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On the preponderance of near-prolate rotors among polyatomic molecules

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Ray's asymmetry parameter[1,2] κ is the most commonly used measure of inertial asymmetry of rigid molecules. Defined in terms of the customary inertial constants A, B, and C by

$$\kappa = (2B - A - C)/(A - C), \tag{1}$$

κ spans the range -1 (prolate symmetric rotor) to $+1$ (oblate symmetric rotor). A casual browsing of the data tables in Herzberg's volume on polyatomic molecules leads to an impression that there seem to be surprisingly many near-prolate rotors among the molecules represented there. This raises two questions: (1) Is this impression correct? (2) If so, why, and is the reason interesting or informative? This Note attempts to shed some light on both.

The first issue was addressed by examining a much larger data base consisting of 477 molecules listed in a recent compilation.[3] In assessing these data, all symmetric-top molecules were excluded as were all linear molecules and molecules with a rigid linear arrangement of all nuclei other than H. Only molecules with four or more heavy nuclei were considered. The resulting distribution of κ values is displayed as a histogram in Fig. 1, and the impression of a predisposition for $\kappa \approx -1$ is clearly borne out by the data. Among those molecules *that have been studied*, the predominance of near-prolate rotors is clear. The distribution would have been even more skewed towards $\kappa = -1$ without the aforementioned exclusions.

The question of possible significance of this imbalance remains. Maybe we tend to choose near-symmetric rotors because they are easier to study. To answer such a question we need some unbiased sample for comparison: What would be the distribution in κ values for a collection of randomly shaped objects? In order to address a possible definition of randomly shaped we consider the principal moments of inertia:

$$I_A = \sum_i M_i y_i^2 + \sum_i M_i z_i^2 = Y + Z, \quad \text{etc.}, \tag{2}$$

where y_i is the y coordinate of the ith nucleus relative to the molecule's center of mass and M_i is its mass. The correspondence $(x,y,z) = (a,b,c)$ is assumed. "Random in shape" is then defined by the assumption that all values of X, Y, and Z up to some maximum (I) are equally probable with the restriction that $X \geqslant Y \geqslant Z$ to preserve the identification of I_A as the smallest principal moment of inertia, I_C the largest. In terms of these quantities, $\kappa = (2Y^2 - X^2 - Z^2)/(X^2 - Z^2)$. The probability function for κ values is given by

$$P(\kappa) = \frac{6}{I^3}\int_0^I dX \int_0^X dY \int_0^Y dZ \times \delta[\kappa - (2Y^2 - X^2 - Z^2)/(X^2 - Z^2)]. \tag{3}$$

$$P(\kappa) = \frac{\sqrt{2}}{(1-\kappa)^{3/2}}\left\{\left(\frac{3-\kappa}{8}\right)\left[\ln\left(1 + \sqrt{\frac{1-\kappa}{2}}\right) - \ln\left(1 - \sqrt{\frac{1-\kappa}{2}}\right)\right] - \frac{1}{2}\sqrt{\frac{1-\kappa}{2}}\right\}. \tag{4}$$

This function, which is weakly divergent as $\kappa \to -1$, is plotted as the solid curve in Fig. 1. The qualitative behavior of the experimental distribution is reproduced, indicating that at least part of the preponderance for $\kappa \approx -1$ reflects an *inherent* bias in the definition of the asymmetry parameter. However, the experimental result is more strongly skewed towards $\kappa \approx -1$ than the theoretical prediction based on our definition of randomly shaped. Other equally defensible definitions of random shape may be possible, and one of these may more accurately represent the distribution for real molecules. It is also possible that there is no reasonable definition of random in shape that would produce the observed preponderance for near-prolate rotors. This would imply that certain molecular shapes are more probable (e.g., that cigar-shaped molecules are more likely than frizbee-shaped molecules) because of the constraints of atomic bonding. It is not clear at present how to put these constraints into a model for κ.

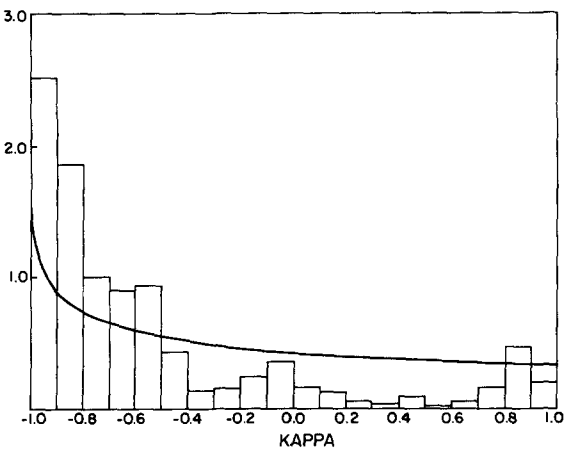

FIG. 1. The histogram shows the distribution in κ values among a set of 477 molecules listed in Ref. 3. The solid line is a theoretical result, from Eq. (4).

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