Journal of Molecular Spectroscopy 325 (2016) 42–49

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

Second moments and rotational spectroscopy

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ARTICLE INFO

Article history:
Received 28 April 2016
In revised form 2 June 2016
Accepted 2 June 2016
Available online 3 June 2016

Keywords:
Second moments
Planar moments
Microwave spectroscopy
Rotational spectroscopy
Zero-point molecular structures
Trifluoroanisole

ABSTRACT

Although determining molecular structure using microwave spectroscopy is a mature technique, there are still simple but powerful insights to analysis of the data which are not generally appreciated. This paper summarizes three applications of second (or planar) moments which quickly and easily provide insights and conclusions about a molecule's structure not easily obtained from the molecule's rotational constants.

If the molecule has a plane of symmetry, group second moments can verify that property and determine which groups are located on that plane. Common groups contribute predictable values to second moments. This study examines the contribution and transferability of CH_2/CH_3, CF_2/CF_3, isopropyl, and phenyl groups to molecular constants.

Structures of related molecules can be critically compared using their second moments.

A third application to any molecule, even those whose structures have only the identity symmetry element, determines bond lengths and angles which exactly reproduce experimentally determined 2nd moments, rotational constants, and moments of inertia. Approximate least squares methods are not needed.

1. Introduction

Rotational spectra are assigned and analyzed in terms of the rotational constants A, B, and C. The structural information contained in rotational constants can equally well be expressed as moments of inertia (I_a, I_b, I_c) or second moments (P_{aa}, P_{bb}, P_{cc}, also called planar moments). The relationships among the three sets are given in Table 1. The $h/8\pi^2$ conversion factor relating rotational constants (expressed in units of MHz instead of joules) and moments of inertia (units of amu-Å^2 instead of kg-m^2) is [A (MHz)][I_a(amu-Å^2)] = 505 379.005(36) using 2006 values of the universal constants h (Planck's constant) and N_A (Avogadro's number) [1]. The universally accepted convention for principal axis labels is that the axis with the smallest moment of inertia is the *a* axis and largest the *c* axis. It follows that $A > B > C$ and $P_{aa} > P_{bb} > P_{cc}$. We show below that second moments are often the simplest parameters to interpret and describe a molecule's structure.

The contribution of each atom in the molecule to a moment of inertia is a mass-weighted sum of the squares of two principal coordinates, i.e., the square of the radial distance of the atom from that axis, summed over all the atoms. Each rotational constant is defined by the reciprocal of those sums. Interpreting a molecular structure from its rotational constants is a challenge. The second moment, $P_{aa} = \Sigma m_i a_i^2$ (and similarly for P_{bb} and P_{cc}), measures the extension of masses along the molecule's *a* axis (or out of the *bc* plane). Interpreting a molecular structure in terms of second moments is simpler because each second moment is a function of only one coordinate per atom, not two, and no reciprocal is involved.

Second moments are linear combinations of moments of inertia as shown in Table 1 and the information contained in the second moments or the moments of inertia or the rotational constants is equivalent. This study emphasizes the simplicity of second moments and their usefulness in understanding molecular structure. One second moment commonly considered is the inertial defect, $\Delta = I_c - I_a - I_b = -2P_{cc}$, usually applied to examine molecular planarity in which case Δ is zero. If isotopolog spectra have been measured, second moments can be used to determine Kraitchman's substitution (r_s) structure [2]. Kraitchman recognized that interpreting a molecule's structure is simpler using second moments rather than moments of inertia or rotational constants. We show below that many structural characteristics can be more easily recognized using second moments than rotational constants.

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http://dx.doi.org/10.1016/j.jms.2016.06.001
0022-2852/© 2016 Published by Elsevier Inc.

Table 1
Fundamental parameters and relationships in rotational spectroscopy.

Rotational constants	Moments of inertia	Second moments
$A = (h/8\pi^2 I_a)$	$I_a = \Sigma m_i\ (b_i^2 + c_i^2) = P_{bb} + P_{cc}$	$P_{aa} = \Sigma m_i a_i^2 = (I_b + I_c - I_a)/2$
$B = (h/8\pi^2 I_b)$	$I_b = \Sigma m_i\ (c_i^2 + a_i^2) = P_{cc} + P_{aa}$	$P_{bb} = \Sigma m_i b_i^2 = (I_c + I_a - I_b)/2$
$C = (h/8\pi^2 I_c)$	$I_c = \Sigma m_i\ (a_i^2 + b_i^2) = P_{aa} + P_{bb}$	$P_{cc} = \Sigma m_i c_i^2 = (I_a + I_b - I_c)/2$
$A \cdot I_a = 505\ 379.005(36) \cdot \text{MHz} \cdot \text{amu} \cdot \text{Å}^2$		
Inertial defect	$\Delta = (I_c - I_a - I_b) = -2P_{cc}$	
Planar molecule	$I_a + I_b = I_c$; P_{cc} and $\Delta = 0$	
Scaling factors	*a* axis;	$SF_a = \{(P_{aa}(\text{exp'l})/(P_{aa}(\text{model})\}^{1/2}$
	b axis;	$SF_b = \{(P_{bb}(\text{exp'l})/(P_{bb}(\text{model})\}^{1/2}$
	c axis;	$SF_c = \{(P_{cc}(\text{exp'l})/(P_{cc}(\text{model})\}^{1/2}$

Table 2
Second moments of CH_3/CH_2 groups.

Compounds with single CH_3/CH_2 groups		P_{cc}/amu-$Å^2$	Refs.
Methylene fluoride	CH_2F_2	1.65	[4]
Methylene chloride	CH_2Cl_2	1.56	[5]
1-Chloro-3-fluoropropyne	$H_2FCC{\equiv}CCl$	1.45	[6]
Methyl fluoroformate	CH_3OCFO	1.56	[7]
S-Methylchlorothiolformate	CH_3SCClO	1.55	[8]
Propene	$CH_3CH{=}CH_2$	1.55	[9]
3-Chloropropene	$CH_2ClCH{=}CH_2$	1.56	[10]
2-Iodopropene	$CH_3CI{=}CH_2$	1.46	[11]
1,1-Difluoropropene	$CH_3CH{=}CF_2$	1.49	[12]
Methyl vinyl ether	$CH_3OCH{=}CH_2$	1.59	[13]
2-Methyl pyridine	$CH_3C_5H_4N$	1.56	[14]
Benzyl cyanide	$C_6H_5CH_2C{\equiv}N$	2.13	[15]
3-Phenyl-1-propyne	$C_6H_5CH_2C{\equiv}CH$	2.14	[16]
Compounds with multiple (n) CH_3/CH_2 groups		P_{cc} and P_{cc}/n	
Butyl cyanide (all trans form)	$CH_3CH_2CH_2CH_2CN$	6.29/4 = 1.57	[17,18]
1-Hexyne (all trans form)	$HC{\equiv}CCH_2CH_2CH_2CH_3$	6.27/4 = 1.57	[19]
Ethyl Formate (*C*$_s$ form)	CH_3CH_2OCHO	3.26/2 = 1.63	[20,21]
Ethyl cyanoformate (*C*$_s$ form)	CH_3CH_2OCCNO	3.18/2 = 1.59	[22]
Ethyl fluoroformate (*C*$_s$ form)	CH_3CH_2OCFO	3.26/2 = 1.63	[23]
3-Hexyne (all trans form)	$CH_3CH_2C{\equiv}CCH_2CH_3$	7.31/4 = 1.83	[24]
Pentane (all trans form)	$CH_3CH_2CH_2CH_2CH_3$	7.90/5 = 1.58	[25]
3-Heptyne (all trans form)	$CH_3CH_2C{\equiv}CCH_2CH_2CH_3$	8.86/5 = 1.77	[25]

Table 3
Second moments of CF_2/CF_3 groups.

		2nd moment	Ref.
Difluoromethane	CH_2F_2	P_{bb} = 46.00/1 = 46.00	[4]
Perfluoropropane	$CF_3CF_2CF_3$	P_{cc} = 134.34/3 = 44.78	[26]
1H-heptafluoropropane	$HCF_2CF_2CF_3$	P_{cc} = 135.31/3 = 45.10	[27]
1H-nonafluorobutane	$HCF_2CF_2CF_2CF_3$	P_{cc} = 181.71/4 = 45.43	[28]
Perfluoropentane	$CF_3(CF_2)_3CF_3$	P_{cc} = 229.61/5 = 45.92	[26]
Perfluorohexane	$CF_3(CF_2)_4CF_3$	P_{cc} = 281.86/6 = 46.98	[29]

Tables 2–6 with accompanying discussion describe the transferability and usefulness of second moments of several common chemical groups. Table 7 with discussion describes the usefulness of comparing structures of related bur different molecules. Table 8 and discussion demonstrates that experimental rotational data may include more information about molecular geometry than is usually recognized. Tables 9–11 describe scaling factors and their use to determine structures which exactly fit the experimental rotational constants.

The equations in Table 1 defining moments of inertia, rotational constants, and second moments are exact for rigid molecules and nearly exact for real molecules with zero-point vibrational motions.

There are elegant and careful studies relating zero-point effective molecular structures and equilibrium structures determined by quantum chemical computations but we are not addressing those differences [3]. Our focus is a simpler understanding of the relationship between effective rotational constants which fit observed rotational frequencies and the fundamental structural information derived from that analysis. The use of second moments to interpret and understand molecular geometry is straightforward and may reveal structural properties not easily deduced from rotational constants. An example is that a planar molecule which is not a symmetric top has only two independent rotational constants, not three, even though its three rotational constants all have different values if the structure is not a symmetric top.

For molecules whose structures include at least a plane of symmetry, contributions from group second moments are transferable among molecules. We discuss transferability of second moments of CH_2/CH_3 groups, CF_2/CF_3 groups, isopropyl groups, phenyl groups, and their combinations. Second moments are useful for identifying and interpreting spectra of isotopologs and revealing which data are independent. Finally, second moments can be used to determine structures which fit rotational constants exactly using scaling factors, SF_i, defined in Table 1. That application of second moments makes least squares calculations of molecular geometry unnecessary.