

Out-of-plane symmetry constraints for in-plane bending vibrations

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Keywords: out-of-plane bendings, charge transfer, dipole moment derivatives, symmetry.

Highlights

Out-of-plane bending vibrations in planar molecules are subjected to symmetry constraints regarding their dipole moment derivatives. Here we show that, under certain conditions, these constraints also apply to in-plane vibrations.

Abstract

Infrared band intensities depend on how the dipole moment changes upon the vibration (dp/dQ). These derivatives can be modeled by charge-charge transfer (C+CT) and/or charge-charge transfer-dipolar polarization (C+CT+DP) models [1]. Planar molecules are special case for such studies because the symmetry of the normal coordinate for the out-of-plane bending vibration makes them subjected to mathematical constraints arising from this symmetry [2], requesting the CT term to be necessarily null ($CT=0$). Recent works have shown that these symmetry constraints might have a noticeable impact on how 2D systems behave within IR spectroscopy compared to 3D systems [3,4].

Here, we expand these concepts by noticing that in-plane vibrations can also feature such constraints as long as the equilibrium position contains a plane of symmetry that is perpendicular to the atoms' directions of motion, and these atoms start the vibration exactly at that plane. Importantly, while true out-of-plane vibrations have all the atoms featuring $CT=0$ individually, for these in-plane constricted vibrations only the atoms lying at the internal symmetry plane will show $CT=0$.

A numerical proof could use any molecule we want as long as it features the mentioned symmetry elements, so benzene was chosen for simplicity; the out-of-plane vibration (699 cm^{-1}) must have all atoms with $CT=0$, but the in-plane bend (1526 cm^{-1}), by having a symmetry plane over C_1, C_4, H_7, H_{10} , makes these atoms (and only them) to have $CT=0$. We highlight that it is not a matter of numbers, but an imposition from the equations that cannot be avoided. Any molecule under the equivalent symmetry situation will necessarily behave exactly as benzene, even if being a very different molecule compared to benzene.

With all that said, we urge for the rational seek (and even the rational design) of molecules and materials by focusing on the mathematical equations behind their properties, by exploring constraints that arise directly from the

equations (i.e. conditions that any molecule *must* obey) rather than simply random testing and checking. This might be a shortcut towards functional materials with specific experimental behaviors, reducing simple testing (we don't need to test a right triangle, as it must obey the pythagorean theorem). The aid from mathematicians is welcomed.

Table 1: Atomic Hirshfeld/CCTDP infrared intensities for the vibrations in benzene (D_{6h}). All values in $km \cdot mol^{-1}$

Atom	691 cm^{-1} / out-of-plane				1072 cm^{-1} / in-plane			
	C	CT	DP	Total	C	CT	DP	Total
C1	0.49	0.00	-0.08	0.41	-0.19	0.00	-0.47	-0.66
C2	0.49	0.00	-0.08	0.41	0.16	-1.04	0.33	-0.55
C3	0.49	0.00	-0.08	0.41	0.16	-1.04	0.33	-0.55
C4	0.49	0.00	-0.08	0.41	-0.19	0.00	-0.47	-0.66
C5	0.49	0.00	-0.08	0.41	0.16	-1.04	0.33	-0.55
C6	0.49	0.00	-0.08	0.41	0.16	-1.04	0.33	-0.55
H7	5.82	0.00	14.16	19.98	1.36	0.00	3.26	4.62
H8	5.82	0.00	14.16	19.98	0.11	-0.59	0.43	-0.04
H9	5.82	0.00	14.16	19.98	0.11	-0.59	0.43	-0.04
H10	5.82	0.00	14.16	19.98	1.36	0.00	3.26	4.62
H11	5.82	0.00	14.16	19.98	0.11	-0.59	0.43	-0.04
H12	5.82	0.00	14.16	19.98	0.11	-0.59	0.43	-0.04
Total	37.86	0.00	84.48	122.34	3.42	-6.52	8.62	5.56

References

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