

## On the thermal expansion of molecules: a sequel

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**Abstract** In a recent article (Varga Z, Hargittai M, Bartell LS (2011) *Struct Chem* 22: 111–121), we showed with the example of lanthanide triiodide that contrary to previous claims by others, simple metal trihalide molecules do expand with increasing temperature. This sequel is meant to strengthen our argument and the validity of the method we used besides correcting a numerical error.

**Keywords** Thermal expansion of bond length · Anharmonicity · Morse potential · Electron diffraction

Recently, we reported the results of our calculations [1] on the thermal expansion of the  $\text{LaI}_3$  molecule when it is heated to 1142 K. The motivation for that work was a series of publications (e.g., [2, 3]) claiming that for very hot  $\text{MX}_3$  molecules the effects of out-of-plane vibrations cancel the thermal expansion of the M–X bonds, hence, the bond lengths are essentially independent of temperature. Our treatment gave results contradicting that claim, for we obtained a substantial thermal expansion for the La–I bonds amounting to 0.023 Å.

There are two reasons for this sequel. One is that at a recent meeting, some theorists asserted that our quantum treatment was incorrect. To get a correct mean bond length

for a hot molecule, it was said that one must calculate mean bond lengths for each level in a series of vibrational levels, then do a Boltzmann weighted average over the ensemble. While such a treatment would work, it is needlessly computer-intensive and entirely unnecessary. One simpler alternative is a path-integral method proposed by Feynman and others [4–7]. Another alternative, the method we used, is also legitimate. It involves using a theorem due to Ehrenfest [8], according to which the quantum space average acceleration over vibrations,  $\left\langle \frac{dV(x)}{dx} \right\rangle$ , vanishes for a given vibrational mode  $x$ . Hence, if, for example,  $V(x) = \frac{1}{2}k(x^2 - ax^3 + \dots)$ , then it follows that the average  $\langle x \rangle \approx \frac{3}{2}a\langle x^2 \rangle$ , where the average over vibrational states is implicit in the term  $\langle x^2 \rangle$ .

The other reason for submitting this sequel is to correct a genuine error in our reported result. In our computation, we introduced a plausible way to determine the effective Morse asymmetry constant  $a$  of the bonds in the asymmetric stretch modes and reported that this asymmetry yielded an amount to the mean displacement in bond lengths of about  $\langle x \rangle_{S_3} = \frac{3}{2}a\langle x^2 \rangle_{S_3}$ , or 0.007 Å, contributed by the asymmetric vibrational modes.

While our inference of the Morse constant for the bonds in the asymmetric stretch mode was essentially correct, it was incorrect to add the Morse result so derived to the total mean displacement. Such an addition amounts to a double-counting of the Morse contributions inasmuch as that source is already contained in the results for the symmetric stretch. The asymmetric stretch does, however, contribute 0.013 Å through the cubic coupling force constant  $F_{133}$  as was shown in our initial publication. Therefore, the corrected total mean displacement from the equilibrium bond length is (0.023–0.007) Å, or 0.016 Å, an amount far larger

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**Table 1** Summary of bond length changes due to the thermal expansion of  $\text{LaI}_3$  from different approaches

Computation, symmetry coordinates, this work	$\langle x \rangle, \text{\AA}$	Computation, normal coordinates, Ref. [3]	$\langle x \rangle, \text{\AA}$	Experiment GED <sup>a</sup> $r_g - r_e, \text{\AA}$
$S_1$	0.005	$Q_1$	0.006	
$S_1$ coupled with $S_3$ via $F_{133}$	0.013			
$S_2$	0.000	$Q_2$	0.000	
$S_2$ coupled with the stretching modes	-0.007	$Q_2$ coupled with the stretching modes	-0.007	
$S_{3a} + S_{3b}$	0.000	$Q_{3a} + Q_{3b}$	0.000	
$S_{4a} + S_{4b}$	0.000	$Q_{4a} + Q_{4b}$	0.000	
$S_4$ coupled with the stretching modes	0.001			
Sum of vibrational contributions	<b>0.012</b>		<b>-0.001</b>	<b>0.013(8)</b>
Centrifugal stretching	0.004		<sup>b</sup>	0.004
Total	<b>0.016</b>		<b>-0.001</b>	<b>0.017(8)</b>

<sup>a</sup> Calculated by us based on the experimental data of Giricheva et al. [9]; for additional data see [1]

<sup>b</sup> Not considered

than the expected error in a modern electron diffraction determination. This value also agrees almost fortuitously well with the experimentally estimated bond length change, 0.017(8) Å, see Table 1. Accordingly, the conclusion of our previous communication [1] holds in that, contrary to Refs. [2, 3], the thermal expansion of bonds considerably exceeds the acceptable experimental errors.

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