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Force Constants and Fundamental Frequencies of the Rare Earth Trihalide Molecules

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Abstract

The effective nuclear charge model has been applied to the rare earth trihalides. A set of the effective nuclear charge values of the rare earth atoms has been evaluated from the bond stretch force constants obtained by normal coordinate analysis of the infrared spectra of the lanthanide trifluorides.

The force constants and the fundamental frequencies of all the lanthanide trihalides have been calculated by means of the effective nuclear charge model. The calculated results are in agreement with the experimental data. The results show that the most probable configuration of the lanthanide trihalides is pyramidal with C_{3v} symmetry, although the geometry of the lanthanide trifluoride molecules is very close to planar. It is also found that the frequency ν_2 (symmetric deformation) and the frequency ν_4 (antisymmetric deformation) will vary with the bond angle (X–Ln–X).

Introduction

Recently, there has been considerable interest in the rare earth trihalides. Some quantum chemical calculations have been performed to estimate whether there may be any covalency in the chemical bonding of the rare earth trihalides, and which geometry these molecules may possess: a planar geometry (D_{3h} symmetry) or a pyramidal geometry (C_{3v} symmetry) [1–4]. Some experimental data of the infrared spectra of the rare earth trihalides based on the matrix isolation technique have been published [5–10]. Also, calculation of the thermodynamic properties of the lanthanide trihalides by using the statistical–mechanical formula from the corresponding infrared spectra data has been reported [11].

The results of some quantum chemical calculations support the following conclusions: the lanthanide trihalide molecules possess a pyramidal configuration (C_{3v} symmetry); there is some covalency in the chemical bonding of the lanthanide trihalides.

However, results from normal coordinate analysis calculations for the infrared spectra of the rare earth trihalides are often in disagreement with each other. For example, Wesley and De Kock interpreted the infrared spectra of some rare earth trifluorides by a planar geometry (D_{3h} symmetry) [7], but Hastie *et al.* interpreted similar infrared spectra data by a pyramidal geometry (C_{3v} symmetry) [5, 6]. As for assignments of the vibrational fundamental frequencies, Wells *et al.* assigned the frequency ν_2 (symmetric deformation) to be higher than the frequency ν_4 (antisymmetric deformation) for the infrared spectra of neodymium trichloride, neodymium tribromide and neodymium triiodide [9]. However, Hastie *et al.* assigned the frequency ν_2 to be lower than the frequency ν_4 for the infrared spectra of the lanthanide trifluorides [6]. Moreover, based on the empirical relation between each fundamental frequency and the atomic number of the rare earth atom, Myers and Graves evaluated the vibrational fundamental frequencies for all the lanthanide trihalide molecules. The results they obtained showed that the frequency ν_2 was always lower than the frequency ν_4 for all the rare earth trihalides [11].

Recently, Ohwada has proposed the effective nuclear charge model to calculate the force constants and the fundamental frequencies for polyatomic molecules [12–14]. The model can be used to calculate and to predict the valence force constants and the fundamental frequencies for polyatomic molecules. The results calculated by using this model show that agreement between the experimental values and the calculated values is moderately good, sometimes very satisfactory. Although the method is an approximate one, we believe that the effective nuclear charge model can be useful for predicting approximate valence force constants and approximate fundamental frequencies, and especially so for predicting the trend in the force constants and the fundamental frequencies for the rare earth series.

To apply the effective nuclear charge model to the lanthanide trihalides we first proposed an empirical formula to evaluate the distances between the rare earth atoms and the halogen atoms in the lanthanide trihalides; then we carried out normal coordinate analysis calculations for the published infrared spectra data of all the rare earth trifluorides to obtain

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the force constants; consequently, we calculated the effective nuclear charge values of all the rare earth atoms from the bond stretch force constants (F_r) by using the corresponding equation of the effective nuclear charge model [13]. Therefore, we could calculate the valence force constants and the vibrational fundamental frequencies for all the rare earth trihalide molecules by means of the effective nuclear charge model and could compare the calculated force constants and calculated fundamental frequencies with experimental results. It was found that the most probable configuration of the lanthanide trihalide molecules was pyramidal geometry (C_{3v} symmetry), also that the frequency ν_2 (symmetric deformation) was lower than the frequency ν_4 (anti-symmetric deformation) if the lanthanide trihalide molecules possessed a very nearly planar geometry (as do lanthanide trifluoride molecules) if not the frequency ν_2 would be higher than the frequency ν_4.

Calculations

Hastie *et al.* have published detailed experimental data of the infrared spectra and some results of normal coordinate analysis calculations for some rare earth trifluorides [5, 6]. Myers and Graves have estimated the fundamental frequencies of all the lanthanide trihalides based on the linear relation between each fundamental frequency and the atomic number of the rare earth atoms, as well as on the ratios between the fundamental frequencies, such as ν_1/ν_3, ν_2/ν_3 and ν_4/ν_3 [11]. For the lanthanide trifluorides, the fundamental frequencies Myers and Graves calculated were in good agreement with the fundamental frequencies Hastie *et al.* observed (there were some misprints in Table 1 of Myers and Graves).

Therefore, we can perform the normal coordinate analysis for the infrared spectral data of the lanthanide trifluorides by means of Wilson's FG matrix method to estimate the valence force constants of these molecules. The FG matrix method will not be described because the method has been given in detail elsewhere [15].

In application of the effective nuclear charge model to the rare earth compounds, it is necessary to know the effective nuclear charge values of atoms and the geometric parameters of molecules. But, for lack of the effective nuclear charge of all the rare earth atoms, we must evaluate the necessary effective nuclear charge by using eqn. (10-a) of ref. [13] from the effective nuclear charge value of the fluorine atom and the molecular geometric parameters as well as the bond stretch force constants (F_r) of the lanthanide trifluoride molecules, which have been obtained from the normal coordinate analysis of the infrared spectra of the rare earth trifluorides. The effective nuclear charge value of the fluorine atom used in the calculations was 1.689 [13]. In this case, we can obtain a set of effective nuclear charge values for all the rare earth atoms.

The distances between the central rare earth atoms and the halogen atoms used in the calculations were evaluated by the following empirical formula proposed by us:

$$R = k(R(\mathrm{re}) - R(\mathrm{x}))$$

where R = distance between the rare earth atom and the halogen atom; $R(\mathrm{re})$ = crystal radius of the rare earth ion (RE^{3+}); $R(\mathrm{x})$ = crystal radius of the halogen ion (X^-); and k = constant.

For the lanthanide trifluorides, $k = 0.88$; for the lanthanide trichlorides, $k = 0.885$; for the lanthanide tribromides, $k = 0.89$; for the lanthanide triiodides, $k = 0.895$. In the calculations, values of $R(\mathrm{re})$ and $R(\mathrm{x})$ were from Pauling [16]. The calculated distances are given in Table I. As the results in Table I show, the calculated distances are in good agreement with some experimental values [11].

Because Ohwada did not give the equation to calculate the angle–angle interaction force constant in the effective nuclear charge model for the XY_3 molecule [13], we obtained the formula to calculate the angle–angle interaction force constant by using the procedure Ohwada described [12–14]. For XY_3 molecules, the bond stretch force constant F_r, the bond–bond interaction force constant F_{rr}, the angle deformation force constant F_α, and the angle–angle interaction force constant $F_{\alpha\alpha}$ can be evaluated by the following equations:

$$F_r = \frac{2Z_1{*}Z_2{*}}{R^3} + \frac{2Z_2{*}Z_2{*}}{q^3}(2s^2 - t^2) \tag{1}$$

$$F_{rr} = \frac{Z_2{*}Z_2{*}}{q^3}(2s^2 + t^2) \tag{2}$$

$$F_\alpha = \frac{Z_2{*}Z_2{*}}{q^3}(2t^2 + s^2) - \frac{Z_2{*}Z_2{*}}{q^3}(s^2 - t^2) \tag{3}$$

$$F_{\alpha\alpha} = \frac{Z_2{*}Z_2{*}}{q^3}t^2 \tag{4}$$

where $Z_1{*}$ = the effective nuclear charge value of the rare earth atom; $Z_2{*}$ = the effective nuclear charge value of the halogen atom; R = the distance between the central rare earth atom and the halogen atom; and q = the distance between the halogen atoms. Also $s = R(1 - \cos\phi)/q$; and $t = R\sin\phi/q$ where ϕ is the bond angle X–Ln–X.

We should point out that the equation used here to calculate the angle deformation force constant does not agree completely with the equation given by Ohwada [13]. In consideration of the angle–angle interaction, the equation to calculate the angle

TABLE I. The Calculated Distances between the Rare Earth Atoms and the Halogen Atoms in the Rare Earth Trihalides (A)[a]

	Ln–F	Ln–Cl	Ln–Br	Ln–I
La	2.209 (2.22)	2.620 (2.62)	2.759 (2.74)	2.962 (2.99)
Ce	2.174	2.584	2.723	2.927
Pr	2.156	2.567	2.706	2.909
Nd	2.147	2.558 (2.56)	2.697	2.900 (2.93)
Pm	2.130	2.540	2.679	2.882
Sm	2.112	2.522	2.661	2.864
Eu	2.103	2.513	2.652	2.855
Gd	2.094	2.505	2.643 (2.64)	2.846
Tb	2.077	2.487	2.626	2.828
Dy	2.068	2.478	2.617	2.819
Ho	2.050	2.460	2.599	2.801
Er	2.042	2.451	2.590	2.792
Tm	2.033	2.443	2.581	2.783
Yb	2.024	2.434	2.572	2.775
Lu	2.015	2.425 (2.42)	2.563 (2.56)	2.766

[a] The values in parentheses are the experimental values [11].

deformation force constant F_α should contain a correction term [14]. Besides, in the procedure to obtain the above-mentioned equations, some approximations were made.

By using the equations mentioned above, we can calculate the valence force constants and the fundamental frequencies for all the lanthanide trihalide molecules from the effective nuclear charge values of the rare earth atoms and the halogen atoms, as well as from the corresponding molecular geometric parameters (the bond lengths and the bond angles). The effective nuclear charge value of the halogen atom used in the calculations was 1.689 for the fluorine atom; 1.759 for the chlorine atom; 1.836 for the bromine atom; and 1.831 for the iodine atom [13].

Results and Discussion

The molecular geometry of the rare earth trihalides possesses either D_{3h} symmetry or C_{3v} symmetry. Four vibrational fundamental frequencies in the infrared spectra can be expected: the ν_1 (a_1) symmetric stretch; the ν_2 (a_1) symmetric deformation; the ν_3 (e) antisymmetric stretch; and the ν_4 (e) antisymmetric deformation. From the infrared spectral data, we can obtain the following valence force constants by means of Wilson's FG matrix method: F_r (the bond stretch); F_{rr} (the bond–bond interaction); F_α (the angle deformation); and $F_{\alpha\alpha}$ (the angle–angle interaction). In normal coordinate analysis calculations, we found that the bond–angle interaction force constant $F_{r\alpha}$ was very small and could be neglected, as Claeys and Van der Kelen have described [15]. Generally, the absolute values of the bond–angle interaction force constant $F_{r\alpha}$ were always smaller than 0.001 for all the lanthanide trifluorides.

From the experimental data of the infrared spectra presented by Hastie *et al.*, and the calculated fundamental frequencies reported by Myers and Graves, we carried out the calculations by means of Wilson's FG matrix method for the lanthanum trifluoride molecules with different bond angle values (F–La–F). The calculated results are shown in Table II.

As the results in Table II show, the bond stretch force constant F_r was rather insensitive to change of the bond angle. However, the angle deformation force constant F_α, and especially the angle–angle interaction force constant $F_{\alpha\alpha}$, were very sensitive to change of the bond angle. If the bond angle (F–La–F) were assumed to be larger than 117°, it meant that lanthanum trifluoride molecule should be rather flat or very close to a planar configuration and the calculated F_α and $F_{\alpha\alpha}$ seemed to be too large. However, if the bond angle (F–La–F) were assumed to be smaller than 110°, the calculated $F_{\alpha\alpha}$ seemed to be too small. Taking into account the results of some quantum chemical calculations [1, 3], we believe that the most probable configuration of the lanthanum trifluoride molecule may be pyramidal with C_{3v} symmetry, and that the bond angle (F–La–F) may have a value between 114° and 117°. Consequently, we performed normal coordinate analysis calculations for all the rare earth trifluoride molecules. In the calculations, the bond angle (F–Ln–F) was taken to be 117° for all the lanthanide trifluoride molecules. In Table III we summarize the calculated force constants. For comparison, the observed and calculated fundamental frequencies are included.

From the bond stretch force constants F_r in Table III, the effective nuclear charge values Z_1* of all the

TABLE II. The Valence Force Constants Calculated by Means of Wilson's FG Matrix Method for the Lanthanum Trifluoride Molecule with Different Bond Angle, ϕ (F–La–F)

ϕ (°)	Force constants (mdyn/Å)				Frequencies[a] (cm^{-1})			
	F_r	F_{rr}	F_α	$F_{\alpha\alpha}$	ν_1	ν_2	ν_3	ν_4
119.5	2.70	0.278	0.321	0.270	539.9	80.4	510.9	125.6
117	2.70	0.264	0.087	0.033	540.4	80.1	511.2	125.6
114	2.69	0.245	0.068	0.011	539.8	83.4	510.7	124.9
110	2.69	0.222	0.061	−0.001	540.5	82.7	511.2	125.3
105	2.68	0.193	0.059	−0.007	540.4	83.2	510.6	123.7
100	2.67	0.163	0.060	−0.011	540.1	83.3	510.6	123.5
95	2.67	0.131	0.062	−0.015	540.1	80.9	510.6	124.4
					(540)	(82)	(511)	(125)

[a] The frequencies in parentheses are the observed values [11].

TABLE III. The Force Constants Calculated by Means of Normal Coordinate Analysis and the Vibrational Fundamental Frequencies for the Lanthanide Trifluoride Molecules (C_{3v} symmetry)

	Frequencies[a] (cm^{-1})				Force constants (mdyn/Å)			
	ν_1	ν_2	ν_3	ν_4	F_r	F_{rr}	F_α	$F_{\alpha\alpha}$
LaF_3	540.4	80.1	511.2	125.6	2.70	0.264	0.087	0.033
	(540)	(82)	(511)	(125)				
CeF_3	549.2	83.8	519.3	114.6	2.79	0.272	0.086	0.041
	(549)	(86)	(519)	(115)				
PrF_3	552.6	84.3	524.6	120.7	2.84	0.268	0.090	0.040
	(552)	(86)	(525)	(121)				
NdF_3	558.7	84.2	534.8	118.1	2.94	0.256	0.089	0.041
	(557)	(84)	(536)	(118)				
PmF_3	559.9	88.1	534.8	124.0	2.95	0.259	0.098	0.045
	(560)	(90)	(535)	(124)				
SmF_3	564.5	90.8	539.8	125.0	3.01	0.258	0.103	0.049
	(565)	(92)	(541)	(126)				
EuF_3	568.3	91.6	542.9	129.5	3.05	0.262	0.107	0.049
	(570)	(92)	(544)	(130)				
GdF_3	573.8	95.1	551.2	135.8	3.14	0.252	0.117	0.053
	(573)	(97)	(552)	(136)				
TbF_3	576.4	95.8	554.7	130.3	3.18	0.249	0.115	0.056
	(577)	(97)	(556)	(131)				
DyF_3	580.5	97.9	559.8	132.4	3.24	0.249	0.12	0.059
	(581)	(98)	(561)	(133)				
HoF_3	584.7	99.9	565.0	134.4	3.30	0.241	0.129	0.064
	(585)	(100)	(566)	(135)				
ErF_3	588.2	101.3	569.2	136.4	3.35	0.241	0.129	0.064
	(589)	(102)	(571)	(137)				
TmF_3	592.3	102.9	574.4	139.4	3.41	0.238	0.134	0.066
	(593)	(103)	(576)	(139)				
YbF_3	596.3	104.5	579.1	140.3	3.47	0.235	0.138	0.069
	(597)	(105)	(581)	(140)				
LuF_3	600.3	106.5	584.4	142.3	3.53	0.232	0.143	0.072
	(601)	(107)	(586)	(142)				

[a] The frequencies in parentheses are from ref. 11.

TABLE IV. The Effective Nuclear Charge Values of the Rare Earth Atoms

Atom	Effective nuclear charge Z^*
La	3.333
Ce	3.277
Pr	3.250
Nd	3.332
Pm	3.256
Sm	3.237
Eu	3.238
Gd	3.298
Tb	3.254
Dy	3.275
Ho	3.246
Er	3.258
Tm	3.275
Yb	3.290
Lu	3.304

rare earth atoms in the lanthanide trifluorides have been evaluated by means of eqn. (1). The calculated effective nuclear charge values Z_1^* are given in Table IV. It should be noted that all the Z_1^* values are larger than 3.0. We must point out that the definition of Z^* in the effective nuclear charge model was different from that of the effective nuclear charge proposed by Slater.

Besides, we assumed that the effective nuclear charge value Z_1^* of each rare earth atom in the lanthanide trifluorides was close to that in the trichlorides, tribromides and triiodides. So, the effective nuclear charge Z_1^*, calculated from the rare earth trifluorides, will be used for all the rare earth trihalides. To check whether the result calculated by using the effective nuclear charge model is reasonable, we have evaluated the force constants and the fundamental frequencies for all the lanthanide trifluorides by using eqns. (1–4) mentioned above. The calculated results are listed in Table V.

TABLE V. The Force Constants and the Fundamental Frequencies of the Lanthanide Trifluoride Molecules Calculated by Using the Effective Nuclear Charge Model (the bond angle (F–Ln–F) was taken as 117°)

	Frequencies[a] (cm^{-1})				Force constants (mdyn/Å)			
	ν_1	ν_2	ν_3	ν_4	F_r	F_{rr}	F_α	$F_{\alpha\alpha}$
LaF_3	531.7 (540)	84.1 (82)	516.2 (511)	142.1 (125)	2.70	0.213	0.101	0.034
CeF_3	541.1 (549)	86.0 (86)	524.0 (519)	145.4 (115)	2.79	0.223	0.106	0.035
PrF_3	546.1 (552)	87.0 (86)	528.2 (525)	147.2 (121)	2.84	0.229	0.108	0.036
NdF_3	554.7 (557)	87.3 (84)	536.9 (536)	147.8 (118)	2.94	0.232	0.110	0.037
PmF_3	556.4 (560)	88.1 (90)	536.6 (535)	149.4 (124)	2.95	0.237	0.112	0.037
SmF_3	562.2 (565)	89.0 (92)	540.9 (541)	151.0 (126)	3.01	0.243	0.115	0.038
EuF_3	565.8 (570)	89.4 (92)	544.0 (544)	151.9 (130)	3.05	0.246	0.117	0.039
GdF_3	573.4 (573)	86.6 (97)	551.1 (556)	152.5 (136)	3.14	0.250	0.118	0.039
TbF_3	577.4 (577)	90.6 (97)	553.7 (556)	154.3 (131)	3.18	0.256	0.121	0.040
DyF_3	582.6 (581)	90.9 (98)	558.2 (561)	155.0 (133)	3.24	0.259	0.123	0.041
HoF_3	588.2 (585)	91.9 (100)	562.5 (566)	156.9 (135)	3.30	0.266	0.126	0.042
ErF_3	592.4 (589)	92.3 (102)	566.3 (571)	157.7 (137)	3.35	0.269	0.128	0.043
TmF_3	597.5 (593)	92.8 (103)	571.0 (576)	158.6 (139)	3.41	0.273	0.129	0.043

(continued)

TABLE V. *(continued)*

	Frequencies[a] (cm^{-1})				Force constants (mdyn/Å)			
	ν_1	ν_2	ν_3	ν_4	F_r	F_{rr}	F_α	$F_{\alpha\alpha}$
YbF_3	602.5	93.1	575.1	159.4	3.47	0.276	0.131	0.044
	(597)	(105)	(581)	(140)				
LuF_3	607.5	93.7	579.8	160.4	3.53	0.280	0.133	0.044
	(601)	(107)	(586)	(142)				

[a] The frequencies in parentheses are from ref. 11.

TABLE VI. The Force Constants and the Fundamental Frequencies Calculated by Using the Effective Nuclear Charge Model for the Neodymium Trichloride Molecule with Different Bond Angle, ϕ (Cl–Nd–Cl)

ϕ (°)	Force constants (mdyn/Å)				Frequencies (cm^{-1})			
	F_r	F_{rr}	F_α	$F_{\alpha\alpha}$	ν_1	ν_2	ν_3	ν_4
119.5	1.820	0.144	0.104	0.036	318.3	29.5	331.2	114.5
117	1.819	0.149	0.109	0.038	321.8	71.8	329.4	113.5
115	1.817	0.152	0.115	0.040	324.7	92.2	328.0	113.0
111	1.813	0.160	0.126	0.044	330.5	123.0	324.9	112.8
105	1.805	0.174	0.146	0.052	339.5	158.6	319.8	114.2
100	1.796	0.188	0.168	0.058	347.4	184.1	314.9	117.0
99.5	1.975	0.190	0.170	0.059	348.2	186.6	314.4	117.4
95	1.783	0.205	0.194	0.066	355.4	208.2	309.4	121.4

From the results in Tables III and V, we found that the calculated force constants and the calculated fundamental frequencies were in good agreement with the force constants obtained by means of normal coordinate analysis and with the fundamental frequencies observed in experiment. This shows that the effective nuclear charge model can be applied to the rare earth trihalide molecules.

The frequency ν_2 (symmetric deformation) reported by Hastie *et al.* was always lower than the frequency ν_4 (anti-symmetric deformation) in the lanthanide trifluorides. However, Wells *et al.* [9] believed that ν_2 was higher than ν_4 in the trichlorides, tribromides and triiodides of neodymium. Therefore, we carried out some calculations for the neodymium trichloride molecule with different bond angles (Cl–Nd–Cl) by using the effective nuclear charge model. The calculated results are given in Table VI. As the results in Table VI show, ν_2 would be higher than ν_4 if the bond angle (Cl–Nd–Cl) were equal to or smaller than 111°. However, ν_2 would be lower than ν_4, and be lower than 100 cm^{-1}, if the bond angle (Cl–Nd–Cl) were larger than 111°.

Wells *et al.* have reported in detail experimental data on the infrared spectra of vaporized neodymium trichlorides [9]. The experimental results show that not only were all the observed frequencies larger than 100 cm^{-1}, but also the frequency ν_2 was higher than the frequency ν_4 according to their assignment. Taking into account the relative intensities of the observed frequencies, we believe that the neodymium trichloride molecule might possess a pyramidal geometry, and the frequency ν_2 might be higher than the frequency ν_4.

To check the fundamental frequencies Myers and Graves calculated for the trichlorides, tribromides and triiodides of lanthanides, we performed normal coordinate analysis calculations for these molecules based on the data reported by Myers and Graves. In the calculations, the bond angle X–Ln–X (where X = Cl, Br and I) was assumed to be 111° for the trichlorides and 114° for the tribromides and the triiodides.

From the calculated results, we found that the calculated bond stretch force constant F_r in the trichloride molecule was always smaller than that in the tribromide molecule for the same rare earth. For example, $F_r(NdCl_3) = 1.82$ mdyne/Å; $F_r(NdBr_3) = 2.08$ mdyne/Å; and $F_r(NdI_3) = 1.43$ mdyne/Å. Besides, $F_r(NdF_3) = 2.94$ mdyne/Å (see Table III). This shows that $F_r(NdF_3) > F_r(NdBr_3) > F_r(NdCl_3) > F_r(NdI_3)$. It is very difficult to give a reasonable interpretation for this obviously anomalous trend because the results of some quantum chemical calculations have shown that the covalency in the chemical bonding of the lanthanide trihalides and the electron populations at the rare earth atoms regularly vary from the trifluoride, the trichloride and the tribromide to the triiodide. Therefore, we have to con-

TABLE VII. The Force Constants and the Fundamental Frequencies of the Lanthanide Trichloride Molecules Calculated by Using the Effective Nuclear Charge Model (the bond angle (Cl–Ln–Cl) was taken as 100°)

	Frequencies (cm^{-1})				Force constants (mdyn/Å)			
	ν_1	ν_2	ν_3	ν_4	F_r	F_{rr}	F_α	$F_{\alpha\alpha}$
$LaCl_3$	336.0	166.0	305.1	107.3	1.67	0.175	0.137	0.046
$CeCl_3$	340.7	169.2	308.6	109.4	1.72	0.183	0.143	0.048
$PrCl_3$	342.9	170.8	310.2	110.5	1.74	0.186	0.145	0.048
$NdCl_3$	347.4	170.9	314.9	110.9	1.79	0.188	0.147	0.049
$PmCl_3$	347.6	172.1	313.9	111.9	1.80	0.192	0.150	0.050
$SmCl_3$	350.0	173.3	315.6	112.9	1.83	0.196	0.153	0.051
$EuCl_3$	351.7	173.9	316.9	113.4	1.85	0.198	0.155	0.052
$GdCl_3$	355.1	173.7	320.4	113.7	1.89	0.200	0.157	0.052
$TbCl_3$	356.9	175.2	321.2	114.8	1.91	0.204	0.160	0.053
$DyCl_3$	359.2	175.5	323.3	115.2	1.94	0.207	0.162	0.054
$HoCl_3$	360.9	176.7	324.3	116.2	1.97	0.211	0.165	0.055
$ErCl_3$	363.8	177.6	326.8	116.9	2.00	0.214	0.167	0.056
$TmCl_3$	366.0	178.1	328.9	117.4	2.03	0.216	0.169	0.056
$YbCl_3$	368.0	178.4	330.7	117.8	2.06	0.218	0.171	0.057
$LuCl_3$	370.6	179.1	333.0	118.4	2.09	0.221	0.173	0.058

TABLE VIII. The Force Constants and the Fundamental Frequencies of the Lanthanide Tribromide Molecules Calculated by Using the Effective Nuclear Charge Model (the bond angle (Br–Ln–Br) was taken as 100°)

	Frequencies (cm^{-1})				Force constants (mdyn/Å)			
	ν_1	ν_2	ν_3	ν_4	F_r	F_{rr}	F_α	$F_{\alpha\alpha}$
$LaBr_3$	231.1	129.5	218.1	75.7	1.501	0.163	0.128	0.043
$CeBr_3$	233.9	131.8	220.2	77.1	1.538	0.170	0.133	0.044
$PrBr_3$	235.2	132.8	221.1	77.7	1.555	0.173	0.135	0.045
$NdBr_3$	237.8	132.6	224.0	77.9	1.606	0.175	0.137	0.046
$PmBr_3$	237.6	133.2	222.8	78.4	1.606	0.178	0.139	0.046
$SmBr_3$	238.8	133.7	223.4	79.0	1.630	0.182	0.142	0.047
$EuBr_3$	239.7	134.0	224.2	79.2	1.647	0.184	0.144	0.048
$GdBr_3$	241.6	133.5	226.0	79.3	1.690	0.186	0.145	0.048
$TbBr_3$	242.3	134.3	226.1	79.9	1.70	0.189	0.148	0.049
$DyBr_3$	243.6	134.2	227.1	80.1	1.73	0.191	0.150	0.050
$HoBr_3$	244.8	135.1	227.8	80.8	1.75	0.195	0.153	0.051
$ErBr_3$	246.1	135.2	228.9	81.0	1.78	0.197	0.154	0.051
$TmBr_3$	247.4	135.5	230.2	81.3	1.80	0.200	0.156	0.052
$YbBr_3$	248.4	135.4	230.9	81.5	1.83	0.202	0.158	0.053
$LuBr_3$	249.9	135.8	232.3	81.8	1.86	0.204	0.159	0.053

sider that, maybe, some fundamental frequencies calculated by Myers and Graves might be somewhat questionable.

The calculations of Myers and Graves were based on the following assumptions: ν_1/ν_3, ν_2/ν_3 and ν_4/ν_3 were assumed to have the same value for all the lanthanide trihalides LnX_3 (X = Cl, Br, I); the ν_3 ratios for $ScCl_3/ScBr_3$ and $ScCl_3/ScI_3$ were assumed to apply to all the LnX_3 molecules.

However, from the experimental data of the infrared spectra of the trichloride, tribromide and triiodide of neodymium published by Wells *et al.*, it was found that $\nu_3(NdCl_3/NdBr_3) = 1.59$ and $\nu_3(NdCl_3/NdI_3) = 2.17$ from the frequencies in Table II of ref. 9. But, it is known from the data of Selivanov *et al.* that $\nu_3(ScCl_3/ScBr_3) = 1.26$ and $\nu_3(ScCl_3/ScI_3) = 1.79$ [8]. Obviously, the differences between them were larger.

As for the ratios ν_2/ν_3 and ν_4/ν_3 for same lanthanide trihalides, we believe that they relate to the molecular geometry, because the frequencies ν_2 and ν_4 are very sensitive to the bond angle X–Ln–X.

We have carried out some calculations for the trichlorides, tribromides and triiodides of all the rare earth atoms by means of the effective nuclear charge model. The calculated results are summarized in Tables VII, VIII, and IX, respectively. The bond angle used in the calculations was 100°.

TABLE IX. The Force Constants and the Fundamental Frequencies of the Lanthanide Triiodide Molecules Calculated by Using the Effective Nuclear Charge Model (the bond angle (I–Ln–I) was taken as 100°)

	Frequencies (cm^{-1})				Force constants (mdyn/Å)			
	ν_1	ν_2	ν_3	ν_4	F_r	F_{rr}	F_α	$F_{\alpha\alpha}$
LaI_3	177.3	106.5	172.8	58.4	1.21	0.131	0.103	0.034
CeI_3	179.1	108.2	174.1	59.4	1.23	0.136	0.106	0.035
PrI_3	180.0	109.0	174.7	59.9	1.25	0.139	0.108	0.036
NdI_3	181.7	108.6	176.7	59.9	1.29	0.140	0.109	0.036
PmI_3	181.2	108.9	175.4	60.2	1.29	0.143	0.111	0.037
SmI_3	181.8	109.1	175.6	60.5	1.30	0.145	0.113	0.038
EuI_3	182.3	109.3	176.0	60.7	1.32	0.147	0.115	0.038
GdI_3	183.4	108.6	177.1	60.6	1.35	0.148	0.116	0.039
TbI_3	183.8	109.2	176.9	61.0	1.36	0.151	0.118	0.039
DyI_3	184.5	109.0	177.5	61.0	1.38	0.152	0.119	0.040
HoI_3	185.2	109.5	177.7	61.5	1.40	0.155	0.121	0.040
ErI_3	185.9	109.5	178.4	61.6	1.41	0.157	0.122	0.041
TmI_3	186.8	109.6	179.2	61.8	1.44	0.158	0.124	0.041
YbI_3	187.1	109.2	179.3	61.8	1.45	0.160	0.125	0.042
LuI_3	188.1	109.5	180.2	62.0	1.47	0.161	0.126	0.042

From the results reported in Tables VII, VIII, and IX, it can be found that the force constants and the fundamental frequencies gradually increase from La to Lu for the rare earth trihalides. The force constants F_r and F_{rr}, and the frequencies ν_1 and ν_3 gradually decrease from the trifluorides, trichlorides and tribromides to the triiodides for each rare earth element.

We should point out that the calculated fundamental frequencies are in agreement with the observed frequencies found in experiment. For example, Selivanov *et al.* have determined that the frequency ν_3 was 316, 320, 324 and 326 cm^{-1} for $LaCl_3$, $PrCl_3$, $NdCl_3$ and $GdCl_3$, respectively [8]. The calculated frequency ν_3 is 305, 310.2, 314.9 and 320.4 cm^{-1}, respectively. The largest deviation between the calculated and observed frequency ν_3 is 11.0 cm^{-1}. On comparing the calculated results with the experimental results of Wells *et al.*, we found that our results support the assignment in Table 2 of ref. 9, although they considered that the force constant $F_{\alpha\alpha}$ was significantly larger for $NdCl_3$.

Loktyushina and Mal'tsev have determined the frequencies in matrix with inert gases for some tribromides and triiodides of rare earths [10]. For the tribromides, the observed frequencies are: $\nu_3(NdBr_3) = 222$ cm^{-1} (Xe); $\nu_3(GdBr_3) = 238$ cm^{-1} (Xe); and $\nu_3(LuBr_3) = 231$ cm^{-1} (Xe), respectively. The calculated frequencies are: $\nu_3(NdBr_3) = 224$ cm^{-1}; $\nu_3(GdBr_3) = 226$ cm^{-1}; and $\nu_3(LuBr_3) = 232.3$ cm^{-1}, respectively. The largest deviation between the calculated and the observed values is 12 cm^{-1}. For the triiodides, the observed frequencies are: $\nu_3(NdI_3) = 181.5$ cm^{-1} (Xe); $\nu_3(GdI_3) = 183.5$ cm^{-1} (Xe); $\nu_3(HoI_3) = 185$ cm^{-1} (Xe); and $\nu_3(LuI_3) = 187$ cm^{-1} (Xe), respectively. The calculated frequencies are: $\nu_3(NdI_3) = 176.7$ cm^{-1}; $\nu_3(GdI_3) = 177.1$ cm^{-1}; $\nu_3(HoI_3) = 177.7$ cm^{-1}; and $\nu_3(LuI_3) = 180.2$ cm^{-1}, respectively. The largest deviation between the calculated and the observed values is 7.3 cm^{-1}. As mentioned above, the calculated frequencies were very close to the observed frequencies, especially for the lanthanide trifluorides. This demonstrates that our calculations are reasonable.

However, on transfering the effective nuclear charge values of the rare earth atoms calculated from the lanthanide trifluorides to other trihalides of the rare earths, maybe, some systematic errors would be included in the calculation of the force constants for the trichlorides, tribromides and triiodides. We feel that the bond stretch force constant F_r calculated for the lanthanide tribromides and triiodides might be somewhat larger, because the bond stretch force constant F_r mainly relates to the effective nuclear charge Z_1* of the rare earth atom.

We should point out that, unlike Ohwada, we obtained the effective nuclear charge values Z_1* for the rare earth atoms not from homonuclear diatomic molecules, but from rare earth compounds. This implies that the calculated effective nuclear charge values Z_1* include some corrections necessary when the effective nuclear charge value obtained from homonuclear diatomic molecule is used for a heteronuclear polyatomic molecule.

We found that the effective nuclear charge Z_1* of the neodymium atom calculated from the bond stretch force constant F_r obtained by normal coordinate analysis from the fundamental frequencies of the neodymium trichloride molecule reported by Wells *et al.* was very close to the value of Z_1* obtained from the neodymium trifluoride molecule.

However, it is certain that the difference between the electronegativities of the bonded atoms must affect the effective nuclear charge of the atom in heteronuclear polyatomic molecules. We believe that the calculated results may be improved if this effect is taken into account.

Conclusions

An empirical formula has been proposed to calculate the distances between the central rare earth atoms and the halogen atoms in lanthanide trihalide molecules. A set of the effective nuclear charge values of the reare earth atoms has been calculated from the bond stretch force constants obtained by using normal coordinate analysis for the infrared spectra data of lanthanide trifluorides.

The effective nuclear charge model has been used for the rare earth trihalides. The calculated fundamental frequencies are in agreement with the observed frequencies. The calculated results show that the lanthanide trihalide molecule is most likely a pyramidal molecule, even if the lanthanide trifluoride molecule is not strictly planar.

The ratio between the frequency ν_2 and the frequency ν_4 will change with decreasing bond angle (X–Ln–X). For the trichlorides, tribromides and triiodides of the rare earths, the frequency ν_2 (symmetric deformation) is higher than the frequency ν_4 (antisymmetric deformation). That shows that the most probable configuration of these molecules is pyramidal (C_{3v} symmetry).

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