

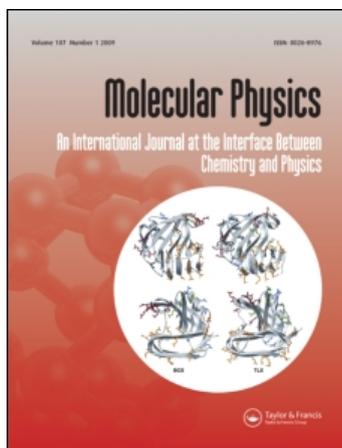
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Vibrational contributions to vicinal proton-proton coupling constants³J_{HH'}

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RESEARCH ARTICLE

Vibrational contributions to vicinal proton–proton coupling constants ${}^3J_{\text{HH}}$

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Vibrational contributions to the ${}^3J_{\text{HH}}$ couplings of six mono- and five 1,1-di-substituted ethanes, three mono-substituted cyclohexanes, three 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 ${}^3J_{\text{HH}}$ couplings since, globally, J_{vib}^{300} contributions amount to about 7% of the J_e values and the correlation coefficient between J_{vib}^{300} and J_e is 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 analysed.

Keywords: vicinal coupling constants; vibrational contributions; numerical precision; DFT/B3LYP

1. Introduction

The development of a practical procedure for accurate prediction of vicinal proton–proton coupling constants ${}^3J_{\text{HH}}$ (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, in general, been carried out using analytical expressions empirically parameterised and of limited precision [6,13–15]. State-of-the-art theoretical methods are the natural alternative to the use of empirical equations for predicting J couplings accurately. 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 to 0.17 Hz versus the larger σ deviation of 0.31 Hz reported for the best empirically parameterised extended Karplus equation [14]. J couplings were calculated at the optimised equilibrium geometries for a series of selected molecules, but vibrational contributions were not estimated [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 considerable interest in vibrational contributions to nuclear spin–spin coupling constants [17–19], which are typically of the same order of magnitude as the differences between the coupling constants calculated theoretically and those observed experimentally. Therefore, these contributions should always be computed when the performance of computational methods is analysed and when

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the temperature dependence of coupling constants or secondary isotope effects is studied [20].

In order to calculate vibrational contributions to coupling constants the first and diagonal second derivatives of J with respect to normal coordinates must be computed. No analytical implementation exists for evaluating these derivatives, therefore a numerical procedure must be used [21]. In principle, first and second derivatives of J with respect to normal coordinates Q_k can be obtained from three values of J computed for the equilibrium geometry J_e and for positively ($+\delta Q_k$) and negatively ($-\delta Q_k$) displaced geometries along the normal coordinate Q_k . This procedure, which uses one δ value and requires the computation of two J_k values, does not provide the computational accuracy necessary for our purposes. Therefore, the performance at the DFT/B3LYP level of procedures that use two or three δ values and require computing four or six J_k values have been analysed, aiming at computational accuracies of 0.01 Hz for vibrational contributions J_{vib} to J and smaller than 0.05 Hz/amu^{1/2} Å and 0.10 Hz/amu Å², respectively, for the first and second derivatives of J with respect to Q_k .

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 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 ,

$$J'_k = \left(\frac{\partial J}{\partial Q_k} \right)_e, \quad 2J''_k = \left(\frac{\partial^2 J}{\partial Q_k^2} \right)_e. \quad (2)$$

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 the k th normal

mode and Φ_{kll} are the cubic anharmonic normal coordinate force constants, defined as

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

According to Equations (3) and (4), the first- and second-order terms in Equation (1), $J'_k \langle Q_k \rangle$ and $J''_k \langle Q_k^2 \rangle$, 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

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

with

$$J_{\text{anh}} = \sum_k J'_k \langle Q_k \rangle = \sum_k J_{\text{anh},k}, \quad (7)$$

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

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

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

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)–(9), the zero point vibrational contributions to J , J_{anh}^0 , J_{har}^0 and J_{vib}^0 are obtained. The differences between vibrational contributions at temperature T , J_{anh}^T , J_{har}^T and J_{vib}^T , and the corresponding values at the zero point can be considered as the thermal vibrational contributions ΔJ_{anh}^T , ΔJ_{har}^T and ΔJ_{vib}^T :

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

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

$\coth(\hbar\omega/2k_B T)$ 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 the respective zero point contributions.

2.2. Computational details

All computations were 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 Carbonnier *et al.* [29] to achieve the best compromise between computer time and quality of results. These authors tested the performance of the 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 basis set used.

Equilibrium geometries were calculated with high numerical accuracy (optimisation 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 using the DFT/B3LYP method with the default G03 options for optimisation (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 procedures for computing J first and second derivatives with respect to Q_k . The BHH basis set was chosen for computing J couplings [16], which uses for H atoms s_H functions from the aug-cc-pV6Z basis set extended with three tight functions. For atoms from Li to Br it uses the standard cc-pVDZ basis set.

3. Results and discussion

3.1. Computational precision

In recent work [12], the 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

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

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

where $J_k(+\delta)$ and $J_k(-\delta)$ are J values computed for molecular geometries obtained by increasing and

decreasing, respectively, the equilibrium geometry by an amount δQ_k . It was found that the $2J''_k$ derivatives sometimes show excessive variation with δ , the optimal value to use being 0.1. However, the precision of the values calculated in this way for J'_k , J''_k and J_{vib} was not then analysed.

The numerical precision of the J'_k , J''_k and J_{vib} values depends on the precision, ε , of the 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 the 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. 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 analysed 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^T_e 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 polynomial fittings were carried out without including the calculated J_e value in the data. Fittings for sets of eight J''_k values calculated for each normal coordinate to a fourth-degree polynome,

$$J''_k(\delta) = J_{ek} + J'_k\delta + J''_k\delta^2 + J'''_k\delta^3 + J''''_k\delta^4, \quad (14)$$

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 are shifted about 0.005 Hz from those for symmetrical vibrations. Fitted values for coefficients in Equation (14) range from -24.5 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 24.3 for J_k'''' .

Taking $\varepsilon = 10^{-7}$ Hz, the precision of J_k' and J_k'' , calculated using Equations (12) and (13), respectively, should be better than 0.01 when $\delta > 10^{-5}$ for the former, and $\delta > 2 \times 10^{-3}$ for the latter. J_k' values thus calculated with δ equal to 0.0001, 0.001 or 0.01 differ from the corresponding fitted values by less than 0.03, 0.01 and 0.003, respectively. For $\delta = 0.1$ the differences are larger, but smaller than 0.4, due to the contributions from the cubic terms, which are not taken into account in Equation (12). For symmetrical vibrations, J_k'' calculated using Equation (13) for δ equal to 0.001 or 0.01 differ by less than 0.3 and 0.01, respectively, from the corresponding fitted values. For $\delta = 0.1$ the differences are larger than for $\delta = 0.01$, but smaller than for 0.3, due to the contamination from quartic terms. For antisymmetrical vibrations there is, in addition, a spurious contribution $-\Delta J_{ek}/\delta^2$ to J_k'' , which amounts to about 0.5 for $\delta = 0.1$.

The spurious contribution $-\Delta J_{ek}/\delta^2$ to J_k'' can be removed by selecting two δ values, instead of only one, and fitting the sets of four J_k^T values calculated for each normal coordinate Q_k to either a second- or third-degree polynome. The differences of the values thus derived for J_k' and J_k'' with respect to those provided by the fittings of eight J_k^T values to the four-degree polynome (Equation (14)) will be taken hereafter as their computational errors. When one of the two selected values is equal to 0.1 and the four J_k^T values calculated are fitted to a second-degree polynome the largest errors for J_k' and J_k'' amount to 0.32 and 0.24, respectively, due to contamination from cubic and quartic terms. However, when one of the two selected δ values is equal to 0.01 and the other is either 0.001 or 0.0001 the errors are smaller than 0.003 since such contamination is then very small. When the two δ values are 0.001 and 0.0001, the largest error for J_k'' increases to 0.3 due to the low precision ε of the calculated J_k^T couplings. However, J_k' errors are smaller than 0.02. On the other hand, when the four calculated J_k^T values are fitted to a third-degree polynome and one of the two selected δ values is equal to 0.1 the errors for J_k'' do not change, but the errors for J_k' decrease below 0.03 since contributions from the cubic terms are taken into account. The precision of the J_k' coefficients derived from the four J_k^T couplings computed for two δ values can be estimated, in principle, by comparison of the four J_k' values, which can be calculated: two by means of Equation (12) and the other two from the second- and third-degree fittings. When the two selected δ values are 0.01 and 0.001 the differences among the four J_k' values are smaller than 0.02. In this

case, clearly, the contamination from cubic and quartic terms is very small.

The precision of the J_k'' coefficients cannot be estimated, in general, by selecting only two J values due to the spurious contributions $-\Delta J_{ek}/\delta^2$ to J_k'' when Equation (13) is applied and to the fact that the second- and third-degree fittings provide nearly the same value for each J_k'' . For these fittings the odd terms $J_k''\delta$ and $J_k'''\delta^3$ are correlated as for the J_{ek} and $J_k''\delta^2$ terms. The J_k'' precision can be estimated, in principle, by selecting three instead of two δ values. When these values are 0.001, 0.01 and 0.1 and the six calculated J_k^T couplings are fitted to a fourth-degree polynome the J_k' , J_k'' , J_k''' and J_k'''' errors are smaller than 0.0001, 0.002, 0.001 and 0.2, respectively. These values increase to 0.02, 0.4, 173 and 3452, when the δ values are 0.0001, 0.001 and 0.01. An inadequate selection of δ values (0.0001 is too small) provides anomalous values for J_k'''' and J_k''' , which indicate larger errors in J_k'' and J_k' , respectively. The precision for J_k'' values can be estimated by comparing the results of the four, third- and second-order fittings for the three values of δ and the results of the second- and third-order fittings for each of the three possible pairs of δ values.

J^C *cis* coupling in cyclopropane was also studied in detail since this is a symmetrical ring molecule with degenerate vibrations. Calculated J_e^C is 10.08 Hz, and J_k^C couplings were calculated taking δ values of 0.001, 0.01 and 0.1, which provide precise J_k' and J_k'' values for only some of the normal vibrations. For other normal vibrations, $\delta = 0.001$ is too small and systematic deviations appear. Additional J_k^C values were calculated for δ values of 0.005, 0.05, 0.075, 0.175 and 0.250 and each set of 16 J_k^C was fitted to both a sixth- and a fourth-order polynome. The differences between the results of these fittings are smaller than 0.01 and 0.03 for J_k' and J_k'' , respectively, showing the small effect of the fifth- and sixth-order terms. On the other hand, when only three δ values are used, the respective maximum deviations for the fourth-degree fittings are 0.01 and 0.03 for δ values of 0.01, 0.05 and 0.10, but increase to 0.07 and 0.44 for δ values of 0.001, 0.01 and 0.10.

On the basis of the above described analysis of the J^T coupling of fluoroethane and the J^C coupling of cyclopropane we decided to compute the vibrational contributions of all couplings for δ values of 0.01, 0.05 and 0.10. The results, multiplied by 0.838, are given in Tables 1–5 for the 84 considered couplings. Deviations with respect to these results of those obtained when less than three δ values are used are considered as computational errors. Excluding the five couplings of bromocyclopropane (see below) the following

Table 1. Predicted^a J^{pre} and experimental^b J^{exp} methyl couplings for mono- and 1,1-di-substituted ethanes (see Figure 1). Vibrational contributions to J^{pre} : zero point anharmonic $J_{\text{anh}}^{0,X}$ and harmonic $J_{\text{har}}^{0,X}$, thermal $\Delta J_{\text{vib}}^{T,X}$, and total $J_{\text{vib}}^{300,X}$ at 300 K (see Equation (20)). Predicted J_c^X couplings for the equilibrium configuration and deviations^c ΔJ_c^X . Values in parentheses in the last column correspond to differences $J^{\text{exp}} - J^{\text{pre}}$ in Ref. [16].

S1	S2		J^X	ΔJ_c^X	$J_{\text{anh}}^{0,X}$	$J_{\text{har}}^{0,X}$	$\Delta J_{\text{vib}}^{T,X}$	$J_{\text{vib}}^{300,X}$	J^{pre}	J^{exp}	$J^{\text{exp}} - J^{\text{pre}}$
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)
		J^T	9.70	0.32	-0.04	0.97	-0.22	0.72	10.42		
F	F	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)
		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		
Cl	Cl	Av	5.60	0.05	-0.09	0.50	-0.02	0.39	5.98	6.04	0.06(0.05)
		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)

Notes: ^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-dibromoethane is the weighted mean of two measures [32,33].

^cDifferences between J_c^X couplings predicted in this work and those predicted in Ref. [16].

maximum errors are found. When only the δ value of 0.10 is used with Equations (12) and (13) the maximum errors for J'_k and J''_k derivatives and vibrational averaged $\langle J \rangle$ couplings are 0.83, -1.02 and -0.31, respectively. When only the two δ values of 0.01 and 0.05 are used the respective values decrease to 0.20, -0.26, and 0.01 due to the fact that the spurious contributions $-\Delta J_{ek}/\delta^2$ to J''_k are eliminated and the contamination from quartic terms is reduced. When

the two δ values are either 0.10 and 0.05, or 0.10 and 0.01, the contamination from quartic terms remains, but the contributions $-\Delta J_{ek}/\delta^2$ are eliminated, consequently the maximum error for the averaged $\langle J \rangle$ couplings decreases below 0.04, but the maximum errors for J'_k and J''_k are similar to those found when only the δ value of 0.10 is used.

The maximum computational error for the averaged $\langle J \rangle$ couplings, given in Tables 1–5 as J^{pre} , is

Table 2. Predicted J^{pre} and experimental^a J^{exp} couplings for some mono-substituted cyclohexanes (see Figure 2). For notation, see Table 1.

X		J^X	ΔJ_c^X	$J_{\text{anh}}^{0,X}$	$J_{\text{har}}^{0,X}$	$\Delta J_{\text{vib}}^{T,X}$	$J_{\text{vib}}^{300,X}$	J^{pre}	J^{exp}	$J^{\text{exp}} - J^{\text{pre}}$
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)
Cl	$J_{1e,2e}$	2.33	-0.06	-0.08	0.20	-0.05	0.07	2.40	2.69	0.29(0.11)
	$J_{1a,2a}$	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)

Note: ^aAll the J^{exp} values are taken from Ref. [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.

C		J^X	ΔJ_c^X	$J_{\text{anh}}^{0,X}$	$J_{\text{har}}^{0,X}$	$\Delta J_{\text{vib}}^{T,X}$	$J_{\text{vib}}^{300,X}$	J^{pre}	J^{exp}	$J^{\text{exp}} - J^{\text{pre}}$
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)	

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

(probably) smaller than 0.01 Hz since, although the maximum errors for J'_k and J''_k when using the three δ values of 0.01, 0.05 and 0.10 are much smaller than when using only the two δ values of 0.01 and 0.05, the differences between the averaged $\langle J \rangle$ couplings at 300 K calculated for both sets of δ values are, in general, smaller than 0.01 Hz. For bromocyclopropane such differences are a bit larger in absolute value, amounting to -0.04 Hz for coupling $J_{1,2'}$, due to the

fact that when, for the lowest vibrational frequency calculated as 213.2 cm^{-1} , results from two δ values are compared with those from three δ values, the J''_k coefficient decreases from 0.48 to 0.35. On the other hand, the average value $\langle Q_k^2 \rangle$ increases from 0.079 at 0 K to 0.168 at 300 K. Consequently, the zero point vibrational contribution J_{vib}^0 decreases 0.02 Hz and the thermal vibrational contribution ΔJ_{vib}^T decreases 0.02 Hz.

Table 4. Predicted J^{pre} and experimental^a J^{exp} couplings for some mono-substituted cyclopropanes (see Figure 4(a)). For notation, see Table 1.

X		J^X	ΔJ_c^X	$J_{\text{anh}}^{0,X}$	$J_{\text{har}}^{0,X}$	$\Delta J_{\text{vib}}^{T,X}$	$J_{\text{vib}}^{300,X}$	J^{pre}	J^{exp}	$J^{\text{exp}} - J^{\text{pre}}$
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)
Cl	$J_{2,3'}$	11.32	-0.06	-0.26	0.84	-0.04	0.54	11.86	12.01	0.15(-0.28)
	$J_{1,2}$	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)
Br	$J_{2,3'}$	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)
	$J_{1,2}$	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)
Li	$J_{2,3}$	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)
	$J_{1,2}$	10.39	0.00	-0.04	0.67	-0.01	0.63	11.02	11.31	0.29(0.09)
CN	$J_{1,2'}$	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)
	$J_{1,2}$	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)

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

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

X	Y		J^X	ΔJ_c^X	$J_{\text{anh}}^{0,X}$	$J_{\text{har}}^{0,X}$	$\Delta J_{\text{vib}}^{T,X}$	$J_{\text{vib}}^{300,X}$	J^{pre}	J^{exp}	$J^{\text{exp}} - J^{\text{pre}}$
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)
O	H	$J_{2,3}$	2.95	-0.03	0.00	0.27	0.00	0.27	3.22	3.80	0.58(0.59)
		$J_{2,3'}$	3.45	-0.02	-0.11	0.22	0.00	0.12	3.57	4.45	0.88(0.71)
O	Cl	$J_{2,3}$	2.12	0.09	0.01	0.24	0.00	0.25	2.37	3.10	0.73(0.91)
		$J_{2,3'}$	2.15	0.00	-0.09	0.07	0.00	-0.02	2.13	2.68	0.55(0.36)
S	H	$J_{2,3}$	0.92	0.06	0.01	0.09	0.01	0.11	1.03	1.42	0.39(0.49)
		$J_{2,3'}$	6.22	-0.05	-0.16	0.41	0.00	0.25	6.47	6.89	0.42(0.12)
PH	H	$J_{2,3}$	5.08	-0.08	0.03	0.50	0.02	0.54	5.63	5.74	0.11(0.17)
		$J_{2,3}$	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)

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

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-di-substituted ethanes, with monovalent and methyl substituents, all three

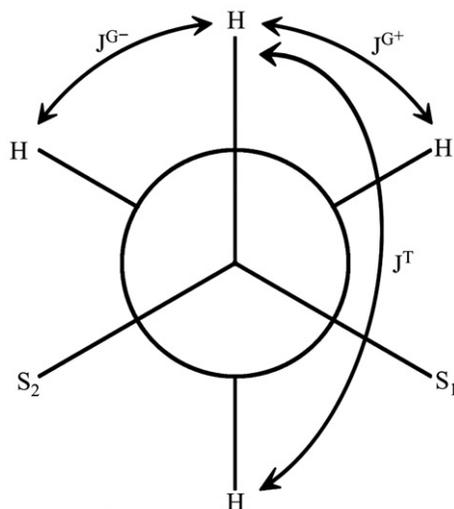


Figure 1. Definitions of J^T , J^{G^+} and J^{G^-} couplings for the equilibrium configuration of an ethane derivative.

rotational isomers are equivalent and J^{RIS} is given by

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

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

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

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

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 six mono- and five 1,1-di-substituted ethanes selected from those used by Altona [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 optimised factor $f = 0.838$ are very close to experimental values, J^{exp} , i.e.

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

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. The differences $J^{\text{exp}} - J^{\text{pre}}$ (see last column of Table 1) are of similar magnitude as those (given in parentheses) reported previously

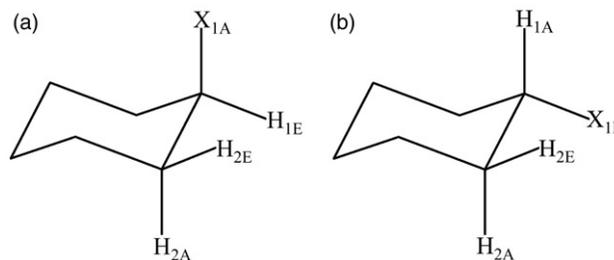


Figure 2. A mono-substituted cyclohexane with substituent X in the axial position (a) and in the equatorial position (b).

without taking into account vibrational contributions [16]. J_e^X (first numeric column of Table 1) were calculated for molecular geometries optimised at the B3LYP/6-31 + G(d,p) level, while in our previous work [16] geometries were optimised using the basis set 6-31G(d) for atoms from H to Cl and 6-311G(d,p) for Br. Deviations ΔJ_e between the present J_e values and those reported previously are of similar magnitude as the $J^{\text{exp}} - J^{\text{pre}}$ differences.

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

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

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

The results obtained for the chair conformations of cyclohexane, cyanocyclohexane and chlorocyclohexane are displayed in Table 2 (see Figure 2). These J couplings are analogous to those for methyl protons: J^{AA} are of *trans*-like J^T type since $|\phi_{\text{HCCH}}| \approx 180$, and J^{AE} and J^{EE} are of *gauche*-like J^{G^+} and J^{G^-} type since $|\phi_{\text{HCCH}}| \approx 60$.

Results obtained for norbornane-type molecules shown in Figure 3 are given in Table 3. The predicted couplings of type *cis* J^C , $|\phi_{\text{HCCH}}| \approx 0$, $J^{2x,3x}$ 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 , $|\phi_{\text{HCCH}}| \approx 120$, $J^{2x,3n}$ and $J^{2n,3x}$, are between 0.32 and 0.38 Hz larger. Except for $J^{2x,3x}$ of **2**, differences $J^{\text{exp}} - J^{\text{pre}}$ for all these couplings are of different sign when the vibrational contributions are considered than when they are neglected (see last column of Table 3). Differences $J^{\text{exp}} - J^{\text{pre}}$ for couplings of type *gauche* J^G ,

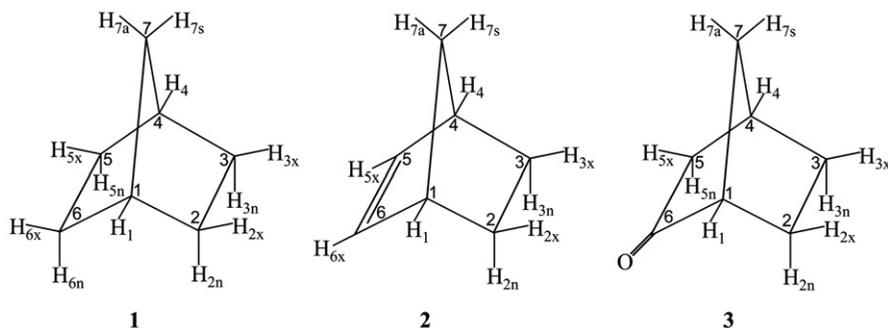


Figure 3. Norbornane-type molecules.

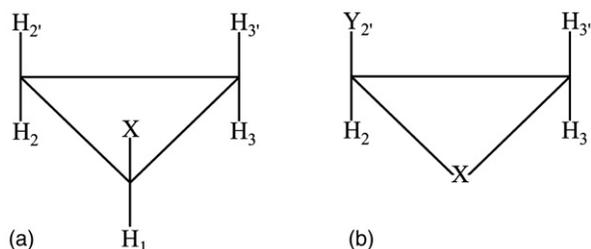
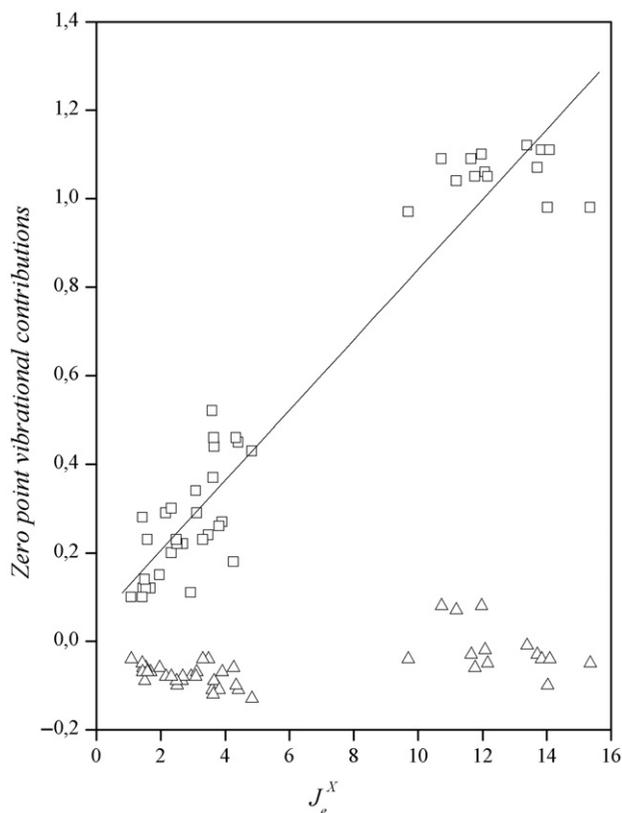


Figure 4. Mono-substituted cyclopropanes (a) and three-membered rings with one heteroatom (b).

$|\varphi_{\text{HCCH}}| \approx 60$, between *apical* H_1 and H_4 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 the low accuracy of the experimental values since the predicted values are close to those predicted for $J^{1,2n}$ of **2** (0.66 Hz), which only deviates -0.11 Hz.

Results for some mono-substituted cyclopropanes are given in Table 4 (see Figure 4). As for norbornane-type molecules, predicted couplings of type *cis* J^C , $|\varphi_{\text{HCCH}}| \approx 0$, $J^{1,2}$, $J^{2,3}$ 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-*skew* J^S type, $|\varphi_{\text{HCCH}}| \approx 145$, $J^{1,2'}$ and $J^{2',3'}$, are smaller in magnitude (between -0.17 and 0.17 Hz). Harmonic contributions $J_{\text{har}}^{0,X}$ for each molecule are similar 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 $J^{2',3'}$, the values for the latter couplings (between 0.52 and 0.84 Hz) being larger than for the former (between 0.28 and 0.54 Hz), except for $X = \text{Li}$.

Results obtained for three-membered heteroatomic rings are given in Table 5. As for the 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).

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

Harmonic contributions $J_{\text{har}}^{0,X}$ are similar for the different couplings in each molecule, ranging from 0.1 for $(X, Y) = (\text{O}, \text{Cl})$ to 0.7 Hz for $(X, Y) = (\text{PH}, \text{H})$.

Zero point anharmonic and harmonic contributions for couplings of the *trans* ($J_{\text{anh}}^{0,T}$ and $J_{\text{har}}^{0,T}$) and *gauche* ($J_{\text{anh}}^{0,G}$ and $J_{\text{har}}^{0,G}$) types for ethane derivatives, six-membered rings, and norbornane type molecules are plotted in Figure 5 versus 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) and linearly correlated to J_e^X

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

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

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

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

with $R = -0.67$ and $\sigma = 0.07$ Hz. As for the cases of *trans* and *gauche* couplings, the larger harmonic

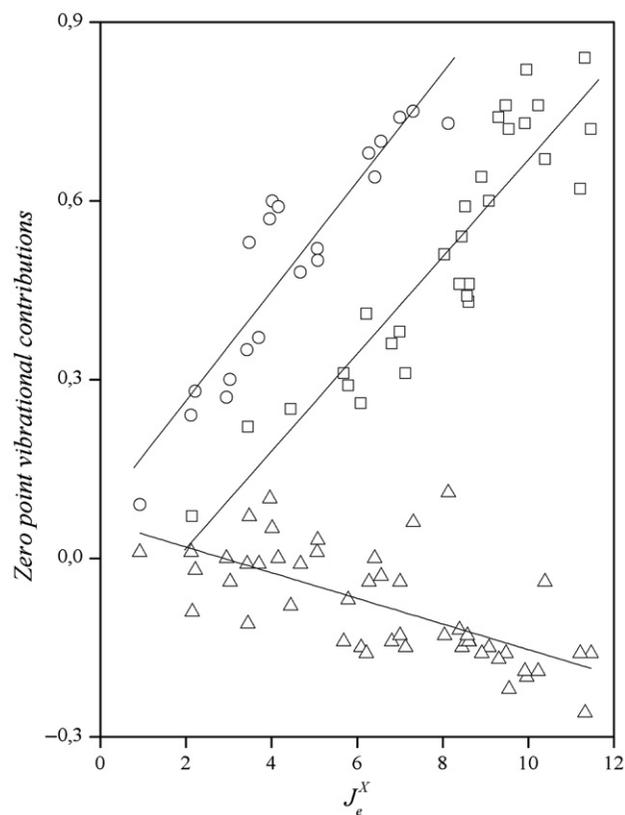


Figure 6. Zero point harmonic (\square and \circ) and anharmonic (Δ) contributions for couplings of types *cis* (\square) and *skew* (\circ) versus J_e^X values.

contributions show positive correlations with J_e^X , but now the contributions for *cis* couplings $J_{\text{har}}^{0,C}$ (\square) appear below those for the *skew* couplings $J_{\text{har}}^{0,S}$ (\circ)

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

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

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

Thermal contributions for *trans* $\Delta J_{\text{vib}}^{300,T}$ and *gauche* $\Delta J_{\text{vib}}^{300,G}$ couplings are relatively large (between -0.34 and 0.17 Hz), showing an approximate negative correlation with J_e^X

$$\Delta J_{\text{vib}}^{300,X} = 0.12 - 0.026J_e^X, \quad (25)$$

with $R = 0.86$ and $\sigma = 0.07$ Hz. On the other hand, thermal contributions for *cis* $\Delta J_{\text{vib}}^{300,C}$ and *skew* $\Delta J_{\text{vib}}^{300,S}$ couplings are small in three-membered rings (between -0.07 and 0.02 Hz), and are a bit larger in magnitude in norbornane-type molecules (between -0.06 and -0.14 Hz).

Vibrational contributions $\Delta J_{\text{vib}}^{300,X}$ at 300 K show an approximate positive correlation with J_e^X

$$J_{\text{vib}}^{300,X} = 0.12 + 0.047J_e^X, \quad (26)$$

with $R = 0.68$ and $\sigma = 0.19$ Hz.

Overall, the deviations between J^{exp} and J^{pre} couplings, calculated including the vibrational contributions (see the last column of Tables 1–5), are of similar magnitude to those (given in parentheses) obtained previously calculating J^{pre} from equilibrium values J_e^X [16]. Fittings to Equation (19) of J couplings computed in this work for equilibrium geometries J_e^X , and including vibrational contributions $J_e^X + J_{\text{vib}}^{300,X}$, yield, respectively, values of 0.9016 and 0.8485 for the f factor and σ deviations of 0.18 Hz. In these fittings, data for three-membered rings with one heteroatom (Table 5) and small couplings between *apical* and *endo* hydrogen atoms for compound **3** were not included. The fact that the inclusion of the vibrational contributions, as calculated in this work, does not improve the agreement between predicted J^{pre} and experimental J^{exp} couplings could be due to errors of the calculated J^{pre} values or to other factors, such as solvent effects, which have not been taken into account. In any case, the vibrational contributions, globally, represent about 7% of J^{pre} and must be considered for a reliable prediction of vicinal couplings.

The accuracy of the vibrational contributions calculated by means of Equations (1) to (9) depends, in addition to the computational accuracy, on the accuracy of the calculated J_k couplings, vibrational frequencies ω_k , and cubic force constants Φ_{klj} .

Equations (3) and (4) show that, the remaining factors being equal, the errors in $\langle Q_k \rangle$ and $\langle Q_k^2 \rangle$ and, therefore, in J_{vib} increase when ω_k decreases. The equations used are, in general, a good approximation for near-rigid molecules with low-amplitude vibrations. However, the approximation will become worse for flexible molecules with large-amplitude vibrations of low frequency, such as the torsional vibrations of methyl groups. The estimation of vibrational contributions to J from these vibrations requires the determination of the energy levels and wave functions for the appropriate Hamiltonian. In the case of a molecule with one methyl group, a Hamiltonian for hindered rotation should be applied [8,9]. Nevertheless, the deviations for the methyl couplings predicted in this work are similar to those for couplings of near-rigid molecules, supporting the conclusion that the contribution to the averaged coupling of one methyl group from the torsional vibration is small [8,9]. It should be realised that, for a methyl group, the three rotational isomers are equivalent with equal populations of one-third, therefore Equation (17) may be a reasonable approximation. On the other hand, when populations of rotational isomers are different, such as in the case of 1,2-di-substituted ethanes, the situation is much more complicated and the contributions from the torsional vibrations can be important [9–11,30,31]. The problem of the conformational analysis then becomes involved and the energy levels and wave functions for the appropriate Hamiltonian for hindered rotation must be calculated in order to estimate the averaged J coupling and the populations of rotational isomers.

The error of a predicted coupling J^{pre} depends, among other factors, on the error of the calculated coupling for the equilibrium configuration J_e . The error of J_e is determined by both the accuracy of the molecular geometry used for the equilibrium configuration and of the theoretical method used to calculate the coupling constant. In the second numerical column of Tables 1–5, differences ΔJ_e^X between the J_e^X couplings predicted in this work and those predicted in Ref. [16] are given. Except for molecules with Br atoms, these differences are due to small changes in local geometry between the molecular geometries used in this work, optimised with the 6-31+G(d,p) basis set, and those used in Ref. [16], optimised with the 6-31G(d) basis set. ΔJ_e^X values provide an indication of the importance of errors in the calculated J_e values from deviations of the optimised molecular configuration with respect to the true equilibrium configuration. In Table 1 the only ethane derivatives which show ΔJ_e^X values larger than 0.1 appear for molecules with F atoms, the most electronegative substituent, reaching 0.32 Hz for J^T of 1,1-difluoroethane and for

1,1-dibromoethane. With respect to the latter molecule it should be noted that the 6-311G(d,p) basis set was used for the Br atoms in Ref. [16] for both the geometry optimisation and for calculating J_e^X . Also, ΔJ_e^X values larger than 0.1 appear in Table 4 for the two cyclopropanes with substituents Br (reaching -0.31 Hz for the coupling $J^{2,3'}$) and Li, the most electropositive substituent.

4. Conclusions

One of the prerequisites to developing a procedure for a reliable and accurate prediction of vicinal J couplings is the feasibility of calculating vibrational contributions J_{vib}^T with good computational accuracy, which we target as 0.01 Hz. The present work shows that, to attain this using Equations (1)–(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 , δ values of 0.01, 0.05 and 0.10 constitute an appropriate set to be used. In general, the computational error increases less than 0.01 Hz when only 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 always be 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 (0.10) is used, the computational error of J_{vib}^T increases 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 the factors discussed above.

Vibrational contributions J_{vib}^{300} are positively correlated with J_e values for the equilibrium configurations with a correlation coefficient of 0.68. This fact explains, in part, the reason why the global agreement between predicted J^{pre} and experimental J^{exp} couplings is good when the predicted couplings are calculated including the vibrational contributions J_{vib}^{300} than when they are calculated from only the J_e values. The main contributions to J_{vib}^{300} are the zero point harmonic contributions $J_{\text{har}}^{0,X}$ which show positive correlations with J_e^X with correlation coefficients greater than 0.9.

The importance of vibrational contributions J_{vib}^T computed for the J couplings of near-rigid molecules

and methyl protons shows that these contributions must be included for a reliable prediction of vicinal couplings and, therefore, for a more accurate application of J couplings in conformational analyses. However, Equations (1)–(5) used in this work are not generally applicable when dealing with the important practical situation of flexible molecules with large-amplitude vibrations involved in conformational equilibria. In these cases the energy levels and wave functions for the large-amplitude vibrations must be calculated from the appropriate Hamiltonian in order to estimate the corresponding vibrational contributions and the conformer populations.

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Appendix 1

Two points were analysed after completion of this work. For the sake of completeness they are included in this appendix, although they do not affect the conclusions presented above.

The first point refers to the temperature dependence of $\langle J \rangle$ due to centrifugal distortions. This is small for one and

two bond coupling constants [45]. The contribution J_{cen} to $\langle J \rangle$ from this source is given in Ref. [24] as

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

with

$$\langle Q_k \rangle_{\text{cen}} = \frac{k_{\text{B}} T}{2\omega_k^2} \sum_{\alpha} \frac{d_k^{(\alpha\alpha)}}{I_{\alpha\alpha}^{(e)}}, \quad (28)$$

where $I_{\alpha\alpha}^{(e)}$ is the moment of inertia at the equilibrium geometry along the principal axis α and $d_k^{(\alpha\alpha)}$ 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.

For cyclic compounds the calculated J_{cen} contributions are smaller in magnitude than 0.01 Hz, and for ethane derivatives they are smaller than 0.03 Hz.

Another interesting point refers to the method chosen to attain a computational accuracy of 0.01 Hz for vibrational contributions J_{vib} based on the exhaustive application of fittings to polynomials of second, third and fourth degree in δ of the calculated J_k values for $\delta = 0.01, 0.05$ and 0.10 . These fittings were carried out excluding the calculated J_e for the equilibrium conformation value in the data because the 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 the use of interpolation formulas or arising from Taylor series approximations could also be used. For instance, Romberg's procedure, based on the second approach, was used by Champagne and coworkers for the numerical evaluation of hyperpolarizabilities [46] and hyper-Raman spectra [47]. Increasingly large values for 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

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

where j is the number of the Romberg iteration and P_0^i is given by Equation (12) for J'_k and Equation (13) for J''_k with $\delta = 2^{i-1}\lambda$. Application of Equation (29) to obtain improved P_1^i derivatives using δ values of 0.05 and 0.10 provides satisfactory results for J'_k and also for J''_k when ΔJ_{ek} is negligible. As the magnitude of ΔJ_{ek} increases the results for J''_k become worse due to the spurious contributions $-\Delta J_{ek}/\delta^2$ to P_0^1 and P_0^2 calculated by means of Equation (13).