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A VCD robust mode analysis of induced chirality: the case of pulegone in chloroform

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Abstract

Vibrational modes in an achiral molecule may acquire rotational strength by complexation to a chiral molecule, as happens for achiral solvent molecules complexed to a chiral solute. We investigate this transfer of chirality in vibrational circular dichroism for the pulegone molecule in CDCl$_3$ solvent from the point of view of the robustness concept introduced recently. It turns out that the transfer of chirality yields non-robust modes, which means that, although they are observed in VCD experiments, the sign of these modes cannot be predicted reliably with standard (DFT) VCD calculations. This limits the usefulness of the induced chirality phenomenon for obtaining information on the intermolecular interactions that give rise to it.
1 Introduction

Although most often associated to a chiral carbon, chirality is a more general geometrical property that is not limited to a chiral center. Indeed, there are many molecules that are chiral without having a chiral center. An example in this regard is the transfer of chirality where an achiral molecule—obviously lacking a chiral center—becomes optically active upon interacting (e.g. by intermolecular hydrogen bonding) with a chiral molecule. The phenomenon is most often encountered when considering (chiral) solute - (achiral) solvent interactions, though it is not limited to this particular case. Experimentally, such cases of induced chirality have been observed using both electronic (ECD) [1] and vibrational (VCD) circular dichroism (VCD) [2–4] spectroscopy.

As suggested in reference [1], the presence of signals associated to the achiral moiety in the ECD spectra might provide information about the relative orientation of the interacting chiral and achiral molecules. Since VCD spectroscopy deals with vibrational transitions rather than electronic transitions, one can expect that under normal circumstances VCD spectroscopy should provide more detailed structural information on the relative orientation of the chiral and achiral moieties than ECD spectroscopy. However, compared to ECD spectroscopy, much less attention has been paid in VCD spectroscopy to the phenomenon of induced chirality in the solvent. For example only six papers have been published on this subject in the period between 2007 and 2009, i.e. the combined experimental and computational studies of Xu et al. [3,5,6] and Debie et al. [4,7], and the theoretical study of Nicu et al. [8].

The studies of Xu et al. [3,5,6] and Debie et al. [4,7] very clearly show that 1) the presence of a chiral solute in an achiral solvent, such as for example H$_2$O and CDCl$_3$, may cause the modes of the achiral solvent to become VCD active, and 2) it is possible not only to find the VCD signals of the achiral solvent experimentally, but also to relate these VCD
signals through calculations to interactions between the solute and solvent molecules.

The theoretical investigation of Nicu et al. [8] has provided a very easy and intuitive explanation of the mechanism responsible for the chirality transfer in VCD. Due to symmetry constraints the electric and magnetic transition dipole moments (ETDM and MTDM) associated to the fundamental transition of a given normal mode are perpendicular in isolated achiral molecules. As a result the rotational strength, i.e. the inner product between the ETDM and MTDM vectors of a given mode, is zero for all vibrational modes of isolated achiral molecules. Since the VCD intensities are proportional to the rotational strengths it is clear that all modes of achiral molecules will have zero VCD intensities. When an achiral molecule is involved in a molecular complex however, its ETDMs and MTDMs are perturbed and no longer perpendicular. Consequently, the modes of the achiral molecule can exhibit non-zero VCD signals. However, because in weak complexation of a solvent molecule to the solute, the perturbation is weak, it is expected that the angle $\xi$ between the ETDM and MTDM will deviate only slightly from $90^\circ$ and as a result the rotational strength will be small.

The findings in the above mentioned papers, i.e. the possibility to measure and compute chirality transfer effects on VCD spectra, and the identification of the mechanism responsible for the chirality transfer, suggest that VCD spectra can indeed provide information about the complexation between solute and solvent molecules involved in a molecular complex, including information on the relative orientation of the molecules. This would indeed be welcome, since current state-of-the-art calculations still have difficulty describing weak complexation accurately, in particular for large solute molecules. In that case one has to take recourse to Density Functional Theory (DFT) calculations, which describe (with a suitable functional) hydrogen bonding reasonably well, but not dispersion interactions. Moreover, the DFT calculations are not sufficiently accurate to compute reliable Boltzmann populations for the various conformations of the molecular complex.
The usefulness of the induced chirality phenomenon is, however, not beyond doubt. Since it is to be expected that the modes of the achiral moiety have angles $\xi$ between the ETDM and MTDM close to $90^\circ$, they should be classified as non-robust modes according to Refs. [8,9]. In general non-robust modes are defined as having angles $\xi$ close to $90^\circ$. They can easily change the angle through $90^\circ$ (hence change sign of the rotational strength) by small computational perturbations (other choice of functional or basis set) or experimental circumstances (e.g. different solvent).

The goal of the present work is to investigate whether induced chirality in VCD spectra yields indeed non-robust signals. It might be hoped that, even though the perturbation due to the complexation is small, it would always lead to a deviation of the $\xi$ angle in the same direction compared to $90^\circ$. In that case we would have weak but still robust induced VCD bands. Using as an example the VCD spectrum of pulegone measured in CDCl$_3$ solvent, we will investigate the robustness of the C–D stretching mode of the achiral CDCl$_3$ solvent which as shown recently by Debie et al. [7] exhibits a non-zero VCD signal in the 1:1 pulegone–CDCl$_3$ molecular complex.

The work is organized as follows: after some experimental, computational and methodological details, the concept of robustness is introduced and exemplified with a discussion of the robust and non-robust normal modes in the VCD spectrum of pulegone between 850 and 1700 cm$^{-1}$. Then the robustness of the C–D stretch mode of the achiral solvent molecule that exhibits induced chirality is investigated in detail. We find that this mode, like other modes with $\xi$ close to $90^\circ$, is non-robust. The sign and magnitude of the rotational strength therefore cannot be reliably reproduced by standard DFT calculations. This limits the usefulness of the induced VCD signals for obtaining information about the structure and strength of the intermolecular interaction giving rise to the complexation and the induced chirality.
2 Experimental and computational details

The samples of R-(+)-pulegone (98%) and S-(−)-pulegone (98%) were obtained from Sigma Aldrich. CDCl₃ (99.8%) and CS₂ (99.9%) were used as solvent, and were obtained from Sigma Aldrich and Riedel-de Haën, respectively. All samples and solvents were used without further purification. The VCD spectra were recorded on a Bruker IFS 66/S FTIR spectrometer, coupled to a PMA37 VCD module. The IR absorbance spectra of pulegone dissolved in CDCl₃ and CS₂ were recorded at a resolution of 4 cm⁻¹; the corresponding VCD spectra were recorded at a resolution of 6 cm⁻¹. Depending on the spectral range to be studied and the solvent used, different experimental parameters were chosen. For the measurements below 1800 cm⁻¹ a demountable KBr cell with a path length of 100 µm was used in combination with a 1850 cm⁻¹ long wave pass filter. The concentration of pulegone for the solutions was set to 0.25 M. The CD stretching region was studied using a demountable CaF₂ cell with a path length of 100 µm and a 3000 cm⁻¹ long wave pass filter. The concentration of pulegone used in these studies was 1.5 M. The collection time for the VCD spectra in the CD stretching region was set to 240 minutes. For all VCD experiments, baseline corrections were introduced by recording the VCD spectra of a racemic mixture, using exactly the same conditions as those used for the samples.

All calculations (geometry optimization, and IR/VCD calculations) are performed using the Amsterdam Density Functional (ADF) program package [10–12]. The vibrational rotational strengths are calculated using the implementation of Stephens’ equations for VCD [13] in the ADF program package [14]. Analytical derivative techniques [15] are employed for the calculation of the atomic polar and axial tensors (APTs and AAT), and harmonic force field, within the framework of density functional theory. For the calculation of AATs, London atomic orbitals [16] based on Slater-type orbitals, and the common origin gauge are used.
The analysis of electric and magnetic transition dipole moments, of the normal modes, and of the angles $\xi$ was done using the ToolsVCD program [8].

The calculated VCD spectra were simulated by representing the peaks as Lorentzian bands [17] with half-width of 4 cm$^{-1}$. The harmonic frequencies obtained from the B3LYP/6-311+G(d,p) calculations were scaled by 0.967 (N-H···Cl stretching). No scaling factor was applied to the frequencies obtained from the OLYP/TZP and BP86/TZP calculations.

3 Methodology

3.1 Normal modes analysis

When comparing modes of a certain molecule in different calculations (e.g. different functional, different basis set) a one-to-one mapping between vibrational modes in the different calculations must be established first. We have done this by calculating overlaps between normal modes.

Using the mass-weighted Cartesian displacement vectors, i.e. the eigenvectors of the mass-weighted Hessian, a normalized $3N$-dimensional vector ($N$ being the number of atoms of the molecule) is constructed for each normal mode:

$$\vec{V}(i) = \vec{V} [v_x^1(i), v_y^1(i), v_z^1(i), ..., v_x^N(i), v_y^N(i), v_z^N(i)]$$  \hspace{1cm} (1)

where $v_k^\lambda(i)$ is the $k^{th}$ Cartesian component of the mass-weighted displacement vector of atom $\lambda$ in the normal mode $i$, and $\vec{V}(i)$ is the $3N$-dimensional vector associated with the mode $i$.

The overlap $\Omega(i, j)$ of two modes $i$ and $j$ obtained from two different calculations can be expressed as the inner product of the vectors $\vec{V}(i)$ and $\vec{U}(j)$ associated with the two
modes:

$$\Omega(i, j) = \vec{V}(i) \cdot \vec{U}(j) = \sum_{\lambda=1}^{N} \sum_{k} v_{\lambda}^{i}(i) u_{\lambda}^{j}(j) \tag{2}$$

The value of the scalar product $\Omega(i, j)$, gives an indication of how well the nuclear displacement vectors of the modes $i$ and $j$ overlap. Two identical modes yield an overlap of 1. Thus, the closer $\Omega$ is to 1, the more similar are the modes $i$ and $j$.

Finally, since the set of normal mode vectors $\{\vec{V}(i)\}$ of a particular calculation are an orthonormal basis (they are the eigenvectors of the mass-weighted Hessian), the normal modes of one calculation can be expressed as linear combinations of the normal modes of another calculation:

$$\vec{V}(i) = \sum_{j} \Omega(i, j) \vec{U}(j) \tag{3}$$

The expansion coefficients, $\Omega(i, j)$, are the normal mode overlaps defined in Eq. (2). They satisfy:

$$\sum_{j} \Omega^{2}(i, j) = 1 \tag{4}$$

Thus, an overlap of 0.90 between two modes means that the two modes differ by 19%, i.e. $1.0 - 0.9^2 = 0.19$, whereas an overlap of 0.70 means that the two modes differ by 51%, i.e. $1.0 - 0.7^2 = 0.51$ (“angle of 45°”).

### 3.2 The concept of robustness in VCD

The VCD intensity of the fundamental transition ($|0\rangle \rightarrow |1\rangle$) of the $i^{th}$ vibrational mode is given by the rotational strength ($R$) [13]:

$$R(i) = \vec{E}_{01}(i) \cdot \text{Im}[\vec{M}_{10}(i)] \tag{5}$$

where $\vec{E}_{01}(i)$ and $\vec{M}_{10}(i)$ are the electric and magnetic transition dipole moments of the fundamental vibrational transition of the $i^{th}$ normal mode. (Note that $\vec{M}_{10}(i)$ is purely imaginary.)
The sign of the \( R(i) \) is determined by the angle \( \xi(i) \) between the vectors \( \vec{E}_{01}(i) \) and \( \text{Im}[\vec{M}_{10}(i)] \):

\[
\cos \xi(i) = \frac{\vec{E}_{01}(i) \cdot \text{Im}[\vec{M}_{10}(i)]}{|\vec{E}_{01}(i)||\text{Im}[\vec{M}_{10}(i)]|} = \frac{R(i)}{|\vec{E}_{01}(i)||\text{Im}[\vec{M}_{10}(i)]|}
\]

where \(|\vec{E}_{01}(i)|\) and \(|\text{Im}[\vec{M}_{10}(i)]|\) are the lengths of the vectors \( \vec{E}_{01}(i) \) and \( \text{Im}[\vec{M}_{10}(i)] \), respectively. Thus, if \( \xi < 90^\circ \) then \( R(i) > 0 \), if \( \xi > 90^\circ \) then \( R(i) < 0 \).

Computational studies of Nicu and Baerends [8, 9] have shown that when the angle \( \xi \) of a normal mode is close to \( 90^\circ \) even a slight perturbation (e.g. the use of slightly different computational parameters) can change it through \( 90^\circ \). This observation led to the introduction of the concept of robustness of the normal modes in a VCD spectrum. Robust modes are characterized by angles \( \xi \) that are far from \( 90^\circ \) (see below for quantification of “far”). The VCD sign of the robust modes is characteristic and can be accurately predicted by calculation as it is not sensitive to small perturbations. The non-robust modes, on the other hand, have angles \( \xi \) that are close to \( 90^\circ \). Their calculated VCD sign should not be trusted as it can be changed by a small change in a computational setting. Also experimental ”perturbations”, e.g. the change from one solvent to another, can change the angle \( \xi \) of a mode, again easily through \( 90^\circ \) if \( \xi \) was close to \( 90^\circ \).

We can thus formulate as criterion for robustness of a normal mode in both experiment and calculation that it should not, in a particular situation (given computational settings, given experimental conditions of solvent, temperature etc.) have a \( \xi \) that deviates more than a given threshold from \( 90^\circ \), i.e. \( \xi < 90^\circ - \tau \) or \( \xi > 90^\circ + \tau \). A sensible value for \( \tau \) has been determined in reference [9] by investigating the changes induced in the angles \( \xi \) upon changing the exchange-correlation functional, i.e. BP86 vs. OLYP, using a test group of 27 molecules. We will summarize the main results of that investigation.

In order to determine a safe value of \( \tau \) we need to obtain an estimate of typical changes \( \Delta \xi \) of the angles \( \xi \) upon changing the functional, e.g. \( \Delta \xi = \xi(\text{BP86}) - \xi(\text{OLYP}) \). For the relevant modes (see below) the differences \( \Delta \xi \) for the modes in a molecule turned out to
have a Gaussian distribution. The $\Delta \xi$ distributions are centered on the $0^\circ$ value, indicating that one functional does not have a systematic bias to larger or smaller $\xi$ for all modes with respect to the other functional. The $\Delta \xi$ distributions have, depending on the molecule, standard deviations between $6^\circ$ and $10^\circ$. The maximum $\Delta \xi$, i.e. $\Delta \xi_{\text{max}}$, was smaller than $30^\circ$ (which represents approximately (more than) three standard deviations) for all 27 molecules considered in reference [9]. Because 99.7% of the members of a distribution fall within the range of three standard deviations, it was concluded in reference [9] that it is a conservative criterium that for a mode to be classified as robust, it should have an angle $\xi$ that differs from $90^\circ$ by at least $30^\circ$ ($\tau$ is $30^\circ$).

A few cautioning remarks need to be made. First, we note that only BP86–OLYP mode pairs with normal mode overlaps of at least 0.90 and significant VCD intensity were considered for the statistics of $\Delta \xi$ (the relevant modes for the analysis mentioned above). Actually, this covers a large fraction of all modes: 90% of the modes exhibit a normal mode overlap of at least 0.90 with the corresponding mode in the calculation with the other functional. The rest of the modes show an overlap with the corresponding mode that is smaller, although usually at least 0.70. As discussed in section 3.1, the two modes then may be very different, e.g. an overlap of 0.7 means the modes differ by 51%. This is a consequence of mode mixing upon change in functional. Very large variation of the $\xi$ angles (thus also of the VCD intensities) can be encountered upon mode mixing, i.e. variations of $60^\circ - 70^\circ$ for $\xi$ are not unusual. Some 10% of the modes exhibit such behavior when going from BP86 to OLYP. When an occasional anomaly is encountered when comparing signs of robust modes with experiment, it may be useful to check on the possibility of mode mixing, or test it computationally. Second, not only modes that mix cannot be used for analysis of the VCD spectrum, also normal modes with small VCD intensities, i.e. small electric and magnetic dipole transition moments (EDTM and MDTM) cannot be used. Large deviations of the angles $\xi$ have been observed for such modes. Although both functionals have predicted small magnitudes for the EDTMs and
MDTs of all these modes, often the relative orientation of these two vectors was very different in the BP86 and OLYP calculation. This suggests that the EDTMs and MDTMs of small magnitude are also very sensitive to small perturbations and therefore cannot be calculated very accurately. We note that an absolute measure, valid for all molecules, to determine what should be considered small in this context cannot be given as the magnitudes of the total EDTM and MDTM of a normal mode depend on the type of mode and on the number of atoms involved in the normal mode motion, i.e. on the molecule. However, unstable sign has been found in Ref. [9] if for a given molecule, the EDTM (or MDTM) is less than 5% of the mean value of the EDTMs (MDTMs) of all the modes of the respective molecule. We take as a conservative threshold a magnitude of 10–20% of the mean value of the EDTM (or MDTM) values of the molecule.

3.3 Applying the concept of robustness

In practice, checking on the robustness of a mode is an additional test that improves the reliability of the VCD predictions. This should be performed in what can be called the “standard procedure” for determining the AC of a molecule from VCD calculation.

1) The standard approach is to perform first a single VCD calculation using computational parameters (basis set, numerical integration accuracy, density functional) that are known to yield both good agreement with experiment and also converged VCD quantities, i.e. nuclear displacement vectors, and atomic axial and polar tensors. Then, using the criteria described above the robustness of the modes in the calculated VCD spectrum should be identified. We advocate to present the robustness of all modes in the plot of the computational VCD spectrum by a dot indicating the value of the angle $\xi$ (90° at the baseline), see Refs. [8,9] and Fig. 4 of this paper.

As the VCD sign of the robust modes can be accurately computed one should expect
to have good agreement between calculation and experiment for the modes identified as 
*robust* (in the calculated VCD spectrum). If this is the case, one can simply ignore the 
discrepancies observed between calculation and experiment for the *non-robust* modes.

This, is a very quick and accurate way of using VCD for determining the absolute con-
figuration of chiral compounds. However, it is important to realize that occasionally one 
can encounter sign differences also for modes identified according to the above criteria as 
*robust*. In case different signs are encountered for one or a few of the *robust* modes, the 
strategy to be followed is to examine whether the cause could be mixing of modes due 
to a perturbation. From the displacement vectors of the calculated mode (e.g., do they 
involve atoms that may participate in hydrogen bonding with the solvent?) and taking 
into account the type of solvent used, one may detect if there is the possibility of mixing of 
modes by solvent effects. In the calculations, one can check on proximity of other modes 
as a cause of mode mixing. Suspicion of mode mixing can then be confirmed by perform-
ing a second calculation where the interaction is explicitly specified (e.g calculation for 
the hydrogen-bonded complex) or a computational perturbation (different functional) is 
applied.

4 Robust modes and non-robust modes in the VCD 
spectrum of pulegone

4.1 Calculated and experimental VCD spectra of pulegone in 
CDCl$_3$

Figure 1 shows a comparison between the experimental VCD spectra measured in CDCl$_3$ 
(continuous line) and CS$_2$ (dotted line) solvents and calculated VCD spectra obtained
from vacuum calculations performed for the pulegone molecule using the BP86, OLYP and B3LYP functionals.

[Figure 1 about here.]

To point out the similarities/differences between the experimental and the various calculated spectra, and to simplify their discussion, we have divided the frequency interval between 1000 and 1800 cm$^{-1}$ into 5 regions labeled from A to E (see Fig. 1).

As can be seen in Fig. 1, there is a fair agreement between calculations and experiment. The calculated spectra reproduce most of the features that stand out in the experimental spectrum. As a result the OLYP, BP86 and B3LYP VCD spectra in Fig. 1 have a similar appearance. However, it should be noted that when compared in detail the calculated spectra are different. Thus, a close examination of the experimental and calculated VCD patterns in the regions A to E reveals the following hierarchies for the three functionals: OLYP ≥ BP86 ≥ B3LYP for region A (none of the calculations is able to reproduce the –/+ patterns in the experimental spectrum); B3LYP ≥ BP86 ≥ OLYP in region B; OLYP ≥ BP86 ≥ B3LYP in region C; OLYP ≥ BP86 ≥ B3LYP in region D; OLYP ≥ BP86 > B3LYP in region E. Clearly, none of the three functionals can be considered as being overall superior.

Regarding the discrepancies between calculation and experiment observed in region A, we note that, as Debie et al. have shown [7], they can be remedied by using continuum solvation models in calculations for simulating the solvent effects, or by performing calculations for the 1:1 pulegone–CDCl$_3$ molecular complex. In reference [7], Debie et al. have found that when using the B3LYP functional, the best agreement between calculation and experiment is obtained when the 1:1 pulegone–CDCl$_3$ molecular complex is embedded in a continuum solvation model.
These conclusions are true also for the calculations performed here with the OLYP and BP86 exchange-correlation functionals. However, there are two reasons we have chosen the vacuum calculations as the reference calculations for the discussion of the normal modes robustness in the next section (hence the comparison between vacuum calculations and experiment in Fig. 1). First, the calculated VCD spectra obtained by embedding the molecular complex into a continuum solvation model reproduce the experimental spectrum only marginally better than the spectra obtained from vacuum calculation for the free pulegone. Second, we are interested to know how significant are the changes induced in the VCD spectra by the use of various computational parameters (e.g. the use of solvation models and/or different functionals).

4.2 Identifying the robust and non-robust modes of pulegone

We illustrate the usefulness of the robust modes concept using the pulegone molecule in CDCl₃. We begin by assigning the robustness of the modes in the VCD spectrum of calculation 1 (the OLYP spectrum in Fig. 1). To do this, the values of the ξ angles of all modes in Fig. 1 have been plotted as dots on top of the calculated VCD spectrum (see Fig. 2). In Fig. 2 the baseline of the calculated VCD spectrum is the 90° line, the Y-coordinate of each dot gives the magnitude of each ξ angle (see the vertical right axis), and the X-coordinate gives the frequency of the mode. For comparison, the experimental spectrum is also shown in Fig. 2.

[Figure 2 about here.]

In the calculated spectrum, there are 38 modes with frequencies between 800 and 1800 cm⁻¹. As can be seen in Fig. 2, only 13 of these 38 modes have angles ξ that differ from 90° by more than 30°. Furthermore, out of these 13 modes, only 9 have significant VCD intensities and therefore can be classified as robust, according to the criteria introduced.
in Section 4. In Fig. 2, the robust modes have been indicated by arrows, and also labeled with numbers. The modes that were not identified as robust, are non-robust modes. For convenience, only the non-robust modes that are numbered will be discussed here.

4.3 Robust modes of pulegone

Having identified the robust and non-robust modes in the VCD spectrum of pulegone obtained from calculation 1, we continue by investigating how the robust modes and (in the next section) the non-robust modes are affected by the use of various computational parameters. To this end we have investigated the differences between calculations performed 1) with different functionals (OLYP [18,19] vs. BP86 [20,21]), 2) with the COSMO solvation models vs. calculations performed for the isolated molecule, 3) with different criteria for geometry optimization, i.e. very tight criterium (10^{-6} Hartree for the energy and 10^{-4} Hartree/Ångstrom for the gradients) vs. the ADF default criterium (10^{-4} Hartree for the energy and 10^{-3} Hartree/Ångstrom for the gradients), and 4) for the free pulegone molecule vs. the 1:1 pulegone—CDCl\textsubscript{3} molecular complex. By combining the computational parameters mentioned above we have performed 16 different calculations for pulegone (labeled from 1 to 16). A list with the computational parameters used in each of the 16 calculations is given in Table 1.

[Figure 3 about here.]

Finally, for the 1:1 pulegone—CDCl\textsubscript{3} molecular complex, we have also investigated how the relative orientation of the pulegone and CDCl\textsubscript{3} molecules influence the VCD spectra. The relative orientation of the solvent molecule towards pulegone was described using the dihedral angles $\tau_1$ and $\tau_2$ (see Fig. 3). A systematic conformational analysis performed using the MMFF force field yielded 9 stable conformations for 1:1 pulegone—CDCl\textsubscript{3} complex (see reference [7] for a detailed description).
The differences between the 16 calculations have been judged with respect to our reference calculation, i.e. the results of the calculations 2 to 16 have been compared against the results of calculation 1. Thus, after establishing a one-to-one correspondence between the modes of all calculations (as described in Section 3), we have monitored the differences between the frequencies, rotational strengths, and $\xi$ angles of the modes obtained from calculation 1 and their homologues obtained from the calculations 2 to 16.

In Fig. 4, the values of the angles $\xi$ predicted by the 16 calculations have been plotted on top of the VCD spectrum of calculation 1. As before, the base line of the VCD spectrum represents the 90° line. The large vertical spreading of the dots in Fig. 4 clearly shows that the angles $\xi$ are very sensitive to the computational parameters used in the calculations. Since the various calculations predict slightly different frequencies for the normal modes, it is not immediately evident from the Fig. 4, without further information like the mode overlaps we discussed earlier, which dots belong to the ”same” mode in the different calculations. Thus, we have encircled the dots associated with one mode; this has been done for the modes that will be discussed in what follows (see Fig. 4).

For the calculations performed with the same functional the differences in the normal modes frequencies caused by the various computational variables used are most of the time smaller than 5 cm$^{-1}$. When comparing different functionals (OLYP and BP86) the differences in frequencies are larger but still small, i.e. smaller than 15 cm$^{-1}$ for modes with frequency below 1300 cm$^{-1}$, and smaller than 25 cm$^{-1}$ for modes with frequency above 1300 cm$^{-1}$. There are some exceptional cases (modes 64 and 65), whose frequencies are much more sensitive (variation up to 61.5 cm$^{-1}$).

[Figure 4 about here.]

The $\xi$ angles associated to robust modes exhibit variations that are always smaller than 30°, i.e. $\Delta \xi < 30^\circ$ (see encircled dots associated with the modes 29, 31, 38, 45, 46,
48, 50 and 56 in Fig. 4). As a result, no changes across 90° have been encountered for these modes (robust modes by definition have ξ angles that differ from 90° by more than 30°). It is therefore clear that all 16 calculations predict the same signs for all robust modes, corroborating the definition of robustness. This is in complete agreement with the conclusions obtained in reference [9], i.e. robust modes have a characteristic sign that is not affected by small perturbations such as the use of slightly different computational parameters.

We should again [9] caution that sometimes modes strongly mix when going from one calculation to another one. A look at the normal mode overlaps reveals that approximately 75% of studied modes, i.e. the modes with frequencies between 800 and 1800 cm\(^{-1}\), are practically identical in all 16 calculations, i.e. the normal mode overlaps are very close to 1 (> 0.95). The rest of the modes (25%) mix when changing computational parameters, i.e. these modes do not have an equivalent in calculation 1 and can be obtained only as linear combinations of the modes of calculation 1. One should realize that the mixing can create modes that can be very different. As discussed in Section 3, two modes that exhibit an overlap of 0.7 differ by 51%. Thus, as shown previously [9], it is not unusual for modes with overlaps of 0.7 to have ξ angles that differ by 60° or more. This can be seen indeed in Fig. 4 when looking at the mode 33 which mixes with mode 32 upon changing computational parameters and exhibits angle variation up to 66.5°.

Finally, we would like to draw attention on the modes 28 and 57 which exhibit very large variation of their angles ξ, i.e. 88.1° and 56.1°, respectively. These modes do not mix upon changing computational parameters. However, they have very small VCD intensities. As discussed in Section 3.2 it is not unusual for modes with weak VCD signals to exhibit large variation in ξ.
4.4 Non-robust modes of pulegone: the case of the C=O stretch vibration

In the case of the non-robust modes, we have two distinct situations: modes that exhibit changes across 90° (e.g. mode 65), and modes that do not (e.g. modes 37, 44, etc.). Since in reference [7] a lot of computational effort was invested in order to reproduce correctly the sign the C=O stretching mode of pulegone, i.e. mode 65 (a non-robust mode), in the following we will investigate this mode in detail.

[Figure 5 about here.]

Figure 5 shows a comparison of the values predicted by the 16 calculations in Table 1 for the angle $\xi$ of the C=O stretching mode of pulegone. In Fig. 5, the Y-coordinate gives the magnitude of the $\xi$ angles, whereas the X-coordinate indicates the calculation (from 1 to 16). The rotational strengths of the 16 calculations are also shown in Fig. 5. As can be seen, all 16 calculations predict values for the angle $\xi$ that are very close to 90°, i.e. $\xi$ differs from 90° by less than 5° for 11 calculations, and by less than 9° for the other 5 calculations. Furthermore, the predicted values for $\xi$ are both larger and smaller than 90°, i.e. in calculations 1, 3, 4, 9, and 11 $\xi > 90^\circ$ (thus, $R < 0$), whereas in the rest of the calculation $\xi < 90^\circ$ (thus, $R > 0$). This clearly shows that even the use of slightly different computational parameters, e.g. different convergence criteria for the geometry optimization, can affect the prediction of the sign for the rotational strength of the C=O stretching mode of pulegone. It should also be mentioned here that all COSMO calculations, i.e. calculations 5, 6, 7, 8, 13, 14, 15 and 16, have predicted the correct sign for the C=O stretching mode. However, in our opinion this is purely fortuitous. Firstly, the use of solvation models in calculation is often unsuccessful [3, 22]. Secondly, as discussed above the changes induced in the $\xi$ angles upon using COSMO in the calculations are too small (compared to the vacuum calculation) to be trusted.
Further, we investigate how the relative orientation of the pulegone and CDCl₃ molecules in the 1:1 pulegone–CDCl₃ molecular complex affects the values of the angles $\xi$ of the C=O stretching mode of pulegone. Figure 6 shows a comparison of the calculated values of the $\xi$ angles for the 9 conformations of the molecular complex (A to I). The computational parameters used to obtain the $\xi$ angles in Fig. 6 are identical to the ones used in calculation 2 (see Table 1 for details). As can be seen, the situation in Fig. 6 is very similar to the one in Fig. 5. That is, the $\xi$ angles have values that are both larger and smaller than $90^\circ$ ($89^\circ < \xi < 94^\circ$).

Thus, based on the comparisons done in Figs. 5 and 6, and keeping in mind the large spread in the values of angle $\xi$ in Fig. 6, it is clear that sign differences between calculated and experimental VCD signals can easily occur for non-robust modes. This clearly shows that sign discrepancies between experiment and calculation should be of no concern, if they are associated to non-robust modes.

5 Transfer of chirality and robustness

In reference [7], Debie et al. have measured a weak but non-zero VCD signal for the C–D stretching mode of CDCl₃. This is a typical case of chirality transfer [1–4]. In this section we investigate whether this mode is robust or non-robust.

We start our analysis of the C–D stretching mode by comparing its frequency, rotational strength and angle $\xi$ in the free CDCl₃ to those in the molecular complex (see Table 2). As can be seen, in the free CDCl₃ (FM) the ETDM and MTDM associated to the C–D stretching mode are perpendicular, i.e. $\xi = 90.00^\circ$, whereas in the molecular complex (MC) the angle $\xi$ is $91.87^\circ$. Since the $\xi$ differs from $90^\circ$ by less than $2^\circ$, it is clear that the
C−D stretching mode (in the molecular complex) would normally be classified as a *non-robust* mode. To substantiate this classification, we investigate how the angle $\xi$ associated to the C−D stretching mode of CDCl$_3$ is affected by 1) the use of various computational parameters, and 2) the relative orientation of the pulegone and CDCl$_3$ molecules. Figure 7 compares the calculated $\xi$ angles of the C−D stretching mode obtained from the 8 calculations (in Table 1) performed for the molecular complex, i.e. calculations 2, 4, 6, 8, 10, 12, 14 and 16. Figure 8 shows a comparison of the calculated $\xi$ angles of the C−D stretching mode for the 9 conformations of the molecular complex (A to I). (Figures 7 and 8 show also the calculated rotational strengths for the C−D stretching mode.)

[Figure 7 about here.]

[Figure 8 about here.]

As can be seen, all calculations predict positive and negative rotational strengths of very small magnitude, and $\xi$ angles that are very close to 90°, i.e. $88^\circ < \xi < 93^\circ$ in Fig. 7, and $88^\circ < \xi < 95^\circ$ in Fig 8. The situation is completely analogous to the one studied in the previous section for the C=O stretching mode of pulegone. This clearly shows that the angle $\xi$ close to 90° for the induced chiral mode behaves precisely as in other cases: it can change through 90° and therefore change sign of the rotational strength by a small perturbation. Induced chirality does not lead to *robust* modes.

It is interesting to point out that upon complexation the magnitudes of both the ETDM and the MTDM of the C−D stretching mode have increased with a factor of approximately 60. This can be seen in Table 3 where the magnitudes and the Cartesian components of both transition moments predicted by calculation 2, i.e. a molecular complex calculation, are compared to those computed for the free CDCl$_3$ using identical computational
parameters. In fact, all 17 calculations performed here for the molecular complex i.e 2, 4, 6, 8, 10, 12, 14 and 16, and A to I, have predicted an enhancement of the magnitudes of the electric and magnetic transition dipole moments.

The enhancement of the electric dipole transition moments results in an significant increase of the IR intensity of the C–D stretching mode. This is observed in both calculation (see Table 3) and experiment (see Fig S5 in the electronic supplementary information of reference [4]).

The VCD intensity of the C–D stretching mode on the other hand, was found to be very weak in experiment and also in most of the calculations (see Figs. 7 and 8). This apparent contradiction can be explained easily. Firstly, all calculations have predicted ξ angles that are very close to 90°, i.e. 88° < ξ < 95° (see Figs. 7 and 8). Thus, the large magnitudes of the two dipole transition moments are counteracted by the very small values take by cos ξ. Secondly, as shown in Fig. 8, the C–D stretching mode has different VCD signs in different conformations of the 1:1 CDCl₃–pulegone complex. Thus, in experiment one can expect that the VCD signal will be even more reduced due to cancelation between various conformations.

We can conclude that there is good qualitative agreement between calculation and experiment for the frequency of the C-D stretching mode and for the enhancement of the EDTM (visible in the IR experiment). However, it should be clear that the VCD sign of the C–D stretching mode studied here can not be computed accurately. Non only is this mode non-robust and therefore its sign can not be computed accurately, also the Boltzmann weights of the various conformations can not be computed accurately. That is because the relative energies of the various conformations of the 1:1 pulegone–CDCl₃ complex are within 1 kcal/mol which is below the accuracy of DFT.

[Figure 9 about here.]
The enhancement of the ETDMs and MTDMs (thus of the IR and VCD intensities) of the stretching modes is a very general phenomenon that is often encountered in complexation phenomena involving intra- and inter-molecular hydrogen bonding interactions. It is a consequence of the electronic charge that flows into the stretched bond affecting both the magnitude of the electronic components of the ETDM and MTDM and also the frequency of the mode. A detailed theoretical description of the mechanism responsible for the enhancement on the IR and VCD intensities can be found in references [8, 23]; experimentally the phenomenon is well documented in references [24, 25]. In the case of the 1:1 pulegone–CDCl₃ molecular complex, the enhancement of the magnitude of the ETDM and MTDM of the C–D stretching mode is caused by the donor-acceptor interaction between the σ* molecular orbital (MO) localized on the C–D bond as the acceptor, and the occupied MO 42 of pulegone as the donor (see Fig. 9). We note that this phenomenon is very often encountered for O–H and N–H bonds and that it is somewhat remarkable that it occurs also for the C–D stretching mode since the σ* MO of the C–D bond is much higher in energy (thus less likely to mix with occupied MOs) than the σ* MOs of the O–H and N–H bonds. The fact that the frequency of the C–D mode shifts with less than 1 cm⁻¹ in the MC compared to the FM supports this last affirmation. (Upon complexation, calculations predict shifts up to a few hundred cm⁻¹ for the frequencies of the O–H and N–Hs stretching modes [8, 23].) It is probable that the abundance of CDCl₃, since it is the solvent, leads in this case to an observable effect. The CDCl₃ do not have to compete with any other complexing agent, indeed the pulegone molecules cannot avoid association with CDCl₃ molecules.

6 Conclusions

In this paper we have investigated the robustness of the C-D stretch mode of an achiral molecule (CDCl₃) that exhibits induced chirality upon complexation to the chiral pulegone
molecule. This case of chirality transfer was recently studied by Debie et al. [7]. In the first part of this work we have defined the robustness concept and illustrated on the example of the pulegone molecule its usefulness for the interpretation of the differences between calculated and experimental VCD spectra. To highlight the difference between robust and non-robust modes we have performed 25 different calculations for pulegone, i.e. the 16 calculations in Table 1 (performed for the free pulegone and for the 1:1 pulegone–CDCl₃ molecular complex using 8 different computational parameters), plus the 9 calculations for the different conformers (labeled A to I) of the molecular complex. The predictions of these 25 calculations have been monitored with respect to the experimental VCD spectrum of pulegone measured in CDCl₃. The results of this detailed analysis have clearly confirmed the general usefulness of the concept of robustness:

Firstly, the analysis of the robust modes of pulegone (with frequencies between 800 and 1700 cm⁻¹) has shown that indeed the sign of these modes is not affected by the use of different computational parameters (e.g. functional, solvation model, different convergence criteria for the geometry optimization). We note that the signs of all signals associated to robust modes in the calculated VCD spectra of pulegone are in agreement with the experiment.

Secondly, the analysis of the C=O stretching mode of pulegone (a non-robust modes) has clearly shown that the VCD sign of a non-robust mode can be affected even by the use of slightly different computational parameters. That is, changes of ξ across 90° can be observed even for normal modes (obtained from calculations performed with slightly different computational parameters) that have overlaps of 0.9 or higher. It is therefore clear that sign discrepancies between experiment and calculations for modes with ξ angles that are close to 90°—which are non-robust by definition—bear little relevance as the VCD sign of these modes can not be computed accurately (see Figs. 5 and 6).

As already mentioned, Debie et al. have invested a lot of computational effort to reproduce correctly the signs of these VCD signals. However, although agreement in sign between
theory and experiment was eventually obtained, the fact remains that the C=O stretching mode is a non-robust mode and the agreement may be (entirely) fortuitous. As shown here, from the moment a single, sufficiently good quality calculation reveals an angle too close to 90°, the reliability of the predicted sign of the VCD band is heavily jeopardized.

In the second part of this work, the C–D stretching mode of the CDCl₃ molecule in the 1:1 pulegone–CDCl₃ molecular complex (a typical case of chirality transfer) has been investigated. The complexation changes the angle between ETDM and MTDM of this mode, which in the free achiral molecule is 90°. Since the complexation perturbation is weak, the angle will not differ much from 90°. This does not rule out that in the transfer of chirality phenomenon the deviation would consistently be in the same direction, and therefore the sign of the VCD signal still be robust. Our study study revealed, however, that this particular case of an angle ξ close to 90° is no exception to the rule: the mode is non-robust. As shown in Fig. 8, the VCD sign of this mode is conformation dependent. Moreover, the use of slightly different computational parameters yields different signs for the rotational strength of a given conformation (see Fig. 7). In view of previous experience we would also expect that if the molecular complex would be in a different solvent (not the neat CDCl₃ of the actual experiment) the sign of the VCD signal could also change. It is therefore clear that in cases like the one studied here, i.e. a molecular complex formed via a hydrogen bond between a chiral solute molecule and an achiral solvent molecule, one can not use the agreement between the calculated and experimental VCD signals of the modes of the achiral moiety to extract information about the molecular interaction, e.g. the relative orientation of the two molecules involved in the molecular complex. This limits the usefulness of the induced chirality phenomenon for the interpretation of the intermolecular interactions that give rise to it. In future works, whenever induced chirality is observed experimentally, first the robustness of the associated modes should be checked carefully. If such a mode is not robust, which will usually be the case if the transfer of chirality is by a relatively weak intermolecular interaction, we feel that no
conclusion on, e.g., the structure of the solvent solute complex can be drawn from an agreement in sign between theory and experiment.

Acknowledgement

This work has been supported (EJB) by Korea Science and Engineering Foundation (World Classs Univ. program: R32-2008-000-10180-0).
[Table 1 about here.]
[Table 2 about here.]
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Table 3: Comparison of the Cartesian components of the total electric and magnetic transition dipole moments (ETDM and MTDM) of the C–D stretching mode in the free CDCl$_3$ (FM) and in the pulegone–CDCl$_3$ molecular complex (MC).