# Ab Initio Studies on the Structures and Vibrational Frequencies of Rare Earth Fluorides $LnF_n$ (Ln = Er, Tm; $n$ = 1, 2, 3) and Their Positive Ions and an Assessment of Their Ionization and Dissociation Energies

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Hartree−Fock and second-order Møller−Plesset calculations are reported of the structural and vibrational parameters of some rare earth fluorides $LnF_n$ neutrals and $LnF_n^+$ ions, where Ln is erbium and thulium and $n = 1$, 2, and 3. Quasi-relativistic pseudopotentials developed by Dolg et al. were applied for a description of the core electrons of the lanthanide atoms. A planar $D_{3h}$ structure resulted from geometry optimization at both levels of calculation for the ground state of erbium and thulium trifluorides. The vertical and adiabatic ionization energies of $LnF_n^+$ are reported and Ln−F bond dissociation energies $D_0(LnF_{n-1}-F)$ evaluated. These quantities are compared to available experimental data.

## I. Introduction

Binary or ternary compounds of rare earth trifluorides and transition-metal oxides with perovskite structure exhibit good magnetic properties. Often a knowledge of the properties of individual components contributes essentially to understanding the fundamental relationship between geometry, bonding, and the chemical and physical properties of these magnetic materials. Rare earth fluorides are experimentally not well-characterized with respect to structural or vibrational parameters. Experimental structural data are known only for La and Nd trifluorides, but these parameters have been estimated for all lanthanide trihalide molecules in a systematic manner by Mayers et al.[1] Jia et al.[2] and Jia[3] proposed empirical relations for bond distances and bond length calculations, respectively, while an effective nuclear charge model has been applied for force constant evaluations. There have been two very recent experimental studies on the vaporization processes and the thermodynamic properties of dysprosyum trifluoride,[4] and of erbium and thulium trifluorides,[5] by means of Knudsen effusion mass spectrometry. The second work also included measurement of the stretching frequencies by matrix isolation infrared spectroscopy. According to these two studies it can be concluded that the electron impact ionization process of the $LnF_3$ molecule is accompanied by the following fragmentation pathway:

$$LnF_3 + e^- \rightarrow LnF_2^+ + F + 2e^- \quad (1)$$

$$\rightarrow LnF^+ + 2F + 2e^- \quad (2)$$

$$\rightarrow Ln^+ + 3F + 2e^- \quad (3)$$

Recent advances in pseudopotential methods[6] and the development of quasi-relativistic pseudopotentials with various core size for rare earth elements[7,8] make it possible to perform ab initio calculations of chemical systems containing these heavy elements. In our study, the HF and MP2 methods were employed in electronic structures and vibrational frequency calculations of erbium and thulium mono-, di-, and trifluorides and their positive ions. Further, the ionization energies and Ln−F bond dissociation energies of the relevant species were calculated. Results were compared to the estimated and individual experimental data to test if the quasi-relativistic pseudopotential[7,8] employed can reproduce known results and could be expected to make accurate preditions where experimental data are absent.

## II. Computational Details

Ab initio calculations were carried out using the GAUSSIAN 94 program[9] installed on an HP-735 workstation. The geometries of the relevant neutral and positive ion species were optimized at the Hartee−Fock (HF) level,[10] and the electron correlation energy was calculated by second-order Møller−Plesset perturbation theory (MP2).[10] The quasi-relativistic pseudopotentials of Dolg et al.[7,8] (in the following text designated as DSSP) were employed to describe the inner shells of individual lanthanide atoms. The pseudopotential comprised 11 and 10 electrons in the valence space for molecular and atomic calculations, respectively. Valence electrons were described by the basis set (7s6p5d/5s4p3d). For fluorine atoms the (4s4p/2s2p) basis set was used to describe seven electrons in the valence space and only $1s^2$ electrons were included in the core. Test calculations were carried out with the all-electron 6-31G(2d) basis set[11] for fluorine. These results will be denoted DZP in the tables. Vibrational frequencies were obtained from analytical calculation of the first energy derivatives and numerical second derivatives of the corresponding optimized structures and were used to provide estimates of zero-point vibrational energy (ZPE) corrections. The optimized structures of neutral species were used to carry out single-point calculations for the corresponding positive ions. The ionization energies were evaluated as the difference of total energies where the vertical ionization energy is defined by

$$IE_{vert} = E(\text{optimized neutral}) - E(\text{positive ion at the neutral equilibrium geometry}) \quad (4)$$

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**TABLE 1: Symmetries, Electronic States, Equilibrium Geometrical Parameters, Total Energies, and Zero-Point Vibrational Energies of Erbium Species**

| species | symmetry | el. state | method | $R$(Er−F) (Å) | ∠(F−Er−F) (deg) | energy (au) | ZPE (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| $ErF_3$ | $D_{3h}$ | $^1A_1'$ | HF | 2.042 | 120.0 | −109.979 434 | 12.0 |
| | | | HF(DZP) | 2.009 | 120.0 | −336.370 827 | 12.6 |
| | | | MP2 | 2.061 | 120.0 | −110.519 261 | 11.5 |
| | | | MP2(DZP) | 2.012 | 120.0 | −337.189 287 | 12.2 |
| | | | SCF[a] | 2.010 | ∼117 | | |
| | | | estd[b] | 2.07 | | | |
| | | | estd[c] | 2.042 | 114−117 | | |
| $ErF_2$ | $C_{2v}$ | $^2A_1$ | HF | 2.030 | 121.3 | −85.902 415 | 7.3 |
| | | | HF(DZP) | 1.985 | 116.9 | −236.831 782 | 8.0 |
| | | | MP2 | 2.046 | 122.0 | −86.317 011 | 7.0 |
| | | | MP2(DZP) | 1.984 | 116.7 | −237.434 410 | 7.9 |
| | | | estd[d] | 1.998 | 112 | | |
| $ErF_2^+$ | $C_{2v}$ | $^1A_1$ | HF | 1.965 | 119.0 | −85.653 637 | 8.4 |
| | | | HF(DZP) | 1.930 | 116.3 | −236.601 223 | 9.0 |
| | | | MP2 | 1.979 | 113.8 | −86.063 116 | 8.1 |
| | | | MP2(DZP) | 1.932 | 111.6 | −237.197 335 | 8.9 |
| ErF | $C_{\infty v}$ | $^1\Sigma_g$ | HF | 2.011 | | −61.826 717 | 3.4 |
| | | | HF(DZP) | 1.960 | | −137.292 894 | 3.7 |
| | | | MP2 | 2.024 | | −62.138 408 | 3.2 |
| | | | MP2(DZP) | 1.954 | | −137.700 009 | 3.7 |
| | | | SCF[e] | 2.029 | | | |
| $ErF^+$ | $C_{\infty v}$ | $^2\Sigma_g$ | HF | 1.948 | | −61.604 157 | 3.9 |
| | | | HF(DZP) | 1.907 | | −137.079 222 | 4.2 |
| | | | MP2 | 1.958 | | −61.887 807 | 3.8 |
| | | | MP2(DZP) | 1.905 | | −137.457 705 | 4.2 |

[a] Ref 12. [b] Ref 1. [c] Ref 2. [d] Ref 3. [e] Ref 14.

and the adiabatic ionization energy by

$$\mathrm{IE}_{\mathrm{ad}} = E(\text{optimized neutral}) - E(\text{optimized positive ion}) \tag{5}$$

The bond dissociation energies were calculated from the relation

$$D(\mathrm{LnF}_{n-1}{-}\mathrm{F}) = E_{\mathrm{LnF}_n}(\text{optimized neutral}) - E_{\mathrm{F}} \tag{6}$$

Already mentioned above, two sets of pseudopotentials were used in the calculations. For ground states of the lanthanide atoms and atomic ions, the energies were derived by pseudopotentials which treat 10 valence electrons explicitly. Structural and vibrational parameters and total energies of trifluorides, difluorides, and monofluorides and their positive ions were calculated by 11 valence electron pseudopotentials. As far as the molecular parameters of all these species are concerned, an 11-electron pseudopotential is appropriate. The evaluation the Ln−F bond dissociation energies also requires 10-electron pseudopotential calculations to take into account different Ln subconfigurations in the monofluoride and in the atomic ground state. Furthermore, it should be noted that the ionization energies were derived from the total energies of neutral halide species and the corresponding positive ions with the same 4f subconfiguration on Ln (i.e., 11-electron pseudopotentials), and thus the calculated ionization energies are related to ionization from halogen p-like orbitals. Here, we could mention the study of Ruščić et al.,[12] who showed that the energies of 4f-orbital ionization are quite close to those of the halogen valence orbitals for most of the lanthanide trihalides, in which the 4f-like ionizations have lower energies.

## III. Results and Discussion

**A. Geometry and Total Energies.** The equilibrium geometries of the ground states of neutral ErF$_n$ species and their positive ions at both levels of calculation are given in Table 1. Point groups, electronic states, calculated total energies, and zero-point vibrational energies of each species are also presented. For comparison, the geometrical parameters from other works are included if available. Geometrical optimizations of the $ErF_3$ molecule were performed for $C_{3v}$ and $D_{3h}$ symmetries. It should be noted that the optimization procedure starting with $C_1$ symmetry of the trifluoride molecule proceeded to the $D_{3h}$ symmetry structure. The Er−F bond length for planar and pyramidal structures differs by only 0.001 Å at the HF and at MP2 levels, but MP2 bond lengths are 0.02 Å longer than HF values. The HF bond length is in excellent agreement with the value of 2.042 Å estimated from the emirical formula proposed by Jia et al.,[2] while the SCF value reported by Dolg et al.[13] is 0.03 Å lower. The energy differences between the $C_{3v}$ and $D_{3h}$ structures are less than 0.001 eV at the HF and MP2 levels of calculation. The F−Er−F bond angles are 120° in both cases, which is close to an estimated value of 117° in the literature.[2] In the $C_{3v}$ structure the Er atom is 0.001 Å above the plane of the fluorine atoms. Thus, the convergent results of all calculated parameters evidently indicate that the deviations obtained are only a consequence of gradient tolerance in the optimization process. The ground state of $ErF_2$ has bond lengths that are shorter by 0.012 and 0.015 Å at the HF and MP2 levels, respectively, compared to the planar structure of $ErF_3$. Here, the empirical value reported by Jia[3] is shorter by 0.032 and 0.048 Å than our bond length, and the bond angle differs by ∼10°. The Er−F bond length of $ErF_2^+$ is significantly less than that of the neutral structure at both levels of calculation. The bond angle decreases by 2° and 8° at the HF and MP2 levels, respectively. The bond lengths for monofluoride are 0.019 and 0.022 Å smaller than for difluoride. Our MP2 bond length is in reasonable agreement with the value of 2.029 Å derived from the SCF calculation of Dolg et al.[7] Again, the bond lengths for positive ions are significantly lower than that of the neutral structure at both levels of calculation.

The optimized geometrical parameters of the ground states of neutral TmF$_n$ species and their positive ions at the HF and MP2 levels of calculation are presented in Table 2, together

**TABLE 2: Symmetries, Electronic States, Equilibrium Geometrical Parameters, Total Energies, and Zero-Point Vibrational Energies of Thulium Species**

| species | symmetry | el. state | method | $R$(Tm−F) (Å) | ∠(F−Tm−F) (deg) | energy (au) | ZPE (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| $TmF_3$ | $D_{3h}$ | $^1A_1'$ | HF | 2.030 | 120.0 | −110.561 369 | 12.2 |
| | | | HF(DZP) | 1.999 | 120.0 | −336.953 450 | 12.7 |
| | | | MP2 | 2.051 | 120.0 | −111.105 659 | 11.6 |
| | | | MP2(DZP) | 2.003 | 120.0 | −337.775 874 | 12.3 |
| | | | SCF[a] | 1.999 | ∼117 | | |
| | | | estd[b] | 2.05 | | | |
| | | | estd[c] | 2.033 | 114−117 | | |
| $TmF_2$ | $C_{2v}$ | $^2A_1$ | HF | 2.021 | 121.8 | −86.484 835 | 7.4 |
| | | | HF(DZP) | 1.976 | 117.5 | −237.414 392 | 8.0 |
| | | | MP2 | 2.036 | 123.1 | −86.903 839 | 7.1 |
| | | | MP2(DZP) | 1.976 | 117.4 | −238.021 057 | 7.9 |
| | | | estd[d] | 1.986 | 113 | | |
| $TmF_2^+$ | $C_{2v}$ | $^1A_1$ | HF | 1.956 | 119.8 | −86.232 967 | 8.4 |
| | | | HF(DZP) | 1.921 | 117.0 | −237.180 780 | 9.0 |
| | | | MP2 | 1.970 | 114.3 | −86.646 672 | 8.2 |
| | | | MP2(DZP) | 1.924 | 112.3 | −237.780 716 | 8.9 |
| TmF | $C_{\infty v}$ | $^1\Sigma_g$ | HF | 2.004 | | −62.411 090 | 3.4 |
| | | | HF(DZP) | 1.953 | | −137.877 199 | 3.7 |
| | | | MP2 | 2.018 | | −62.727 353 | 3.2 |
| | | | MP2(DZP) | 1.948 | | −138.288 719 | 3.7 |
| | | | SCF[e] | 2.020 | | | |
| $TmF^+$ | $C_{\infty v}$ | $^2\Sigma_g$ | HF | 1.940 | | −62.185 689 | 3.9 |
| | | | HF(DZP) | 1.899 | | −137.660 752 | 4.2 |
| | | | MP2 | 1.951 | | −62.473 700 | 3.7 |
| | | | MP2(DZP) | 1.897 | | −138.043 342 | 4.2 |

[a] Ref 12. [b] Ref 1. [c] Ref 2. [d] Ref 3. [e] Ref 14.

with point groups, electronic states, total energies, and zero-point vibrational energies. Available structural parameters from other works are also included in the table. The predicted bond lengths for $TmF_3$ of $C_{3v}$ and $D_{3h}$ symmetries are almost exactly the same, i.e., 2.030 and 2.051 Å at the HF and MP2 levels, respectively. In the pyramidal structure the Tm atom is located 0.001 Å above the plane of the fluorine atoms, and the energy difference of ∼0.001 eV between two structures was found. As in the case of $ErF_3$, these deviations originated in a gradient tolerance, and hence, a planar structure of $TmF_3$ is favored. These findings accord well with the MCSCF and HF study reported by Cundari et al.[15] In this context, it should be stressed that in our calculations a planar structure resulted from an optimization process started with $C_1$ symmetry, in contrast to the cited study where 3-fold molecular symmetry was assumed. The experimentally based empirical estimated bond length of Meyers and Graves[1] coincides with our MP2 values, while the HF bond length is quite close to that of Jia and Zhang.[2] The smallest bond length, 1.999 Å, was given by the SCF calculation reported by Dolg et al.[13] The Tm−F bond length of $TmF_2$ is slightly shorter than that of the trifluoride and amounts to 2.021 Å at the HF level and 2.036 Å at the MP2 level of calculation. Our theoretical bond lengths and bond angles are again above the estimated values obtained by Jia.[3] However, for $TmF_2^+$ the HF and MP2 levels of theory predict bond lengths of 1.956 and 1.970 Å, respectively. The HF bond angle decreases by only 2°, while the MP2 value is 9° lower in comparison with the neutral $TmF_2$ structure. The equilibrium bond length of TmF is approximately 0.02 Å lower than that of $TmF_2$, and the MP2 bond length is comparable with Dolg et al.'s SCF result.[7] A further decrease in bond length is observed going from the neutral to the positive ion monofloride molecule. In summary, an inspection of Tables 1 and 2 reveals that the Ln−F bond length decreases from $LnF_3$ to LnF, on average decreasing by 0.02 Å between subsequent fluorides. The difference of bond lengths in $ErF_2^+$ and $ErF^+$ is also 0.02 Å. The bond lengths of $ErF_2^+$ and $ErF^+$ are about 0.06 Å lower compared to their neutral molecules. The same trend is evident for thulium species. The bond angle in $LnF_2$ decreases by only a few degrees upon ionization.

A study of the $LnF_3^+$ structure did not lead to a significant minimum on the potential energy surface either in $D_{3h}$ or $C_{3v}$ symmetries.

It is evident from Tables 1 and 2 that the bond lengths of studied $LnF_n$ molecules and ions are shorter by 0.04 and 0.06 Å on average at the HF and $MP_2$ levels, respectively, if the 6-31G(2d) basis set for the fluorine atom was used in the calculations. Otherwise, the trends in variation of the structural parameters are consistent with those where the lanthanide and fluorine atoms were treated by pseudopotentials and are not further discussed.

Table 3 lists the relevant total single-point energies of ground-state positive ions calculated at equilibrium geometries of neutral species by removing an electron. The electronic states of $LnF_2^+$ and $LnF^+$ are identical with those of the optimized structure (shown in Tables 1 and 2), while the electronic structure of $LnF_3^+$ could not be determined due to the partially filled degenerate orbitals. Total energies of atomic erbium, thulium, and fluorine are also evaluated. These data were necessary for the vertical ionization and bond dissociation energy computations discussed below.

**B. Harmonic Vibrational Frequencies.** All optimized $LnF_n$ and $LnF_n^+$ structures were confirmed to be minima by the evaluation of their harmonic vibrational frequencies at both methods. These frequencies for Er species are summarized in Table 4, and those of Tm species in Table 5. Vibrational frequencies of the $LnF_3$ molecule of either the $C_{3v}$ or $D_{3h}$ point group are as follows: symmetric stretching ($\nu_s$), doubly degenerate asymmetric stretching ($\nu_{a_1}$, $\nu_{a_2}$), doubly degenerate asymmetric deformation ($\delta_{a_1}$, $\delta_{a_2}$), and out-of-plane bending ($\pi$). We can see that there are practically no differences between the HF frequencies of the two symmetry groups. MP2 stretching frequencies of the $ErF_3$ molecule are lower by 25 cm$^{-1}$, and deformation and out-of-plane bending frequencies by only 5

**TABLE 3: Total Energies of Positive Ions at Neutral Equilibrium Geometry and Atoms**

| | energy (au) | | | | | |
|---|---|---|---|---|---|---|
| | $ErF_3^+$ | $ErF_2^+$ | $ErF^+$ | $Er^+$ | Er | F |
| HF | −109.524 285 | −85.650 000 | −61.602 437 | −31.359 491 | −31.542 561 | −23.910 415 |
| HF(DZP) | −335.931 633 | −236.598 098 | −137.077 757 | | | −99.366 165 |
| MP2 | −110.012 767 | −86.059 421 | −61.886 025 | −31.503 878 | −31.712 951 | −23.983 204 |
| MP2(DZP) | −336.685 851 | −237.194 611 | −137.456 467 | | | −99.518 971 |

| | energy (au) | | | | |
|---|---|---|---|---|---|
| | $TmF_3^+$ | $TmF_2^+$ | $TmF^+$ | $Tm^+$ | Tm |
| HF | −110.104 237 | −86.229 330 | −62.183 911 | −31.859 825 | −32.044 946 |
| HF(DZP) | −336.512 182 | −237.177 605 | −137.659 238 | | |
| MP2 | −110.597 288 | −86.643 003 | −62.471 885 | −32.001 692 | −32.213 356 |
| MP2(DZP) | −337.270 382 | −237.777 952 | −138.042 054 | | |

**TABLE 4: Vibrational Frequencies ($cm^{-1}$) of Erbium Species**

| | | | frequency | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $\nu_s$ | $\nu_{a_1}$ | $\nu_{a_2}$ | $\delta_{a_1}$ | $\delta_{a_2}$ | $\pi$ |
| $ErF_3$ | $D_{3h}$ | HF | 560 | 555 | 554 | 136 | 132 | 80 |
| | | HF(DZP) | 601 | 590 | 590 | 140 | 140 | 46 |
| | | MP2 | 537 | 529 | 529 | 131 | 127 | 77 |
| | | MP2(DZP) | 592 | 583 | 583 | 134 | 134 | 22 |
| | | estd[a] | 592 | 566 | | 158 | | 92 |
| | | estd[b] | 589 | 571 | | 137 | | 102 |
| | | exptl[c] | 561 | 539 | | | | |
| $ErF_2$ | | HF | 560 | 549 | | 120 | | |
| | | HF(DZP) | 614 | 597 | | 123 | | |
| | | MP2 | 540 | 525 | | 112 | | |
| | | MP2(DZP) | 611 | 592 | | 114 | | |
| | | estd[d] | 457 | 437 | | 166 | | |
| $ErF_2^+$ | | HF | 643 | 631 | | 132 | | |
| | | HF(DZP) | 690 | 673 | | 137 | | |
| | | MP2 | 621 | 605 | | 134 | | |
| | | MP2(DZP) | 682 | 663 | | 140 | | |
| ErF | | HF | 562 | | | | | |
| | | HF(DZP) | 623 | | | | | |
| | | MP2 | 541 | | | | | |
| | | MP2(DZP) | 624 | | | | | |
| | | CI(SD)[e] | 545 | | | | | |
| $ErF^+$ | | HF | 648 | | | | | |
| | | HF(DZP) | 702 | | | | | |
| | | MP2 | 631 | | | | | |
| | | MP2(DZP) | 698 | | | | | |

[a] Ref 2. [b] Ref 1. [c] Ref 5. [d] Ref 3. [e] Ref 7.

**TABLE 5: Vibrational Frequencies ($cm^{-1}$) of Thulium Species**

| | | | frequency | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $\nu_s$ | $\nu_{a_1}$ | $\nu_{a_2}$ | $\delta_{a_1}$ | $\delta_{a_2}$ | $\pi$ |
| $TmF_3$ | $D_{3h}$ | HF | 565 | 559 | 559 | 138 | 134 | 84 |
| | | HF(DZP) | 604 | 593 | 593 | 140 | 140 | 51 |
| | | MP2 | 540 | 533 | 533 | 132 | 127 | 80 |
| | | MP2(DZP) | 594 | 586 | 586 | 134 | 134 | 31 |
| | | estd[a] | 598 | 571 | | 159 | | 93 |
| | | estd[b] | 593 | 576 | | 139 | | 103 |
| | | expl[c] | 566 | 545 | | | | |
| $TmF_2$ | | HF | 564 | 553 | | 121 | | |
| | | HF(DZP) | 616 | 598 | | 123 | | |
| | | MP2 | 543 | 530 | | 112 | | |
| | | MP2(DZP) | 611 | 593 | | 113 | | |
| | | estd[d] | 462 | 442 | | 166 | | |
| $TmF_2^+$ | | HF | 645 | 634 | | 131 | | |
| | | HF(DZP) | 693 | 675 | | 136 | | |
| | | MP2 | 623 | 608 | | 133 | | |
| | | MP2(DZP) | 683 | 665 | | 140 | | |
| TmF | | HF | 561 | | | | | |
| | | HF(DZP) | 623 | | | | | |
| | | MP2 | 538 | | | | | |
| | | MP2(DZP) | 622 | | | | | |
| | | CI(SD)[e] | 544 | | | | | |
| $TmF^+$ | | HF | 646 | | | | | |
| | | HF(DZP) | 702 | | | | | |
| | | MP2 | 628 | | | | | |
| | | MP2(DZP) | 698 | | | | | |

[a] Ref 2. [b] Ref 1. [c] Ref 5. [d] Ref 3. [e] Fef 7.

and 3 $cm^{-1}$, respectively. The estimated frequency data from the literature[1,2] are higher compared with our HF and MP2 values, and stretching and deformation frequencies on average by 4 and 10%, respectively. Experimentally only stretching frequencies have been reported.[5] The symmetric stretching frequency, 561 $cm^{-1}$, coincides with our HF values, but the asymmetric one, 539 $cm^{-1}$, lies between the corresponding HF and MP2 results. The symmetric stretching frequency of the $ErF_2$ molecule remains the same as that of $ErF_3$, while its asymmetric vibration is hardly lower and the deformation frequency increases by about 20 $cm^{-1}$. In previous work,[3] estimated asymmetric stretching and deformation frequencies are under- and overestimated, respectively. The MP2 frequency of TmF is shifted by 4 $cm^{-1}$ compared with CI(SD) frequency reported by Dolg et al.[7]

From the calculated results for Tm fluorides, we found that their behavior and tendencies are similar to those of Er fluorides. All but one of the frequencies of Tm fluorides were higher than those of Er fluorides; however, these differences did not exceed 5 $cm^{-1}$. This is true also for the experimental stretching frequencies of the trifluoride measured by means of matrix isolation infrared spectroscopy.[5]

For illustration, Figure 1 displays individual HF normal modes of the $TmF_3$ molecule. Arrows in the figure represent core-sponding eigenvectors.

The calculated vibrational spectral features of $ErF_3$ and $TmF_3$ are in satisfactory agreement with the available experimental data. A small deviation of the vibrational frequencies determined at the HF and MP2 levels using the pseudopotential proposed by Dolg et al. suggests that the HF level is sufficient for frequency calculations for lanthanide trifluorides, regardless of the well-known fact that HF frequencies are generally 10−15% higher than the observed fundamental vibrational frequencies.[16] Finally, it is noted that, using the 6-31G(2d) basis set for fluorine, the calculated symmetric stretching frequencies of $LnF_n$ are 60 $cm^{-1}$ higher on average. The asymmetric stretching and deformation frequencies of tri- and difluorides increase by 50 and 4 $cm^{-1}$, respectively. The most pronounced difference is found in the calculated frequency associated with the out-of-plane mode (∼50% on average).

**C. Ionization Energies.** The calculated ionization energies for adiabatic and vertical transitions of Er and Tm fluorides and both atoms are quoted in Table 6. The values were corrected for zero-point vibrational energy. Also listed are some

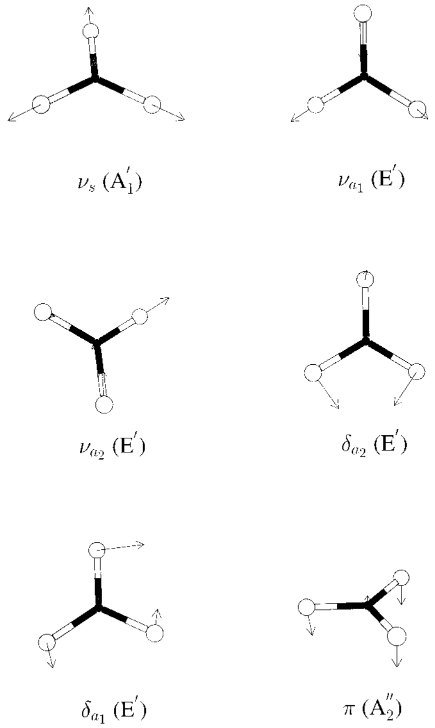

**Figure 1.** 1. Normal modes of vibration of the $TmF_3$ molecule.

experimental results available in the literature.[17,18] In the case of the trifluorides only vertical ionization energies were presented. The calculated ionization energies for $ErF_3$ and $TmF_3$ are equal, while the MP2 values are rather higher, by 1.4 eV. Ruščić et al.[12] utilized the $X_\alpha$ method to calculate the transition-state orbital energies of selected lanthanide trihalides. They reported valence band ionization energies for $ErF_3$ extending from 12.76 to 13.73 eV and 14.04 to 14.44 eV for the ionization process from 4f erbium-based molecular orbitals and from halogen-based molecular orbitals, respectively. The ionization energies calculated in this work might be compared with the latter, while the pseudopotential used is not suitable for evaluation of metal-based ionization. Our MP2 values of 13.8 and 13.7 eV lie near this range. The analysis of net atomic charges from Mulliken population analysis confirms the evolution of an electron from halogen atoms. For the difluorides and monofluorides the adiabatic ionization energies are only 0.1 eV lower than the vertical values where a difference exists. Our MP2 adiabatic ionization enegy of $ErF_2$ agrees quite well with the experimental value, and the HF value is only 0.1 eV lower. For ErF, the experimental result is closer to the HF values and the MP2 ionization energy is 0.5 eV higher. We can see that the calculated ionization energy of $TmF_2$ increases by 0.1 eV with respect to $ErF_2$, but for monofluoride no difference exists at the HF level. The ionization energy of Er and Tm atoms at the MP2 level approaches the experimental values, but the HF values are rather lower. The ionization energies of studied species predicted by the 6-31G(2d) basis set are generally 0.2−0.6 eV lower than those predicted using the pseudopotential for the fluorine atom.

It can be concluded that the calculated ionization energies of $ErF_2$, ErF, $TmF_2$, TmF, and the two atoms are consistent with experimental data. The lack of experimental data for the gaseous trifluorides did not allow checking of the calculated values.

As stated above, $ErF_3^+$ and $TmF_3^+$ could not be found as minima in the framework of $D_{3h}$ or $C_{3v}$ symmetries. Two or three imaginary frequencies resulted when frequencies were calculated for the positive ion at equilibrium geometries of the neutral species. Geometrical optimization for both trifluoride positive ions was sucessful if the molecular symmetry was reduced. Starting from geometry of $C_1$ symmetry, the minimization of all variables results in $C_{2v}$ symmetry. In this case one of the Ln−F bonds is considerably elongated (by ~0.7 Å), and also this structure possesses imaginary frequencies. This indicates that positive trifluoride ions are not stable, which is in accordance with experimental findings.[5,17,18]

**D. Bond Dissociation and Atomization Energies.** The energies for dissociation of the fluorine atom from $LnF_n$, where $n = 1, 2, 3$, are given in Table 7. Note that these neutral bond dissociation energies are $D_0$ values. We evaluated the dissociation energies for vertical and adiabatic processes and found that the two values are in most cases equal. Therefore, the values in the table are regarded as the energy differences of the optimized structures, corrected for zero-point vibrational energy. The Ln−F dissociation energies were derived from dissociation energies of corresponding the Ln subconfiguration of monofluorides with respect to the separated neutral atoms and corrected for the energy separation between the atomic subconfiguration on Ln[20] taken from experimental data.[21]

Immediately we observed that HF and MP2 bond dissociation energies differ considerably, but the differences between dissociation energies of identical bonds for Er and Tm species are insignificant. MP2 values for the dissociation of one Ln−F bond from the trifluorides and difluorides are ~150 and ~80 kJ $mol^{-1}$, respectively, higher than the corresponding HF values, whereas for the monofluorides these difference amounted to 100 kJ $mol^{-1}$. The $D_0$(LnF−F) bond dissociation energy is a little lower than $D_0$($LnF_2$−F), while $D_0$(Er−F) is rather higher with respect to $D_0$($LnF_2$−F) for both levels of calculation. The agreement of calculated data with that of other data is mixed. The dissociation energies of 491 and 426 kJ $mol^{-1}$ for ErF and TmF, respectively, calculated by Dolg et al.[7] at the CI(SD) level including Davidson's correction approach our values calculated at HF levels of approximation. In column *b* we list the bond dissociation energy derived from the appearance potentials of the relevant ions[5] resulting from the fragmentation pathway mentioned in the Introduction. We see that they are closer to our MP2 values. The values of dissociation energies quoted in column *c* and *d* were derived from gaseous equilibrium studies carried out by mass spectrometry.[17,18] For all fluorides they can be compared with our MP2 dissociation energies.

Finally, the atomization energies of the difluorides and trifluorides of Er and Tm were evaluated. The results, together with available theoretical and experimental data, are summarized in Table 8. Again, the values obtained at the HF level are lower than the corresponding MP2 values. An inspection of the table reveals that our MP2 atomization energies are in good agreement with the work of Zmbov et al.[17] for $ErF_3$ and $ErF_2$ and with the experimental atomization energies reported by Kleinschmidt et al.[18] for $TmF_3$.

## IV. Concluding Remarks

In this article, we report a study on the structure and vibrational parameters of erbium and thulium mono-, di-, and trifluorides and their positive ions where quasi-relativistic pseudopotentials developed by the Stuttgart group were applied in calculations for atomic descriptions. We examined the structures of $ErF_3$ and $TmF_3$ in $C_{3v}$ and $D_{3h}$ symmetries. The present ab initio results indicate that these molecules assume a planar configuration. The Ln−F bond length decreases going

**TABLE 6: Adiabatic and Vertical Ionization Energies (eV)**

| | method | $IE_{ad}$ | $IE_{vert}$ | | method | $IE_{ad}$ | $IE_{vert}$ |
|---|---|---|---|---|---|---|---|
| $ErF_3$ | HF | | 12.4 | $TmF_3$ | HF | | 12.4 |
| | HF (DZP) | | 12.0 | | HF (DZP) | | 12.0 |
| | MP2 | | 13.8 | | MP2 | | 13.8 |
| | MP2(DZP) | | 13.7 | | MP2(DZP) | | 13.8 |
| $ErF_2$ | HF | 6.8 | 6.9 | $TmF_2$ | HF | 6.9 | 7.0 |
| | HF (DZP) | 6.3 | 6.4 | | HF (DZP) | 6.4 | 6.4 |
| | MP2 | 6.9 | 7.0 | | MP2 | 7.0 | 7.1 |
| | MP2(DZP) | 6.6 | 6.5 | | MP2(DZP) | 6.5 | 6.6 |
| | exptl[a] | 7.0 ± 0.3 | | | | 6.96 ± 0.10 | |
| ErF | HF | 6.1 | 6.1 | TmF | HF | 6.1 | 6.2 |
| | HF (DZP) | 5.8 | 5.9 | | HF (DZP) | 5.9 | 5.9 |
| | MP2 | 6.8 | 6.9 | | MP2 | 6.9 | 7.0 |
| | MP2(DZP) | 6.6 | 6.6 | | MP2(DZP) | 6.7 | 6.7 |
| | exptl[a] | 6.3 ± 0.3 | | | | 5.8 ± 0.3 | |
| Er | HF | 5.0 | | Tm | HF | 5.1 | |
| | MP2 | 5.7 | | | MP2 | 5.8 | |
| | exptl[a] | 6.1 ± 0.1 | | | | 6.1 ± 0.3[b] | |

[a] Ref 17. [b] Ref 18.

**TABLE 7: Bond Dissociation Energies ($kJ\ mol^{-1}$) of the Ground State of $LnF_n$**

| | | | | | other works | | | |
|---|---|---|---|---|---|---|---|---|
| | HF | HF(DZP) | MP2 | MP2(DZP) | *a* | *b* | *c* | *d* |
| $D_0(ErF_2-F)$ | 442 | 459 | 598 | 624 | | | 636 ± 46 | |
| $D_0(ErF-F)$ | 438 | 458 | 517 | 570 | | 593 | 561 ± 35 | |
| $D_0(Er-F)$ | 446 | 477 | 544 | 580 | 491 | 578 | 569 ± 17 | |
| $D_0(TmF_2-F)$ | 441 | 459 | 579 | 624 | | | | 597 ± 8 |
| $D_0(TmF-F)$ | 433 | 453 | 511 | 565 | | 568 | | 561 ± 8[e] |
| $D_0(Tm-F)$ | 439 | 439 | 535 | 535 | 426 | 570 | | 506 ± 8 |

[a] Ref 14. [b] Ref 5. [c] Ref 17. [d] Ref 18. [e] At 298 K.

**TABLE 8: Atomization Energies ($kJ\ mol^{-1}$) of the Ground State of $LnF_n$**

| | | | | | other works | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | HF | HF(DZP) | MP2 | MP2(DZP) | *a* | *b* | *c* | *d* | *e* |
| $ErF_3$ | 1364 | 1431 | 1769 | 1936 | 1671 | 1850 | 1657 | 1764 ± 48 | |
| $ErF_2$ | 927 | 977 | 1317 | 1195 | | | | 1130 ± 39 | |
| $TmF_3$ | 1368 | 1434 | 1771 | 1938 | 1597 | 1821 | 1645 | | 1703 ± 25 |
| $TmF_2$ | 932 | 980 | 1197 | 1319 | | | | | |

[a] Ref 13. [b] Ref 5. [c] Ref 19. [d] Ref 17. [e] Ref 18.

from trifluorides to monofluorides and for the Er species is only slightly higher than for relevant species of thulium. For the corresponding positive ions it is lower compared to their precursor neutral molecules.

The calculated vibrational frequencies at the HF and MP2 level of the $ErF_n$ and $TmF_n$ series differ by a few percent (4%), the latter being lower. The stretching vibrational frequencies of $ErF_3$ or $TmF_3$ are in good agreement with experiment. The symmetric stretching frequency is identical in each $LnF_n$ species. Degeneracy of asymmetric stretching and deformation frequencies in $LnF_2$ molecules disappears, but the former is comparable to that in $LnF_3$ and the latter is shifted to a lower value. The frequencies of the $TmF_n$ series are usually higher than those of Er fluorides.

The calculated ionization energies for adiabatic and vertical processes are almost the same. The ionization energies of difluorides and monofluorides are in good agreement with experimental values, whereas that of Er and Tm atoms deviates a little more with respect to the quoted experimental results.

Trends in the calculated bond dissociation energy indicated the sequence $D_0(Ln-F) > D_0(LnF_2-F) > D_0(LnF-F)$ at both levels of theory. The difference between the relevant HF and MP2 values is substantial; the MP2 method predicts bond dissociation energies within experimental errors, except that of $D_0(Ln-F)$, which is rather too high. The atomization energies of $LnF_3$ and $LnF_2$ are in reasonable agreement with experimental results when the MP2 method is applied.

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