

Mean Amplitudes of Vibration of the Novel [ReFBr₅]²⁻ Anion

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Mean amplitudes of vibration of the recently described square-bipyramidal [ReFBr₅]²⁻ anion have been calculated from vibrational spectroscopic data, over a wide temperature range. The results are briefly discussed in relation with its structural peculiarities and some comparisons with related species are made.

Key words: Monfluoropentabromhenate (IV); Mean Amplitudes of Vibration; Bond properties.

The interesting halogeno-heteroleptic [ReFBr₅]²⁻ anion has recently been obtained as partner in the crystalline salt of the voluminous organic bis(triphenylphosphor-anilido) ammonium cation [1]. Its single crystal X-ray structure analysis revealed the presence of a square-bipyramidal species with C_{4v} symmetry [1].

We have recently started some studies on the fundamental vibrational properties of simple third-row transition metal compounds in order to obtain a wider insight into its bond peculiarities. In this context we have now calculated the mean amplitudes of vibration of this new Re(IV) anion.

The calculations were performed in the temperature range between 0 and 1000 K with the method of the characteristic vibrations of Müller and co-workers [2–4]. The necessary vibrational frequencies and structural parameters were taken from [1]. The obtained values, in the temperature range between 0 and 1000 K, are shown in Table 1.

A comparison of the obtained mean amplitudes of vibration with the corresponding force constants of the different Re-halogen bonds (Re-F = 2.94; Re-Br(ax) = 1.43; Re-Br(eq) = 1.32 mdyn/Å [1]) shows some interesting features. The amplitude values follow the trends suggested by the force constants only at temperatures above 298.16 K, i.e., the lower mean amplitude values are related to the stronger bonds. The fact that at the lowest temperatures this trend is not followed may be related to the so called “low temperature anomaly” which is observed

Table 1. Calculated mean amplitudes of vibration (in Å) for [ReFBr₅]²⁻.

T (K)	<i>u</i> _{Re-Br(eq)}	<i>u</i> _{Re-Br(ax)}	<i>u</i> _{Re-F}	<i>u</i> _{BrBr(eq)}	<i>u</i> _{Br(eq)Br(ax)}	<i>u</i> _{BrF}
0	0.0387	0.0374	0.0427	0.059	0.064	0.080
100	0.0409	0.0391	0.0427	0.072	0.076	0.089
200	0.0492	0.0463	0.0436	0.095	0.098	0.110
298.16	0.0577	0.0540	0.0461	0.114	0.117	0.131
300	0.0579	0.0541	0.0461	0.114	0.118	0.131
400	0.0658	0.0614	0.0494	0.131	0.135	0.150
500	0.0730	0.0681	0.0531	0.147	0.151	0.167
600	0.0797	0.0742	0.0567	0.160	0.165	0.182
700	0.0859	0.0799	0.0603	0.173	0.178	0.196
800	0.0916	0.0853	0.0638	0.185	0.190	0.209
900	0.0971	0.0903	0.0672	0.196	0.201	0.222
1000	0.1022	0.0952	0.0704	0.206	0.212	0.234

when the mean amplitudes of vibrations are dominated by the masses rather than by the bond strengths [5, 6].

At temperatures above 298.16 K, the expected correlation between force constants and mean amplitudes of vibration exists in the full temperature range, with the strongest bond (Re-F) showing the lowest temperature dependence. On the other hand, the obtained results also agree with the spectroscopically observed strengthening of the Re-Br(ax) bond: the mean amplitudes for this bond are always lower than those of the corresponding Re-Br(eq) bonds.

Despite the fact of the different oxidation state of rhenium in both compounds, the values calculated for both types of Re-Br bonds in [ReFBr₅]²⁻ are comparable to that found in ReO₃Br [7]. However, those calculated for the Re-F bond are somewhat higher than those found in the structurally related Re(VII) or Re(VI) species (for example, at 298 K, 0.0386 Å in ReOF₄ [8], 0.0376 Å in ReF₆ [9]; 0.0385 Å in ReOF₅ [8], 0.0386 Å in ReO₃F [10], and 0.0365 Å in ReF₆⁺ [11]). Unfortunately, for more direct comparisons with other halogenated Re(IV) compounds no data are available. Nevertheless, it is evident that in the case of the Re-F bonds the mean amplitudes of vibration depend more on the metal oxidation state, whereas in the case of the heavier bromine atom the mean amplitudes of Re-Br bonds depend less on the oxidation state.

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