

## On negative inertial defect<sup>☆</sup>

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### Abstract

Morino's general formula for inertial defect has been applied to planar molecules with very low out-of-plane vibrations in order to explain negative inertial defects reported for such molecules. The obtained simple formula is combined with an empirical proportionality relation between zero point inertial defect  $\Delta_0$  and  $\sqrt{I_{cc}}$  for ordinary molecules to give semi-empirical relations between the inertial defect  $\Delta_0$ , the wavenumber of the lowest out-of-plane vibration  $\nu_1$ , and  $\sqrt{I_{cc}}$ . The relation explains well the observed negative inertial defects and allows us to estimate the value of  $\nu_1$  from the observed  $\Delta_0$ .

### 1. Introduction

The inertial defect of a molecule is defined as

$$\Delta = I_{cc} - I_{aa} - I_{bb} \quad (1)$$

where  $I_{\alpha\alpha}$  ( $\alpha = a, b, c$ ) are the principal moments of inertia of the molecule. According to the convention, we choose the molecule-fixed axes such that  $I_{aa} \leq I_{bb} \leq I_{cc}$ . Because of the definition of moments of inertia,

$$I_{\alpha\alpha} = \sum_i m_i (\beta_i^2 + \gamma_i^2) \quad (2)$$

the inertial defect of a hypothetical rigid molecule is given by

$$\Delta = -2 \sum_i m_i c_i^2 \quad (3)$$

where  $m_i$  and  $c_i$  are the mass and the coordinate along the  $c$  axis of the  $i$ th particle, respectively.

Because of the small mass of an electron,  $\Delta$  is very nearly 0 for a planar molecule, as pointed out by Fermi for triatomic molecules [1]. Eq. (3) indicates that  $\Delta$  is negative for non-planar molecules but is never positive for any molecule.

Mecke and Baumann [2] showed, however, that the moments of inertia of  $\text{H}_2\text{O}$ , calculated from their experimentally determined rotational constants in the analysis of its vibration-rotation spectrum, gave small *positive* inertial defects for several vibrational states, including the ground state. Mecke's ground state value [3]  $\Delta_0 = 0.077(\pm 0.001) \times 10^{-40} \text{ g cm}^2$  is very close to the modern value. A complication arises from the fact that the vibrational averages of the *inverse* of moments of inertia  $\langle 1/I \rangle$  are obtained from the spectroscopic experiment rather than  $\langle I \rangle$ . Darling and Dennison [4] developed a detailed calculation of the vibration-rotation interaction and explained the observed values of inertial defect in their classic paper on  $\text{H}_2\text{O}$ . Their expression of inertial defect was generalized for any planar asymmetric top

<sup>☆</sup> Dedicated to Professor Yonezo Morino on his 87th birthday.

molecule by Morino and Oka [5]. Their theory explained the then-available experimental values of ground state inertial defects of triatomic [6], four-atomic [7] and ethylene-type planar molecules [8] with amazing accuracy. The theory has recently been extended to planar symmetric top molecules [9]. Quite independently, Herschbach and Laurie [10] developed a theory on inertial defect which gave identical results to Morino's [5] but which allowed a different perspective. This latter point has been recently amplified by Watson [11] who clarified the qualitative aspects of the vibration–rotation interaction leading to the inertial defect and gave a convenient approximate formula based on centrifugal distortion constants.

All these works provided theoretical values of inertial defect in the ground vibrational state that agreed remarkably well with experimental values for many planar molecules of small size. A few serious discrepancies at the time of publication (such as  $F_2O$  in Ref. [6] and  $ClF_3$  in Ref. [7]) were resolved when their experimental values were revised [10,12]. Thus, it has been well-established that small planar molecules have *positive* inertial defect of the order of  $\kappa^2 I$  (where  $\kappa \approx 0.1$  is the Born–Oppenheimer constant  $(m/M)^{1/4}$ ) in the ground state and that they can be reliably estimated even when approximate potential constants are used. An observed small positive inertial defect has been regarded as evidence for the planarity of a molecule.

There have been planar molecules, however, which showed abnormally small or *negative* inertial defects. Morino's first paper [5] already mentions formamide  $NH_2CHO$  whose inertial defect varies from  $0.018 \text{ amu}\text{\AA}^2$  to  $-0.022 \text{ amu}\text{\AA}^2$  for isotopic species [13], and phenol  $C_6H_5OH$  for which Kojima reported [14]  $-0.032 \text{ amu}\text{\AA}^2$ . For those molecules, the slight non-planarity of the  $NH_2$  and  $OH$  group with respect to the  $CHO$  and benzene planes, respectively, was suspected. Later studies showed that the vibrational potential for the  $NH_2$  out-of-plane motion in  $NH_2CHO$  is highly quartic [15,16]. Hirota et al. [15] explained the anomalous values of inertial defects of  $NH_2CHO$  and its isotopic species based on the very anharmonic potential. Quite apart from such

“quasiplanar” molecules, there are planar molecules which have been observed to show negative inertial defects in the ground vibrational state. The purpose of the present paper is to discuss the negative inertial defects of such molecules within the realm of the harmonic out-of-plane vibrational potential.

## 2. Observed negative inertial defects

Vinyl formate  $CHO-O-CH=CH_2$  studied by Rao and Curl [17] was the first planar molecule which showed a large negative inertial defect  $\Delta_0 = -0.243 \text{ amu}\text{\AA}^2$ . The existence of a very low out-of-plane vibration was suspected to be the cause of this large negative inertial defect. This is supported by the fact that malonaldehyde  $CHO-CH=CHOH$  with a similar framework show a small positive inertial defect [18] of  $\Delta_0 = 0.1026 \text{ amu}\text{\AA}^2$ . In this latter molecule, the large amplitudes of out-of-plane vibrations are suppressed by the strong hydrogen bonding between  $CHO$  and  $OH$  [8]. Hanyu et al. found a large negative inertial defect of  $-0.146 \text{ amu}\text{\AA}^2$  for nitrosobenzene [19]. They observed the variation of inertial defect with the excitation of the low frequency torsional out-of-plane vibration and found that the value of inertial defect decreases drastically by  $\Delta_t \approx -0.82 \text{\AA}^2$  for each excitation of the vibration. They proposed the Hanyu–Britt–Boggs (HBB) formula to explain the variation. The large increase of the magnitude of negative inertial defect has been observed for many other molecules and the HBB formula has been used to estimate the magnitude of the low frequency out-of-plane vibration from the observed value of  $\Delta_t$ .

Planar molecules which have large negative inertial defects ( $|\Delta_0| > 0.050 \text{ amu}\text{\AA}^2$ ) are listed in Table 1. The table is not meant to be exhaustive, but is to give representative molecules for which the values of negative inertial defects are accurately determined. All molecules in the table have at least one out-of-plane vibration whose wave-number is much less than that of any of the in-plane vibrations. When available, the wavenumbers of the low out-of-plane vibrations are also listed in the table. Most of them were determined from the relative intensities of their microwave

spectra in the vibrationally excited states. Some of them (marked with an asterisk) were determined by the HBB formula. When direct far infrared measurements are quoted in the reference, they are listed. No effort has been made to search for their values other than those quoted in the references.

Molecules in Table 1 are classified into three groups. The first five are aliphatic molecules with low frequency torsional vibrations. There are several other molecules in this category such as acrolein CHO–CHCH<sub>2</sub> [51–53], thioacrolein CHS–CHCH<sub>2</sub> [54], acryloyl fluoride CFO–CHCH<sub>2</sub> [55], vinyl isocyanate CH<sub>2</sub>CHNCO [56], acrylic acid CH<sub>2</sub>CHCOOH [57], and vinyl imine CH<sub>2</sub>CHCHNH [58], which all have negative inertial defects with magnitudes less than 0.050 amuÅ<sup>2</sup>. The second group of molecules is the five-membered and six-membered ring compounds with low frequency torsional out-of-plane vibrations due to the attached NO, NO<sub>2</sub>, CHO, CFO, CClO, NCO, CHCH<sub>2</sub>, NSO, BF<sub>2</sub>, or BCl<sub>2</sub> groups. Here the entry of many similar molecules allows us to observe some qualitative aspects of Δ<sub>0</sub>. The similarity of the values of Δ<sub>0</sub> for the group (nitrobenzene, 3-fluoro- and 4-fluoro-nitrobenzene) and the group (styrene, 3-fluoro-, 4-fluoro-styrene, and vinylpyridine) suggests that the value of Δ<sub>0</sub> is determined mostly by the wavenumber of the lowest out-of-plane vibration and is not sensitive to the variation of the planar ring frame. By and large, this is observed for all molecules listed in Table 1. The two groups of ring compounds mentioned above also show subtle variation of planarity depending on the relative positions of the substituents. Correll et al [35] showed that unlike 3-fluoro- and 4-fluoro-nitrobenzene, 2-fluoronitrobenzene has a large negative inertial defect of –17.8349(16) amuÅ<sup>2</sup> clearly indicating that it is non-planar (32°) due to the F...O repulsion. The case of 2-fluorostyrene is a little subtle because of relatively small negative inertial defect Δ<sub>0</sub> = –1.215 amuÅ<sup>2</sup>. However, the observed zigzag variations of the three rotational constants, as the vibration is excited, convinced Villamañán et al. [59] to conclude that the molecule is quasiplanar with a potential hump of 16 cm<sup>–1</sup>. It is often from the absence of such

zigzag variation of rotational constants that planarity of molecules is concluded in spite of their negative inertial defect. The third group is composed of the last five molecules in Table 1. They are large ring compounds and the low out-of-plane vibration is not a torsional motion but is a bending of the ring.

### 3. Theoretical calculations

The negative inertial defects for molecules with very low out-of-plane vibrations can be explained by using Morino's general expression [5] for inertial defect,

$$\Delta = \frac{h}{\pi^2 c} \left\{ \sum_n (v_n + \frac{1}{2}) \sum_m' \frac{\nu_m^2}{\nu_n(\nu_n^2 - \nu_m^2)} \times [(\zeta_{mn}^a)^2 + (\zeta_{mn}^b)^2 - (\zeta_{mn}^c)^2] + \sum_t \frac{3}{2\nu_t} (v_t + \frac{1}{2}) \right\} \quad (4)$$

where  $\zeta_{mn}^\alpha$  are Coriolis constants expressing the instantaneous angular momentum along the  $\alpha$  axis due to normal modes  $n$  and  $m$ . The value of  $h/\pi^2 c$  is 134.861 amuÅ<sup>2</sup>/cm<sup>–1</sup>. The first summations in Eq. (4) on  $n$  and  $m$  go over all vibrational modes while the latter summation on  $t$  goes only over out-of-plane vibrations. We here use Morino's formula for asymmetric top molecules because all molecules in Table 1 are such molecules. It turns out, however, that the following analysis applies also to planar symmetric top molecules since the additional term containing the first-order Coriolis coupling  $\zeta_{nn}^c$  in the theory of symmetric top molecules [9] does not exist if  $n$  is an out-of-plane vibration.

There is a quadratic  $\zeta$  sum rule which greatly simplifies the analysis of inertial defect [5,10,11,19],

$$\sum_m (\zeta_{mn}^\alpha)^2 = A_{nn}^{\alpha\alpha} - \frac{1}{4} \sum_\xi \frac{(a_n^{\alpha\xi})^2}{I_{\xi\xi}} \quad (5)$$

where

$$a_n^{\alpha\xi} \equiv \partial I_{\alpha\xi} / \partial Q_n \quad \text{and} \quad A_{nn}^{\alpha\alpha} \equiv (\frac{1}{2}) \partial^2 I_{\alpha\alpha} / \partial Q_n^2$$

are the first and second derivatives of moments of inertia with respect to the normal coordinate  $Q_n$ . In the context of this paper, we consider the case when  $n$  in Eq. (5) is an out-of-plane vibration  $t$ . From the

Table 1  
Molecules with negative zero-point inertial defect

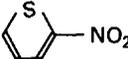
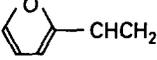
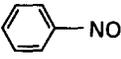
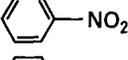
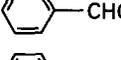
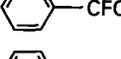
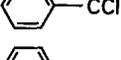
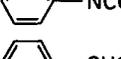
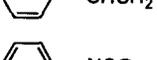
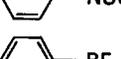
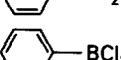
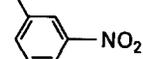
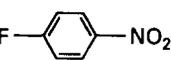
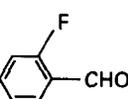
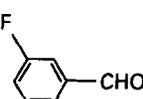
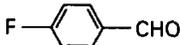
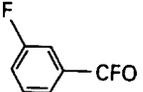
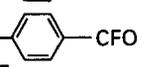
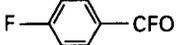
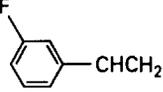
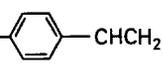
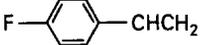
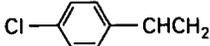
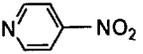
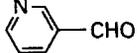
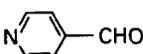
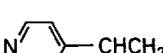
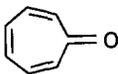
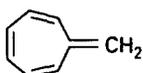
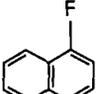
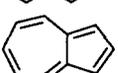
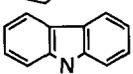
Molecules		$\Delta_{0, \text{obs}}^a$	$\nu_1^b$	$\Delta_{0, \text{calc}}^c$	$\nu_{1, \text{est}}^f$	Ref.
<i>cis</i> -Glyoxal	CHO-CHO	-0.1286	108(10)	-0.126(29)	107	20
<i>trans</i> -Thioglyoxal	CHO-CHS	-0.070			104	21
Nitroethylene	CH <sub>2</sub> CH-NO <sub>2</sub>	-0.0665	100(20)	-0.109(67)	114	22
Formicanhydride	CHO-O-CHO	-0.1909	85(8)	-0.148(37)	77	23
Vinylformate	CHO-O-CHCH <sub>2</sub>	-0.243			68	17
2-Nitrothiophene		-0.164	90(20)	-0.201(83)	100	24
<i>trans</i> - $\alpha$ -Vinylfuran		-0.1018	119(27)	-0.143(64)	139	25
Nitrosobenzene		-0.146	100	-0.176	110	19
Nitrobenzene		-0.4811	50(15)	-0.49(20)	51	26
Benzaldehyde		-0.128	110.85 <sup>c</sup>	-0.138	115	27
Benzoyl fluoride		-0.325	63.36 <sup>c</sup>	-0.344	66	28
Benzoyl chloride		-0.486	44.6 <sup>c</sup>	-0.543	48	29
Phenylisocyanate		-0.127	57(16)	-0.39(17)	103	30
Styrene		-0.6958	38.1 <sup>d</sup>	-0.720	39	31
<i>N</i> -Sulphinylaniline		-0.4518	41.1*	-0.606	51	32
Phenylboron difluoride		-0.2537	49*	-0.492	75	33
Phenylboron dichloride		-0.45	37*	-0.670	49	34
3-Fluoronitrobenzene		-0.4984	55.6*	-0.393	47	35
4-Fluoronitrobenzene		-0.4874	55.4*	-0.388	48	35
2-Fluorobenzaldehyde		-0.112			114	36
<i>cis</i> -3-Fluorobenzaldehyde		-0.078			125	36
<i>trans</i> -3-Fluorobenzaldehyde		-0.121			107	36

Table 1. Continued

Molecules		$\Delta_{0, \text{obs}}^a$	$\nu_1^b$	$\Delta_{0, \text{calc}}^c$	$\nu_{1, \text{est}}^f$	Ref.
4-Fluorobenzaldehyde		-0.162	64*	-0.327	93	37
<i>cis</i> -3-Fluorobenzoyl fluoride		-0.3264	52.29*	-0.427	62	38
<i>trans</i> -3-Fluorobenzoyl fluoride		-0.3315	56.24*	-0.381	61	38
4-Fluorobenzoyl fluoride		-0.3384	61.01*	-0.327	60	39
<i>cis</i> -3-Fluorostyrene		-0.591	50(20)	-0.48(27)	43	40
<i>trans</i> -3-Fluorostyrene		-0.789			34	40
4-Fluorostyrene		-0.775	30(15)	-0.92(56)	35	41
4-Chlorostyrene		-0.801	35(15)	-0.73(41)	33	42
4-Nitropyridine		-0.475	55(15)	-0.430	51	43
3-Pyridinecarbaldehyde		-0.1097	135(30)	-0.087(55)	124	44
4-Pyridinecarbaldehyde		-0.1313	124(30)	-0.108(66)	114	44
4-Vinylpyridine		-0.682	35(15)	-0.80(41)	40	45
Tropone		-0.516	60(20)	-0.40(19)	50	46
Heptafulvene		-0.5008	70(11)	-0.323(76)	51	47
1-Fluoronaphthalene		-0.1444			94	48
Azulene		-0.1517	<sup>g</sup>		98	49
Carbazole		-0.3602			54	50

<sup>a</sup> Observed zero-point inertial defect in  $\text{amu}\text{\AA}^2$  reported in the given reference.

<sup>b</sup> The lowest out-of-plane vibration in  $\text{cm}^{-1}$  reported in the reference. Many of them are from the observed relative intensities. The numbers in parentheses are uncertainties. Numbers with asterisks are determined from the HBB formula.

<sup>c</sup> From Ref. [60].

<sup>d</sup> From Ref. [61].

<sup>e</sup> Calculated zero-point inertial defect from Eqs. (14) and (15), using reported  $\nu_1$ .

<sup>f</sup> Estimated  $\nu_1$  using Eqs. (14) and (15) from observed  $\Delta_0$ .

<sup>g</sup> See text.

definition of angular momentum, we see that  $\zeta_{mn}^{\alpha}$  is non-vanishing only when  $m$  is an in-plane vibration (which will be denoted by  $s$ ), and  $\alpha$  is one of the in-plane axes  $a$  or  $b$ . From the expressions of  $A_{nn}^{\alpha\alpha}$  and  $a_n^{\alpha\xi}$ , we see [5]

$$A_{tt}^{aa} = A_{tt}^{bb} = 1 \quad \text{and} \quad a_t^{\alpha\xi} = a_t^{b\xi} = 0$$

for any out-of-plane vibration  $t$  and any axis  $\xi$ . Eq. (5) is thus reduced to [19]

$$\sum_s (\zeta_{st}^a)^2 = \sum_s (\zeta_{st}^b)^2 = 1 \quad (6)$$

### 3.1. The Hanyu–Britt–Boggs formula

In order to derive the HBB formula, we rewrite Eq. (4) as [8]

$$\Delta = \sum_n \left(\nu_n + \frac{1}{2}\right) \Delta_n \quad (7)$$

and write down the expression of  $\Delta_n$  for an out-of-plane vibration  $t$ ,

$$\begin{aligned} \Delta_t &= \frac{h}{\pi^2 c} \left\{ \sum_s \frac{\nu_s^2}{\nu_t(\nu_t^2 - \nu_s^2)} [(\zeta_{st}^a)^2 + (\zeta_{st}^b)^2] + \frac{3}{2\nu_t} \right\} \\ &= -\frac{h}{\pi^2 c} \left\{ \frac{1}{2\nu_t} + \sum_s \frac{\nu_t}{\nu_s^2 - \nu_t^2} [(\zeta_{st}^a)^2 + (\zeta_{st}^b)^2] \right\} \end{aligned} \quad (8)$$

where Eq. (6) has been used to derive the second expression. For the lowest out-of-plane vibration 1, we often have  $\nu_s \gg \nu_1$  for all  $\nu_s$ . For such a case, neglecting the second term, we have the HBB formula,

$$\Delta_1 = -\left(\frac{h}{2\pi^2 c}\right) \frac{1}{\nu_1} \quad \text{or} \quad \nu_1 = -\left(\frac{h}{2\pi^2 c}\right) \frac{1}{\Delta_1} \quad (9)$$

Since the neglected second term in the bracket of Eq. (8) is always positive for  $\Delta_1$ , the HBB formula underestimates the value of  $\nu_1$ . The formula is a good approximation when  $(\zeta_{st}^a)^2$ , normalized by Eq. (6), is distributed over many in-plane vibrations. If  $(\zeta_{st}^a)^2$  is dominated by the lowest in-plane vibrations, i.e.,  $(\zeta_{s1}^a)^2 \approx 1$ , the correction could amount to  $-(2\nu_1^2/\nu_s^2)\nu_1$ .

### 3.2. Zero-point inertial defect $\Delta_0$

The expression for zero-point inertial defect  $\Delta_0 = \sum_n \Delta_n/2$  can be obtained from Eq. (4) by straightforward algebra to be

$$\begin{aligned} \Delta_0 &= \frac{h}{2\pi^2 c} \left\{ \sum_{s>s'} \left( \frac{1}{\nu_s} + \frac{1}{\nu_{s'}} - \frac{1}{\nu_s + \nu_{s'}} \right) (\zeta_{ss'}^c)^2 \right. \\ &\quad + \sum_t \frac{3}{2\nu_t} - \sum_s \sum_t \left( \frac{1}{\nu_s} + \frac{1}{\nu_t} - \frac{1}{\nu_s + \nu_t} \right) \\ &\quad \left. \times [(\zeta_{st}^a)^2 + (\zeta_{st}^b)^2] \right\} \end{aligned}$$

where  $s$  and  $s'$  denote in-plane vibrations while  $t$  denotes out-of-plane vibrations. Using Eq. (6), we find

$$\begin{aligned} \Delta_0 &= \frac{h}{2\pi^2 c} \left\{ -\sum_t \frac{1}{2\nu_t} - \sum_s \sum_t \left( \frac{1}{\nu_s} - \frac{1}{\nu_s + \nu_t} \right) \right. \\ &\quad \left. \times [(\zeta_{st}^a)^2 + (\zeta_{st}^b)^2] \right. \\ &\quad \left. + \sum_{s>s'} \left( \frac{1}{\nu_s} + \frac{1}{\nu_{s'}} - \frac{1}{\nu_s + \nu_{s'}} \right) (\zeta_{ss'}^c)^2 \right\} \end{aligned} \quad (10)$$

This equation indicates that if one of the out-of-plane vibrations  $\nu_1$  is very much lower than the other of vibrations, its effect dominates. It amounts to

$$\Delta_{01} = -\left(\frac{h}{4\pi^2 c}\right) \frac{1}{\nu_1} = -\frac{33.715}{\nu_1} \text{amu}\text{\AA}^2 \text{cm}^{-1} \quad (11)$$

This formula gives the observed dependence of  $\Delta_0$  on  $\nu_1$  as seen in Table 1 but overestimates the magnitude of  $\Delta_0$ , clearly indicating that the positive contribution from the rest of the terms in Eq. (10) is not negligible. Since the normal coordinate analysis of all molecules in Table 1 is prohibitive, here I use a simple empirical formula to estimate the latter contribution,

$$\Delta_0 = \Delta_{01} + \alpha \sqrt{I_{cc}} \quad (12)$$

The approximate proportionality between  $\Delta_0$  and  $\sqrt{I_{cc}}$  is empirically observed for a group of mechanically similar molecules. As an example, a plot of experimentally determined  $\Delta_0$  versus  $\sqrt{I_{cc}}$  is shown in Fig. 1 for planar molecules containing three or four heavy atoms with no very low frequency out-of-plane vibrations. All triatomic

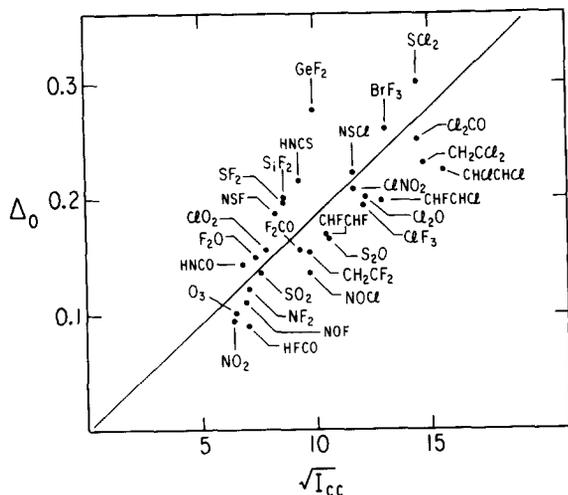


Fig. 1. A plot of the ground state inertial defect  $\Delta_0$  (in  $\text{amu}\text{\AA}^2$ ) versus  $\sqrt{I_{cc}}$  ( $I_{cc}$  in  $\text{\AA}^2$ ). All triatomic molecules from Lovas' table [62] containing three heavy atoms and molecules from Refs. [7] and [8] are used in the plot. The proportionality between  $\Delta_0$  and  $\sqrt{I_{cc}}$  given in Eq. (13) of the text is shown by the straight line. All  $\Delta_0$  values fall to within 25% from the straight line except for  $\text{GeF}_2$  and  $\text{HFCO}$ .

molecules containing three heavy atoms from Lovas' table [62] and molecules from Refs. [7] and [8] are used in the plot. The average relation of the straight line in Fig. 1,

$$\Delta_0 = 0.0186\sqrt{I_{cc}} \quad (13)$$

where  $\Delta_0$  and  $I_{cc}$  are in  $\text{\AA}^2$ , fits to all molecules within 25% of  $\Delta_0$  except for  $\text{GeF}_2$  and  $\text{HFCO}$ .

In order to determine  $\alpha$  in Eq. (12), the values of  $\Delta_0 = \Delta_{0l}$  calculated from  $\Delta_{0,\text{obs}}$  and  $\nu_1$  in Table 1 are plotted versus  $\sqrt{I_{cc}}$  in Fig. 2. The molecules in Fig. 2 are limited to those whose  $\nu_1$  were experimentally measured without using the HBB formula. Some molecules with large uncertainties in  $\nu_1$  and thus in  $\Delta_{0l}$  are also excluded. It is noted that the three aliphatic molecules lie along the straight line whose slope is identical to that shown in Fig. 1 and given by Eq. (13). We thus adopt  $\alpha = 0.0186$  for aliphatic molecules. For aromatic molecules, we have  $\alpha = 0.00803$  from Fig. 2. We therefore have the expression of zero-point inertial defect

$$\Delta_0 = -\frac{33.715}{\nu_1} + 0.0186\sqrt{I_{cc}} \quad (14)$$

for the aliphatic molecules and

$$\Delta_0 = -\frac{33.715}{\nu_1} + 0.00803\sqrt{I_{cc}} \quad (15)$$

for the aromatic molecules with low frequency torsional vibrations. There are insufficient experimental data to arrive at a formula for the third group of molecules (the last five molecules in Table 1). Unlike other molecules in Table 1, they do not have isolated low frequency out-of-plane vibrations but may have a few grouped low frequency vibrations. We here use Eq. (15) for them with reservation.

Values of  $\Delta_0$  calculated by using Eqs. (14) and (15) are shown in Table 1 as  $\Delta_{0,\text{calc}}$ . It is noted that they agree well with the experimentally determined values of  $\Delta_0$  with the possible exception of phenylisocyanate and 4-fluorobenzaldehyde. The discrepancy may be due to underestimated values of  $\nu_1$ .

Eqs. (14) and (15) may also be used to estimate the values of  $\nu_1$  from observed  $\Delta_0$ . The values of  $\nu_1$  thus determined are also listed in Table 1 as  $\nu_{1,\text{est}}$ . I believe they are close to real values assuming that the experimentally determined  $\Delta_{0,\text{obs}}$  are accurate for the first two groups of molecules. For the last group of molecules, however, they may give a gross underestimate because these molecules may have more than one very low frequency out-of-plane vibration. For example, three low frequency out-of-plane vibrations at  $272.7(50)\text{cm}^{-1}$ ,  $188.0(24)\text{cm}^{-1}$  and  $180.3(19)\text{cm}^{-1}$  are reported for azulene by Christen et al. [49] instead of the estimated value of  $98\text{cm}^{-1}$ . Obviously, more sophisticated treatment is needed for such molecules.

#### 4. Final remarks

Morino's general formula for inertial defect has been used together with an empirical relation between  $\Delta_0$  and  $\sqrt{I_{cc}}$  to explain negative inertial defects observed for planar molecules. The obtained formulae Eqs. (14) and (15) reproduce the observed values of zero-point inertial defect well and may also be used to estimate the value of lowest out-of-plane vibration from observed  $\Delta_0$ . This formalism may also be useful for

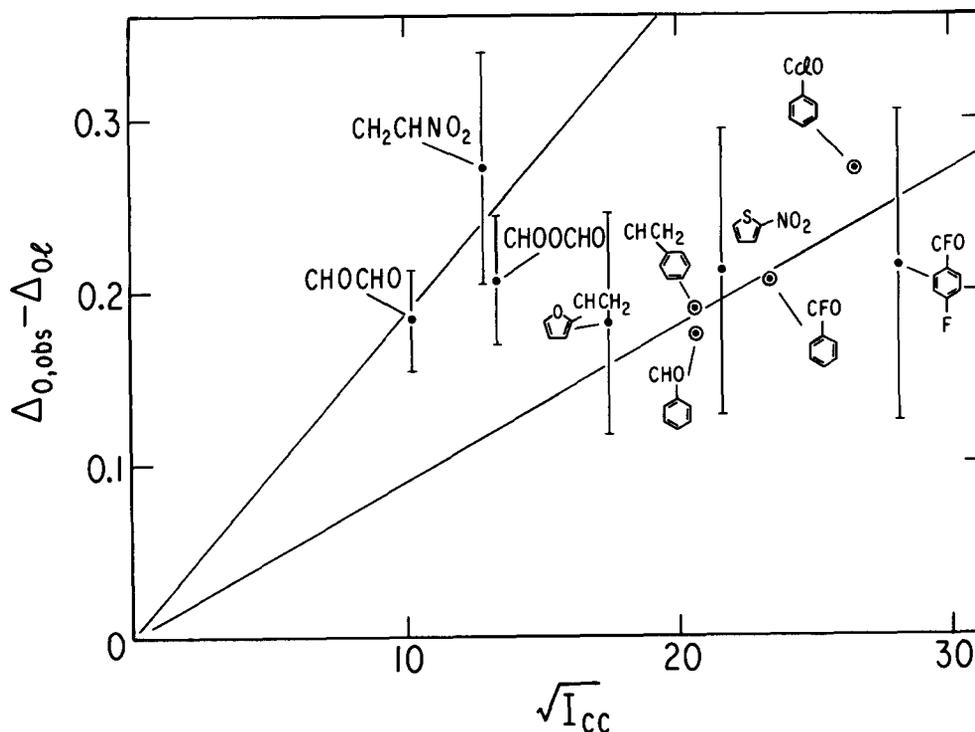


Fig. 2. A plot of  $\Delta_{0,obs} - \Delta_{0,c}$  (in  $\text{amu}\text{\AA}^2$ ) versus  $\sqrt{I_{cc}}$ , where  $\Delta_{0,c}$  is calculated from Eq. (11) and the  $\nu_1$  values are listed in Table I. Points denoted with open circles are those for which  $\nu_1$  were directly measured by far infrared spectroscopy. Other points are calculated using  $\nu_1$  determined from relative intensities of vibrationally excited microwave spectral lines with bars showing the uncertainty. Only values with small uncertainties are shown. The straight line for the three aliphatic molecules is identical to the one in Fig. 1. The two straight lines lead us to the empirical formulae Eqs. (14) and (15).

judging the planarity of a molecule when a small negative inertial defect is observed [63].

The progress in recent years of the spectroscopy of weakly bound molecules has introduced large values of inertial defects amounting to  $3 \text{ amu}\text{\AA}^2$  or more. Treatment of large negative inertial defects for such molecules is an interesting theme. I have not been able to incorporate it into this paper.

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