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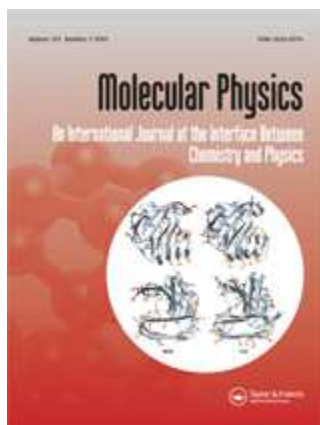
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Vibrational contributions to vicinal proton-proton coupling

constants ${}^3J_{HH}$.

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precision; DFT/B3LYP.

Abstract

Vibrational contributions to the ${}^3J_{HH}$ couplings of 6 mono- and 5 1,1-disubstituted ethanes, 3 monosubstituted cyclohexanes, 3 norbornane type molecules, and 11 three-membered rings have been calculated at the DFT/B3LYP level for the Fermi contact term using a moderate sized basis set. When, for a data set of 70 couplings, the sums of the values for the equilibrium configurations J_e and the respective vibrational contributions J_{vib}^{300} at 300 K are multiplied by a factor of 0.8485, the corresponding predicted couplings J^{pre} are in good agreement with the experimental couplings J^{exp} with a standard deviation σ of 0.18 Hz. The same σ results when J^{pre} values are obtained by multiplying the J_e values by 0.9016. However, the vibrational contributions must be taken into account, together with the J_e values, in order to achieve a procedure for a reliable and accurate prediction of ${}^3J_{HH}$ couplings since, globally considered, J_{vib}^{300} contributions amount to about 7% of the J_e values and the correlation coefficient between the J_{vib}^{300} and J_e is of only 0.68 with a σ deviation of 0.20. The first and diagonal second derivatives of J with respect to each normal coordinate Q_k , required to estimate the vibrational contributions, have been obtained from six J_k values computed for molecular geometries positively ($+\delta Q_k$) and negatively ($-\delta Q_k$) displaced from the equilibrium geometry along the normal coordinate Q_k and using for δ the values 0.01, 0.05 and 0.10. The computational precision of the results obtained when using one, two and three δ values is analyzed.

1. Introduction

The development of a practical procedure for accurate prediction of vicinal proton-proton coupling constants ${}^3J_{HH}$ (written hereafter J) is an objective of great importance for investigating the conformational behaviour in solution of organic and biochemical compounds, as well as biopolymers, because of the strong dependence of J on the dihedral angle φ between the coupled protons [1-2]. After the angular dependence, the next factor that determines the magnitude of J couplings is the effect of the substituents [3-7]. In addition to these two important factors there is a series of secondary factors that influence the magnitude of the J couplings such as changes in local geometry and contributions from torsional vibrations [3,8-12]. Predictions of J couplings have been carried out, in general, using analytical expressions empirically parameterized of limited precision [6,13-15]. State-of-the-art theoretical methods are the natural alternative to the use of empirical equations for predicting accurately J couplings. A procedure to predict J from DFT/B3LYP calculations using a moderate sized basis set was developed recently [16]. For a dataset of 163 couplings the σ deviation between predicted J^{pre} and experimental J^{exp} couplings amounted 0.17 Hz against the larger σ deviation of 0.31 Hz reported for the best empirically parameterized extended Karplus equation [14]. J couplings were calculated at the optimized equilibrium geometries for a series of selected molecules but vibrational contributions were not estimated in Ref. [16]. In this paper, these contributions are calculated for a representative dataset of 84 J couplings in order to determine their effect on the prediction of vicinal J couplings.

In recent years, there has been a considerable interest on vibrational contributions to nuclear spin-spin coupling constants [17-19] which are typically of the

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2
3 same order of magnitude as the differences between the coupling constants calculated
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5 theoretically and those observed experimentally. Therefore, these contributions should
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7 always be computed when the performance of computational methods is analyzed and
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9 when the temperature dependence of coupling constants or secondary isotope effects is
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11 studied [20].
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16 In order to calculate vibrational contributions to coupling constants the first and
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18 diagonal second derivatives of J with respect to normal coordinates must be computed.
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20 No analytical implementation exists for evaluating these derivatives, therefore, some
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22 numerical procedure must be used [21]. In principle, first and second derivatives of J
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24 with respect to normal coordinates Q_k can be obtained from three values of J computed
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26 for the equilibrium geometry J_e and for positively ($+\delta Q_k$) and negatively ($-\delta Q_k$)
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28 displaced geometries along the normal coordinate Q_k . This procedure, that uses one δ
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30 value and requires the computation of two J_k values, does not provide the
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32 computational accuracy necessary for our purposes. Therefore, the performance at the
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34 DFT/B3LYP level of procedures that use two or three δ values and require computing
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36 four or six J_k values have been analyzed aiming at getting computational accuracies of
37
38 0.01 Hz for vibrational contributions J_{vib} to J and smaller than 0.05 Hz/amu^{1/2} Å and
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40 0.10 Hz/amu Å², respectively, for first and second derivatives of J with respect to Q_k .
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2. Methods

2.1. Vibrational contributions

At the second-order perturbation level, a vibrational averaged $\langle J \rangle$ coupling for a near rigid molecule with low amplitude vibrations is given by [22-23],

$$\langle J \rangle = J_e + \sum_k (J'_k \langle Q_k \rangle + J''_k \langle Q_k^2 \rangle), \quad (1)$$

where Q_k 's are the vibrational normal coordinates, J_e is the J value for the equilibrium configuration, and J'_k and $2J''_k$ are the first and diagonal second derivatives of J with respect to the normal coordinate Q_k ,

$$J'_k = (\partial J / \partial Q_k)_e, \quad 2J''_k = (\partial^2 J / \partial Q_k^2)_e. \quad (2)$$

The average values of Q_k and Q_k^2 in thermal equilibrium at temperature T , using the harmonic oscillator partition function, are given by [24],

$$\langle Q_k \rangle = -\frac{\hbar}{4\omega_k^2} \sum_l \frac{\Phi_{kll}}{\omega_l} \coth\left(\frac{\hbar\omega_l}{2k_B T}\right), \quad (3)$$

$$\langle Q_k^2 \rangle = \frac{\hbar}{2\omega_k} \coth\left(\frac{\hbar\omega_k}{2k_B T}\right), \quad (4)$$

where k_B is the Boltzmann constant, ω_k is the vibrational angular frequency of k-th normal mode and Φ_{kll} 's are the cubic anharmonic normal coordinate force constants defined as

$$\Phi_{kll} = (\partial^3 E / \partial Q_k \partial Q_l^2)_e. \quad (5)$$

According to equations (3) and (4), the first and second order terms in equation (1), $J'_k < Q_k >$ and $J''_k < Q_k^2 >$, correspond, respectively, to anharmonic and harmonic vibrational contributions to $\langle J \rangle$ from the k-th normal coordinate Q_k . Therefore, a vibrationally averaged coupling can be written as

$$\langle J \rangle = J_e + J_{anh} + J_{har}, \quad (6)$$

with

$$J_{anh} = \sum_k J'_k < Q_k > = \sum_k J_{anh,k}, \quad (7)$$

$$J_{har} = \sum_k J''_k < Q_k^2 > = \sum_k J_{har,k}. \quad (8)$$

Combining contributions J_{anh} and J_{har} yields the vibrational contribution J_{vib} to $\langle J \rangle$,

$$J_{vib} = J_{anh} + J_{har} = \sum_k (J_{anh,k} + J_{har,k}). \quad (9)$$

On the other hand, when $T = 0$ K the coth functions in equations (3) and (4) are equal to 1, and the zero point values are obtained for $\langle Q_k \rangle$ and $\langle Q_k^2 \rangle$. Substituting these values in equations (7) to (9), the zero point vibrational contributions to J , J_{anh}^0 , J_{har}^0 and J_{vib}^0 , are obtained. Differences between vibrational contributions at temperature T , J_{anh}^T , J_{har}^T and J_{vib}^T , and the corresponding ones at the zero point can be considered as the thermal vibrational contributions ΔJ_{anh}^T , ΔJ_{har}^T and ΔJ_{vib}^T , being

$$\langle J^T \rangle = J_e + J_{anh}^0 + J_{har}^0 + \Delta J_{vib}^T, \quad (10)$$

$$\Delta J_{vib}^T = \Delta J_{anh}^T + \Delta J_{har}^T. \quad (11)$$

$\coth(\hbar\omega/2k_B T)$ increases with T and decreases with ω , and at $T = 300$ K for vibrational frequencies ω_k of 1000, 300 and 100 cm^{-1} becomes, respectively, 1.017, 1.62 and 4.24.

Therefore, thermal contributions from low frequency vibrations can be important as compared with the respective zero point contributions.

2.2. Computational details

All computations have been performed with the G03 system of programs [25] at the Density Functional Theory (DFT) level using the hybrid functional B3LYP [26-28]. Several outputs were modified in order to increase the number of printed digits.

The harmonic frequencies ω_k and the cubic force constants Φ_{kll} in equations (3) and (4) were computed at different levels of theory as the hybrid force field B3LYP/6-31+G(d,p)//B3LYP/6-31G(d) proposed by Carbonier *et al* [29] to achieve the best compromise between computer time and quality of results. These authors tested the performance of B3LYP density functional for computing harmonic and anharmonic frequencies for a set of near rigid molecules. That study revealed that the relatively cheap 6-31+G(d,p) basis set performs a very good job for harmonic frequency calculations and that B3LYP anharmonicities are in close agreement with the reference values irrespective of the used basis set.

Equilibrium geometries were calculated with high numerical accuracy (optimization criterion Opt=VeryTight and numerical grid Int=Ultrafine) at the B3LYP/6-31+G(d,p) level obtaining harmonic frequencies ω_k and normal coordinates Q_k . Cubic force constants Φ_{kll} were computed at the B3LYP/6-31G(d) level [29].

J couplings were computed for equilibrium geometries and at positively ($+\delta Q_k$) and negatively ($-\delta Q_k$) displaced geometries along Q_k by using the DFT/B3LYP method with the default G03 options for optimization (Opt=Tight) and grid (Int=FineGrid). Tighter convergence criteria and more accurate numerical grids were also used for several couplings in order to check the performance of the selected

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3 procedures for computing J first and second derivatives with respect to Q_k . The BHH
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6 basis set was chosen for computing J couplings [16], which uses for H atoms s_H
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9 functions from the aug-cc-pV6Z basis set extended with three tight functions. For atoms
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11 from Li to Br it uses the standard cc-pVDZ basis set.
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3. Results and discussion

3.1. Computational precision

In a recent work [12], first J'_k and second $2J''_k$ derivatives of J with respect to Q_k , equation (2), were computed by numerical differentiation using the standard three points formula,

$$J'_k = [J_k(+\delta) - J_k(-\delta)]/2\delta, \quad (12)$$

$$J''_k = [J_k(+\delta) + J_k(-\delta) - 2J_e]/2\delta^2, \quad (13)$$

where $J_k(+\delta)$ and $J_k(-\delta)$ are J values computed for molecular geometries obtained increasing and decreasing, respectively, the equilibrium geometry in an amount δQ_k . It was found that the $2J''_k$ derivatives show, sometimes, an excessive variation with δ being the optimal value to be used of 0.1. However, the precision of values calculated in this way for J'_k , J''_k and J_{vib} was not then analyzed.

The numerical precision of the J'_k , J''_k and J_{vib} values depends on the precision ε of calculated J couplings and on the δ value used in the finite difference procedure. For a given ε , there is an optimum δ value such that numerical errors due to ε , which decrease with increasing δ , are equal to truncation errors due to the neglect of higher derivatives, which increase with increasing δ [21]. Unfortunately, neither the ε error nor the optimum δ value to be used for each normal coordinate is known in principle. Therefore, in order to determine the precision of J'_k , J''_k and J_{vib} more than three points must be used for calculating the J'_k and $2J''_k$ derivatives.

Two couplings were analyzed in detail in this work, namely, J^T *trans* coupling of fluoroethane and J^C *cis* coupling of cyclopropane. J^T was selected due to both its high calculated J_e^T value, 15.97 Hz, and because fluoroethane presents an inner rotation mode with a low calculated frequency of 252.5 cm⁻¹. J^T contributions J_{anh} and J_{har} were calculated at four δ values, i.e. 0.0001, 0.001, 0.01 and 0.1, and the corresponding J'_k and J''_k were obtained by means of equations (12) and (13). J'_k values show small variations with δ , while J''_k values do not, in particular those belonging to antisymmetrical vibrations. In the case of symmetrical vibrations, J''_k values are anomalous for $\delta = 0.0001$ but for $\delta > 0.0001$ they show only small variations. Since equation (13) contains J_e for the equilibrium conformation, a series of polynomic fittings were carried out without including the calculated J_e value in data. Fittings for sets of eight J_k^T values calculated for each normal coordinate to a fourth degree polynome,

$$J_k^T(\delta) = J_{ek} + J'_k \delta + J''_k \delta^2 + J'''_k \delta^3 + J''''_k \delta^4, \quad (14)$$

provide ΔJ_{ek} values,

$$\Delta J_{ek} = J_{ek} - J_e, \quad (15)$$

which are smaller than 10⁻⁷ in the case of symmetrical vibrations but which are equal to 0.0051468 Hz for antisymmetrical vibrations. This difference explains the bad results obtained for J''_k from equation (13) for the latter vibrations. On the other hand, ΔJ_{ek} values indicate that the precision ε for calculated J^T couplings is about 10⁻⁷ Hz but figures for antisymmetrical vibrations being shifted about 0.005 Hz from those for symmetrical vibrations. Fitted values for coefficients in equation (14) range from -24.5

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3 to 28.7 for J'_k , from -2.8 to 39.9 for J''_k , from -29.1 to 32.0 for J'''_k , and from -1.8 to
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6 24.3 for J''''_k .
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9 Taking $\varepsilon = 10^{-7}$ Hz, the precision of J'_k and J''_k , calculated using equations (12)
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11 and (13), respectively, should be better than 0.01 when the $\delta > 10^{-5}$ for the former, and
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13 $\delta > 2 \times 10^{-3}$ for the latter. J'_k values thus calculated with δ equal to 0.0001, 0.001 or 0.01
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15 differ from the corresponding fitted ones less than 0.03, 0.01 and 0.003, respectively.
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17 For $\delta = 0.1$ the differences are larger, but smaller than 0.4, due to the contributions from
18
19 the cubic terms which are not taken into account in equation (12). For symmetrical
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21 vibrations, J''_k calculated by using equation (13) for δ equal to 0.001 or 0.01 differ less
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23 than 0.3 and 0.01, respectively, from the corresponding fitted ones. For $\delta = 0.1$ the
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25 differences are larger than for $\delta = 0.01$, but smaller than 0.3, due to the contamination
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27 from quartic terms. For antisymmetrical vibrations there is, in addition, a spurious
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29 contribution $-\Delta J_{ek} / \delta^2$ to J''_k , which amounts to about 0.5 for $\delta = 0.1$.
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37 The spurious contribution $-\Delta J_{ek} / \delta^2$ to J''_k can be removed by selecting two δ
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39 values, instead of only one, and fitting the sets of four J_k^T values calculated for each
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41 normal coordinate Q_k to either a second or third degree polynome. Differences of the so
42
43 derived values for J'_k and J''_k with respect to those provided by the fittings of eight J_k^T
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45 values to the four degree polynome, equation (14), will be taken hereafter as their
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47 computational errors. When one of the two selected values is equal to 0.1 and the four
48
49 J_k^T values calculated are fitted to a second degree polynome the largest errors for J'_k
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51 and J''_k amount to 0.32 and 0.24, respectively, due to contamination from cubic and
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53 quartic terms. However, when one of the two selected δ values is equal to 0.01 and the
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55 other one is either 0.001 or 0.0001 the errors are smaller than 0.003 since such
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3 contaminations are then very small. When the two δ values are 0.001 and 0.0001, the
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5 largest error for J_k'' increases up to 0.3 due to the low precision ε of the calculated J_k^T
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8 couplings. However, J_k' errors are smaller than 0.02. On the other hand, when the four
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11 J_k^T values calculated are fitted to a third degree polynome and one of the two selected δ
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14 values is equal to 0.1 the errors for the J_k'' do no change but the errors for the J_k'
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16 decreases below 0.03 since contributions from the cubic terms are taken into account.
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18 The precision of the J_k' coefficients derived from the four J_k^T couplings computed for
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20 two δ values can be estimated, in principle, by comparison of the four J_k' values which
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23 can be calculated: two by means of equation (12) and the other two from the second and
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25 third degree fittings. When the two selected δ values are 0.01 and 0.001 the differences
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27 among the four J_k' values are smaller than 0.02. In this case, clearly, the contamination
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29 from cubic and quartic terms is very small.
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35 The precision of the J_k'' coefficients cannot be estimated, in general, by
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37 selecting only two J values due to the spurious contributions $-\Delta J_{ek}/\delta^2$ to J_k'' when
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39 equation (13) is applied and to the fact that the second and third degree fittings provide
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41 near the same value for each J_k'' . For these fittings the odd terms $J_k' \delta$ and $J_k''' \delta^3$ are
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43 correlated as the J_{ek} and $J_k'' \delta^2$ terms do. The J_k'' precision can be estimated, in
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45 principle by selecting three instead of two δ values. When these values are 0.001, 0.01
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47 and 0.1 and the six calculated J_k^T couplings are fitted to a fourth degree polynome the
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51 J_k' , J_k'' , J_k''' and J_k'''' errors are smaller than 0.0001, 0.002, 0.001 and 0.2, respectively.
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54 These values increase to 0.02, 0.4, 173 and 3452, when the δ values are 0.0001, 0.001
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56 and 0.01. An inadequate selection of δ values, 0.0001 is too small, provides anomalous
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58 values for J_k'''' and J_k''' which indicate larger errors in J_k'' and J_k' , respectively. The
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3 precision for J_k'' values can be estimated comparing the results of the four, third and
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5 second order fittings for the three values of δ and the results of the second and third
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7 order fittings for each of the three possible pairs of δ values.
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11 J^C cis coupling in cyclopropane was also studied in detail since this is a
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13 symmetrical ring molecule with degenerate vibrations. Calculated J_e^C is 10.08 Hz, and
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15 J_k^C couplings were calculated taking δ values of 0.001, 0.01 and 0.1, which provide
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17 precise J_k' and J_k'' values for only a part of normal vibrations. For other normal
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19 vibrations $\delta = 0.001$ results too small and systematic deviations appear. Additional J_k^C
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21 values were calculated for δ values of 0.005, 0.05, 0.075, 0.175 and 0.250 and each set
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23 of sixteen J_k^C was fitted to both a sixth and a fourth order polynome. The differences
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25 between the results of these fittings are smaller than 0.01 and 0.03 for J_k' and J_k'' ,
26
27 respectively, showing the small effect of the fifth and sixth order terms. On the other
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29 hand, when only three δ values are used, the respective maximum deviations for the
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31 fourth degree fittings are 0.01 and 0.03 for δ values of 0.01, 0.05 and 0.10 but increase
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33 to 0.07 and 0.44 for δ values of 0.001, 0.01 and 0.10.
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43 On the basis of the above described analysis of the J^T coupling of fluoroethane
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45 and the J^C coupling of cyclopropane we decided to compute the vibrational
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47 contributions of all couplings for δ values of 0.01, 0.05 and 0.10. Results, multiplied by
48
49 0.838, are given in tables 1 to 5 for the 84 considered couplings. Deviations with respect
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51 to these results of those obtained when less than three δ values are used are considered
52
53 as computational errors. Excluding the 5 couplings of bromocyclopropane (see below)
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55 the following maximum errors are found. When only the δ value of 0.10 is used with
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57 equations (12) and (13) the maximum errors for J_k' and J_k'' derivatives and vibrational
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2
3 averaged $\langle J \rangle$ couplings are 0.83, -1.02 and -0.31, respectively. When only the two δ
4 values of 0.01 and 0.05 are used the respective values decrease to 0.20, -0.26, and 0.01
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6 due to the fact that the spurious contributions $-\Delta J_{ek}/\delta^2$ to J_k'' are eliminated and the
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8 contamination from quartic terms is reduced. When the two δ values are either 0.10 and
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10 0.05, or 0.10 and 0.01, the contamination from quartic terms remains but the
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12 contributions $-\Delta J_{ek}/\delta^2$ are eliminated, consequently, the maximum error for the
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14 averaged $\langle J \rangle$ couplings decreases below 0.04 but the maximum errors for J_k' and J_k''
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16 are close to those found when only the δ value of 0.10 is used.
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24 The maximum computational error for the averaged $\langle J \rangle$ couplings, given in
25 tables 1 to 5 as J^{pre} , is, probably, smaller than 0.01 Hz since, though the maximum
26 errors for the J_k' and J_k'' when using the three δ values of 0.01, 0.05 and 0.10 are much
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28 smaller than when using only the two δ values of 0.01 and 0.05, differences between the
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30 averaged $\langle J \rangle$ couplings at 300 K calculated for both sets of δ values are, in general,
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32 smaller than 0.01 Hz. For bromocyclopropane such differences are a bit larger in
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34 absolute value, amounting to -0.04 Hz for coupling $J_{1,2'}$, due to the fact that when, for
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36 the lowest vibrational frequency calculated as 213.2 cm^{-1} , results from two δ values are
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38 compared with those from three δ values, the J_k'' coefficient decreases from 0.48 to
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40 0.35. On the other hand, the average value $\langle Q_k^2 \rangle$ increases from 0.079 at 0 K up to
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42 0.168 at 300 K. Consequently, the zero point vibrational contribution J_{vib}^0 decreases in
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44 0.02 Hz and the thermal vibrational contribution ΔJ_{vib}^T decreases in 0.02 Hz.
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3.2. Vibrational contributions

When vibrational contributions are neglected, averaged vicinal couplings to methyl protons can be estimated making use of the rotational isomeric state (RIS) approximation which assumes the molecule exists only in the most stable rotational isomers. For mono and 1,1-disubstituted ethanes, with monovalent and methyl substituents, all three rotational isomers are equivalent and J^{RIS} is given by

$$J^{RIS} = \frac{1}{3} (J_e^T + J_e^{G^+} + J_e^{G^-}), \quad (16)$$

where J_e^X , $X=T, G^+$ and G^- , are vicinal couplings for the equilibrium conformation defined in figure 1.

Figure 1 about here

Similarly, when vibrational contributions are taken into account, such averaged coupling J is given by

$$J = \frac{1}{3} (J^T + J^{G^+} + J^{G^-}), \quad (17)$$

with

$$J^X = J_e^X + J_{anh}^X + J_{har}^X, \quad (18)$$

where the anharmonic J_{anh}^X and harmonic J_{har}^X vibrational contributions are given by equations (7) and (8).

J^X couplings were calculated for 6 mono- and 5 1,1-disubstituted ethanes selected from those used by Altona *et al* [14] to derive a substituent parameter λ scale based on the relationship between J couplings and substituent electronegativities. Calculated couplings, J^{cal} , are overestimated but predicted J^{pre} couplings obtained by scaling J^{cal} with an optimized factor $f = 0.838$ are very close to experimental values, J^{exp} , i.e.

$$J^{pre} = f J^{cal} . \quad (19)$$

The rms deviation σ between J^{exp} and J^{pre} amounts to 0.07 Hz. J^{pre} values are shown in table 1 together with their vibrational contributions and the respective experimental values. Differences $J^{exp} - J^{pre}$, see last column of table 1, are of similar magnitude than those, given in parenthesis, reported previously without taking into account vibrational contributions [16]. J_e^X , first numeric column of table 1, were calculated for molecular geometries optimized at the B3LYP/6-31+G(d,p) level while in our previous work [16] geometries were optimized by using the basis set 6-31G(d) for atoms from H to Cl and 6-311G(d,p) for Br. Deviations ΔJ_e between present J_e values and those reported previously are of similar magnitude than $J^{exp} - J^{pre}$ differences.

Table 1 about here

In table 1 are also reported zero point vibrational contributions $J_{anh}^{0,X}$ and $J_{har}^{0,X}$, changes $\Delta J_{vib}^{T,X}$ of vibrational contributions when the temperature increases from 0 to 300 K, and vibrational contributions $J_{vib}^{300,X}$ at 300 K,

$$J_{vib}^{300,X} = J_{anh}^{0,X} + J_{har}^{0,X} + \Delta J_{vib}^{T,X} . \quad (20)$$

Thermal contributions, $\Delta J_{vib}^{T,X}$, for average couplings are small, they are between -0.04 and -0.02 Hz, compared with zero point vibrational contributions, $J_{vib}^{0,Av}$, between 0.35 and 0.58 Hz, which are dominated by $J_{har}^{0,Av}$, between 0.42 and 0.67 Hz. $J_{anh}^{0,Av}$ contributions are between -0.10 and -0.05 Hz.

Figure 2 about here

Table 2 about here

Results obtained for the chair conformations of cyclohexane, cyanocyclohexane and chlorocyclohexane are displayed in table 2. These J couplings are analogous to those for methyl protons: J^{AA} are of type *trans* like J^T since $|\phi_{HCCH}| \approx 180$, and J^{AE} and J^{EE} are of type *gauche* like J^{G^+} and J^{G^-} since $|\phi_{HCCH}| \approx 60$. Comparison of vibrational contributions with those of the same type given in table 1 shows two small but remarkable differences: anharmonic contributions $J_{anh}^{0,AA}$ are positive and thermal contributions $J_{vib}^{T,EE}$ are negative.

Figure 3 about here

Table 3 about here

Results obtained for norbornane-type molecules shown in figure 3 are given in table 3. The predicted couplings of type *cis* J^C , $|\phi_{HCCH}| \approx 0$, $J^{2x,3x}$ and $J^{2n,3n}$, are between 0.40 and 0.55 Hz smaller than those reported previously neglecting vibrational contributions [16] while those of type *skew* J^S , $|\phi_{HCCH}| \approx 120$, $J^{2x,3n}$ and $J^{2n,3x}$, are between 0.32 and 0.38 Hz larger. Except for $J^{2x,3x}$ in **2**, differences $J^{exp} - J^{pre}$ for all these couplings are of different sign when the vibrational contributions are considered than when they are neglected, (see last column in table 3). Differences $J^{exp} - J^{pre}$ for couplings of type *gauche* J^G , $|\phi_{HCCH}| \approx 60$, between *apical*, H₁ and H₄, and *bridge*, H_{7a} and H_{7s}, hydrogen atoms are small. On the other hand, for the small couplings between *apical* and *endo* hydrogen atoms, the larger deviations found for **3** seem to be due to low accuracy of experimental values since the predicted values are close to those predicted for $J^{1,2n}$ in **2**, 0.66 Hz, which only deviates -0.11 Hz.

Figure 4 about here

Table 4 about here

Results for some monosubstituted cyclopropanes are given in table 4. Like in norbornane type molecules, predicted couplings of type *cis* J^C , $|\phi_{HCCH}| \approx 0$, $J^{1,2}$, $J^{2,3}$ and $J^{2',3'}$, are smaller than those predicted previously [16], between 0.18 and 0.60 Hz, while the corresponding differences for couplings of near type *skew* J^S , $|\phi_{HCCH}| \approx 145$, $J^{1,2'}$ and $J^{2,3'}$, are smaller in magnitude, between -0.17 and 0.17 Hz. Harmonic contributions $J_{har}^{0,X}$ in each molecule are very close for the two couplings $J^{1,2}$ and $J^{1,2'}$ as well as for the three couplings $J^{2,3}$, $J^{2,3'}$ and $J^{2',3'}$, being the values for the latter couplings, between 0.52 and 0.84 Hz, larger than for the former ones, between 0.28 and 0.54 Hz, except for X=Li.

Table 5 about here

Results obtained for three-membered heteroatomic rings are given in table 5. Like data reported in table 4, couplings of type *cis* J^C , ($J^{2,3}$ and $J^{2',3'}$), are smaller than those predicted previously, between 0.17 and 0.38 Hz, but couplings of type *skew* J^S , ($J^{2,3'}$), are larger, between 0.01 and 0.18 Hz. Harmonic contributions $J_{har}^{0,X}$ are similar for the different couplings in each molecule ranging from 0.1 for (X,Y) = (O,Cl) to 0.7 Hz for (X,Y) = (PH,H).

Figure 5 about here

Zero point anharmonic and harmonic contributions for couplings of the *trans* ($J_{anh}^{0,T}$ and $J_{har}^{0,T}$) and *gauche* ($J_{anh}^{0,G}$ and $J_{har}^{0,G}$) types for ethane derivatives, six membered rings, and norbornane type molecules, are plotted in figure 5 against the J_e^X equilibrium values. J_e^X values are smaller than 5.0 Hz for *gauche* couplings and larger than 9.5 Hz for *trans* couplings. Anharmonic contributions (Δ) are small and negative, between $-$

0.16 and -0.03 Hz, except for *trans* couplings of six-membered rings which are positive and close to 0.1 Hz. On the other hand, harmonic contributions (\square) are larger and positive, between 0.10 and 1.11 Hz, being linearly correlated to J_e^X ,

$$J_{har}^{0,X} = 0.05 + 0.079J_e^X, \quad (21)$$

with a correlation coefficient R of 0.97 and a standard deviation σ of 0.10 Hz. The range for the $J_{har}^{0,T}$ contributions, between 0.94 and 1.11 Hz, is smaller than that for $J_{har}^{0,G}$, which is between 0.10 and 0.52 Hz.

Figure 6 about here

Zero point anharmonic and harmonic contributions for *cis* ($J_{anh}^{0,C}$ and $J_{har}^{0,C}$) and *skew* ($J_{anh}^{0,S}$ and $J_{har}^{0,S}$) couplings for norbornane type molecules and three-membered rings are plotted in figure 6 against J_e^X equilibrium values. Anharmonic contributions (Δ), between -0.26 and 0.10 Hz, show a rough negative correlation with J_e^X ,

$$J_{anh}^{0,X} = 0.06 - 0.022J_e^X, \quad (22)$$

with $R = -0.67$ and $\sigma = 0.07$ Hz. Like in the cases for *trans* and *gauche* couplings the larger harmonic contributions show positive correlations with J_e^X but now the contributions for *cis* couplings $J_{har}^{0,C}$ (\square) appear below those for the *skew* couplings $J_{har}^{0,S}$ (\circ),

$$J_{har}^{0,C} = -0.15 + 0.082J_e^X, \quad (23)$$

$$J_{har}^{0,S} = 0.08 + 0.092J_e^X, \quad (24)$$

being $R = 0.91$ and $\sigma = 0.08$ Hz.

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3 Thermal contributions for *trans* $\Delta J_{vib}^{300,T}$ and *gauche* $\Delta J_{vib}^{300,G}$ couplings are
4
5 relatively large, between -0.34 and 0.17 Hz, showing a rough negative correlation
6
7 with J_e^X ,
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$$10 \quad \Delta J_{vib}^{300,X} = 0.12 - 0.026 J_e^X, \quad (25)$$

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12 with $R = 0.86$ and $\sigma = 0.07$ Hz. On the other hand, thermal contributions for *cis* $\Delta J_{vib}^{300,C}$
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14 and *skew* $\Delta J_{vib}^{300,S}$ couplings are small in three-membered rings, between -0.07 and 0.02
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16 Hz, being a bit larger in magnitude in norbornane type molecules, between -0.06 and $-$
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18 0.14 Hz.
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25 Vibrational contributions $\Delta J_{vib}^{300,X}$ at 300 K show a rough positive correlation with
26
27 J_e^X ,
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$$30 \quad J_{vib}^{300,X} = 0.12 + 0.047 J_e^X, \quad (26)$$

31
32 with $R = 0.68$ and $\sigma = 0.19$ Hz.
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36 Overall deviations between J^{exp} and J^{pre} couplings, calculated including the
37
38 vibrational contributions, see last column of tables 1 to 5, are of similar magnitude than
39
40 those, given in parentheses, obtained previously calculating J^{pre} from equilibrium
41
42 values J_e^X [16]. Fittings to equation (19) of J couplings computed in this work for
43
44 equilibrium geometries, J_e^X , and including vibrational contributions, $J_e^X + J_{vib}^{300,X}$, yield,
45
46 respectively, values of 0.9016 and 0.8485 for the f factor and equal σ deviations of 0.18
47
48 Hz. In these fittings data for three-membered rings with one heteroatom, table 5, and
49
50 small couplings between *apical* and *endo* hydrogen atoms for compound **3** were not
51
52 included. The fact that the inclusion of the vibrational contributions, as calculated in this
53
54 work, does not improve the agreement between predicted J^{pre} and experimental J^{exp}
55
56 couplings could be due to errors of calculated J^{pre} values or to other factors, such as
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3 solvent effects, which have not been taken into account. In any case, the vibrational
4 contributions, globally considered, represent about 7% of J^{pre} and must be considered
5
6 for a reliable prediction of vicinal couplings.
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9

10 The accuracy of vibrational contributions calculated by means of equations (1)
11 to (9) depends, besides on the computational accuracy, on the accuracy of the calculated
12
13 J_k couplings, vibrational frequencies ω_k , and cubic force constants Φ_{kll} . Equations (3)
14
15 and (4) show that, the remaining factors being equal, the errors in $\langle Q_k \rangle$ and $\langle Q_k^2 \rangle$
16
17 and, therefore, in J_{vib} increase when ω_k decrease. The used equations are, in general, a
18
19 good approximation for near rigid molecules with low amplitude vibrations. However,
20
21 the approximation will be less good for flexible molecules with large amplitude
22
23 vibrations of low frequency, such as the torsional vibrations of methyl groups. The
24
25 estimation of vibrational contributions to J from these vibrations requires the
26
27 determination of the energy levels and wave functions for the appropriate Hamiltonian.
28
29 In the case of a molecule with one methyl group, a Hamiltonian for hindered rotation
30
31 should be applied [8-9]. Nevertheless, the deviations for the methyl couplings predicted
32
33 in this work are similar to those for couplings of near rigid molecules supporting the
34
35 conclusion that the contribution to the averaged coupling of one methyl group from the
36
37 torsional vibration is small [8-9]. It should be realized that for a methyl group the three
38
39 rotational isomers are equivalent with equal populations of 1/3, therefore, equation (17)
40
41 may be a reasonable approximation. On the other hand, when populations of rotational
42
43 isomers are different, such as in the case of 1,2-disubstituted ethanes, the situation is
44
45 much more complicated and the contributions from the torsional vibrations can be
46
47 important [9-11,30-31]. The problem of the conformational analysis is then involved
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49 and the energy levels and wave functions for the appropriate Hamiltonian for hindered
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3 rotation must be calculated in order to estimate the averaged J coupling and the
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5 populations of rotational isomers.
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8 The error of a predicted coupling J^{pre} depends, among other factors, on the
9
10 error of the calculated coupling for the equilibrium configuration J_e . The error of J_e is
11
12 determined by both the accuracy of the molecular geometry used for the equilibrium
13
14 configuration and of the theoretical method used to calculate the coupling constant. In
15
16 the second numerical column of tables 1 to 5 differences ΔJ_e^X between the J_e^X
17
18 couplings predicted this work and those predicted in reference [16] are given. Except for
19
20 molecules with Br atoms, these differences are due to small changes in local geometry
21
22 between the molecular geometries used in these work, optimized with the 6-31+G(d,p)
23
24 basis set, and those used in [16], optimized with the 6-31G(d) basis set. ΔJ_e^X values
25
26 provide an idea about the importance of errors in the calculated J_e values from
27
28 deviations of the optimized molecular configuration with respect to the true equilibrium
29
30 configuration. In table 1 the only ethane derivatives which show ΔJ_e^X values larger than
31
32 0.1 appear for molecules with F atoms, the most electronegative substituent, reaching
33
34 0.32 Hz for J^T of 1,1-difluoroethane, and for 1,1-dibromoethane. With respect to the
35
36 latter molecule it should be noted that the 6-311G(d,p) basis set was used for the Br
37
38 atoms in [16] for both the geometry optimization and for calculating J_e^X . Also, ΔJ_e^X
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40 values larger than 0.1 appear in table 4 for the two cyclopropanes with substituents Br,
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42 reaching -0.31 Hz for the coupling $J^{2,3'}$, and Li, the most electropositive substituent.
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4. Conclusions

One of the prerequisites to develop a procedure for a reliable and accurate prediction of vicinal J couplings is the feasibility of calculating vibrational contributions J_{vib}^T with a good computational accuracy which we target in 0.01 Hz. The present work shows that to reach this aim from equations (1) to (5), at the DFT/B3LYP level, and using the G03 programs, six values of J_k must be computed, in principle, for each normal coordinate Q_k . When J_k values are calculated for molecular geometries positively ($+\delta Q_k$) and negatively ($-\delta Q_k$) displaced from the equilibrium geometry along the normal coordinate Q_k the three δ values of 0.01, 0.05 and 0.10 constitute an appropriate set to be used. The computational error increases, in general, less than 0.01 Hz when only the two δ values of 0.01 and 0.05 are used but, in some cases, errors are introduced by contributions to J_{vib}^T from low frequency vibrations. Therefore, three δ values should be always used for these vibrations. On the other hand, although the precision of the first J'_k derivative of J with respect to the normal coordinate Q_k can be estimated from four J_k calculated for two δ values, estimation of the precision of the second $2J''_k$ derivative requires calculating six J_k for three δ values. When only one δ value of 0.10 is used, the computational error of J_{vib}^T increases up to 0.3 Hz for some couplings. The actual errors of calculated vibrational contributions J_{vib}^T are, of course, larger than the computational accuracy due to several factors discussed above.

Vibrational contributions J_{vib}^{300} are positively correlated with J_e values for the equilibrium configurations being the correlation coefficient equal to 0.68. This fact explains, in part, the reason why the global agreement between predicted J^{pre} and experimental J^{exp} couplings is near equal when the predicted couplings are calculated

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3 including the vibrational contributions J_{vib}^{300} than when they are calculated from only the
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6 J_e values. The main contributions to J_{vib}^{300} are the zero point harmonic contributions
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9 $J_{har}^{0,X}$ which show positive correlations with the J_e^X being the correlation coefficients
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12 larger than 0.9.

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14 The importance of vibrational contributions J_{vib}^T computed for the J couplings of
15
16 near rigid molecules and methyl protons shows that these contributions must be
17
18 included for a reliable prediction of vicinal couplings and, therefore, for a more accurate
19
20 application of J couplings in conformational analyses. However, equations (1) to (5)
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22 used in this work are not applicable, in general, when dealing with the important
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24 practical situation of flexible molecules with large amplitude vibrations involved in
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26 conformational equilibriums. In these cases the energy levels and wave functions for the
27
28 large amplitude vibrations must be calculated from the appropriate Hamiltonian in order
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30 to estimate the corresponding vibrational contributions and the conformer populations.
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42 Appendix

43 Two points have been analyzed after completion of this work. The obtained
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45 results are presented here for the sake of completeness but they do not affect to our
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47 conclusions.
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50 The first point refers to the temperature dependence of $\langle J \rangle$ due to centrifugal
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52 distortions. This is small for one and two bond coupling constants [45]. The
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54 contribution J_{cen} to $\langle J \rangle$ from this source is given by [24],
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56

$$57 J_{cen} = \sum_k J'_k \langle Q_k \rangle_{cen} \quad , \quad (27)$$

58
59
60 with

$$\langle Q_k \rangle_{cen} = \frac{k_B T}{2\omega_k^2} \sum_{\alpha} \frac{a_k^{(\alpha\alpha)}}{I_{\alpha\alpha}^{(e)}}, \quad (28)$$

where $I_{\alpha\alpha}^{(e)}$ is the moment of inertia at equilibrium geometry along the principal axis α and $a_k^{(\alpha\alpha)}$ is the derivative of $I_{\alpha\alpha}$ with respect to the coordinate Q_k evaluated at equilibrium. In equation (28) a classical average is used for the rotational part.

The calculated J_{cen} contributions are smaller in magnitude than 0.01 Hz for cyclic molecules and than 0.03 Hz for ethane derivatives.

Another interesting point refers to the method chosen to get a computational accuracy of 0.01 Hz for vibrational contributions J_{vib} based on the exhaustive application of fittings to polynomes of second, third and fourth degrees in δ of the calculated J_k values for δ equal to 0.01, 0.05 and 0.10. These fittings were carried out without including the calculated J_e for the equilibrium conformation value in data because differences ΔJ_{ek} between fitted values J_{ek} and J_e are often several orders of magnitude larger than the precision ε for calculated J_k values. Alternatively, differentiation methods based on using interpolation formulas or arisen from Taylor series approximations could be used, in principle. The Romberg's procedure, based on the second approach, has been used by Champagne and coworkers for numerical evaluation of hyperpolarizabilities [46] and hyper-Raman spectra [47]. Increasingly large values of the step size $\delta=2^{i-1}\lambda$, $i=1,2,3,\dots$ are used. The elimination of the higher order contamination terms is then performed by applying the iterative formula

$$P_j^i = \frac{4^j P_{j-1}^i - P_{j-1}^{i+1}}{4^j - 1}, \quad j = 1, 2, \dots, \quad (29)$$

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3 Where j is the number of the Romberg iteration and P_0^i is given by equations (12) for
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5
6 J_k' and (13) for J_k'' with $\delta=2^{i-1}\lambda$. Application of equation (29) to get improved P_1^i
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9 derivatives using δ values of 0.05 and 0.10 provides satisfactory results for J_k' and, also,
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11
12 for J_k'' when ΔJ_{ek} is negligible. As the magnitude of ΔJ_{ek} increases the results for J_k''
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15 become worse due to the spurious contributions $-\Delta J_{ek}/\delta^2$ to P_0^1 and P_0^2 calculated by
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18 means of equation (13).
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Table 1. Predicted^a J^{pre} and experimental^b J^{exp} methyl couplings for mono- and 1,1-disubstituted ethanes, see figure 1. Vibrational contributions to J^{pre} : zero point anharmonic $J_{anh}^{0,X}$ and harmonic $J_{har}^{0,X}$, thermal $\Delta J_{vib}^{T,X}$, and total $J_{vib}^{300,X}$ at 300 K, see equation (20). Predicted J_e^X couplings for the equilibrium configuration and deviations^c ΔJ_e^X . Values in parentheses in the last column correspond to differences $J^{exp} - J^{pre}$ in [16].

S1	S2		J^X	ΔJ_e^X	$J_{anh}^{0,X}$	$J_{har}^{0,X}$	$\Delta J_{vib}^{T,X}$	$J_{vib}^{300,X}$	J^{pre}	J^{exp}	$J^{exp} - J^{pre}$
H	H	J^T	15.35	-0.07	-0.05	0.98	-0.31	0.61	15.96		
		J^G	3.60	-0.01	-0.11	0.52	0.12	0.53	4.12		
		Av	7.52	-0.03	-0.09	0.67	-0.02	0.56	8.07	8.02	-0.05(-0.12)
Me	H	J^T	13.71	-0.03	-0.03	1.07	-0.28	0.75	14.46		
		J^{G^+}	3.66	0.01	-0.09	0.44	0.11	0.46	4.12		
		J^{G^-}	3.09	0.02	-0.08	0.34	0.11	0.37	3.47		
		Av	6.82	0.00	-0.07	0.62	-0.02	0.53	7.35	7.35	0.00(-0.02)
CN	H	J^T	14.03	-0.01	-0.10	0.98	-0.34	0.54	14.57		
		J^{G^+}	3.65	0.00	-0.09	0.46	0.11	0.47	4.12		
		J^{G^-}	3.63	0.02	-0.12	0.37	0.10	0.35	3.98		
		Av	7.10	0.00	-0.10	0.60	-0.04	0.45	7.56	7.63	0.07(-0.03)
F	H	J^T	13.39	0.20	-0.01	1.12	-0.27	0.84	14.23		
		J^{G^+}	4.83	-0.08	-0.13	0.43	-0.01	0.29	5.12		
		J^{G^-}	1.43	0.08	-0.07	0.28	0.17	0.38	1.81		
		Av	6.55	0.07	-0.07	0.61	-0.04	0.50	7.05	7.00	-0.05(0.00)
Cl	H	J^T	13.84	0.01	-0.04	1.11	-0.24	0.84	14.68		
		J^{G^+}	4.41	0.00	-0.11	0.45	0.02	0.36	4.78		
		J^{G^-}	2.16	0.04	-0.08	0.29	0.13	0.33	2.50		
		Av	6.80	0.02	-0.08	0.62	-0.03	0.51	7.32	7.26	-0.06(-0.07)
Br	H	J^T	14.09	0.00	-0.04	1.11	-0.24	0.83	14.92		
		J^{G^+}	4.34	0.01	-0.10	0.46	0.03	0.38	4.72		
		J^{G^-}	2.33	0.05	-0.08	0.30	0.12	0.34	2.67		
		Av	6.92	0.02	-0.07	0.62	-0.03	0.52	7.44	7.35	-0.09(-0.10)
Me	F	J^T	11.65	0.22	-0.03	1.09	-0.26	0.80	12.45		
		J^{G^+}	3.82	0.00	-0.11	0.26	0.00	0.15	3.97		
		J^{G^-}	1.59	0.08	-0.07	0.23	0.16	0.32	1.92		
		Av	5.69	0.10	-0.07	0.53	-0.03	0.42	6.11	6.11	0.00(0.08)
Me	Me	J^T	12.08	-0.04	-0.02	1.06	-0.23	0.82	12.90		

		J^G	3.12	0.02	-0.07	0.29	0.09	0.31	3.43		
		Av	6.11	0.00	-0.05	0.55	-0.02	0.48	6.59	6.61	0.02(0.02)
F	F	J^T	9.70	0.32	-0.04	0.97	-0.22	0.72	10.42		
		J^G	1.50	0.03	-0.09	0.14	0.07	0.12	1.62		
		Av	4.23	0.13	-0.07	0.42	-0.03	0.32	4.55	4.52	-0.03(0.09)
Cl	Cl	J^T	11.77	0.06	-0.06	1.05	-0.17	0.82	12.59		
		J^G	2.51	0.04	-0.10	0.22	0.05	0.17	2.68		
		Av	5.60	0.05	-0.09	0.50	-0.02	0.39	5.98	6.04	0.06(0.05)
Br	Br	J^T	12.16	-0.14	-0.05	1.05	-0.15	0.86	13.02		
		J^G	2.49	-0.09	-0.09	0.23	0.04	0.18	2.67		
		Av	5.71	-0.11	-0.08	0.50	-0.02	0.41	6.12	6.27	0.15(-0.01)

^aTheoretical values in this table correspond to computed values multiplied by 0.836, see equation 17. ^b J^{exp} values are taken from the dataset constructed by Altona et al.[4]. The value for 1,1-dibromo ethane is the weighted mean of two measures [32-33]. ^cDifferences between J_e^X couplings predicted in this work and those predicted in [16]

Table 2. Predicted J^{pre} and experimental^a J^{exp} couplings for some monosubstituted cyclohexanes, see figure 2. For notation see table 1.

X		J^X	ΔJ_e^X	$J_{anh}^{0,X}$	$J_{har}^{0,X}$	$\Delta J_{vib}^{T,X}$	$J_{vib}^{300,X}$	J^{pre}	J^{exp}	$J^{exp} - J^{pre}$
H	$J_{1a,2a}$	11.97	0.00	0.08	1.10	-0.05	1.12	13.10	12.85	-0.25(-0.07)
	$J_{1a,2e}$	3.48	0.04	-0.04	0.24	0.08	0.28	3.77	3.61	-0.16(-0.10)
	$J_{1e,2e}$	2.66	0.00	-0.09	0.22	-0.04	0.09	2.76	2.92	0.16(0.04)
CN	$J_{1a,2a}$	11.19	0.02	0.07	1.04	-0.07	1.04	12.23	12.66	0.43(0.60)
	$J_{1a,2e}$	3.31	0.03	-0.04	0.23	0.08	0.28	3.59	3.53	-0.06(-0.01)
	$J_{1e,2a}$	4.26	0.13	-0.06	0.18	0.12	0.24	4.49	4.27	-0.22(-0.18)
	$J_{1e,2e}$	2.33	-0.06	-0.08	0.20	-0.05	0.07	2.40	2.69	0.29(0.11)
Cl	$J_{1a,2a}$	10.73	0.03	0.08	1.09	-0.06	1.11	11.84	11.88	0.04(0.34)
	$J_{1a,2e}$	3.91	0.05	-0.07	0.27	0.04	0.23	4.14	4.08	-0.06(-0.08)
	$J_{1e,2a}$	2.93	0.07	-0.08	0.11	0.09	0.13	3.06	2.97	-0.09(-0.12)
	$J_{1e,2e}$	2.68	-0.01	-0.08	0.22	-0.06	0.08	2.76	3.03	0.27(0.12)

^a All the J^{exp} values are taken from [34].

Table 3. Predicted J^{pre} and experimental^a J^{exp} couplings for some norbornane type molecules, see figure 3. For notation see table 1.

<i>C</i>		J^X	ΔJ_e^X	$J_{anh}^{0,X}$	$J_{har}^{0,X}$	$\Delta J_{vib}^{T,X}$	$J_{vib}^{300,X}$	J^{pre}	J^{exp}	$J^{exp} - J^{pre}$
1	$J_{2x,3x}$	11.46	-0.02	-0.16	0.72	-0.14	0.42	11.88	12.22	0.34(-0.18)
	$J_{2x,3n}$	4.02	0.00	0.05	0.60	0.06	0.70	4.72	4.62	-0.10(0.28)
	$J_{2n,3n}$	8.62	0.01	-0.14	0.46	-0.10	0.21	8.84	9.05	0.21(-0.25)
2	$J_{2x,3x}$	8.61	-0.01	-0.14	0.43	-0.05	0.24	8.85	9.38	0.53(0.07)
	$J_{2x,3n}$	3.48	0.00	0.07	0.53	0.03	0.63	4.10	3.91	-0.19(0.16)
	$J_{2n,3n}$	8.39	-0.01	-0.12	0.46	-0.06	0.28	8.67	9.02	0.35(-0.05)
	$J_{1,2x}$	3.34	0.01	-0.11	0.15	-0.02	0.02	3.37	3.66	0.29(0.06)
	$J_{1,2n}$	0.59	0.01	-0.03	0.10	0.01	0.08	0.66	0.55	-0.11(-0.07)
	$J_{1,7s}$	1.45	0.00	-0.06	0.12	0.00	0.06	1.50	1.51	0.01(-0.05)
	$J_{1,7a}$	1.68	0.01	-0.07	0.12	-0.01	0.05	1.72	1.83	0.11(0.03)
3	$J_{2x,3x}$	11.21	0.01	-0.16	0.62	-0.13	0.33	11.54	12.05	0.51(-0.04)
	$J_{2x,3n}$	4.16	0.03	0.00	0.59	0.03	0.62	4.78	4.70	-0.08(0.24)
	$J_{2n,3x}$	3.96	-0.03	0.10	0.57	0.05	0.72	4.69	4.59	-0.10(0.28)
	$J_{2n,3n}$	8.57	0.00	-0.13	0.44	-0.11	0.20	8.77	9.12	0.35(-0.13)
	$J_{1,2x}$	4.47	-0.01	-0.09	0.22	-0.05	0.08	4.55	4.72	0.17(-0.12)
	$J_{1,2n}$	0.56	0.01	-0.03	0.12	0.02	0.11	0.67	0.12	-0.55(-0.47)
	$J_{1,7s}$	1.08	0.01	-0.04	0.10	0.01	0.07	1.15	1.19	0.04(0.03)
	$J_{1,7a}$	1.54	0.00	-0.06	0.12	-0.01	0.05	1.59	1.64	0.05(-0.02)
	$J_{4,7s}$	1.96	-0.01	-0.06	0.15	-0.01	0.08	2.04	2.10	0.06(-0.03)
	$J_{4,7a}$	1.42	-0.06	-0.05	0.10	0.00	0.04	1.46	1.60	0.14(0.08)
	$J_{4,3x}$	4.10	0.00	-0.11	0.19	-0.03	0.05	4.15	4.30	0.15(-0.12)
$J_{4,5x}$	4.41	0.00	-0.09	0.24	-0.02	0.13	4.54	4.76	0.22(0.00)	
$J_{4,3n}$	0.48	0.01	-0.02	0.12	0.03	0.12	0.61	0.12	-0.49(-0.39)	
$J_{4,5n}$	0.42	0.00	-0.03	0.12	0.02	0.12	0.54	0.00	-0.54(-0.46)	

^a J^{exp} values are taken from [35] for **1**, [36] for **2**, and [37] for **3**.

Table 4. Predicted J^{pre} and experimental^a J^{exp} couplings for some monosubstituted cyclopropanes, see figure 4a. For notation see table 1.

X		J^X	ΔJ_e^X	$J_{anh}^{0,X}$	$J_{har}^{0,X}$	$\Delta J_{vib}^{T,X}$	$J_{vib}^{300,X}$	J^{pre}	J^{exp}	$J^{exp} - J^{pre}$
H	$J_{1,2}$	8.45	-0.02	-0.15	0.54	-0.01	0.38	8.83	8.97	0.14(-0.17)
	$J_{1,2'}$	5.07	-0.02	0.01	0.52	0.00	0.53	5.61	5.58	-0.03(0.08)
F	$J_{1,2}$	5.69	0.02	-0.14	0.31	-0.01	0.17	5.85	5.89	0.04(-0.23)
	$J_{1,2'}$	2.22	-0.03	-0.02	0.28	0.02	0.28	2.50	2.39	-0.11(-0.04)
	$J_{2,3}$	9.96	-0.08	-0.20	0.82	-0.03	0.59	10.56	10.80	0.24(-0.04)
	$J_{2,3'}$	7.00	0.03	-0.04	0.74	-0.01	0.70	7.70	7.70	0.00(0.17)
	$J_{2',3'}$	11.32	-0.06	-0.26	0.84	-0.04	0.54	11.86	12.01	0.15(-0.28)
Cl	$J_{1,2}$	6.81	0.01	-0.14	0.36	-0.01	0.21	7.03	7.01	-0.02(-0.33)
	$J_{1,2'}$	3.43	0.02	-0.01	0.35	0.02	0.36	3.79	3.58	-0.21(-0.10)
	$J_{2,3}$	9.48	-0.08	-0.16	0.76	-0.02	0.58	10.06	10.26	0.20(-0.06)
	$J_{2,3'}$	6.56	-0.08	-0.03	0.70	-0.01	0.67	7.23	7.14	-0.09(-0.03)
	$J_{2',3'}$	10.23	-0.08	-0.19	0.76	-0.03	0.54	10.77	10.58	-0.19(-0.55)
Br	$J_{1,2}$	7.00	0.04	-0.13	0.38	-0.01	0.23	7.23	7.13	-0.10(-0.38)
	$J_{1,2'}$	3.70	0.01	-0.01	0.37	0.02	0.39	4.08	3.80	-0.28(-0.18)
	$J_{2,3}$	9.31	-0.18	-0.17	0.74	-0.02	0.54	9.85	10.16	0.31(-0.08)
	$J_{2,3'}$	6.28	-0.28	-0.04	0.68	-0.01	0.63	6.91	7.01	0.10(-0.07)
	$J_{2',3'}$	9.92	-0.31	-0.19	0.73	-0.03	0.52	10.44	10.45	0.01(-0.59)
Li	$J_{1,2}$	10.39	0.00	-0.04	0.67	-0.01	0.63	11.02	11.31	0.29(0.09)
	$J_{1,2'}$	8.13	-0.08	0.11	0.73	0.01	0.85	8.98	9.12	0.14(0.26)
	$J_{2,3}$	7.13	-0.12	-0.15	0.31	-0.04	0.13	7.25	7.71	0.46(-0.11)
	$J_{2,3'}$	3.03	-0.09	-0.04	0.30	-0.04	0.22	3.25	3.17	-0.08(-0.19)
	$J_{2',3'}$	5.79	-0.12	-0.07	0.29	0.00	0.21	6.00	6.42	0.42(0.05)
CN	$J_{1,2}$	8.04	0.01	-0.13	0.51	0.07	0.45	8.49	8.43	-0.06(-0.24)
	$J_{1,2'}$	4.68	0.02	-0.01	0.48	0.05	0.52	5.20	5.12	-0.08(0.09)
	$J_{2,3}$	8.53	-0.06	-0.14	0.59	-0.06	0.38	8.92	9.18	0.26(-0.09)
	$J_{2,3'}$	6.41	-0.06	0.00	0.64	-0.04	0.60	7.02	7.08	0.06(0.10)
	$J_{2',3'}$	9.08	-0.03	-0.15	0.60	-0.08	0.37	9.44	9.49	0.05(-0.34)

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^a J^{exp} values are taken from [38] for $X = \text{H}$, [39] for $X = \text{Cl}$, Br , and CN , and [40] for $X = \text{Li}$ and F .

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Table 5. Predicted J^{pre} and experimental^a J^{exp} couplings for some three-membered rings with one heteroatom, see figure 4b. For notation see table 1.

X	Y		J^X	ΔJ_e^X	$J_{anh}^{0,X}$	$J_{har}^{0,X}$	$\Delta J_{vib}^{T,X}$	$J_{vib}^{300,X}$	J^{pre}	J^{exp}	$J^{exp} - J^{pre}$
NH	H	$J_{2,3}$	6.09	-0.05	-0.15	0.26	-0.01	0.10	6.19		
		$J_{2',3'}$	4.45	-0.08	-0.08	0.25	0.00	0.17	4.62		
		A_v	5.27	-0.07	-0.12	0.26	-0.01	0.14	5.41	6.30	0.89(0.54)
		$J_{2',3}$	2.95	-0.03	0.00	0.27	0.00	0.27	3.22	3.80	0.58(0.59)
O	H	$J_{2,3}$	3.45	-0.02	-0.11	0.22	0.00	0.12	3.57	4.45	0.88(0.71)
		$J_{2,3'}$	2.12	0.09	0.01	0.24	0.00	0.25	2.37	3.10	0.73(0.91)
O	Cl	$J_{2,3}$	2.15	0.00	-0.09	0.07	0.00	-0.02	2.13	2.68	0.55(0.36)
		$J_{2,3'}$	0.92	0.06	0.01	0.09	0.01	0.11	1.03	1.42	0.39(0.49)
S	H	$J_{2,3}$	6.22	-0.05	-0.16	0.41	0.00	0.25	6.47	6.89	0.42(0.12)
		$J_{2,3'}$	5.08	-0.08	0.03	0.50	0.02	0.54	5.63	5.74	0.11(0.17)
PH	H	$J_{2,3}$	9.55	-0.08	-0.22	0.72	-0.02	0.47	10.02	10.05	0.03(-0.35)
		$J_{2',3'}$	8.91	-0.07	-0.16	0.64	-0.02	0.47	9.38	9.26	-0.12(-0.44)
		$J_{2,3'}$	7.31	-0.10	0.06	0.75	0.01	0.82	8.13	7.80	-0.33(-0.20)

^a J^{exp} values are taken from [41] for $X = \text{NH}$ and $Y = \text{H}$, and for $X = \text{O}$ and $Y = \text{H}$, [42] for $X = \text{O}$ and $Y = \text{Cl}$, [43] for $X = \text{PH}$ and $Y = \text{H}$, and [44] for $X = \text{S}$ and $Y = \text{H}$.

Figure 1.

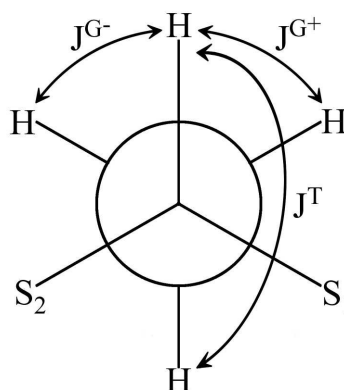


Figure 2

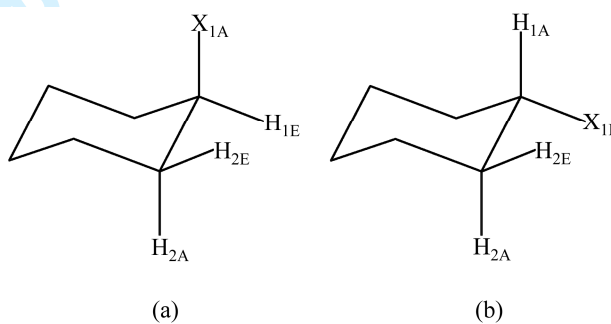


Figure 3

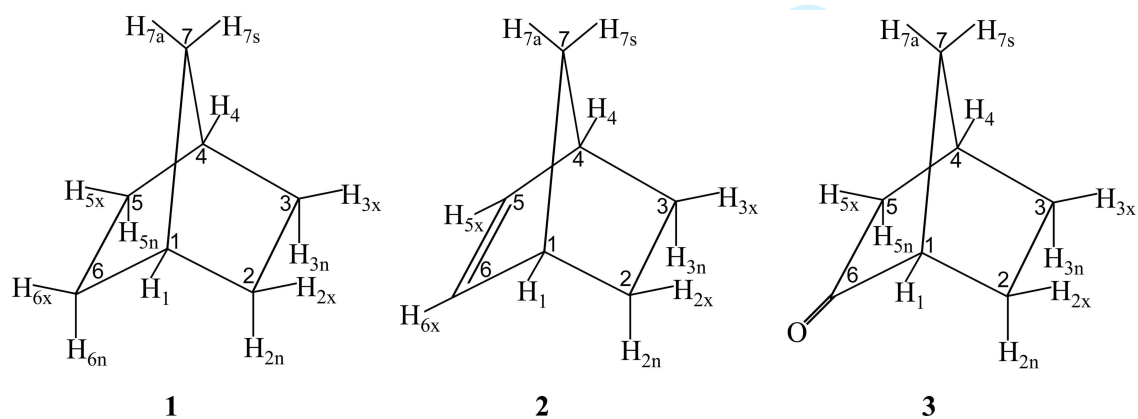


Figure 4

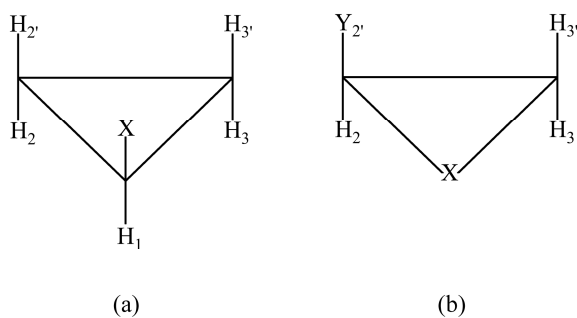


Figure 5

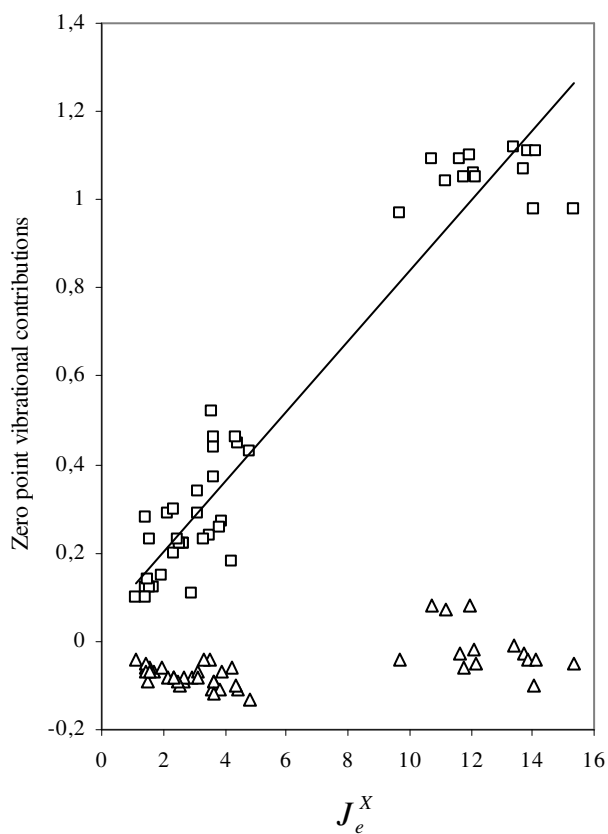
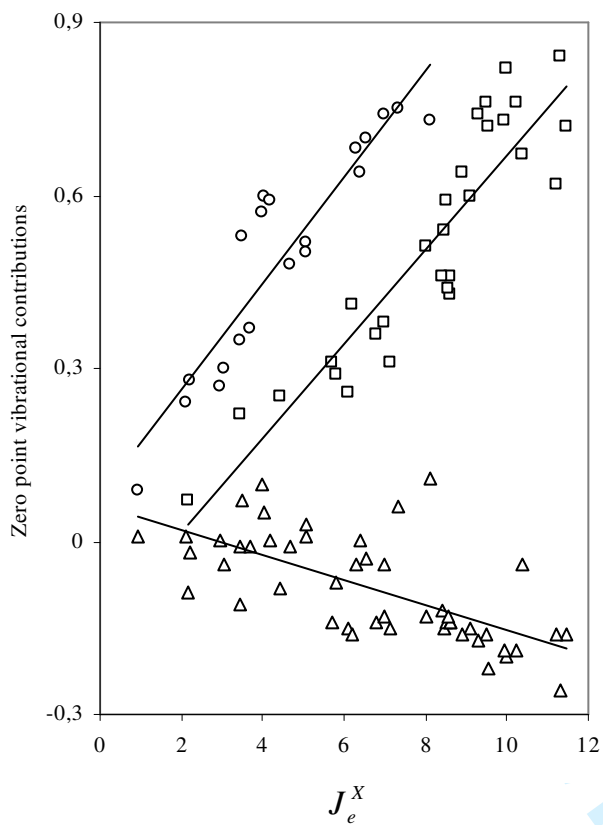


Figure 6



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Figure captions

Figure 1. Definitions of J^T , J^{G^+} and J^{G^-} couplings for the equilibrium configuration of an ethane derivative.

Figure 2. A monosubstituted cyclohexane with the substituent X in axial position (a) and in equatorial position (b).

Figure 3. Norbornane type molecules.

Figure 4. Monosubstituted cyclopropanes (a) and three-membered rings with one heteroatom (b).

Figure 5. Zero point harmonic (\square) and anharmonic (Δ) contributions for couplings of types *trans* and *gauche* versus J_e values.

Figure 6. Zero point harmonic (\square and \circ) and anhamonic (Δ) contributions for couplings of types *cis* (\square) and *skew* (\circ) versus J_e values.