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 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 PrF_3, GdF_3 and HoF_3 molecular monomers. All 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 La_2F_6 and Ce_2F_6 dimers, as a further test of the proposed model. – PACS 36.40.Wa (Charged clusters)

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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 D_{3h} symmetry exhibited by the Group-IIIA (Al, Ga, In) and Fe trihalides, most experimental work on rare-earth trifluorides indicates C_{3v} equilibrium geometries.

The strongest evidence comes from the infrared spectra of matrix-isolated RF_3 molecules and from electric dipole deflection experiments. The symmetric stretch ν_1 mode is infrared-active in addition to the other fundamental frequencies only in the C_{3v} configuration and has been observed in most RF_3 species from LaF_3 to LuF_3 [4, 5]. The electric deflection studies of most 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 - 92° 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

only for PrF_3, GdF_3, and 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 ν_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 agrement 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 PrF_3, GdF_3 and 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 La_2F_6 and Ce_2F_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 $\boldsymbol{r}_{ij}$ and of the dipole moments $\boldsymbol{p}_i$ carried by the ions. The form that we adopt for the function $U(\{\boldsymbol{r}_{ij}\}, \{\boldsymbol{p}_i\})$ is

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

$$+ U_{\text{pol}}^{\text{cl}}(\{\boldsymbol{r}_{ij}\}, \{\boldsymbol{p}_i\}) + U_{\text{shell}}(\{\boldsymbol{r}_{ij}\}, \{\boldsymbol{p}_i\}).$$

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]

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

where R_i and ρ_i are characteristic radii and hardness parameters for the ions and f has the standard value $f = 0.05\, e^2/\text{Å}^2$; 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_{shell} of the fluorines. The electrically induced dipoles are described by the electronic polarizabilities α_F and α_R, whereas a short-range α_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 ($R_F = 1.32$ Å, $\rho_F = 0.215$ Å, $C_F = 2.08$ eÅ$^{5/2}$, $\alpha_F = 0.88$ Å^3 and $\alpha_s = 0.48$ Å^3/e) as well as simple proportionality between R_R and ρ_R for metal ions ($R_R/\rho_R = 18.6$), the model involves for each rare-earth trifluoride three disposable parameters. These are the effective valence z_R, the radius

R_R and the electronic polarizability α_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 LaF_3 to LuF_3 from the data on the PrF_3, GdF_3 and 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 $R_R = (1.42 - 0.01\, n_{4f})$Å; 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 ± 0.1) and a constant value for the ratio α_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 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 PrF_3, GdF_3, and 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 RF_3 monomers (bond lengths in Å, bond angles in degrees and frequencies in 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_{R-F}	∠ F-R-F	ν_1	ν_2	ν_3	ν_4
LaF_3:	2.12	107.8	547	84	527	121
			540	82	510	125
CeF_3:	2.11	107.9	550	85	530	121
			549	80	519	115
PrF_3:	2.10	108.0	554	85	532	122
	2.091		542	86	458	99
NdF_3:	2.09	108.1	557	85	534	123
			557	80	535	115
PmF_3:	2.08	108.2	560	85	537	124
			(560)	(90)	(535)	(124)
SmF_3:	2.07	108.3	563	85	538	125
			(564)	92	508	123
EuF_3:	2.06	108.4	567	86	541	126
			572	90	544	120
GdF_3:	2.05	108.5	568	86	541	127
	2.053		583	95	552	130
TbF_3:	2.03	108.7	573	86	545	128
			580	97	554	131
DyF_3:	2.02	108.8	578	86	547	129
			(581)	(98)	(561)	(133)
HoF_3:	2.01	108.9	580	86	549	131
	2.007		585	102	569	120
ErF_3:	2.00	109.0	584	87	551	132
			(589)	(102)	(571)	(137)
TmF_3:	1.99	109.1	588	87	554	133
			(593)	(103)	(576)	(139)
YbF_3:	1.98	109.2	592	87	556	134
			597	100	579	144
$LuF3$:	1.97	109.3	595	87	558	135
			598	109	585	150

bond length show the same trend, but are larger than ours by a few hundredths of an Å. 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° in LaF_3 and the monomer is apparently found to be planar from DyF_3 onwards.

The other four columns in Table 1 report our calculated values for the vibrational frequencies of each monomer: the ν_1 symmetric stretch, the ν_2 out-of-plane bending, the ν_3 antisymmetric stretch, and the ν_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_2, Ar, and Ne matrices and carry an estimated uncertainty of up to ± 15 cm^{-1}. 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_2F_6 and Ce_2F_6 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_2F_6 dimer embedded in N_2, Ar, and Ne matrices is available from the work of Hastie et al. [4]. By extrapolation of these spectra they propose modes at 542 ± 8, 532 ± 8, 378 ± 6, 323 ± 8 and 166 ± 20 cm^{-1} for the isolated dimer in the gas phase. These correspond in our calculated spectra to a singlet at 536 cm^{-1}, a triplet near 524 cm^{-1}, and three doublets near 353, 300 and 149 cm^{-1}. In addition we find two triplets at about 95 and 40 cm^{-1}, and a doublet near 30 cm^{-1}.

The spectrum that we calculate for the Ce_2F_6 dimer is very similar to that reported above for La_2F_6, except that the mode frequencies are shifted upward typically by about 3 cm^{-1}. 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.

	$r_{R\text{-}F^B}$	$r_{R\text{-}F^T}$	$\angle\, F^T\text{-}R\text{-}F^T$	$\angle\, F^B\text{-}R\text{-}F^B$	$\angle\, R_1\text{-}F^B\text{-}R_2$
La_2F_6:	2.34	2.13	114.3	72.0	108.0
Ce_2F_6:	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_6 octahedra, which depending on composition may bind together by edge sharing.

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