The insignificance of long-distance interactions for molecular frequencies. Analyses of sparse force-constant matrices.

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Abstract

The experimentally observed group additivity of temperature dependent molecular properties of organic molecules *i.e.* the heat capacity, suggests that molecular vibrational frequencies primarily are determined by short-distance atomic interactions. Based on the molecular graph a consistent hierarchy of molecular force constant (FC) matrices has be constructed. These sparse and low-density matrices systematically include the force constants for the uncoupled atomic displacement, neighbour (1-2), next-neighbour (1-3) and longer-range atomic interactions. Such FC matrices were constructed for a number of hydrocarbons and hetero atomic molecules, and the error on the vibrational frequencies decrease rapidly with the inclusion of more interactions in the matrices. With inclusion of 1-4 interactions average relative errors between 1.3 % and 3.8 % are obtained based on B3LYP/6-311(d,p) calculations. The largest relative errors are found for low frequency vibrations below 50 cm^{-1}. The results were largely independent of the calculational level. The insignificance of the long-distance interactions was confirmed by the improvement in the calculated frequencies of hetero atomic molecules when FC matrices with only short-distance interactions is complemented with matric elements from a FC matrix of a hydrocarbon with similar geometry. Further confirmation is provided by calculations of molecular frequencies from the FC matrices constructed from fragments and supplemented with matrix elements for the interactions between atoms belonging to different fragments taken from appropriate compounds. The difference between the vibrational frequencies obtained in this way without the molecular FC matrix an those obtained from the full FC matrix are within a few cm^{-1}.

Keywords:Group additivity, molecular vibrations, sparse matrices, graph theory.

I Introduction

The concept of the chemical group has a central role in the qualitative description of the reactive properties of organic molecules. It can be expressed quantitatively by group additivity schemes for thermochemical properties of which that developed by Benson for molecules in the gas phase is the most well-known.[1-5] Discussions of the foundation of group additivity are commonly based on the "atoms in molecules" theory of Bader[6-9]. However, this theory deal only with the electronic energy and group additivity of thermochemical properties, at temperatures different from absolute zero include temperature dependent terms that are not directly connected to the energy of the unperturbed molecule. Consequently, a full explanation for the origin of this central concept in organic chemistry is still lacking.

In an attempt to provide an explanation for the group additivity of the temperature dependent properties, an hypothesis based on molecular and group frequency distributions has been proposed.[10,11] The hypothesis is based on the rigid rotator-harmonic oscillator approximation and introduces the group frequency distribution (GFD) as an important variable. The central claim of the hypothesis is that when the molecular frequency distributions (MFD) is a weighted sum of group frequency distributions (GFDs), the temperature dependent properties will be additive in the groups. It is worth pointing out that the vibrational frequencies of a molecule are completely determined by the MFD and the number of atoms. The hypothesis is supported by the fact that calculated MFD's of polymers approach a limiting value as the degree of polymerization increases. Furthermore, when the MFD in the limit of an infinite polymeric chain is equated with the GFD's of the monomeric units, and following the rules for transformation of statistical distributions, it can be shown that the hypothesis provides an explanation for the group additivity of thermochemical values.[11] The hypothesis is supported by model calculations of vibrational frequencies but experimental support for the hypothesis would require measurements of total molecular frequency distributions. In the absence of such experimental tests, further support for the hypothesis must be found in fundamental physics and calculational investigations.

The limiting behaviour of the MFD in polymeric chains and the derived significance of the GFDs is only possible when the MFDs dependency on long distance interactions is insignificant. This is also implicit in the hierarchy of additivity approximations constructed by Benson and Buss[1].

Benson and Buss classified the group-additivity concept as a second order approximation for estimation of molecular properties from atomic properties. The zero'th order approximation was defined as an estimation of molecular properties by adding atomic properties. This is nearly exact for the mass and approximate for a few other properties but obviously of limited chemical interest, as the atoms are unchanged in chemical reactions. In the first order approximation each atom is considered together with its neighbours (1-2 interactions). This is equivalent to estimating the properties of a molecule from its constituent bonds. For certain classes of compounds this is a useful mean for estimating molecular properties and is often used in qualitative analyses of chemical reactivity. In the second order approximation next-neighbour (1-3) interactions are included in the estimation of molecular properties.

However, in order to limit the number of different groups to what is necessary and practical, the Benson and Buss hierarchy is not consistent beyond the zero'th and first order approximations in the way next-neighbour interactions are treated when all the atoms of a group are taken into account. This can be seen by considering an α-methylene group in a ketone and in an ester. They are regarded as identical groups in

Benson additivity schemes but the 1-3 interaction between the methylene carbon and the alkoxy oxygen of the ester is clearly absent in the ketone. On the other hand, for the hydrogen atoms 1-4 interactions are taken into account in so far as an α-methylene group is different from a methylene group in a hydrocarbon chain.

Benson and Buss based their group additivity scheme on a system of exchange reactions. An alternative system in which next-neighbour and longer range interactions is treated systematically is presented here and is based on a graph theoretical analysis of the molecular graph and its adjacency matrix.[12-16] As will be shown, molecular frequencies can be accurately estimated from sparse and low-density force constant matrices where the selection of the matrix elements is based on the properties of the molecular graph.

The primary purpose of the present work is to give a better theoretical foundation to the concept of the chemical group through an investigation of the properties of the FC-matrix; in particular the influence of eliminating long distance interactions from the matrix. A secondary purpose is to investigate the potential for estimation of molecular vibrational frequencies from sparse and low-density matrices which only include short-distance atomic interactions. The calculation of the full force constant (FC) matrix is often regarded as a bottleneck in the calculations of the properties of large systems, and various procedures have been suggested to simplify the task.[17-25] The results presented here will focus on results obtained from alkylbenzenes and a selection of their nitrogen, oxygen and silicon derivatives.

Several different calculational levels have been used in the investigation but the Tables and Figures of the main text are based on results obtained at the B3LYP/6-311G(d,p) level. Results with other calculational levels and methods are given in the Supporting Information.

II Spare matrices and molecular graphs

Molecular frequencies are found by solving an eigenvalue problem[26,27]:

$$\mathbf{M}^{-1/2}\mathbf{K}\mathbf{M}^{-1/2}\,\mathbf{x} = \omega^2\,\mathbf{x} \tag{1}$$

where **K** is the force constant matrix, **x** represents the displacement in cartesian coordinates, ω are the angular frequencies. $\mathbf{M}^{-1/2}$ is a diagonal matrix in which each element is equal to $1/\sqrt{m_i}$ where m_i is the mass of the atom associated with the row and the column of the matrix element. The matrix product on the left-hand side of Equation 1 is equal to the force constant matrix in mass-weighted Cartesian coordinates. The sparse matrices analysed in the following are versions of the FC matrix **K** in Equation 1. A sparse matrix is by definition a matrix in which a majority of the matrix elements is equal to zero. For convenience, the term will in the following also be used for low density matrices where less than half of the matrix elements are equal to zero.

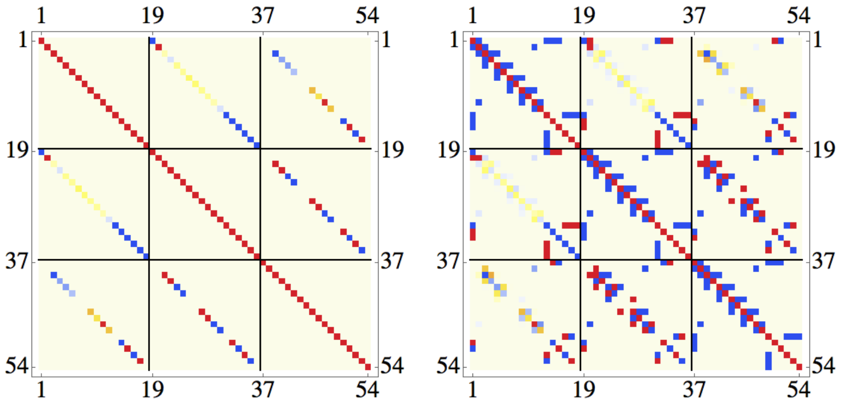
It is useful to think of a FC matrix as consisting of nine blocks:

$$\mathbf{K} = \begin{pmatrix} \left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right) & \left(\frac{\partial^2 V}{\partial x_i \partial y_j}\right) & \left(\frac{\partial^2 V}{\partial x_i \partial z_j}\right) \\ \left(\frac{\partial^2 V}{\partial y_i \partial x_j}\right) & \left(\frac{\partial^2 V}{\partial y_i \partial y_j}\right) & \left(\frac{\partial^2 V}{\partial y_i \partial z_j}\right) \\ \left(\frac{\partial^2 V}{\partial z_i \partial x_j}\right) & \left(\frac{\partial^2 V}{\partial z_i \partial y_j}\right) & \left(\frac{\partial^2 V}{\partial z_i \partial z_j}\right) \end{pmatrix} \tag{2}$$

Independently of how the force constant matrix is calculated and the atoms are numbered, elementary row and column operations can always lead to the form shown in Equation 2 where V is the molecular energy. When the matrix is written in this way, each of the nine blocks can be regarded as a weighted adjacency matrix of the molecule considered as a complete graph, *i.e.* a graph where all pairs of vertices (atoms) are connected by an edge. However, in order to include the uncoupled displacements (the diagonals) a loop must be added at each vertex. The edges describe the interaction between the two atoms that are connected by the edge, and the weight of a particular edge is then equal to the change in potential energy associated with infinitesimal displacements of the two atoms along one of three axes.

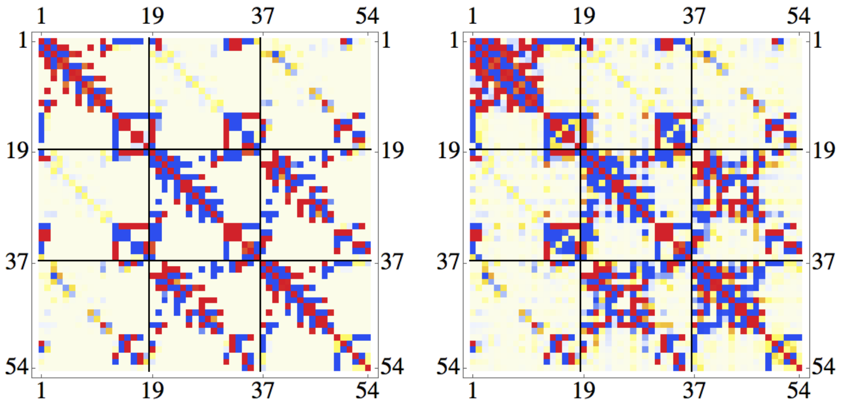
A consistent hierarchy of approximations can be based on the molecular graph as follows. The zero'th order (atomic) approximation is given by a graph consisting of a number of vertices equal to the number of atoms with no edges but with a loop at each vertex (atom). The adjacency matrix for such a graph will only have elements different from zero at the diagonal. For the first order FC matrix the coupled displacements of neighbouring atoms are added to the diagonal elements and for the second order matrix the next-neighbour interactions are added, and so forth for the higher orders. The pairs of neighbouring atoms in the first order matrix are given by the adjacency matrix of the molecular graph and the pairs of next-neighbouring atoms are given by the adjacency matrix of the molecular graph raised to the 2nd. power. Similarly, for the longer-range interactions that are determined by the molecular graph when raised to the appropriate power.

The zero'th order FC matrix will then only include the elements in the diagonal of the nine block matrices (Equation 2), and the first order matrix will a be block matrix in which each of the nine blocks is a weighted adjacency matrix of the molecular graph to which loops have been added at each atom. The higher order FC matrices will be blocks of the adjacency matrix of the 1st. order molecular graph raised to the appropriate power with addition of ones in the diagonal, and subsequently weighted according to the magnitudes of the interactions. To illustrate this, three sparse FC matrices are shown together with the full FC matrix of Ethylbenzen in Figure 1 and the associated graphs are shown in Figure 2:



0th. order matrix

1st. order matrix



2nd. order matrix

Full matrix

Figure 1. Plots of the lowest order FC matrices and the full FC matrix for Ethylbenzen (B3LYP/6-311G(d,p)). The colours are drawn with a temperature scale for matrix elements with absolute values above $10^{-2.5}$ *a.u.*

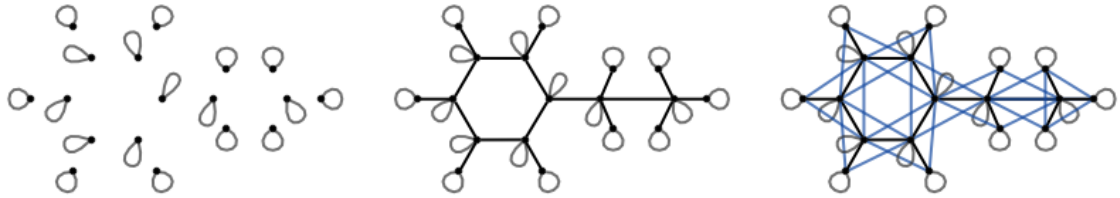


Figure 2. Zero'th, first, and second order molecular graphs of Ethylbenzene. Grey: uncoupled displacements, black: 1-2 interactions, blue: 1-3 interactions.

The overall appearance of the plots in Figure 1 is largely determined by the orientation of the molecule and the numbering of the atoms. The 12 atoms of the phenyl group and the benzylic carbon, numbered 1 - 12, are located in the *y-z* plane and as can be seen from the plot of the full matrix, the out-of-plane displacements of these atoms in the *x*-dimension are poorly coupled to their displacements in the *y-z* plane. The diagonals of the nine blocks are evident in the zero'th order matrix and all the elements in the main diagonal are positive. The selection of added elements in the first and second order matrixes are determined by the adjacency matrices of the first and second order molecular graphs shown in Figure 2 and it is clear that even in the 2nd. order matrix a significant fraction of large force constants has been omitted.

The relative magnitude of the force constants included in the various levels of approximation is shown in Figure 3.

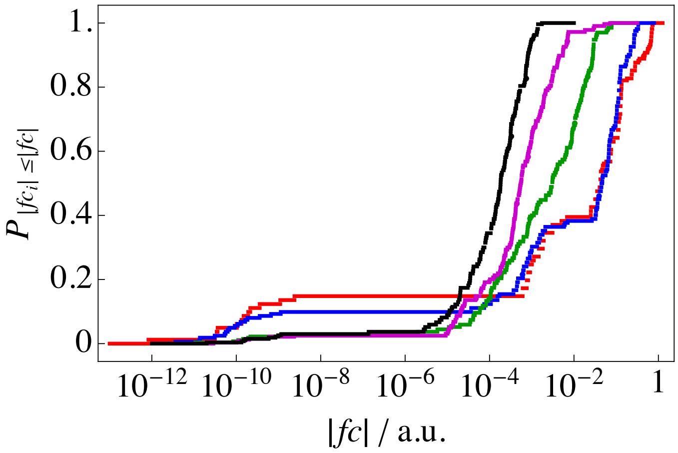


Figure 3. Distributions of force constants (absolute values) from Ethylbenzene (B3LYP/6-311G(d,p)). Red: Uncoupled displacements (162); blue: 1-2 interactions (325); green: 1-3 interactions (540); magenta: 1-4 interactions (648); black: 1-5 interactions (540). The number in parentheses is the total number of force constant of the given distance.

It is clear that all distributions cover a wide range of magnitudes and that a selection of matrix elements based on interatomic distances is very different from one based on magnitude of the matrix elements. This changes when the total interatomic interactions are considered. Here and in the following, distance is used in the graph theoretical sense as the number of edges (bonds) between vertices (atoms).

The total interaction between a pair of atoms can be found from vector addition of the appropriate matrix elements from each of the nine blocks of the force constant matrix (Equation 2) and the results are shown in Figure 4 as distribution functions for interactions associated with different atomic distances (notice the change of scale on the abscissa).

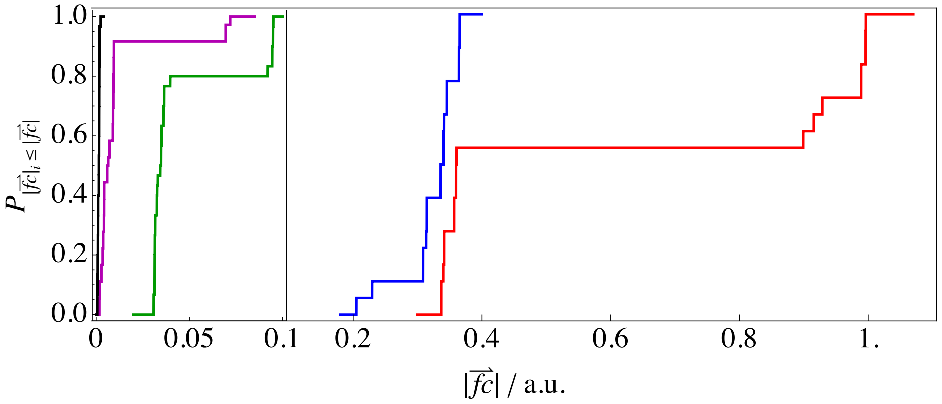


Figure 4. Distributions of the magnitudes of the total atomic interactions in Ethylbenzene (B3LYP/6-311G(d,p)). Red: uncoupled displacements (diagonals) (18); blue: 1-2 interactions (36); green: 1-3 interactions (60); magenta: 1-4 interactions (72); black: 1-5 interactions (60). The number in parentheses is the total number of interactions of the given type. Notice the change of scale on the abscissa

The red curve in Figure 4 shows the magnitude of the uncoupled displacements of the atoms and for all the hydrogen atoms they fall in a narrow interval below 0.4 *a.u.* The values for displacement of the carbon atom are all larger.

Whereas the elements in the force constant matrix depends on the orientation of the molecule, the magnitudes of the total interaction between two atoms is independent of the molecular orientation. Although there are large overlaps in the magnitudes of the force constants for interactions at different distances (Figure 3), the total interactions associated with the uncoupled displacements and with the 1-2 interactions are all larger than the total interactions at longer distances (Figure 4). However, the potentially large number of long-distance interactions may add to their significance. In Ethylbenzene with 18 atoms, there is a total of $18^2 = 324$ interactions. The number of interactions for each distance is shown in the parentheses of the legend to Figure 4. In Ethylbenzene, the longest interactions are 1-8 which are between the hydrogen atom at the paraposition and the hydrogens of the methyl group. The properties of the FC matrix elements for Ethylbenzene reported here are found for all the compounds included in this study (Figure S1) with the expected changes arising from the variation in the number of atoms.

It is worth noticing that for a given compound, the trace of the sparse FC matrices is identical to the trace of the full matrix which means that the sum of eigenvalues is identical for all the matrices associated with the compound independent of the order of the matrix. This follows from elementary matrix algebra and ensures that at least one molecular parameter *i.e.* the zero-point vibrational energy is independent of the number of off-diagonal elements included in the matrix and hence of the order of the sparse matrix when the six eigenvalues corresponding to molecular translation and rotation can be ignored.

In the calculation of molecular frequencies, the sparse matrices can be treated as the full matrices, and surprisingly they are generally well behaved in that a few negative eigenvalues are only obtained from sparse matrices of low orders that are calculated from molecules with many repeating groups (see below).

The hierarchy of sparse matrices based on the molecular graph, ensures that the largest total atomic interactions that are excluded from the sparse FC matrix decreases systematically as the order of the approximation increases (Figure 4). A similar hierarchy based on a random graph will also give positive eigenvalues with improved frequencies as the order of the graph increases. However, the errors remain large and the properties of the molecular graph and the adjacency matrix are essential for the accuracy of the frequencies calculated from the sparse and low-density FC-matrices. An example is shown in Figure S2.

III Results

Frequencies and heat capacities from sparse matrices. This section is organized as follows. Firstly, the results from sparse FC matrices of a selection of hydrocarbons are reported. Subsequently, the results from sparse FC matrices of heteroatomic analogues of Pentylbenzene are presented, and finally the results from FC matrices constructed from molecular fragments are presented.

In Figure 5 is shown the Ethylbenzene molecular frequencies obtained from a selection of sparse matrices and plotted against the frequencies obtained from the full matrix.

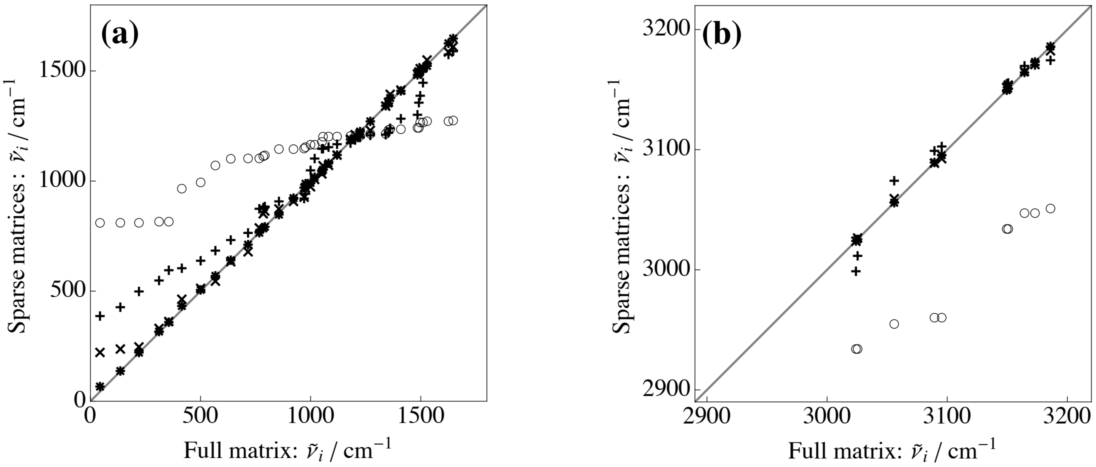


Figure 5. Ethylbenzene (B3LYP/6-311G(d,p)) frequencies from sparse FC matrices plotted against the frequencies from the full FC matrix. The sparse matrices were of the orders: 0th. (○), 1st. (+), 2nd. (×) and 3rd. (*). The line is drawn with a slope of 1.

The zero'th and first order sparse matrices are very poor approximations but already the second order matrix gives acceptable values, which further improve at higher approximations.

The benign behaviour of the sparse matrices when the matrix elements are selected according to the properties of the molecular graph, and the good approximations of the frequencies obtained with these sparse matrices, is also obtained with other hydrocarbons as shown in Table 1. The results obtained at other calculational levels for a selection of the molecules are summarized in Table S1 (Supporting Information).

Table 1 (located at the end of the manuscript)

The results summarized in Table 1 confirm that matrices, which only include short-range interactions, can give frequencies that are close to those obtained from the full matrix. Taking the data from the 3rd. order approximation (1-4 interactions included) as an example, the average error on the frequencies varies between 1.3 % (Propylbenzene) and 3.8 % ((8-Methylnonyl)benzene)). However, the errors are concentrated in the low end of the frequency range as shown in Figure 6, in which the dependency of the errors on the frequency and the level of approximation have been plotted for the five lowest levels of approximation. An example of the error distributions is shown for 2-Pentylnaphthalene in Figure S3 in the Supporting Information.

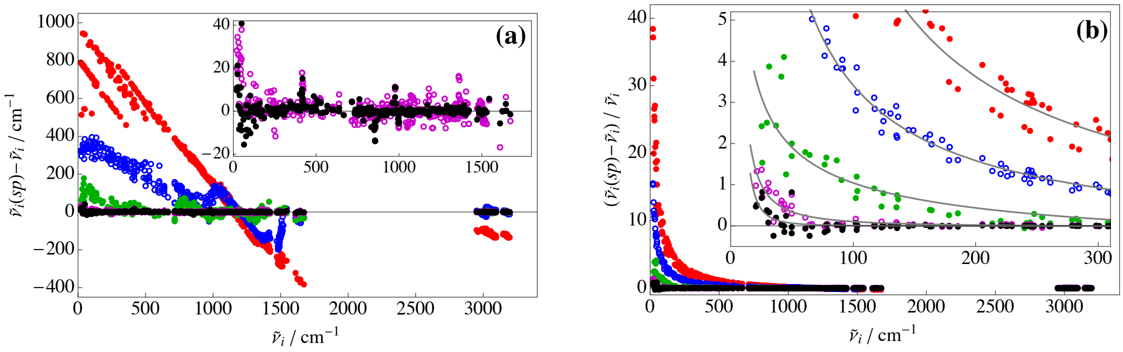


Figure 6. Hydrocarbons (B3LYP/6-311(d,p)): Error (a) and relative error (b) of the frequencies obtained from sparse matrices when compared to frequencies from the full matrix. The sparse matrices were of the orders: 0th. (red), 1st. (blue), 2nd. (green), 3rd. (magenta), and 4th. (black). The frequencies are calculated from the same matrices as the results summarized in Table 1 excluding those that give rise to negative eigenvalues (imaginary frequencies). In the insert of panel (a), is shown the error of the frequencies below 1800 cm^{-1} from the 3rd. and 4th. order matrices. The insert in panel (b) shows the lower part of the graphs with fits according to $y = a x^{-b} + c$ based on frequencies below 600 cm^{-1}.

A surprising systematic variation of the error with the level of approximation and the frequency wave-number is evident from Figure 5, panel A and underlined by the fits to the relative errors included in the insert of panel B. As pointed out above, all the FC matrices, independently of their order, include the same main diagonal and all the elements in this diagonal are positive numbers (see Equation 2 and Figure 1). The trace of a matrix is invariant under diagonalization and consequently the sum of the frequencies must be the same whether they are obtained from the full FC matrix or from one of the sparse matrices studied here. In principle, the error on the frequencies calculated from the sparse matrices could be randomly distributed over the full frequency interval but as is clear from Figure 6 this is not the case. For the zero'th order FC matrices, the calculated frequencies fall in two groups: those below approximately 1200 cm^{-1} larger than the frequencies from the full matrix whereas those above are smaller. As the order of the matrix increases, the magnitude of the errors on the frequencies becomes decreases but the pattern is maintained for the first and second order matrices. For the third and fourth order matrices the relative error is only significant at very low wave-numbers below 50 cm^{-1} but still biased towards positive values.

The systematic variation in the error of the calculated frequencies is reflected in the calculated heat capacity values, which are included in Table 1 and calculated from the rigid rotator-harmonic oscillator approximation at two different temperatures. The lowest frequencies are most sensitive to the errors introduced by the approximations used here and consequently the differences introduced at low temperatures are most significant. The results show that with the second order approximation the results for the vibrational heat capacity at 300 K are within a few percent of the values obtained from the full matrix. The fraction of force constants included varies between 35 % for the smallest molecule (Ethylbenzene) and 16 or 17 % for the largest ((8-Methylnonyl)benzene or 3-Pentyldecalin). When 1-4 interactions are included (3rd. order approximation), the values are within one percent even at 200 K. At this approximation, the fraction of force constants varies between 28 and 57 %. As can be seen from Figure 6, at this approximation the only significant error is obtained for frequencies at wave-numbers below 50 cm^{-1}. Large molecules will have more frequencies at low wave-numbers and consequently this increase in the error below 50 cm^{-1} primarily affects the larger molecules. However, the effect is small as can be seen on the heat capacity values, where for a given approximation the error hardly changes with the size of the molecule in the range included here.

Two of the sparse FC matrices of the molecules (8-Methylnonyl)benzene and 3-Pentyldecalin in Table 1 give rise to imaginary frequencies that are a consequence of negative eigenvalues of the matrix. The origin of this remains unclear.

The level of calculation appears to have only a minor influence (Table S1) on the quality of the vibrational frequencies obtained from the sparse matrices.

Heteroatomic analogues and complemented matrices. A consequence of the insignificance of long-distance interactions is that introduction of heteroatoms should only have local effects on the FC matrix. Consequently, it should be possible to obtain a significant improvement of the frequency calculations from a low order FC matrix of a molecule with heteroatoms by complementing the matrix with the long-distance interactions from a hydrocarbon with the same geometry. This has been tested for a series of compounds with geometries similar to Pentylbenzene and the results are summarized in Table 2.

Table 2 (located at the end of the manuscript)

The compounds include nitrogen species that are isoelectronic with the Pentylbenzene and which have one or two cationic sites, as well as molecules with heavier atoms (O, Cl and Si). For each compound two sets of calculations have been carried out. One set of frequencies was obtained from sparse FC matrices similar to the results summarized in Table 1. The second set was obtained from the sparse matrices but complemented with matrix elements from the FC matrix of Pentylbenzene. Taking the 2nd. order approximations of (4-Phenylbutyl)ammonium as example, in the first column is shown the relative error when the frequencies are calculated from the matrix elements of all the uncoupled displacements, all 1-2, and all 1-3 interactions. This is equal to 1593 matrix elements out of a total of 6561. The average error on the frequencies is 10.4 %. When the 1593 matrix elements of the sparse matrix are complemented with 4968 matrix elements from the FC matrix of the Pentylbenzen for all interactions beyond 1-3, the error is reduced to 2.3 % as seen in the second column. For complementing the sparse matrices of 4-Phenylbutanol, the matrix elements for two hydrogen atoms were removed from the complementing matrix.

The 3rd. order matrix of Pentylbenzene gives frequencies with an average error of 1.9 % (Table 1) whereas the frequencies of the heteoratom analogues listed in Table 2 at the same level of approximation have errors between 1.8 % ((4-Phenylbutyl)ammonium and N-Phenyl-1,3-diammoniopropane) and 2.9 % N-(4-Chlorobutyl)anilinium.

When the sparse FC matrices are complemented with matrix elements from the Pentylbenzene FC matrix the accuracy is significantly improved for all the chosen molecules. For the lowest order approximations, the improvement is smallest for the charged molecules with the dicationic N-Phenyl-1,3 diammonipropane giving an error of 36.3 % on the frequencies from the zero'th order complemented matrix. It is not surprising that all interatomic interactions in this dication are poorly described by the interatomic interactions in the neutral Pentylbenzene. Among the neutral molecules the largest errors on the frequencies is obtained from the complemented matrices of 4-Phenylbutanol. Among the complemented third order approximations the ionic molecules give errors between 1.4 % and 2.0 % whereas the error for the neutrals lies between 0.1 % and 1.0 %. For the ions, the improvement obtained by complementing the sparse matrices is low or absent for the third order approximations and above. In the Supporting Information (Table S2) is shown results obtained from ωB97XD/6-

311+G(2df, 2p) calculations. They do not appear to be significantly different from those described here.

These results confirm that the differences in the interatomic interactions in two molecules with and without a heteroatom is primarily a localized phenomenon, and that the differences at longer ranges are of little significance for the magnitude of the molecular frequencies.

With regard to the dependency of the errors on the wave-number and the level of approximation, the heteroatomic molecules are very similar to the hydrocarbons as shown in Figure 7.

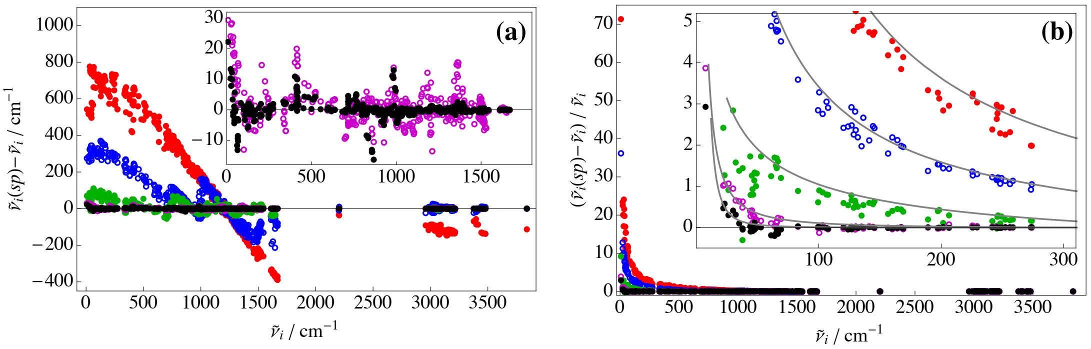


Figure 7. Heteroatomic compounds (B3LYP/6-311(d,p)): Error (a) and relative error (b) of the frequencies obtained from sparse matrices when compared to the full matrix. The sparse matrices were of the orders: 0th. (red), 1st. (blue), 2nd. (green), 3rd. (magenta), and 4th. (black). In the insert in panel **a** is shown the error of the frequencies below 1800 cm^{-1} from the 3rd. and 4th. order matrices. The lines in the insert in panel (b) are plotted according to the fits obtained from the data in Figure 6b.

Comparison of Figures 6 and 7 show that the error on the frequencies from lowest order approximations have much the same systematic variation for the heteroatomic molecules as for the hydrocarbon.

As shown in Figure 8, the systematic variation of the error on the frequencies disappears when the sparse FC matrices are complemented matrix elements from the hydrocarbon matrix. However, the general improvement in the frequencies from the complemented 3rd. order FC matrices is clearly seen from the inserts in Figure 8a and 8b when compared to the inserts in Figures 7a and 7b.

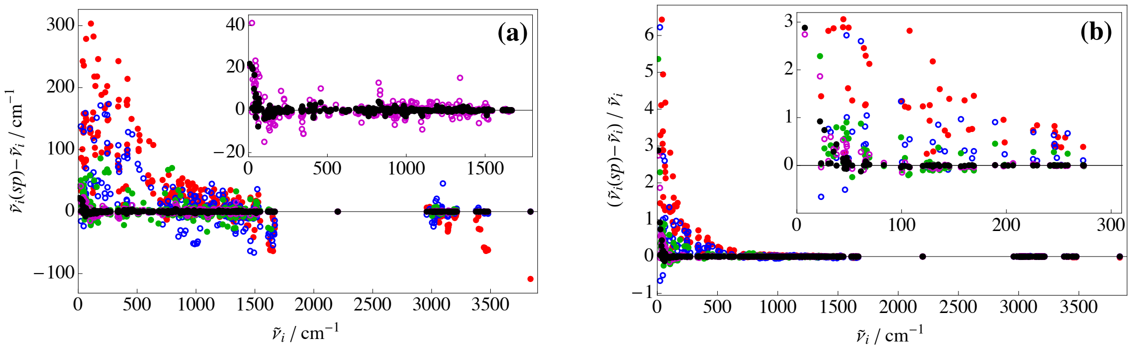


Figure 8. Heteroatomic compounds (B3LYP/6-311(d,p)): Sparse matrices complemented with matrix elements from Pentylbenzene: Error (a) and relative error (b) of the frequencies obtained from complemented sparse matrices when compared with frequencies from the full matrix. The sparse matrices were of the orders: 0'th (red), 1st. (blue), 2nd. (green), 3rd. (magenta), and 4th. (black). Only data from calculations summarized in Table 2 without imaginary frequencies have been included. The insert in panel (a) shows the errors on frequencies below 1800 cm^{-1} from the complemented 3rd. and 4th. order matrices.

Matrices from molecular fragments. The third set of results has been obtained from composite FC matrices constructed from molecular fragments. From a FC matrix of a molecule, the matrix elements of a fragment can be extracted by selection of the rows and columns associated with the atoms belonging to the fragment. Such fragment matrices can then be combined to produce a sparse FC matrix of a molecule composed of the chosen fragments. A composite FC matrix assembled from fragment matrices will be a sparse matrix or low-density matrix with no matrix elements for the interaction between the atoms of different fragments. However, if only short-range interactions are significant it should be possible to calculate molecular frequencies by supplementing the composite matrix with the relatively few matrix elements that describe the short-range coupling between atoms belonging to separate fragments (Figure 9).

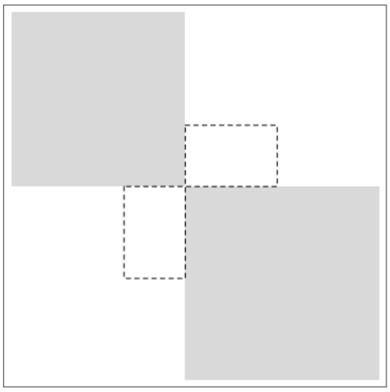


FIGURE. 9. Schematic of coupling matrix. The grey squares contain the matrix elements of the two fragments and the areas within the dashed lines indicate coupling elements for atoms belonging to different fragments.

This has been tested for the molecules and fragments listed in Tables 3. The sparse FC matrix of the molecule that only consists of the matrix elements of the fragments is called a zero'th order coupling matrix. This can be supplemented with 1-2 interactions between the two atoms that connect the two fragments to give the first order coupling matrix. The second order coupling matrix includes 1-2 and 1-3 interactions, and so forth with each higher order coupling matrices including matrix elements from consecutively longer-range interactions between the atoms of the different fragments.

Table 3. Molecules and the fragments (*incl. origin*) from which their sparse composite matrices were constructed. The composite matrices were supplemented with matrix elements from Octylbenzene and Decane. (B3LYP/6-311G(d,p))

2 fragments:

1-(4-Chlorophenyl)-6-methylheptane:
(4-Chlorophenyl)ethyl (*4-Chloro-1-butylbenzene*) + 4-Methylpentyl (*2-Methyloctane*)

2-Chloro-8-(4-chlorophenyl)octane:
(4-Chlorophenyl)ethyl (*4-Chloro-1-butylbenzene*) + 5-Chlorohexyl (*2-Chlorononane*)

8-(4-Trifluoromethylphenyl)-1-octene:
(4-Trifluoromethylphenyl)ethyl (*1-Butyl-4-Trifluoromethylbenzene* + Hex-5-en-1-yl (*1-Nonene*)

3 fragments:

4-(10-Chlorodecyl)phenol:
(4-Hydroxyphenyl)ethyl (*4-Butylphenol)* + Butane-1,4-diyl (*Octane*) + 4-Chlorobutyl (*1-Chlorooctane*)

10-(2-Naphthyl)decanol:
(2-Naphthyl)butyl (*2-Butylnaphthalene)* + Butane-1,4-diyl (*Octane*) + 4-Hydroxybutyl (*Octanol*)

1-(4-Trifluoromethylphenyl)-10-methylundecane:
(4-Trifluoromethylphenyl)ethyl (*1-Butyl-4-Trifluoromethylbenzene* + Butane-1,4-diyl (*Octane*) + 4-Methylpentyl (*2-Methyloctane*)

In order to test possibility of calculating frequencies of molecule without access to the molecular force constant matrix, the supplementary elements were taken from the compounds Octylbenzene and Decane. Elements from the FC-matrix of Octylbenzene was used for the coupling elements between the Phenethyl fragment and the aliphatic chain, and in the calculations based on three fragments the FC-matrix of Decane was used as the source for the elements coupling the two aliphatic moities.

In Figure 10 is shown how the frequencies from the sparse matrices compare to those obtained from the full FC-matrix and a statistical summary of all the results is given as Table S2 in the Supporting Information.

As with the other sparse matrices, the error on frequencies obtained from the sparse coupling matrices is largest for the frequencies at low wavenumbers

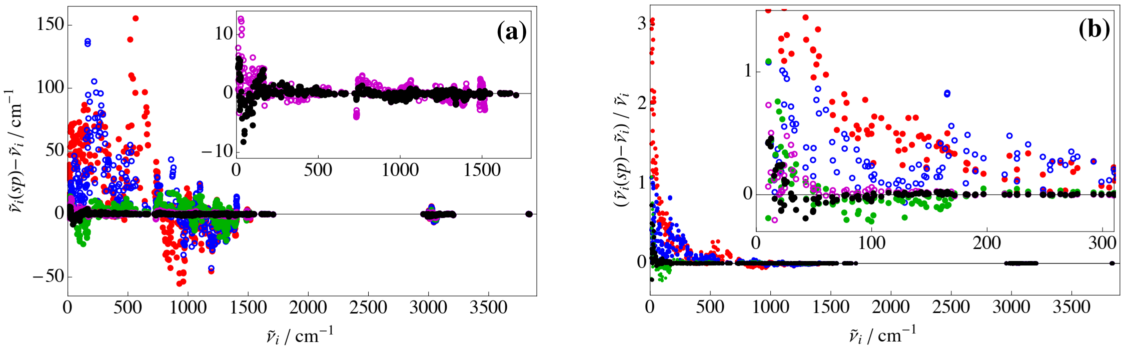


FIGURE. 10 Coupling matrices (B3LYP/6-311(d,p): Error **(a)** and relative error **(b)** of the frequencies obtained from sparse coupling FC matrices and compared to frequencies from the full matrix. The red points are with no supplementing elements. The blue, green, magenta and black points are sparse coupling matrices of 1st., 2nd., 3rd., and 4th. order.

As for the frequencies from other sparse matrices examined here, the distribution of the errors is far from Gaussian (Figure 11):

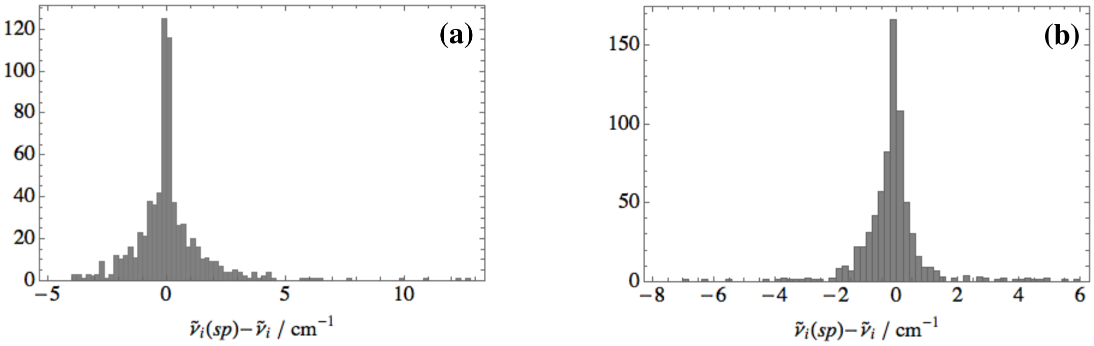


Figure 11. Densities of the errors (bin width: 0.2 cm^{-1}) on the frequencies obtained from the 3th. order (a) and the 4th. order (b) coupling matrices for the compounds listed in Table 3.

The large majority of the errors from the 4th. order approximations are within ±2 cm^{-1} and from the insert in Figure 10a it can be seen that most of the frequencies with larger errors are associated with the vibrational frequencies below 50 cm^{-1}.

It is informative to look at how the level of approximation changes the total interaction between atoms that are included in the calculations. This is shown for 1-(4-Chlorophenyl)-6-methylheptane in Figure 12.

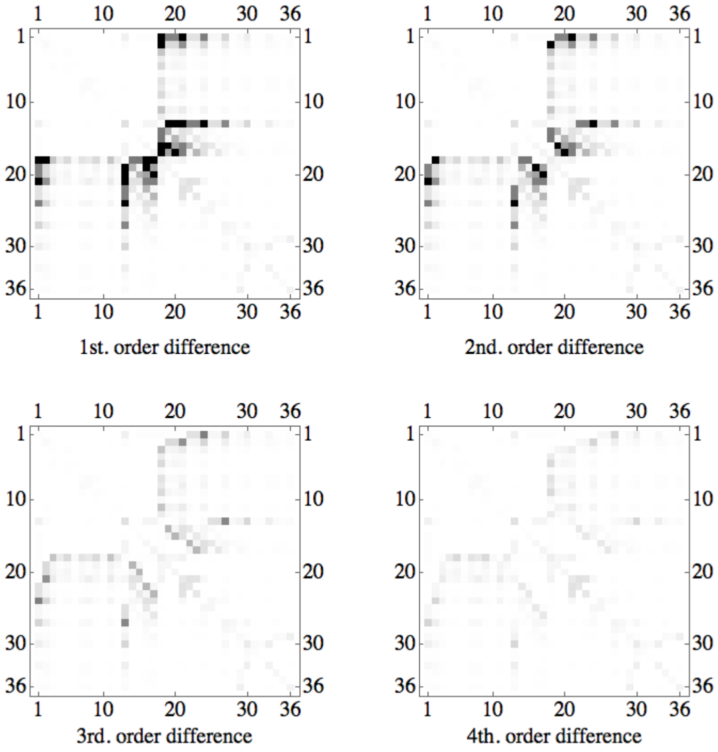


Figure 12. Difference matrices showing the absolute difference between the total atomic interactions calculated from the full FC matrix and from four different coupling matrices for 1-(4-Chlorophenyl)-6-methylheptane (B3LYP/6-311G(d,p)). The shading is done according to a greyscale for values between 0 and 5 10^{-3} *au*.

For all matrices the total interactions between a pair of atoms was found by vector addition of the appropriate matrix elements and the values were compared to the total interactions found from the full FC matrix. The interactions within each fragment are very close to those of the test molecule as indicated by the light regions at the top left and lower right of the difference matrices shown in Figure 12. The single largest absolute difference (0.179 *a.u.*) is found between the full FC matrix and the matrix without any coupling elements. This difference matrix is not shown in Figure 12. As coupling elements are added the largest difference decrease to 0.038 *a.u.* (1st. order), 6.9 10^{-3} *a.u.* (2nd. order), 2.4 10^{-3} *a.u.* (3rd. order), and 0.83 10^{-3} *a.u.* (4th. order). The Figure illustrates how the selection of the coupling elements, based on the molecular graph in increasing order, picks out the total interactions of decreasing magnitude, in agreement with the trend in total interactions illustrated by Figure 4.

IV Discussion

The success of group additivity schemes and indeed the central position of the group concept in organic chemistry is a strong indication for the insignificance of long-distance atomic interactions for molecular properties. The primary purpose of the present work is to find evidence for this in the calculation of vibrational frequencies. The results presented above all support the conclusion that in general vibrational frequencies are indeed determined by relatively short-distance interactions. The very lowest frequencies cannot be determined solely by short-distance interactions as the calculations presented here demonstrate and which is also clear from the inability for group additivity schemes to account for molecular properties at low temperatures.

Although the calculational investigations described above necessarily is based on a limited number of molecules (see Figure S1), they include a variety of structural elements (aliphatic as well as aromatic structures, several different hetero atoms) to enable some general conclusions to be drawn from the results.

In the first part of the results section it is shown that the vibrational frequencies from hydrocarbons can indeed, except for the very lowest, be calculated from FC matrices which only include the short-distance interactions. This conclusion is independent of the method and the calculational level as shown from the data summarized in Table I and Table S1. This is also the case when heteroatoms are included as described in the second part.

The results presented here show that group additivity of vibrationally dependent properties arise from the mathematical properties of the FC matrices. Previously it was shown that the same properties can be explained by regarding the molecular frequency distribution as a linear combination of group frequency distributions.[11] Frequency distributions are directly linked to the eigenvalue distribution or spectral properties of the Hermitian FC matrices (Equation 1). The spectral properties of Hermitian matrices is an area of intense study, and in particular random Hermitian and Toeplitz matrices appear to have been extensively studied.[30,31] A better understanding of the mathematical properties of the FC matrix may lead to an explanation for the systematic variations in the error that are noticeable features of the data summarized in Figures 6 and 7, and may lead to improved accuracy of the frequencies calculated from sparse FC matrices.

A secondary purpose of this study has been to explore the potential for calculating molecular frequencies without access to the molecular FC matrix. The results reported in on FC matrices formed from fragments give an indication that this may indeed be possible. Very little optimization was done in connection with the results presented here except for testing that calculations based on Phenylethyl fragments gave smaller errors than those based on Benzyl fragments.[32] Wider applications of the method will require investigations of how to optimize the choice of fragments, and of course on the quality of the results when it is applied to large molecules.

Supporting information

Figure S1: Molecular structures. Figure S2: Errors from calculations based on a random graph. Figure S3: Error distribution of frequencies from sparse FC matrices for 2-Pentylnaphthalene (B3LYP/6-311G(d,p)). Table S1: Statistical analysis of frequencies from sparse matrices obtained with different calculational levels. TableS2: Statistical analysis of frequencies from sparse matrices obtained from fragment matrices.

Computational methods

Molecular frequencies were calculated with the Gaussian 09 suite of programmes at the following levels: HF/6-31G(d), HF/6-311G(d, p), B3LYP/6-31G(d), B3LYP/6-311G(d, p), ωB97XD/6-311+G(2df, 2p), MP2/6-31G(d), MP2/6-311G(d, p).[33] The optimization criterion was set at "VeryTight" and in the DFT-based calculations the grid was specified as "UltraFine". The conformation of the alkylchains were *all-anti*, and with the alkyl group equatorial in Pentyldecalin. All other calculations were done with MATHEMATICA.[34] The matrix elements of the FC matrices were extracted from the formatted Gaussian checkpoint files.[35] The reported frequencies were calculated directly from the matrices after mass-weighting and the six lowest frequencies were discarded. Comparison of the frequencies from the Gaussian output files and from the frequencies obtained from the extracted FC matrices without coordinate transformation gave differences below 0.2 cm^{-1}. Consequently, conversion to a rotating and translating frame of reference, which is done to compensate for inadequate optimization, was not carried out.[28,29] The factors for conversion from atomic to SI units were taken from reference 36.

All calculations of heat capacities were based on the harmonic oscillator-rigid rotator approximation.

In the calculations based on molecular fragments, the matrix elements of the fragments will only have the appropriate values when the various fragments are orientated as in the intact molecule. Consequently, the FC matrices of the fragments were modified according to:

$$\mathbf{K}_{\mathbf{FR}} = \mathbf{R}\ \mathbf{K}_{\mathbf{F}}\ \mathbf{R}^{-1}$$

where $\mathbf{K}_{\mathbf{FR}}$ is the FC matrix of the fragment when orientated as in the intact molecule and $\mathbf{R}$ is a diagonal block matrix constructed from the rotation matrix that gives the fragment the appropriate orientation. $\mathbf{K}_{\mathbf{F}}$ is the part of FC matrix of the molecule from which the fragment is taken. The FC-matrices of the molecules (Octylbenzene and Decane) from which the coupling elements where taken were similarly modified.

Acknowledgements

I am grateful to Steen Hammerum, University of Copenhagen for assistance with the Gaussian calculations, for many discussions on group additivity, and for his continual interest in my work. Computational resources were generously provided by the Department of Chemistry, University of Copenhagen.

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Table 1. Frequency statistics and the derived vibrational heat capacities from comparison of frequenices obtained from sparse and low-density matrices compared to the frequencies from the full matrix (B3LYP/6-311G(d,p)) .

Ethylbenzene

Approx. order[a]	FC fraction[b]	M.A.R.D.[c]	C_{vib}[d]	
			200 K	300 K
0	0.06	0.786	8.66	45.26
1	0.17	0.328	29.84	75.85
2	0.35	0.121	48.97	90.66
3	0.57	0.015	52.48	92.64
4	0.76	0.003	52.80	92.78
5	0.91	0.000	52.97	92.89
Full	1.00	n.a.	52.97	92.89

Propylbenzene

Approx. order	FC fraction	M.A.R.D.	C_{vib}	
			200 K	300 K
0	0.05	0.924	9.90	53.12
1	0.14	0.391	36.36	90.68
2	0.31	0.133	62.42	110.30
3	0.51	0.013	67.52	113.25
4	0.69	0.005	67.85	113.41
5	0.82	0.001	68.01	113.51
Full	1.00	n.a.	68.02	113.52

Butylbenzene

Approx. order	FC fraction	M.A.R.D.	C_{vib}	
			200 K	300 K
0	0.04	1.105	11.13	60.93
1	0.12	0.476	42.97	105.56
2	0.27	0.139	76.19	130.06
3	0.46	0.017	82.39	133.73
4	0.62	0.010	82.66	133.87
5	0.76	0.002	82.87	134.00
Full	1.00	n.a.	82.88	134.01

Pentylbenzene

Approx. order	FC fraction	M.A.R.D.	C_{vib}	
			200 K	300 K
0	0.04	1.253	12.22	68.33
1	0.11	0.538	49.64	120.15
2	0.24	0.124	90.40	149.74
3	0.42	0.019	97.00	153.83
4	0.57	0.011	97.37	154.02
5	0.70	0.002	97.57	154.14
Full	1.00	n.a.	97.58	154.15

(4-Methylpentyl)benzene

Approx. order	FC fraction	M.A.R.D.	C_{vib}	
			200 K	300 K
0	0.03	1.353	13.80	77.38
1	0.10	0.566	58.18	137.31
2	0.22	0.123	106.16	172.99
3	0.38	0.033	112.99	177.02
4	0.55	0.013	113.44	177.26
5	0.67	0.002	113.67	177.40
Full	1.00	n.a.	113.68	177.41

(8-Methylnonyl)benzene

Approx. order	FC fraction	M.A.R.D.	C_{vib}	
			200 K	300 K
0	0.02	1.819	18.72	108.67
1	0.07	0.749	85.63	197.46
2	0.16	n.a. [e]	n.a. [e]	
3	0.28	0.038	172.28	258.89
4	0.41	0.012	172.89	259.23
5	0.51	0.004	173.12	259.38
Full	1.00	n.a.	173.15	259.40

2-Pentylnaphthalene

Approx. order	FC fraction	M A.R.D.	C_{vib}	
			200 K	300 K
0	0.03	1.001	24.26	100.58
1	0.09	0.480	73.22	165.32
2	0.20	0.088	122.24	199.95
3	0.35	0.027	127.91	203.66
4	0.49	0.024	128.01	203.66
5	0.61	0.003	128.65	204.00
Full	1.00	n.a.	128.65	204.01

3-Pentyldecalin

Approx. order	FC fraction	M A.R.D.	C_{vib}	
			200 K	300 K
0	0.02	1.197	16.18	104.71
1	0.07	0.494	67.56	177.26
2	0.17	n.a. [f]	n.a. [e]	
3	0.32	0.012	152.62	240.48
4	0.47	0.007	153.03	240.71
5	0.61	0.001	153.15	240.79
Full	1.00	n.a.	153.16	240.79

[a] The highest order interactions included in the FC matrix. [b] The fraction of matrix elements included in the sparse FC matrix. [c] The mean of the absolute relative difference. [d] The vibrational heat capacity calculated from the frequencies. [e] The 2nd. order approximations for (8-Methylnonyl)benzene and 3-Pentyldecalin gave rise to respectively two and one imaginary frequency.

Table 2. Statistical analysis of frequencies obtained from sparse matrices and from sparse matrices complemented with matrix elements from the FC matrix of pentylbenzene (B3LYP/6-311G(d,p)).

	(4-Phenylbutyl)ammonium		N-Butylanilinium	
	Sparse matrices	Sparse matrices + complement	Sparse matrices	Sparse matrices + complement
Approx. order[a]	M.A.R.D.[b]	M.A.R.D.[c]	M.A.R.D.	M.A.R.D.
0	1.235	0.236	1.207	0.180
1	0.526	0.046	0.519	n.a. [d]
2	0.104	0.023	0.110	0.023
3	0.018	0.014	0.019	0.016
4	0.009	0.002	0.005	0.008
5	0.002	0.001	0.001	0.001

	N-Phenyl-1,3-diammoniopropane		N-(4-Chlorobutyl)anilinium	
	Sparse matrices	Sparse matrices + complement	Sparse matrices	Sparse matrices + complement
Approx. order	M.A.R.D.	M.A.R.D.	M.A.R.D.	M.A.R.D.
0	1.172	0.363	1.226	0.252
1	0.494	0.073	0.559	n.a. [d]
2	0.087	0.032	0.098	0.014
3	0.018	0.015	0.029	0.020
4	0.006	0.010	0.008	0.012
5	0.001	0.001	0.002	0.001

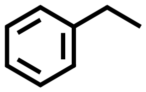
	(5-Chloropentyl)benzene		1-Chloro-4-pentylbenzene	
	Sparse matrices	Sparse matrices + complement	Sparse matrices	Sparse matrices + complement
Approx. order	M.A.R.D.	M.A.R.D.	M.A.R.D.	M.A.R.D.
0	1.260	0.093	1.195	0.021
1	0.583	0.029	0.551	0.025
2	0.108	0.004	0.110	0.006
3	0.024	0.001	0.023	0.010
4	0.012	0.001	0.005	0.010
5	0.004	0.000	0.001	0.001

	Butylphenylsilane		4-Phenylbutanol[d]	
	Sparse matrices	Sparse matrices + complement	Sparse matrices	Sparse matrices + complement
Approx. order	M.A.R.D.	M.A.R.D.	M.A.R.D.	M.A.R.D.
0	1.060	0.068	1.067	0.162
1	0.553	0.434	0.484	0.055
2	0.115	0.015	0.134	0.016
3	0.022	0.008	0.021	0.005
4	0.010	0.001	0.010	0.001
5	0.003	0.001	0.003	0.000

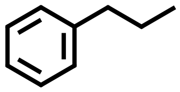
[a] The highest order interactions included in the FC matrix of the molecule. [b] Mean of the absolute relative error for frequencies obtained from the sparse matrices compared to frequencies from the full matrix. [c] Mean of the absolute relative error for frequencies obtained from the sparse matrices complemented with matrix elements from Pentylbenzene and compared to the full matrix. [d] For complementing the 4-Phenylbutanol matrices the matrix elements from two hydrogens were removed from the Pentylbenzene matrix.

Figure S1

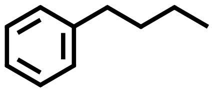
Gustav Bojesen: *The insignificance of long-distance interactions for molecular frequencies. Analyses of sparse force-constant matrices.*



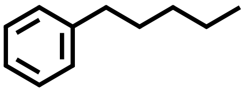
Ethylbenzene



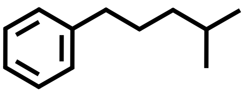
Propylbenzene



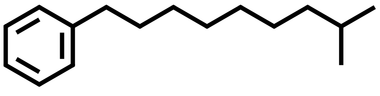
Butylbenzene



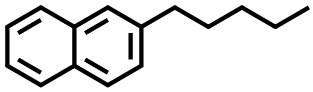
Pentylbenzene



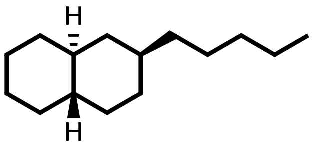
(4-Methylpentyl)benzene



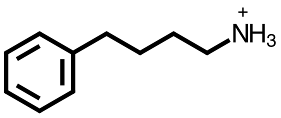
(8-Methylnonyl)benzene



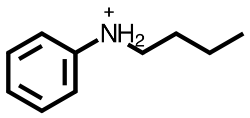
2-Pentylnaphthalene



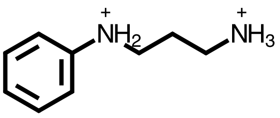
3-Pentyldecalin



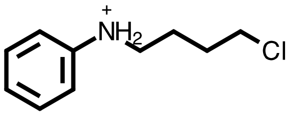
(4-Phenylbutyl)ammonium



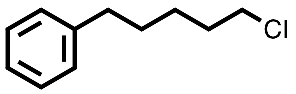
N-Butylanilinium



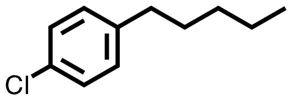
N-Phenyl-1,3-diammoniopropane



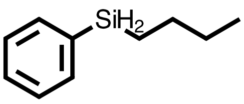
N-(4-Chlorobutyl)anilinium



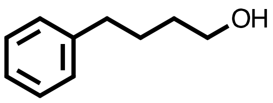
(5-Chloropentyl)benzene



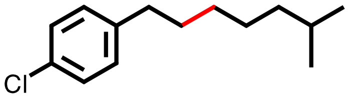
1-Chloro-4-pentylbenzene



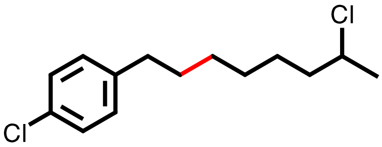
Butylphenylsilane



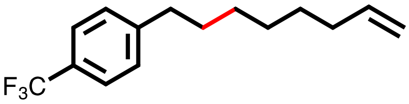
4-Phenylbutanol



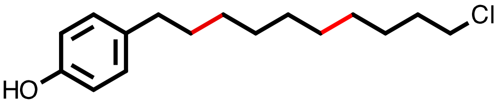
1-(4-Chlorophenyl)-6-methylheptane



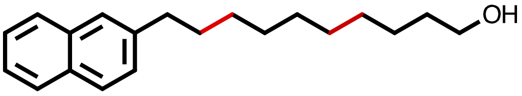
2-Chloro-8-(4-chlorophenyl)octane



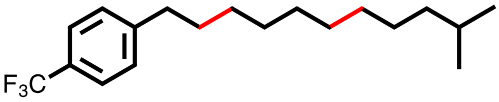
8-(4-Trifluoromethylphenyl)-1-octene



4-(10-Chlorodecyl)phenol



10-(2-Naphthyl)decanol

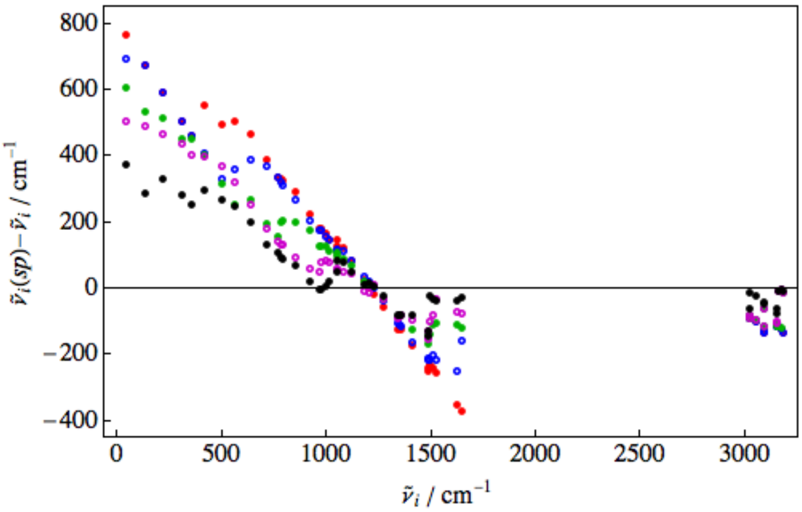


1-(4-Trifluoromethylphenyl)-10-methylundecane

Figure S2

Gustav Bojesen: *The insignificance of long-distance interactions for molecular frequencies. Analyses of sparse force-constant matrices.*

Errors and relative errors from calculations of frequencies for Ethylbenzene with the selection of force constants based on a random graph (B3LYP/6-311G(d,p)). Colour coding as for Figures 6 and 7.



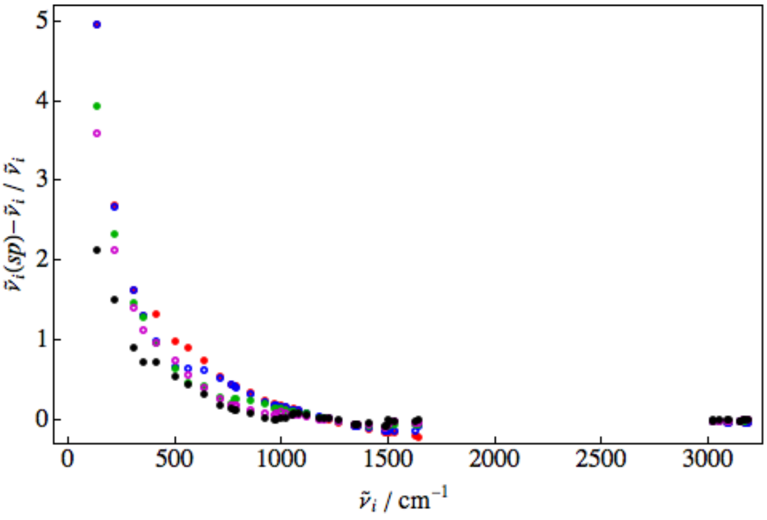
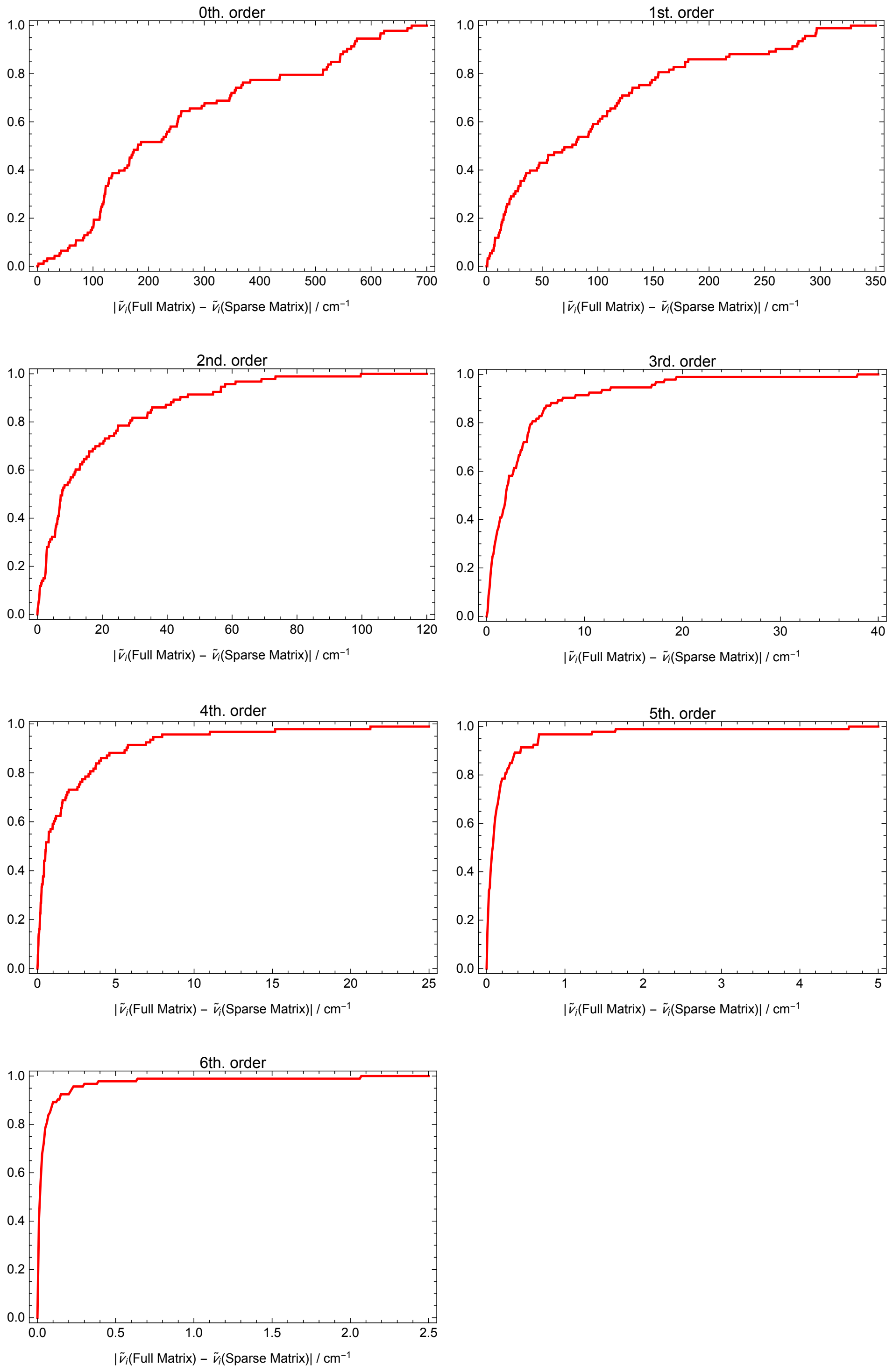
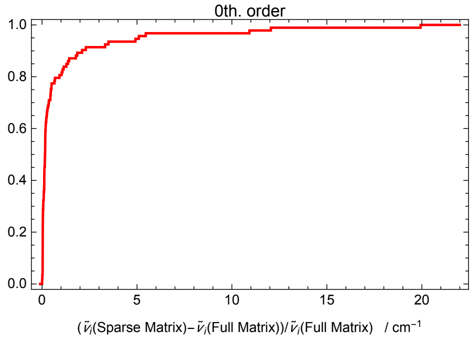


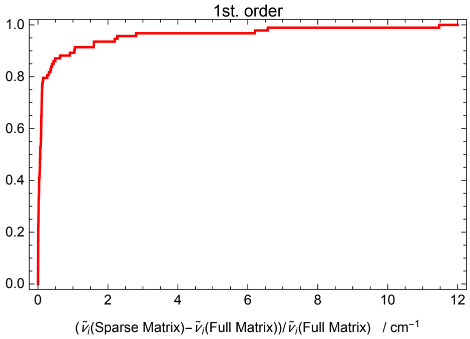
Figure S3

Gustav Bojesen: *The insignificance of long-distance interactions for molecular frequencies. Analyses of sparse force-constant matrices.*

Error and relative errors distributions from frequency calculations for 2-Pentylnaphthalene from sparse force constant matrices. B3LYP/6-311G(d,p)




0th. order
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
$(\tilde{\nu}_i$(Sparse Matrix)$-\tilde{\nu}_i$(Full Matrix))/$\tilde{\nu}_i$(Full Matrix)   / cm^{-1}


1st. order
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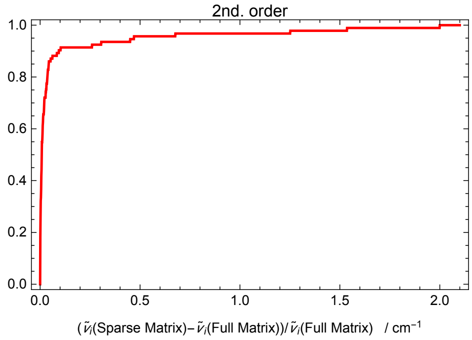
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
12
$(\tilde{\nu}_i$(Sparse Matrix)$-\tilde{\nu}_i$(Full Matrix))/$\tilde{\nu}_i$(Full Matrix)   / cm^{-1}


2nd. order
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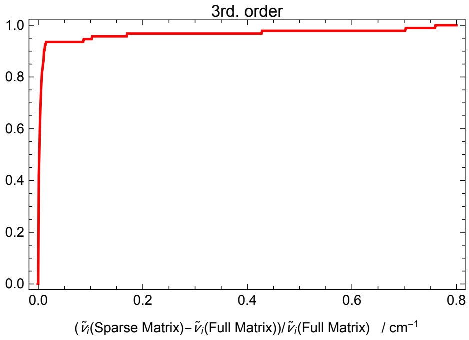
0.8
0.6
0.4
0.2
0.0
0.0
0.5
1.0
1.5
2.0
$(\tilde{\nu}_i$(Sparse Matrix)$-\tilde{\nu}_i$(Full Matrix))/$\tilde{\nu}_i$(Full Matrix)   / cm^{-1}


3rd. order
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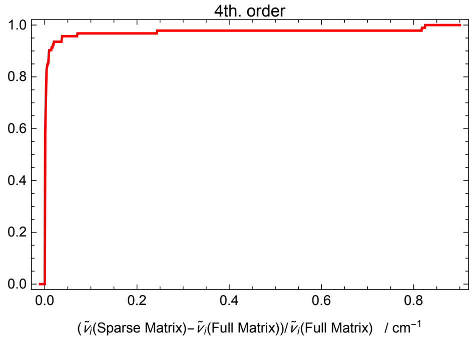
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
$(\tilde{\nu}_i$(Sparse Matrix)$-\tilde{\nu}_i$(Full Matrix))/$\tilde{\nu}_i$(Full Matrix)   / cm^{-1}


4th. order
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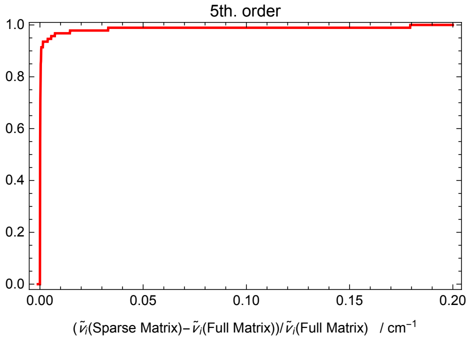
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
$(\tilde{\nu}_i$(Sparse Matrix)$-\tilde{\nu}_i$(Full Matrix))/$\tilde{\nu}_i$(Full Matrix)   / cm^{-1}


5th. order
1.0
0.8
0.6
0.4
0.2
0.0
0.00
0.05
0.10
0.15
0.20
$(\tilde{\nu}_i$(Sparse Matrix)$-\tilde{\nu}_i$(Full Matrix))/$\tilde{\nu}_i$(Full Matrix)   / cm^{-1}

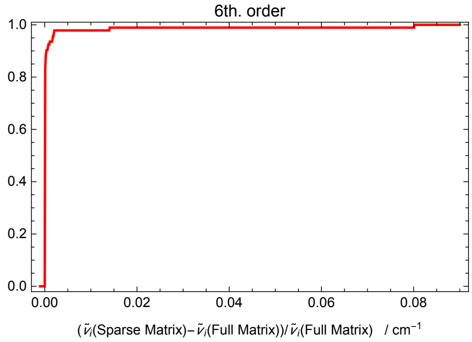

6th. order
1.0
0.8
0.6
0.4
0.2
0.0
0.00
0.02
0.04
0.06
0.08
$(\tilde{\nu}_i$(Sparse Matrix)$-\tilde{\nu}_i$(Full Matrix))/$\tilde{\nu}_i$(Full Matrix)   / cm^{-1}

Table S1

Gustav Bojesen: *The insignificance of long-distance interactions for molecular frequencies. Analyses of sparse force-constant matrices.*

Summary of frequency calculations from sparse matrices of the orders 0 to 6.

Ethylbenzen

HF/6-31G(d)		FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
	0	0,06	271,239	205,472	0,829	2,85
	1	0,17	93,16	86,702	0,318	1,146
	2	0,35	27,616	36,398	0,137	0,653
	3	0,57	3,822	5,928	0,02	0,114
	4	0,76	1,54	2,834	0,003	0,008
	5	0,91	0,082	0,131	0	0,002
	6	0,98	0,02	0,038	0	0

HF/6-311G(d,p)		FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
	0	0,06	265,078	202,88	0,807	2,738
	1	0,17	91,364	85,769	0,31	1,103
	2	0,35	27,668	36,159	0,134	0,63
	3	0,57	3,569	5,295	0,017	0,092
	4	0,76	1,44	2,621	0,003	0,008
	5	0,91	0,086	0,146	0	0,002
	6	0,98	0,02	0,041	0	0

MP2/6-31G(d)		FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
	0	0,06	271,437	185,718	0,828	2,701
	1	0,17	85,338	81,025	0,322	1,22
	2	0,35	20,825	35,604	0,147	0,762
	3	0,57	3,785	6,723	0,024	0,132
	4	0,76	2,141	3,543	0,007	0,023
	5	0,91	0,105	0,285	0,001	0,007
	6	0,98	0,021	0,047	0	0,001

MP2/6-311G(d,p)		FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
	0	0,06	265,403	183,936	0,84	2,739
	1	0,17	83,796	79,627	0,321	1,215
	2	0,35	21,839	35,898	0,151	0,768
	3	0,57	4,264	7,706	0,029	0,163
	4	0,76	2,029	3,56	0,006	0,021
	5	0,91	0,112	0,299	0,001	0,007
	6	0,98	0,021	0,049	0	0,001

B3LYP/6-31G(d)		FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
	0	0,06	253,452	182,633	0,837	2,917
	1	0,17	88,316	82,954	0,346	1,308
	2	0,35	21,573	32,393	0,134	0,682
	3	0,57	3,761	6,024	0,022	0,121
	4	0,76	1,886	3,399	0,006	0,021
	5	0,91	0,07	0,125	0,001	0,003
	6	0,98	0,02	0,035	0	0

B3LYP/6-311G(d,p)		FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
	0	0,06	245,726	180,69	0,786	2,623
	1	0,17	87,22	83,054	0,328	1,177
	2	0,35	21,406	31,284	0,121	0,597
	3	0,57	3,308	5,042	0,015	0,077
	4	0,76	1,598	3,034	0,003	0,009
	5	0,91	0,07	0,132	0	0,002
	6	0,98	0,019	0,037	0	0

ωB97XD/6-311+G(2df,2p)		FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
	0	0,06	247,783	185,696	0,884	3,274
	1	0,17	87,306	83,666	0,367	1,446
	2	0,35	23,061	33,798	0,154	0,804
	3	0,57	3,475	5,835	0,021	0,12
	4	0,76	1,661	2,917	0,008	0,033
	5	0,91	0,078	0,13	0,001	0,002
	6	0,98	0,021	0,038	0	0,001

Propylbenzene

MP2/6-311+G(d,p)		FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
	0	0,05	271,121	204,726	0,956	2,811
	1	0,14	93,739	87,965	0,378	1,198
	2	0,31	23,367	34,475	0,15	0,624
	3	0,51	3,737	6,667	0,023	0,135
	4	0,69	1,814	3,242	0,007	0,021
	5	0,82	0,16	0,465	0,002	0,012
	6	0,93	0,038	0,089	0	0,001

B3LYP/6-311G(d,p)		FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
	0	0,05	255,198	199,539	0,924	2,8
	1	0,14	94,201	93,24	0,391	1,216
	2	0,31	22,454	31,713	0,133	0,537
	3	0,51	3,125	4,513	0,013	0,071
	4	0,69	1,548	2,968	0,005	0,015
	5	0,82	0,13	0,328	0,001	0,007
	6	0,93	0,039	0,1	0	0,001

ωB97XD/6-311+G(2df,2p)		FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
	0	0,05	256,73	205,32	0,98	3,181
	1	0,14	94,096	93,392	0,407	1,329
	2	0,31	24,068	33,693	0,15	0,637
	3	0,51	3,279	5,198	0,018	0,104
	4	0,69	1,555	2,81	0,007	0,027
	5	0,82	0,138	0,374	0,002	0,01
	6	0,93	0,039	0,094	0	0,002

Butylbenzene

MP2/6-31G(d)		FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
	0	0,04	284,364	220,122	1,105	3,381
	1	0,12	100,957	93,572	0,454	1,502
	2	0,27	23,141	31,99	0,158	0,637
	3	0,46	3,303	6,373	0,027	0,182
	4	0,62	1,911	3,606	0,013	0,06
	5	0,76	0,129	0,499	0,002	0,016
	6	0,86	0,041	0,136	0	0,002

MP2/6-311G(d,p)		FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
	0	0,04	276,62	219,392	1,128	3,433
	1	0,12	99,783	92,136	0,46	1,506
	2	0,27	23,724	31,599	0,161	0,632
	3	0,46	3,67	6,255	0,028	0,173
	4	0,62	1,854	3,478	0,012	0,054
	5	0,76	0,124	0,434	0,002	0,014
	6	0,86	0,043	0,139	0,001	0,003

B3LYP/6-31G(d)		FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
	0	0,04	269,668	215,729	1,147	3,745
	1	0,12	101,889	98,045	0,488	1,629

B3LYP/6-311G(d,p)		FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
	0	0,04	262,056	214,042	1,105	3,48
	1	0,12	100,606	98,532	0,476	1,53

2	0,27	20,848	29,859	0,147	0,61
3	0,46	3,348	4,796	0,02	0,127
4	0,62	1,822	3,601	0,013	0,066
5	0,76	0,128	0,51	0,002	0,018
6	0,86	0,047	0,154	0,001	0,003

2	0,27	20,373	29,641	0,139	0,549
3	0,46	3,171	4,516	0,017	0,103
4	0,62	1,551	3,049	0,01	0,045
5	0,76	0,126	0,472	0,002	0,015
6	0,86	0,045	0,143	0,001	0,002

ωB97XD/6-311+G(2df,2p)	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	263,473	220,255	1,186	4,067
1	0,12	100,03	98,833	0,499	1,719
2	0,27	22,32	30,784	0,158	0,666
3	0,46	3,251	5,546	0,026	0,17
4	0,62	1,593	3,223	0,014	0,073
5	0,76	0,144	0,613	0,003	0,023
6	0,86	0,044	0,132	0,001	0,003

Pentylbenzene

B3LYP/6-31G(d)	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	274,886	227,472	1,287	4,049
1	0,11	107,301	100,949	0,545	1,73
2	0,24	20,766	25,844	0,127	0,427
3	0,42	3,282	4,684	0,022	0,127
4	0,57	1,748	3,105	0,013	0,067
5	0,7	0,146	0,549	0,003	0,02
6	0,81	0,041	0,141	0,001	0,003

HF/6-311G(d,p)	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	292,027	247,128	1,27	3,859
1	0,11	112,738	103,03	0,493	1,442
2	0,24	25,509	29,117	0,111	0,331
3	0,42	3,653	5,103	0,023	0,122
4	0,57	1,402	2,595	0,008	0,037
5	0,7	0,18	0,68	0,003	0,02
6	0,81	0,046	0,149	0,001	0,003

MP2/6-311G(d,p)	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	281,796	231,613	1,27	3,731
1	0,11	105,158	95,777	0,524	1,63
2	0,24	22,258	27,823	0,131	0,409
3	0,42	3,488	5,593	0,027	0,126
4	0,57	1,719	3,238	0,011	0,05
5	0,7	0,126	0,348	0,002	0,011
6	0,81	0,048	0,171	0,001	0,004

B3LYP/6-311G(d,p)	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	267,837	225,859	1,253	3,838
1	0,11	106,186	101,74	0,538	1,658
2	0,24	20,765	25,9	0,124	0,41
3	0,42	3,023	4,233	0,019	0,108
4	0,57	1,588	2,813	0,011	0,051
5	0,7	0,149	0,525	0,002	0,018
6	0,81	0,043	0,145	0,001	0,003

ωB97XD/6-311+G(2df,2 p)	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	269,301	232,582	1,32	4,311
1	0,11	105,286	102,117	0,552	1,792
2	0,24	21,969	26,615	0,132	0,45
3	0,42	3,084	5,046	0,025	0,159
4	0,57	1,579	3,198	0,014	0,075
5	0,7	0,156	0,624	0,003	0,024
6	0,81	0,043	0,137	0,001	0,003

(4-Methylpentyl)benzene

MP2/6-31G(d)	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,03	294,446	239,255	1,358	4,317
1	0,1	111,272	96,526	0,555	1,866
2	0,22	19,084	26,839	0,135	0,48
3	0,38	4,077	6,793	0,041	0,212
4	0,55	1,724	3,133	0,015	0,095
5	0,67	0,143	0,341	0,002	0,011
6	0,78	0,035	0,119	0	0,002

B3LYP/6-31G(d)	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,03	280,758	234,602	1,39	4,558
1	0,1	111,507	98,592	0,572	1,889
2	0,22	17,706	23,902	0,126	0,452
3	0,38	4,278	5,93	0,037	0,19
4	0,55	1,641	3,088	0,016	0,097
5	0,67	0,153	0,449	0,003	0,015
6	0,78	0,031	0,112	0	0,002

MP2/6-311G(d,p)	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,03	285,443	238,185	1,375	4,353
1	0,1	109,757	95,619	0,562	1,88
2	0,22	18,603	26,455	0,137	0,481
3	0,38	4,367	6,73	0,04	0,204
4	0,55	1,646	3,204	0,014	0,086
5	0,67	0,138	0,28	0,002	0,008
6	0,78	0,039	0,131	0,001	0,003

B3LYP/6-311G(d,p)	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,03	273,08	232,354	1,353	4,35
1	0,1	109,998	98,595	0,566	1,829
2	0,22	17,374	23,909	0,123	0,437
3	0,38	3,834	5,371	0,033	0,172
4	0,55	1,477	2,754	0,013	0,077
5	0,67	0,151	0,422	0,002	0,013
6	0,78	0,032	0,117	0	0,002

ωB97XD/6-311+G(2df,2p)	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,03	273,921	238,787	1,466	5,141
1	0,1	109,113	98,454	0,6	2,101
2	0,22	18,266	25,419	0,144	0,545
3	0,38	4,134	6,16	0,042	0,238
4	0,55	1,508	2,988	0,018	0,121
5	0,67	0,173	0,556	0,004	0,023
6	0,78	0,034	0,115	0,001	0,003

(4-Phenylbutyl)ammonium

B3LYP/6-311G(d,p)

	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff	SD A.R.Diff.
0	0,04	278,697	220,421	1,235	3,631
1	0,11	107,709	101,089	0,526	1,571
2	0,24	18,868	23,282	0,104	0,322
3	0,42	3,142	3,95	0,018	0,079
4	0,57	1,477	2,804	0,009	0,043
5	0,7	0,127	0,38	0,002	0,011
6	0,81	0,033	0,096	0	0,002

ωB97XD/6-311+G(2df,2p)

	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff	SD A.R.Diff.
0	0,04	281,209	227,158	1,265	3,864
1	0,11	106,571	101,651	0,526	1,616
2	0,24	19,852	24,113	0,109	0,34
3	0,42	3,395	4,637	0,023	0,119
4	0,57	1,435	2,786	0,01	0,053
5	0,7	0,139	0,511	0,002	0,017
6	0,81	0,035	0,096	0	0,002

With matrix complement from Pentylbenzen:

Empty rows below indicate calculations with imaginary frequencies (negativ eigenvalues)

B3LYP/6-311G(d,p)

M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
38,394	60,162	0,236	0,689
12,291	20,742	0,046	0,118
2,405	4,866	0,023	0,09
1,264	3,024	0,014	0,072
0,253	0,52	0,002	0,009
0,072	0,216	0,001	0,006
0,03	0,105	0,001	0,003

ωB97XD/6-311+G(2df,2p)

M.A.Diff.	SD A.Diff.	M A.R.Diff	SD A.R.Diff.
281,209	227,158	1,265	3,864
106,571	101,651	0,526	1,616
19,852	24,113	0,109	0,34
3,395	4,637	0,023	0,119
1,435	2,786	0,01	0,053
0,139	0,511	0,002	0,017
0,035	0,096	0	0,002

N-Butylanilinium

HF/6-311G(d,p)

	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	290,639	245,616	1,23	3,591
1	0,11	108,937	99,419	0,479	1,39
2	0,24	29,353	55,291	0,247	1,31
3	0,42	3,389	5,269	0,023	0,109
4	0,57	1	1,667	0,004	0,012
5	0,7	0,136	0,295	0,001	0,006
6	0,81	0,041	0,126	0	0,002

MP2/6-311G(d,p)

	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	281,929	225,329	1,24	3,508
1	0,11	101,146	95,755	0,518	1,596
2	0,24	20,184	27,074	0,115	0,359
3	0,42	3,718	5,697	0,028	0,12
4	0,57	1,327	2,37	0,007	0,027
5	0,7	0,137	0,246	0,001	0,004
6	0,81	0,049	0,188	0,001	0,004

B3LYP/6-311G(d,p)

	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	268,068	221,241	1,207	3,507
1	0,11	102,514	99,098	0,519	1,564
2	0,24	20,328	24,854	0,11	0,336
3	0,42	3,003	4,034	0,019	0,087
4	0,57	1,183	1,914	0,005	0,019
5	0,7	0,129	0,215	0,001	0,003
6	0,81	0,041	0,138	0,001	0,002

ωB97XD/6-311+G(2df,2p)

	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	269,893	227,937	1,196	3,492
1	0,11	100,925	99,837	0,502	1,508
2	0,24	20,553	25,605	0,108	0,33
3	0,42	3,209	4,131	0,02	0,093
4	0,57	1,152	1,936	0,005	0,019
5	0,7	0,131	0,228	0,001	0,005
6	0,81	0,036	0,118	0	0,002

With matrix complement from Pentylbenzen:

HF/6-311G(d,p)

M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
31,648	44,844	0,182	0,559
2,965	5,401	0,02	0,103
1,765	3,63	0,015	0,072
0,621	1,543	0,007	0,034
0,12	0,276	0,001	0,006
0,009	0,02	0	0

MP2/6-311G(d,p)

M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
28,352	40,843	0,192	0,607
3,23	5,758	0,031	0,135
1,793	3,67	0,018	0,087
0,624	1,463	0,007	0,035
0,079	0,15	0,001	0,002
0,013	0,041	0	0,001

B3LYP/6-311G(d,p)

M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
28,274	40,326	0,18	0,558
3,117	5,245	0,023	0,099
1,786	3,427	0,016	0,074
0,648	1,575	0,008	0,038
0,107	0,273	0,001	0,007
0,007	0,014	0	0

ωB97XD/6-311+G(2df,2p)

M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
28,173	40,874	0,171	0,522
2,976	4,938	0,021	0,09
1,713	3,237	0,014	0,067
0,579	1,555	0,007	0,04
0,105	0,275	0,001	0,007
0,007	0,013	0	0

N-Phenyl-1,3-diammoniumpropane

B3LYP/6-311G(d,p)

	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	282,436	216,258	1,172	3,263
1	0,11	107,741	98,817	0,494	1,431
2	0,24	18,885	22,922	0,087	0,265
3	0,42	3,409	3,917	0,018	0,066
4	0,57	1,224	2,059	0,006	0,023
5	0,7	0,151	0,315	0,001	0,005
6	0,81	0,04	0,112	0	0,002

ωB97XD/6-311+G(2df,2p)

	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	284,37	224,127	1,149	3,191
1	0,11	106,715	99,47	0,474	1,362
2	0,24	18,422	23,545	0,08	0,256
3	0,42	3,381	3,858	0,017	0,067
4	0,57	1,162	1,984	0,005	0,02

With matrix complement from Pentylbenzen:

B3LYP/6-311G(d,p)

M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
57,461	81,333	0,363	1,108
18,567	24,683	0,073	0,193
4,077	6,395	0,032	0,126
2,238	3,333	0,015	0,062
0,877	2,249	0,01	0,054
0,108	0,253	0,001	0,002
0,033	0,099	0	0,002

ωB97XD/6-311+G(2df,2p)

M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
57,141	82,219	0,348	1,059
18,595	26,352	0,082	0,215
4,083	6,785	0,032	0,134
2,123	2,959	0,012	0,05
0,769	1,966	0,009	0,046

5	0,7	0,157	0,325	0,001	0,006
6	0,81	0,036	0,101	0	0,002

0,103	0,235	0,001	0,002
0,031	0,1	0	0,002

N-(4-Chlorobutyl)anilinium

B3LYP/6-311G(d,p)

	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	258,829	194,162	1,226	3,249
1	0,11	92,407	92,197	0,559	1,617
2	0,24	20,442	22,468	0,098	0,24
3	0,42	3,502	4,756	0,029	0,132
4	0,57	1,203	1,984	0,008	0,037
5	0,7	0,161	0,373	0,002	0,012
6	0,81	0,042	0,095	0	0,002

WB97XD/6-311+G(2df,2p)

	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	260,626	201,002	1,198	3,153
1	0,11	91,405	91,96	0,531	1,526
2	0,24	20,968	22,746	0,098	0,241
3	0,42	3,717	5,048	0,03	0,136
4	0,57	1,206	1,824	0,008	0,035
5	0,7	0,172	0,447	0,002	0,015
6	0,81	0,037	0,082	0	0,001

With matrix complement from Pentylbenzen:

B3LYP/6-311G(d,p)

M.A.Diff.	SD A.Diff	M A.R.Diff.	SD A.R.Diff.
34,49	49,638	0,252	0,717
2,561	2,728	0,014	0,047
1,952	3,326	0,02	0,08
0,7	2,308	0,012	0,086
0,087	0,177	0,001	0,004
0,012	0,027	0	0

WB97XD/6-311+G(2df,2p)

M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
44,023	65,376	0,357	1,129
3,817	6,162	0,032	0,133
2,155	3,826	0,022	0,093
0,683	2,234	0,011	0,078
0,079	0,178	0,001	0,004
0,011	0,027	0	0,001

(5-Chloropentyl)benzene

B3LYP/6-311G(d,p)

	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	258,026	197,614	1,26	3,457
1	0,11	95,762	93,72	0,583	1,735
2	0,24	20,788	23,048	0,108	0,282
3	0,42	3,346	4,095	0,024	0,122
4	0,57	1,491	2,777	0,012	0,067
5	0,7	0,171	0,662	0,004	0,028
6	0,81	0,043	0,102	0	0,002

ωB97XD/6-311+G(2df,2p)

	FC fraction	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	259,987	204,185	1,295	3,711
1	0,11	95,423	93,517	0,586	1,813
2	0,24	21,956	23,819	0,115	0,312
3	0,42	3,364	4,892	0,03	0,17
4	0,57	1,472	2,831	0,014	0,084
5	0,7	0,186	0,822	0,005	0,038
6	0,81	0,037	0,088	0	0,001

With matrix complement from Pentylbenzen:

B3LYP/6-311G(d,p)

	FC fraction SF	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	10,787	22,578	0,093	0,301
1	0,11	3,544	7,375	0,029	0,11
2	0,24	0,635	1,056	0,004	0,011
3	0,42	0,183	0,246	0,001	0,005
4	0,57	0,065	0,145	0,001	0,005
5	0,7	0,019	0,043	0	0,001
6	0,81	0,011	0,037	0	0,001

ωB97XD/6-311+G(2df,2p)

	FC fraction SF	M.A.Diff.	SD A.Diff.	M A.R.Diff.	SD A.R.Diff.
0	0,04	9,37	21,124	0,084	0,282
1	0,11	3,106	7,165	0,019	0,076
2	0,24	0,591	0,973	0,003	0,009
3	0,42	0,196	0,368	0,002	0,008
4	0,57	0,056	0,116	0,001	0,005
5	0,7	0,016	0,035	0	0,001
6	0,81	0,01	0,031	0	0,001

1-Chloro-4-pentylbenzene

B3LYP/6-311G(d,p)

	FC fraction	M.A.Diff.	SD A.Diff.	M.A.R.Diff.	SD A.R.Diff.
0	0,04	273,698	213,185	1,195	3,049
1	0,11	107,111	91,47	0,551	1,6
2	0,24	19,873	20,356	0,11	0,35
3	0,42	3,106	4,226	0,023	0,103
4	0,57	1,117	1,97	0,005	0,017
5	0,7	0,148	0,324	0,001	0,007
6	0,81	0,035	0,088	0	0,002

ωB97XD/6-311+G(2df,2p)

	FC fraction	M.A.Diff.	SD A.Diff.	M.A.R.Diff.	SD A.R.Diff.
0	0,04	274,454	220,749	1,236	3,328
1	0,11	106,385	91,531	0,56	1,71
2	0,24	19,245	21,14	0,113	0,377
3	0,42	3,153	4,809	0,029	0,138
4	0,57	1,129	1,853	0,006	0,019
5	0,7	0,151	0,312	0,002	0,008
6	0,81	0,035	0,082	0	0,002

With matrix complement from Pentylbenzen:

B3LYP/6-311G(d,p)

	M.A.Diff.	SD A.Diff.	M.A.R.Diff.	SD A.R.Diff.
0	4,222	6,6	0,021	0,078
1	2,866	7,148	0,025	0,127
2	1,003	1,787	0,006	0,027
3	0,687	1,985	0,01	0,067
4	0,603	2,054	0,01	0,071
5	0,041	0,122	0,001	0,003
6	0,02	0,06	0	0,001

ωB97XD/6-311+G(2df,2p)

	M.A.Diff.	SD A.Diff.	M.A.R.Diff.	SD A.R.Diff.
0	19,486	34,879	0,226	0,919
1	5,471	9,323	0,054	0,228
2	3,002	5,765	0,034	0,155
3	1,008	2,217	0,013	0,081
4	0,675	2,493	0,013	0,1
5	0,041	0,102	0,001	0,003
6	0,022	0,067	0	0,001

(4-Phenylbutyl)silane

B3LYP/6-311G(d,p)

	FC fraction	M.A.Diff.	SD A.Diff.	M.A.R.Diff.	SD A.R.Diff.
0	0,04	222,489	163	1,06	2,956
1	0,11	90,903	100,069	0,553	1,629
2	0,24	20,336	22,515	0,115	0,333
3	0,42	3,042	4,378	0,022	0,099
4	0,57	1,413	2,899	0,01	0,046

With matrix complement from Pentylbenzen:

B3LYP/6-311G(d,p)

	M.A.Diff.	SD A.Diff.	M.A.R.Diff.	SD A.R.Diff.
0	22,188	26,802	0,068	0,148
1	26,602	92,506	0,434	3,213
2	1,869	4,408	0,015	0,063
3	0,64	1,848	0,008	0,043
4	0,126	0,28	0,001	0,005

5	0,7	0,169	0,673	0,003	0,023
6	0,81	0,042	0,128	0	0,002

ωB97XD/6-311+G(2df,2p)

	FC fraction	M.A.Diff	SD A.Diff	M A.R.Diff	SD M.A.R.Diff
0	0,04	224,155	165,903	1,129	3,359
1	0,11	89,12	100,5	0,575	1,775
2	0,24	22,049	23,803	0,128	0,386
3	0,42	3,167	4,964	0,03	0,147
4	0,57	1,473	2,922	0,013	0,065
5	0,7	0,188	0,617	0,004	0,023
6	0,81	0,044	0,116	0	0,002

5	0,067	0,19	0,001	0,004
6	0,018	0,054	0	0,001

ωB97XD/6-311+G(2df,2p)

	FC fraction S	M.A.Diff	SD A.Diff	M.A.R.Diff	SD A.R.Diff
0	0,04				
1	0,11				
2	0,24	2,033	4,802	0,02	0,081
3	0,42	0,654	1,875	0,01	0,049
4	0,57	0,127	0,297	0,001	0,006
5	0,7	0,074	0,203	0,001	0,005
6	0,81	0,024	0,072	0	0,002

4-Phenylbutanol

MP2/6-311G(d,p)

	FC fraction	M.A.Diff.	SD A.Diff.	M.A.R.Diff.	SD A.R.Diff.
0	0,04	263,702	200,524	1,049	2,567
1	0,12	81,781	87,141	0,473	1,453
2	0,26	22,931	29,105	0,149	0,471
3	0,44	3,691	5,916	0,029	0,143
4	0,6	1,697	3,117	0,012	0,057
5	0,74	0,149	0,527	0,003	0,018
6	0,84	0,053	0,174	0,001	0,005

B3LYP/6-31G(d)

	FC fraction	M.A.Diff.	SD A.Diff.	M.A.R.Diff.	SD A.R.Diff.
0	0,04	257,161	197,528	1,085	2,925
1	0,12	87,168	89,951	0,488	1,523
2	0,26	21,047	24,911	0,133	0,439
3	0,44	3,472	4,985	0,023	0,131
4	0,6	1,659	3,398	0,013	0,07
5	0,74	0,137	0,584	0,003	0,021
6	0,84	0,038	0,122	0,001	0,003

B3LYP/6-311G(d,p)

	FC fraction	M.A.Diff.	SD A.Diff.	M.A.R.Diff.	SD A.R.Diff.
0	0,04	251,968	196,688	1,067	2,825
1	0,12	87,452	90,625	0,484	1,463
2	0,26	20,905	25,229	0,134	0,444
3	0,44	3,226	4,585	0,021	0,115
4	0,6	1,455	2,968	0,01	0,052
5	0,74	0,141	0,57	0,003	0,019
6	0,84	0,042	0,13	0,001	0,003

ωB97XD/6-311+G(2df,2p)

	FC fraction	M.A.Diff.	SD A.Diff.	M.A.R.Diff.	SD A.R.Diff.
0	0,04	254,061	204,548	1,119	3,121
1	0,12	86,852	91,037	0,495	1,559
2	0,26	22,261	26,444	0,138	0,454
3	0,44	3,292	5,348	0,027	0,169
4	0,6	1,463	2,921	0,013	0,076
5	0,74	0,157	0,683	0,003	0,026
6	0,84	0,046	0,143	0,001	0,004

With matrix complement from Pentylbenzen:

MP2/6-311G(d,p)

	M.A.Diff.	SD A.Diff.	M.A.R.Diff.	SD A.R.Diff.
0	35,903	45,051	0,186	0,502
1	9,258	14,314	0,061	0,183
2	2,63	4,083	0,014	0,048
3	0,808	1,632	0,006	0,022
4	0,125	0,217	0,001	0,004
5	0,056	0,114	0	0,002
6	0,011	0,027	0	0,001

B3LYP/6-31G(d)

	M.A.Diff.	SD A.Diff.	M.A.R.Diff.	SD A.R.Diff.
0	33,025	40,996	0,163	0,459
1	9,043	15,049	0,057	0,173
2	2,776	4,551	0,017	0,059
3	0,697	1,297	0,005	0,018
4	0,129	0,27	0,001	0,006
5	0,05	0,122	0,001	0,003
6	0,013	0,037	0	0,001

B3LYP/6-311G(d,p)

	M.A.Diff.	SD A.Diff.	M.A.R.Diff.	SD A.R.Diff.
0	33,553	42,066	0,162	0,435
1	8,753	14,999	0,055	0,167
2	2,531	4,217	0,016	0,051
3	0,654	1,261	0,005	0,018
4	0,125	0,255	0,001	0,005
5	0,045	0,105	0	0,002
6	0,014	0,038	0	0,001

ωB97XD/6-311+G(2df,2p)

	M.A.Diff.	SD A.Diff.	M.A.R.Diff.	SD A.R.Diff.
0	34,358	42,389	0,172	0,491
1	8,571	14,303	0,058	0,182
2	2,466	3,837	0,017	0,061
3	0,703	1,412	0,007	0,026
4	0,118	0,247	0,001	0,006
5	0,047	0,108	0	0,002
6	0,017	0,048	0	0,001

Table S2

Gustav Bojesen: *The insignificance of long-distance interactions for molecular frequencies. Analyses of sparse force-constant matrices.*

Summary of frequency calculations from coupling matrices based on fragment matrices and coupling elements from Octylbenzene and Decane

1-(4-Chlorophenyl)-6-methylheptane:

(4-Chlorophenyl)ethyl (*4-Chloro-1-butylbenzene*) + 4-Methylpentyl (*2-Methyloctane*)

B3LYP/6-311G(d,p	M.A.Diff	SD A.Diff	M.A.R.Diff	SD A.R.Diff
0	12,701	19,852	0,094	0,300
1	8,875	13,580	0,047	0,127
2	2,613	3,635	0,010	0,031
3	0,783	1,385	0,007	0,043
4	0,443	0,507	0,003	0,015

2-Chloro-8-(4-chlorophenyl)octane:

(4-Chlorophenyl)ethyl (*4-Chloro-1-butylbenzene*) + 5-Chlorohexyl (*2-Chlorononane*)

B3LYP/6-311G(d,p	M.A.Diff	SD A.Diff	M.A.R.Diff	SD A.R.Diff
0	13,284	18,170	0,106	0,333
1	8,851	13,351	0,044	0,123
2	2,940	3,696	0,014	0,044
3	0,810	1,427	0,008	0,049
4	0,487	0,633	0,005	0,020

8-(4-Trifluoromethylphenyl)-1-octene:

(4-Trifluoromethylphenyl)ethyl (*1-Butyl-4-Trifluoromethylbenzene* + Hex-5-en-1-yl (*1-Nonene*)

B3LYP/6-311G(d,p	M.A.Diff	SD A.Diff	M.A.R.Diff	SD A.R.Diff
0	12,948	16,725	0,108	0,338
1	8,548	14,553	0,054	0,157
2	2,690	3,651	0,021	0,110

3	0,869	1,435	0,014	0,081
4	0,560	0,733	0,008	0,045

4-(10-Chlorodecyl)phenol:

(4-Hydroxyphenyl)ethyl (*4-Butylphenol)* + Butane-1,4-diyl (*Octane*) + 4-Chlorobutyl (*1-Chlorooctane*)

B3LYP/6-311G(d,p	M.A.Diff	SD A.Diff	M.A.R.Diff	SD A.R.Diff
0	20,686	28,344	0,168	0,516
1	14,123	22,937	0,071	0,181
2	4,303	4,685	0,027	0,096
3	1,175	1,263	0,009	0,048
4	0,820	1,245	0,012	0,054

10-(2-Naphthyl)decanol:

(2-Naphthyl)butyl (*2-Butylnaphthalene)* + Butane-1,4-diyl (*Octane*) + 4-Hydroxybutyl (*Octanol*)

B3LYP/6-311G(d,p	M.A.Diff	SD A.Diff	M.A.R.Diff	SD A.R.Diff
0	17,826	24,367	0,142	0,463
1	12,077	18,727	0,060	0,148
2	3,385	4,339	0,019	0,075
3	0,970	1,335	0,008	0,035
4	0,655	1,038	0,008	0,041

1-(4-Trifluoromethylphenyl)-10-methylundecane:

(4-Trifluoromethylphenyl)ethyl (*1-Butyl-4-Trifluoromethylbenzene +* Butane-1,4-diyl (*Octane*) + 4-Methylpentyl (*2-Methyloctane*)

B3LYP/6-311G(d,p	M.A.Diff	SD A.Diff	M.A.R.Diff	SD A.R.Diff
0	17,112	22,295	0,143	0,431
1	11,643	17,105	0,053	0,121
2	3,558	4,552	0,017	0,050
3	0,982	1,152	0,009	0,033
4	0,687	1,034	0,009	0,046