.07                 | 108.3                 | 563<br>(564) | 85<br>92    | 538<br>508   | 125<br>123   |
| $\text{EuF}_3$ : | 2.06                 | 108.4                 | 567<br>572   | 86<br>90    | 541<br>544   | 126<br>120   |
| $\text{GdF}_3$ : | 2.05<br><u>2.053</u> | 108.5                 | 568<br>583   | 86<br>95    | 541<br>552   | 127<br>130   |
| $\text{TbF}_3$ : | <u>2.03</u>          | 108.7                 | 573<br>580   | 86<br>97    | 545<br>554   | 128<br>131   |
| $\text{DyF}_3$ : | 2.02                 | 108.8                 | 578<br>(581) | 86<br>(98)  | 547<br>(561) | 129<br>(133) |
| $\text{HoF}_3$ : | 2.01<br><u>2.007</u> | 108.9                 | 580<br>585   | 86<br>102   | 549<br>569   | 131<br>120   |
| $\text{ErF}_3$ : | <u>2.00</u>          | 109.0                 | 584<br>(589) | 87<br>(102) | 551<br>(571) | 132<br>(137) |
| $\text{TmF}_3$ : | 1.99                 | 109.1                 | 588<br>(593) | 87<br>(103) | 554<br>(576) | 133<br>(139) |
| $\text{YbF}_3$ : | 1.98                 | 109.2                 | 592<br>597   | 87<br>100   | 556<br>579   | 134<br>144   |
| $\text{LuF}_3$ : | 1.97                 | 109.3                 | 595<br>598   | 87<br>109   | 558<br>585   | 135<br>150   |

bond length show the same trend, but are larger than ours by a few hundredths of an  $\text{\AA}$ . The trends in the apical angles are again similar, but quantitatively the values from the quantum chemical calculations are larger than ours. The apical angle is reported as  $112.9^\circ$  in  $\text{LaF}_3$  and the monomer is apparently found to be planar from  $\text{DyF}_3$  onwards.

The other four columns in Table 1 report our calculated values for the vibrational frequencies of each monomer: the  $\nu_1$  symmetric stretch, the  $\nu_2$  out-of-plane bending, the  $\nu_3$  antisymmetric stretch, and the  $\nu_4$  in-plane bending mode. The Table also includes the mode frequencies as reported by Boghosian and Papatheodorou [3] from infrared measurements on matrix-isolated molecules, supplemented in a few cases by estimates (shown in parentheses in Table 1).

As discussed by Hastie *et al.* [4] in reporting such infrared spectra of a number of trifluorides, the effect of the matrix on the observed spectra is very large: the values of the mode frequencies that are believed to be appropriate to the molecule in the gas phase are obtained by extrapolation from data taken on monomers embedded in N<sub>2</sub>, Ar, and Ne matrices and carry an estimated uncertainty of up to  $\pm 15$  cm<sup>-1</sup>. Bearing in mind these facts, it appears that our results are well compatible with the experimental data, especially for the lighter members of the rare-earth series.

#### 4. Static and Dynamic Structure of Trifluoride Dimers

The dimeric species is believed to be present, but hard to identify, in the equilibrium vapour of the rare-earth trifluorides [3]. We find the ground-state structure of the La<sub>2</sub>F<sub>6</sub> and Ce<sub>2</sub>F<sub>6</sub> dimers to consist of two edge-sharing distorted tetrahedra, with the values of the geometrical parameters as reported in Table 2. We also find a stable, asymmetric excited-state structure in which the two rare-earth ions share a fluorine triple bond. This asymmetric structure is stabilized by the inclusion of the metal-ion polarizability.

Evidence on infrared-active modes for the La<sub>2</sub>F<sub>6</sub> dimer embedded in N<sub>2</sub>, Ar, and Ne matrices is available from the work of Hastie *et al.* [4]. By extrapolation of these spectra they propose modes at  $542 \pm 8$ ,  $532 \pm 8$ ,  $378 \pm 6$ ,  $323 \pm 8$  and  $166 \pm 20$  cm<sup>-1</sup> for the isolated dimer in the gas phase. These correspond in our calculated spectra to a singlet at 536 cm<sup>-1</sup>, a triplet near 524 cm<sup>-1</sup>, and three doublets near 353, 300 and 149 cm<sup>-1</sup>. In addition we find two triplets at about 95 and 40 cm<sup>-1</sup>, and a doublet near 30 cm<sup>-1</sup>.

The spectrum that we calculate for the Ce<sub>2</sub>F<sub>6</sub> dimer is very similar to that reported above for La<sub>2</sub>F<sub>6</sub>, except that the mode frequencies are shifted upward typically by about 3 cm<sup>-1</sup>. The available infrared spectral data on this matrix-isolated species do not, however, allow an extrapolation to the gas phase to be made [4].

Table 2. Geometrical parameters of dimers in their ground state (bond lengths in Å, bond angles in degrees). The indices T and B denote terminal and bonding fluorines.

|                                  | $r_{R-F^B}$ | $r_{R-F^T}$ | $\angle F^T-R-F^T$ | $\angle F^B-R-F^B$ | $\angle R_1-F^B-R_2$ |
|----------------------------------|-------------|-------------|--------------------|--------------------|----------------------|
| La <sub>2</sub> F <sub>6</sub> : | 2.34        | 2.13        | 114.3              | 72.0               | 108.0                |
| Ce <sub>2</sub> F <sub>6</sub> : | 2.33        | 2.12        | 114.2              | 72.2               | 107.8                |

#### 5. Conclusions

In summary, we have evaluated a simple ionic model for all the rare-earth trifluorides from the rather scanty experimental evidence which is available on the bond lengths of their gaseous monomers. As in previous work on the other rare-earth halides [11], our main attention has been on the model parameters (effective valence, ionic radius and electronic polarizability) of the rare-earth ions, for which we have proposed some simple and reasonable trends across the whole series of lanthanide trifluorides.

The main uses of our results should be in studies of the gaseous complexes formed by rare-earth trifluorides with the alkali and trivalent-metal fluorides, as well as in computer simulation studies of their melts. Particularly interesting data have become available from Raman scattering experiments on binary melts of lanthanide and potassium fluorides at various compositions [16]. These experiments indicate formation of RF<sub>6</sub> octahedra, which depending on composition may bind together by edge sharing.

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