

## ARE LINEAR MOLECULES REALLY LINEAR? I. THEORETICAL PREDICTIONS

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In spectroscopic parlance, a linear triatomic molecule is one whose potential energy minimum occurs at a linear geometry. We have recently discussed<sup>a,b,c</sup> that any linear triatomic molecule will be observed as being “bent” on ro-vibronic average in any ro-vibronic state. As quantum mechanics asserts, we have to characterize Nature through “observation.” Theoretically we make observations of molecular structures by calculating the expectation values of the structural parameters over the relevant ro-vibronic wavefunctions.

In computational molecular spectroscopy studies, we have shown that for many linear triatomic molecules such as  ${}^6\Delta$  FeNC,  ${}^6\Delta$  FeCN,  ${}^2\Pi$  BrCN<sup>+</sup>,  ${}^3\Phi$  CoCN,  ${}^2\Delta$  NiCN,  ${}^1\Sigma^+$  CsOH,  ${}^3\Sigma^-$  FeCO, and  ${}^2\Pi$  NCS, the ro-vibrationally averaged structure (zero-point structure, for example) is slightly bent with a bond angle supplement  $180^\circ - \angle(\text{A-B-C})$  [where  $\angle(\text{A-B-C})$  is the bond angle] in the range from  $7.5^\circ$  (NCS) to  $22.5^\circ$  ( $\text{C}_3$ ). We have also described the theoretical background<sup>b</sup> for this fact using a Laguerre-Gauss type wavefunction for the doubly degenerate bending oscillator; the average “bentness” is basically caused by the inseparability of the bending motion from the free rotation about the molecular axis.

Our finding is in contradiction to the well-established paradigm in spectroscopy that the ro-vibrationally averaged structure of a linear molecule is linear. In particular, it throws doubt on the so-called  $r_0$  structures routinely determined for linear triatomic molecules under the *a priori* assumption that ro-vibrationally averaged bond-angle of a linear molecule should be  $180^\circ$ .

In the following talk, we discuss how experimentally derived rotational-constant values are to be interpreted.

<sup>a</sup>T. Hirano, U. Nagashima, *J. Mol. Spectrosc.*, **314**, 35–47 (2015)

<sup>b</sup>T. Hirano, U. Nagashima, P. Jensen, *J. Mol. Spectrosc.* **343**, 54–61 (2018).

<sup>c</sup>T. Hirano, U. Nagashima, P. Jensen, *J. Mol. Spectrosc.* (2018), <https://doi.org/10.1016/j.jms.2017.12.011>; and references therein.