

# The connection between robustness angles and dissymmetry factors in vibrational circular dichroism spectra

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## 1. Introduction

In 2009 Nicu and Baerends [1] introduced a very simple and useful concept for analyzing the individual bands in vibrational circular dichroism (VCD) spectra [2]. They defined robust normal modes using the angle  $\theta$  formed by the electric and magnetic dipole transition moment vectors, the dot product of which determines the rotational strength of the vibrational transition associated with the normal mode under consideration. Gobi and Magyarfalvi [3] pointed out that  $\theta$  is not origin independent, owing to the origin dependent nature of the magnetic dipole transition moments. Fruitful discussions [4] arose from this consideration and resulted in a limited adoption of this concept. In a different direction, the origin independent dissymmetry factors were suggested for identifying and analyzing the robust regions of VCD spectra [5,6].

Nicu's robustness concept using the angle  $\theta$  has a remarkable virtue of simplicity [1,4]. However the origin dependence of this

angle has not been fully understood. An illuminating example of the behavior of  $\theta$  for a normal mode of methyloxirane was presented in Fig. 2 of Gobi and Magyarfalvi [3]. A connection between the robustness angles and origin independent dissymmetry factors will be useful to bring these two different concepts into a unifying scheme for analyzing the VCD spectra [3–5]. In this article we develop the formulation for origin dependence of robustness angles and their connection to the dissymmetry factors.

## 2. Theoretical Formulation

The robustness angle  $\theta$  for the normal mode associated with a fundamental vibrational transition 0–1 is given by the relation:

$$\cos \theta = \frac{\text{Im}(\tilde{\mu}_{01} \cdot \tilde{m}_{10})}{\sqrt{(\tilde{\mu}_{01} \cdot \tilde{\mu}_{01})(\tilde{m}_{10} \cdot \tilde{m}_{10})}} = \frac{\tilde{\mu}_{01} \cdot \text{Im}(\tilde{m}_{10})}{\sqrt{(\tilde{\mu}_{01} \cdot \tilde{\mu}_{01})(\tilde{m}_{10} \cdot \tilde{m}_{10})}} \quad (1)$$

Herein we indicate  $\tilde{\mu}_{01} = \langle 0 | \hat{\mu} | 1 \rangle$  and  $\tilde{m}_{10} = \langle 1 | \hat{m} | 0 \rangle$  (tilde indicates complex conjugate and caret indicates operator). Of course the definition of the operators is  $\hat{\mu} = \sum_j q_j \hat{r}_j$  and  $\hat{m} = \frac{1}{2c} \sum_j \frac{q_j}{m_j} \hat{r}_j \times \hat{p}_j$  ( $m_j$  is the particle mass). Upon shifting the origin from  $\vec{O}$  to  $\vec{O}'$ , such that  $\vec{O}' = \vec{O} - \vec{T}$  where vector  $\vec{T}$  points from  $\vec{O}'$  to  $\vec{O}$ , the positional vector  $\vec{r}_j$  changes from  $\vec{r}_j$  to  $\vec{r}'_j = \vec{r}_j + \vec{T}$ , for a neutral molecule the electric dipole transition moments is origin independent while

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the magnetic dipole transition moment vector varies as follows [7,8]:

$$\Delta \vec{m}_{10} = \vec{m}'_{10} - \vec{m}_{10} = i \frac{\Omega}{2c} \vec{T} \times \vec{\mu}_{01} = i\pi \bar{v} \vec{T} \times \vec{\mu}_{01} \quad (2)$$

In Eq. (2)  $\Omega$  is in rad/s, and  $\bar{v}$  in  $\text{cm}^{-1}$ . The modulus of  $\vec{T}$  is in cm and all other quantities are in electrostatic units, both types of dipole moments being in esu cm. To arrive at Eq. (2) one uses the fundamental quantum mechanical identity (valid for exact wavefunctions) [8]:  $\frac{\hat{p}_i}{m_j} = -\frac{i}{\hbar} [\hat{r}_j, \hat{H}]$  and applies it to calculate the transition moments  $\vec{m}_{10} = \langle 1 | \hat{m} | 0 \rangle$  in the new coordinate system. Since  $\vec{m}_{10}$  is purely imaginary, from here on we set  $\vec{m}_{10} = i\vec{M}_{10}$ , with  $\vec{M}_{10}$  real. Eqs. (1) and (2) have been discussed in the literature and they are included here mostly for setting the notation we are working with.

Applying such a generic translation, the robustness angle  $\theta$  changes to  $\theta'$ . Then the ratio  $(\cos \theta / \cos \theta')$  can be shown (consider Appendix 1) to be:

$$\left( \frac{\cos \theta}{\cos \theta'} \right)^2 = 1 + \left( \frac{\Omega}{2c} \right)^2 \frac{(\vec{T} \times \vec{\mu}_{01}) \cdot (\vec{T} \times \vec{\mu}_{01})}{M_{10}^2} + \left( \frac{\Omega}{c} \right)^2 \frac{\vec{M}_{10} \cdot \vec{T} \times \vec{\mu}_{01}}{M_{10}^2} \quad (3)$$

As noted by Gobi and Magyarfalvi and depicted in Fig. 1 of their paper [4], one can move the origin of coordinate system by a translation vector  $\vec{T}^*$  such that the electric and magnetic dipole transition vectors be either parallel ( $\theta = 0^\circ$ ) or anti-parallel ( $\theta = 180^\circ$ ). Such translations are not unique, given that any additional component 'along'  $\vec{\mu}_{10}$  does not produce further changes in the angle  $\theta$ ; furthermore different  $\vec{T}^*$  are found for different vibrations. To formally rephrase the above, we may state that the  $\vec{T}^*$  vector we are looking for is such that the generated  $\Delta \vec{M}_{10} = \pi \bar{v} \vec{T} \times \vec{\mu}_{10}$  cancels the component of  $\vec{M}_{10}$  perpendicular to  $\vec{\mu}_{10}$ . Noting that the projection of any vector  $\vec{b}$  on to  $\vec{a}$  is given as  $\frac{\vec{b} \cdot \vec{a}}{a^2} \vec{a}$ , this perpendicular component can be expressed as the difference between  $\vec{M}_{10}$  and the projection of  $\vec{M}_{10}$  along  $\vec{\mu}_{01}$ , i.e.:

$$\Delta \vec{M}_{10} = - \left[ \vec{M}_{10} - \left( \frac{\vec{\mu}_{01} \cdot \vec{M}_{10}}{\mu_{01}^2} \right) \left( \frac{\vec{\mu}_{01}}{\mu_{01}} \right) \right] \quad (4)$$

$\vec{T}^*$  can be decomposed along three mutually orthogonal axes: one parallel to  $\vec{\mu}_{01}$ , one parallel to the cross product of  $\vec{\mu}_{01}$  and  $\vec{M}_{10}$ , and a third one, along which it can be shown that  $\vec{T}^*$  has no projection (see Appendix 2 for the proof of this statement and the next equation), i.e.:

$$\vec{T}^* = -k_1(\vec{\mu}_{01} \times \vec{M}_{10}) + k_2 \vec{\mu}_{01} \quad (5)$$

By substituting Eq. (5) into Eq. (2) and assuming that  $\Delta \vec{M}_{10}$  has the form of Eq. (4), through the identity  $\vec{A} \times (\vec{B} \times \vec{C}) = \vec{B}(\vec{A} \cdot \vec{C}) - \vec{C}(\vec{A} \cdot \vec{B})$ , we find:

$$\vec{T}^* = -\frac{2c}{\Omega} \frac{\vec{\mu}_{01} \times \vec{M}_{10}}{\mu_{01}^2} + k_2 \vec{\mu}_{01} = -\frac{\vec{\mu}_{01} \times \vec{M}_{10}}{\pi \bar{v} \mu_{01}^2} + k_2 \vec{\mu}_{01} \quad (6)$$

where  $k_2$  is arbitrary. The magnetic dipole transition moment vector  $\vec{M}_{10}^*$  in the new origin, resulting from the translation  $\vec{T}^*$ , is obtained by Eqs. (2) and (6), which leads to the following result:

$$\begin{aligned} \vec{M}_{10}^* &= \vec{M}_{10} + \left( \frac{1}{\mu_{01}} \right)^2 (\vec{M}_{10} \times \vec{\mu}_{01}) \times \vec{\mu}_{01} \\ &= \frac{\vec{\mu}_{01}}{\mu_{01}^2} (\vec{M}_{10} \cdot \vec{\mu}_{01}) = \vec{\mu}_{01} \left( \frac{g}{4} \right) \end{aligned} \quad (7)$$

The penultimate term may be obtained by applying once more the identity for the triple cross product, while in the last term we made use of the definition of dissymmetry factor  $g = 4R/D = (\Delta \epsilon / \epsilon)$ ,  $R$  and  $D$  being respectively the rotational and dipole strength.

The translation  $\vec{T}^*$  defined by Eq. (6), differing for each normal mode, defines the *robust point* i.e.  $(\cos \theta)^2 = 1$  and  $\vec{M}_{10}^*$  either parallel or antiparallel to  $\vec{\mu}_{01}$  (i.e.  $\cos \theta$  equals +1 or -1 respectively). However, what truly matters to distinguish the behavior of different normal modes, is the rapidity by which the robustness angle changes in the neighborhood of respective *robust points*. In fact, a further translation  $\vec{t}$  from the *robust point* gives a  $\cos \theta'$  value such that in the LHS of Eq. (3) the numerator is 1, the linear term in  $\bar{v}$  drops off ( $\vec{M}_{10}^*$  is parallel to  $\vec{\mu}_{01}$ ), and thus one obtains:

$$\left( \frac{1}{\cos \theta'} \right)^2 = 1 + \pi^2 \bar{v}^2 \frac{(\vec{t} \times \vec{\mu}_{01})^2}{M_{10}^{*2}} \quad (8)$$

By orienting the z-axis parallel to  $\vec{\mu}_{01}$  and expressing  $\vec{t}$  as  $(t_x, t_y, t_z)$ , we have:

$$\cos \theta' = \pm \frac{1}{\sqrt{1 + \kappa^2 (t_x^2 + t_y^2)}} = \pm \frac{1}{\sqrt{1 + \tau_x^2 + \tau_y^2}} \quad (9)$$

where the parameter  $\kappa$  is defined by the equation:

$$\kappa^2 = \left( \frac{\Omega}{2c} \frac{\mu_{01}}{M_{10}^*} \right)^2 = \left( \pi \bar{v} \frac{\mu_{01}}{M_{10}^*} \right)^2 = \left( \frac{4\pi \bar{v}}{g} \right)^2 \quad (10)$$

which clearly shows that  $\kappa$  is translationally invariant. In Eq. (9), since the sign of  $\cos \theta'$  must be equal to the sign of  $\cos \theta$  due to the invariance of the rotational strength, the  $\pm$  sign is the rotational strength sign.

In Figure 1a we plot  $\theta'$  as function of the two variables  $(\tau_x, \tau_y)$ ; in

Figure 1b we plot  $\theta'$  as function of one variable  $\tau$  (where  $\tau^2 = \tau_x^2 + \tau_y^2$ ). The cusp behavior envisioned in the example of Fig. 2 of Gobi and Magyarfalvi [3] is proved here on mathematical grounds. The tangent of the cusp at  $t = 0$  is provided by evaluating the first derivative  $(d\theta'/dt)_0$  which exactly gives  $\pm|\kappa|$  (see Eq. (9)). Being  $\pm$  the sign of the rotational strength we can attribute to  $\kappa$  the sign of the rotational strength itself, that is:

$$\kappa = \frac{\Omega}{2c} \frac{\mu_{01}}{M_{10}^*} = \pi \bar{v} \frac{\mu_{01}}{M_{10}^*} = \frac{4\pi \bar{v}}{g}$$

Not only the parameter  $\kappa$  does acquire importance *per se*, but it also provides a firm foundation to employ the  $g$  factor to judge the VCD and VA (Vibrational Absorption) spectra [5,6].

To further appreciate the physical meaning of the parameter  $\kappa$ , we report in Table 1 the values for the calculated frequencies, for the  $\kappa$  parameter (as derived by the values of  $\vec{M}_{10}^*$  and  $\mu_{01}$  in the next two columns) and for the rotational strengths of all fundamental vibrational transitions in (R)-methyloxirane. The values of  $\kappa$  range from ca.  $7^\circ/\text{\AA}$  to ca.  $5500^\circ/\text{\AA}$  (these values are calculated on the basis of Gaussian 09 program [9]). In Figure 2 we plot  $\theta'$  as function of the modulus  $t$  of the translation vector from the robust point, centering functions at their respective  $\vec{T}^*$ , for the three selected modes #6, 20 and 23 (the last normal mode was discussed by Gobi and Magyarfalvi [3]), which are characterized by three quite different  $\kappa$  values ( $7.7$ ,  $5529.7$  and  $396.3^\circ/\text{\AA}$ , respectively). The three cusps are quite different and the most acute one is the one with largest  $\kappa$  (smallest  $g$ ); the most obtuse is the one with smallest  $\kappa$  (largest  $g$ ). For the latter, one can state that Nicu's angle is least affected by translations. This supports considering either the  $\kappa$ -value (small) or the  $g$ -value (large) to trust a VCD band. In Table 1 we report also the values for  $\vec{T}^*$  (in  $\text{\AA}$ ) for  $k_2 = 0$ , starting from the origin defined in the standard orientation of GAUSSIAN 09 [9] (see Appendix 3).

**Table 1**

Nicu's angle derivatives  $\kappa$  ( $^\circ/\text{\AA}$ : these units relate to  $\text{cm}^{-1}$  by the constant  $(180/\pi) \times 10^8$ ), absolute values for magnetic ( $10^{-24}$  esu cm) and electric ( $10^{-20}$  esu cm) transition dipole moments evaluated at robust points and VCD intensities ( $10^{-44}$  esu<sup>2</sup> cm<sup>2</sup>) for all the 24 normal modes of (R)-methyloxirane (B3LYP/aug-cc-pVTZ). Last three columns: components (in Å) defined in the standard orientation as calculated by GAUSSIAN 09 [9].

Mode #	$\bar{\nu}$	$\kappa$	$ M_{10}^* $	$ \mu_{01} $	R	$T_x^*$	$T_y^*$	$T_z^*$
1	211	7.6	1.31	2.62	3.43	-3.293	23.293	0.838
2	367	-22.1	1.93	6.44	-12.43	0.000	1.281	3.683
3	410	-66.6	0.73	6.58	-4.81	-0.329	2.220	2.602
4	770	42.4	2.04	6.24	12.72	-1.171	1.478	0.617
5	842	903.3	0.24	14.55	3.55	-0.700	-0.163	-0.656
6	908	7.7	7.36	3.49	25.69	-2.900	-1.637	1.314
7	972	-31.9	4.35	7.92	-34.47	-1.816	0.673	0.564
8	1043	96.0	1.11	5.68	6.32	3.243	0.155	0.920
9	1129	-68.5	1.45	4.89	-7.10	2.443	-0.130	-0.059
10	1157	33.6	1.73	2.80	4.85	3.193	3.518	-1.030
11	1167	-18.2	3.83	3.33	-12.74	2.057	1.825	-0.364
12	1189	93.9	0.41	1.79	0.73	1.664	-1.001	2.982
13	1293	-47.2	2.22	4.51	-10.01	-2.019	-0.423	-0.679
14	1408	96.5	0.76	2.89	2.19	1.209	0.200	0.261
15	1439	106.0	1.87	7.64	14.27	-0.061	-0.252	0.771
16	1484	217.8	0.47	3.81	1.78	0.500	-0.066	-0.422
17	1498	-327.5	0.33	4.04	-1.34	-0.587	-0.387	0.000
18	1529	74.9	1.44	3.92	5.65	-0.455	-1.064	0.628
19	3028	979.0	0.27	4.85	1.31	-0.006	0.259	0.176
20	3080	5529.7	0.06	5.92	0.35	-0.565	0.310	-0.128
21	3085	-794.0	0.34	4.93	-1.70	2.516	-0.267	0.473
22	3089	-86.4	2.16	3.35	-7.24	-0.031	-0.895	0.599
23	3110	396.3	0.97	6.89	6.71	1.490	-0.169	0.481
24	3163	-357.2	0.93	5.85	-5.46	-1.086	-1.840	0.400

Please notice that  $|\bar{T}^*|$  is large for small wavenumber normal modes and this is consistent with Eq. (6). As of Eq. (6) and from Table 1, smaller translations  $\bar{T}^*$  are associated also to large dipole moment (IR intense) normal modes.

Robustness concept has been introduced recently for Raman Optical Activity (ROA) [10] and the origin dependence issue present for ROA robustness angles will be addressed in the near future.

### 3. Discussion

The concept of robustness was introduced by Nicu et al. [1] inspired by their finding that the signs of certain calculated VCD bands changed upon minor variations in computational parameters. They noted that these changes occurred when the angle  $\theta$  between electric and magnetic dipole transition moment vectors is close to  $90^\circ$ . As a consequence they suggested that vibrational normal modes for which  $\theta$  is close to  $90^\circ$  are considered as non-robust and those with  $\theta$  farther away from  $90^\circ$  as robust normal modes.

The robustness of normal modes can depend on several criteria. To avoid confusion in the terminology, we rephrase the original terminology as follows: when  $\theta$  is close to  $90^\circ$ , this angle will be referred to as the *non-robust angle* and when  $\theta$  is farther away from  $90^\circ$  it will be referred to as the *robust angle*. The vibrational normal modes with robust angles may be referred to as *normal modes with robust angles*, and those with non-robust angles as *normal modes with non-robust angles*. However, since the angle  $\theta$  is origin dependent [3,4], the use of  $\theta$  obtained from a chosen origin of coordinate system (for example, center of mass or center of charge) cannot reflect its robustness.

In this article we have shown that  $\theta$  associated with a given vibrational normal mode can always be made robust by an appropriate translation of the coordinate system to the robust point of that normal mode. Although this artificially rendered robustness for angle  $\theta$  cannot by itself be of practical value, we have shown that for vibrational normal modes with larger dissymmetry factor ( $g$ ),  $\theta$  changes slowly from its robust point and *vice versa*. This connection between the rate of change of angle  $\theta$  and origin

independent  $g$  values provides a better approach for characterizing the robustness in terms of  $g$  values.

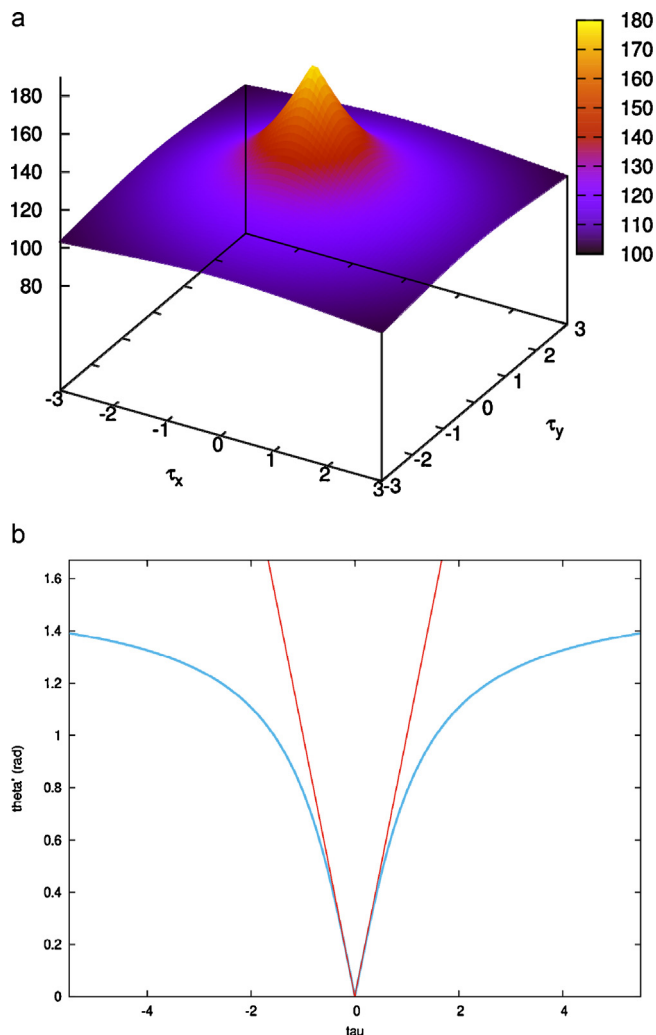
The signal to noise (S/N) associated with a VCD band in the experimental VCD measurements is determined by its  $g$  value. VCD bands with larger  $g$  values have higher S/N and those with smaller  $g$  values have lower S/N. The reliability of VCD bands with  $g$  values less than  $\sim 10^{-5}$  is low with the current state of the instrumentation. For this reason, the experimental VCD bands with larger  $g$  values, somewhat arbitrarily set at  $\geq 5 \times 10^{-5}$  and may be changed as the sensitivity of instrumentation improves, may be referred to as *robust VCD bands* and these  $g$  values can be referred to as *robust  $g$  values*. The vibrational normal modes associated with robust experimental VCD bands can be termed as *normal modes with robust  $g$  values*.

The robust criterion suggested for quantum chemical computations by Gobi and Magyarfalvi [3] is  $\chi = R_i/D_i = 10^{-5}$ . Since the dissymmetry factor is defined as  $4R_i/D_i$ , the criterion chosen earlier from experimental considerations for robust  $g$  values (*i.e.*  $\sim 5 \times 10^{-5}$ ) is in close accordance with that chosen from computational considerations by Gobi and Magyarfalvi [3].

There are various other factors, besides  $\theta$  and  $g$ , that should also be considered in analyzing the quantum chemical computations for robustness.

In obtaining the predicted spectra, Boltzmann populations are used when multiple conformers are present for a molecule for obtaining the conformer average. These computed Boltzmann populations depend on the type of energy used for that purpose and can be subject to large uncertainties. Thus even though a normal mode for a given conformer may have robust  $g$  value, in the presence of multiple conformers, the Boltzmann weighting may lead to uncertainties in the weighted sum. If the Boltzmann population of a conformer is unstable, then that conformer can be associated with non-robust conformer population. The vibrational normal modes of conformers with non-robust populations may be referred to as *normal modes with non-robust conformer populations*.

A different, but related, scenario is that some conformers may individually have flat potential energy surface (PES) with respect to a specific distance or angle in the molecule (or between solute and

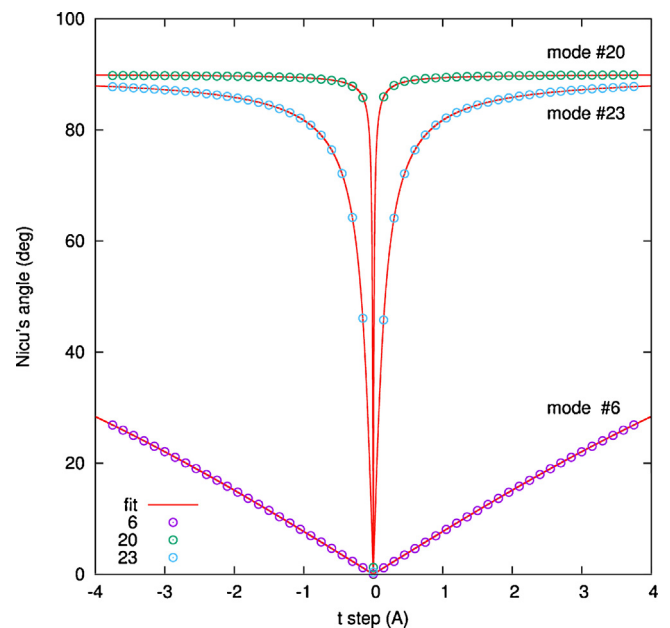


**Figure 1.** (a) Plot of the function  $\theta' = \cos^{-1} \left( -\frac{1}{\sqrt{1 + \tau_x^2 + \tau_y^2}} \right)$ ; (b) Plot of the function  $\theta' = \cos^{-1} \left( \frac{1}{\sqrt{1 + \tau^2}} \right)$ . The straight lines are tangent to the function at  $\tau = 0$  and have the expression  $\theta' = \pm \tau$ .

solvent molecules). The presence of a flat PES can cause variations in the predicted VCD signs for certain normal modes, depending on the chosen location of flat PES [11–13]. Conformers with flat potential energy surface may be referred to as *non-robust PES conformers*, and the corresponding vibrational normal modes as *normal modes of non-robust PES conformers*.

From the different scenarios discussed above, the difficulty in identifying, or defining, a *robust normal mode* is evident. However, it is possible to identify the *normal modes with robust parameters/characteristics* as described in the previous paragraphs.

In this context, it is necessary to introduce a different concept of *robust spectral regions* [5,6]. In comparing the experimental spectra with corresponding quantum chemically predicted spectra, it was proposed [5,6] that, besides comparing the unpolarized vibrational absorption and VCD spectra, the comparison of *dissymmetry factor spectra* can be advantageous. For such comparisons, the calculated dipole and rotational strengths, which respectively represent integrated absorption and VCD intensities, are to be converted to absorption and VCD spectra assuming certain band shapes and widths for each vibrational transition. In these spectral simulations, the contributions from different vibrational transitions overlap and a distributed sum of the contribution of all transitions



**Figure 2.** Dependence of Nicu's angle upon translation of modes #6, 20, 23 of (*R*)-methyl oxirane molecule (B3LYP/aug-cc-pVTZ calculations). The reference geometry (step 0) is obtained from the standard orientation considered by Gaussian [7] by rigidly displacing all coordinates by the vector  $\vec{T}^*$  given by Eq. (2) with  $k_2 = 0$ . By normalizing the vector  $\vec{u} = \vec{\mu}_{01} \times \vec{M}_{10}$  to unit length ( $\vec{u}$  is evaluated at the standard orientation, with no translation applied) each data point is obtained by considering a rigid translation of the reference (step 0) geometry by  $\vec{t}_n = (n\Delta)\vec{u}$ , with  $\Delta = 0.15$  Å. Mode # 23 was discussed by Gobi and Magyarfalvi [3]. The fitting function is given by  $\theta' = \cos^{-1} \left( \pm \frac{1}{\sqrt{1 + (\kappa t)^2}} \right)$  (see text). Mode #6 can be deemed robust, since Nicu's angle is less sensitive to translation, i.e. it has a low  $\kappa$ . The fitted  $\kappa$  values are as follows:  $\kappa_6 = 7.7^\circ/\text{Å}$ ,  $\kappa_{20} = 5319.1^\circ/\text{Å}$ ,  $\kappa_{23} = 394.7^\circ/\text{Å}$ . These compare favorably with the corresponding values given in Table 1, which have been computed analytically by means of Eqs. (7) and (10) using the transition dipole moments  $\vec{\mu}_{01}$  and  $\vec{M}_{10}$  available in Gaussian standard orientation [9].

is included in the resulting spectrum. As a consequence, it may not be possible to identify a robust band associated with one particular vibrational normal mode in the simulated spectra (unless the energy of one particular transition is located farther away from the rest). Instead, the robust dissymmetry factor spectral regions can be identified and compared with corresponding experimental robust dissymmetry factor spectral regions. This approach does not look for individual normal modes (or their associated bands), so the aforementioned concept of individual normal modes with robust parameters is not evaluated in this approach.

#### 4. Summary

It is demonstrated that each VCD band can be made robust by a suitable translation  $\vec{T}^*$  of the origin of coordinate system to a *robust point*, where  $\theta = 0^\circ$  or  $180^\circ$ . However, each normal mode differs in the rapidity at which the robustness angle changes in the neighborhood of the robust point. The robustness angle changes slowly for VCD bands with larger dissymmetry factors and rapidly for VCD bands with smaller dissymmetry factors. This connection between robustness angle and dissymmetry factor clarifies the roles of robustness angles and dissymmetry factors in analyzing the VCD spectra. It is hoped that the above discussion will clarify the concept and use of robustness in interpreting and analyzing the VCD spectra.

## Appendix 1.

*Dependence of Nicu's angle upon a rigid translation of the molecule*

Upon a translation  $\vec{T}$  of the molecule, the magnetic dipole transition moment of a given vibrational transition changes from  $\vec{m}_{10}$  to  $\vec{m}'_{10} = \vec{m}_{10} + \Delta\vec{m}_{10}$  according to:

$$\Delta\vec{m}_{10} = i \left( \frac{\Omega}{2c} \right) \vec{T} \times \vec{\mu}_{01} \quad (\text{A1-1})$$

The imaginary part being (according to the notation introduced in the text):

$$\Delta\vec{M}_{10} = \left( \frac{\Omega}{2c} \right) \vec{T} \times \vec{\mu}_{01} \quad (\text{A1-1}')$$

where  $\hbar\Omega$  is the vibrational energy quantum. For numerical evaluation purposes it is handy to drop the imaginary unit in Eq. (A1-1) above and adopt  $\vec{M}_{10}$  instead of  $\vec{m}_{10}$ . From Eq. (A1-1), it is evident that  $\vec{\mu}_{01} \cdot \Delta\vec{M}_{10} = \left( \frac{\Omega}{2c} \right) \vec{\mu}_{01} \cdot \vec{T} \times \vec{\mu}_{01} = 0$  so that the invariance of rotational strength is satisfied. Starting from the definition of Nicu's angle:

$$\cos \theta = \frac{\text{Im}(\vec{\mu}_{01} \cdot \vec{m}_{10})}{\sqrt{(\vec{\mu}_{01} \cdot \vec{\mu}_{01})(\vec{m}_{10} \cdot \vec{m}_{10})}} = \frac{\vec{\mu}_{01} \cdot \vec{M}_{10}}{\mu_{01} \cdot M_{10}} \quad (\text{A1-2})$$

and considering Eq. (A1-1), it is straightforward to evaluate the cosine of the robustness angle  $\theta'$  obtained by the translation  $\vec{T}$  of the molecule and relate it to the cosine of the robustness angle in the un-translated geometry ( $\theta$ ). Right after definition of  $\cos\theta$  as the cosine of the angle between  $\vec{\mu}_{01}$  and  $\vec{m}'_{10}$ , it is:

$$\begin{aligned} \cos \theta' &= \frac{\text{Im}(\vec{\mu}_{01} \cdot (\vec{m}_{10} + \Delta\vec{m}_{10}))}{\sqrt{(\vec{\mu}_{01} \cdot \vec{\mu}_{01})(\vec{m}_{10} + \Delta\vec{m}_{10}) \cdot (\vec{m}_{10} + \Delta\vec{m}_{10})}} \\ &= \frac{\vec{\mu}_{01} \cdot (\vec{M}_{10} + \Delta\vec{M}_{10})}{\mu_{01} \sqrt{(\vec{M}_{10} + \Delta\vec{M}_{10}) \cdot (\vec{M}_{10} + \Delta\vec{M}_{10})}} \end{aligned} \quad (\text{A1-3})$$

Keeping in mind that  $\vec{\mu}_{01} \cdot \Delta\vec{M}_{10} = 0$ , one obtains for the ratio  $\cos\theta/\cos\theta'$  the following:

$$\begin{aligned} \left( \frac{\cos \theta}{\cos \theta'} \right)^2 &= \frac{m_{10}^2 + (\Delta m_{10})^2 + \vec{m}_{10} \cdot \Delta\vec{m}_{10} + \Delta\vec{m}_{10} \cdot \vec{m}_{10}}{m_{10}^2} \\ &= 1 + \left( \frac{\Omega}{2c} \right)^2 \frac{(\vec{T} \times \vec{\mu}_{01}) \cdot (\vec{T} \times \vec{\mu}_{01})}{M_{10}^2} \\ &\quad + \left( \frac{\Omega}{c} \right) \frac{\vec{M}_{10} \cdot \vec{T} \times \vec{\mu}_{01}}{M_{10}^2} \end{aligned} \quad (\text{A1-4})$$

This equation corresponds to Eq. (3) in the text, if one changes the angular frequency  $\Omega$  to the corresponding wavenumber  $\bar{\nu}$ , i.e.  $\Omega = 2\pi c\bar{\nu}$ .

## Appendix 2.

*The Robust Point  $\vec{T}^*$*

Since the angle between  $\vec{\mu}_{01}$  and  $\vec{M}_{10}$  is origin dependent, as shown by Eq. (4) in the text, it is possible to select a suitable translation  $\vec{T}^*$  such that the two dipole vectors are either parallel or anti-parallel. This could be done by solving  $(\vec{M}_{10} + \Delta\vec{M}_{10}) \times \vec{\mu}_{01} = 0$  with respect to  $\vec{T}$ . Alternatively, we can simply consider that  $\vec{T}^*$

must be such that  $\Delta\vec{M}_{10}$  of Eq. (A1-1') is opposite to the component of  $\vec{M}_{10}$  perpendicular to  $\vec{\mu}_{01}$ , so that effectively  $\vec{M}_{10} + \Delta\vec{M}_{10}$  becomes parallel to  $\vec{\mu}_{01}$ . This corresponds to the following formula, which is Eq. (4) in the text:

$$\Delta\vec{M}_{10} = - \left[ \vec{M}_{10} - \left( \frac{\vec{\mu}_{01} \cdot \vec{M}_{10}}{\mu_{01}} \right) \left( \frac{\vec{\mu}_{01}}{\mu_{01}} \right) \right] \quad (\text{A2-1})$$

This condition univocally determines the component of  $\vec{T}^*$  perpendicular to  $\vec{\mu}_{01}$  and  $\vec{M}_{10}$ . Consider the vectors  $\vec{\mu}_{01}$  and  $\vec{\mu}_{01} \times \vec{M}_{10}$ , and a third vector  $\vec{V}_3$  in order to have three mutually orthogonal directions. For suitable values of  $k_1$ ,  $k_2$ , and  $k_3$  one may write:

$$\vec{T}^* = -k_1(\vec{\mu}_{01} \times \vec{M}_{10}) + k_2\vec{\mu}_{01} + k_3\vec{V}_3 \quad (\text{A2-2})$$

Plugging this expression of  $\vec{T}^*$  into ( $\kappa_2$  arbitrary constant) Eq. (2) of text, and using Eq. (A2-1) one obtains:

$$\begin{aligned} \Delta\vec{M}_{10} &= \left( \frac{\Omega}{2c} \right) \vec{T}^* \times \vec{\mu}_{01} \\ &= - \left( \frac{\Omega}{2c} \right) k_1(\vec{\mu}_{01} \times \vec{M}_{10}) \times \vec{\mu}_{01} + \left( \frac{\Omega}{2c} \right) k_3\vec{V}_3 \times \vec{\mu}_{01} \\ &= - \left[ \vec{M}_{10} - \left( \frac{\vec{\mu}_{01} \cdot \vec{M}_{10}}{\mu_{01}} \right) \left( \frac{\vec{\mu}_{01}}{\mu_{01}} \right) \right] \end{aligned} \quad (\text{A2-3})$$

That is, by making use of the fundamental algebraic identity  $\vec{A} \times (\vec{B} \times \vec{C}) = \vec{B}(\vec{A} \cdot \vec{C}) - \vec{C}(\vec{A} \cdot \vec{B})$ :

$$\begin{aligned} & - \frac{\Omega}{2c} k_1 [\mu_{01}^2 \vec{M}_{10} - (\vec{\mu}_{01} \cdot \vec{M}_{10}) \vec{\mu}_{01}] + \frac{\Omega}{2c} k_3 \vec{V}_3 \times \vec{\mu}_{01} \\ &= -\vec{M}_{10} + \left( \frac{\vec{\mu}_{01} \cdot \vec{M}_{10}}{\mu_{01}} \right) \left( \frac{\vec{\mu}_{01}}{\mu_{01}} \right) \end{aligned} \quad (\text{A2-4})$$

which implies  $k_1 = \frac{2c}{\Omega\mu_{01}^2}$  and  $k_3 = 0$ . Thus all translations  $\vec{T}^*$  that satisfy the equation:

$$\vec{T}^* = - \frac{2c}{\Omega} \frac{\vec{\mu}_{01} \times \vec{M}_{10}}{\mu_{01}^2} + k_2\vec{\mu}_{01} = - \frac{\vec{\mu}_{01} \times \vec{M}_{10}}{\pi\bar{\nu}\mu_{01}^2} + k_2\vec{\mu}_{01} \quad (\text{A2-5})$$

give a magnetic dipole transition moment  $\vec{M}_{10}^*$  which is parallel to the (origin invariant) vector  $\vec{\mu}_{01}$ . The expression of  $\vec{T}^*$  just derived corresponds to Eq. (6) in the text. From the expression of  $\vec{T}^*$  above and the expression of the change of magnetic dipole moment upon translation, Eq. (A2-1), one straightforwardly obtains the expression of the magnetic dipole moment  $\vec{M}_{10}^*$  at the robust points. This is explicitly given by:

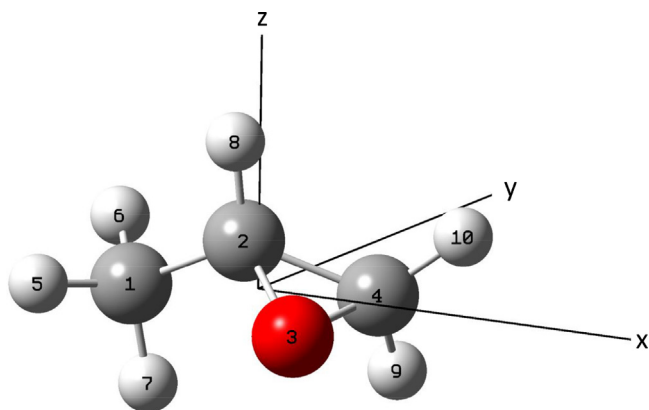
$$\vec{M}_{10}^* = \vec{M}_{10} + \left( \frac{1}{\mu_{01}} \right)^2 (\vec{M}_{10} \times \vec{\mu}_{01}) \times \vec{\mu}_{01} \quad (\text{A2-6})$$

This result corresponds to Eq. (7) of the text.

## Appendix 3.

Cartesian Coordinates of (R)-methyloxirane ( $\text{\AA}$ ) in the standard orientation by GAUSSIAN 09 [9].

	x	y	z
C	-1.508213	0.097098	-0.148875
C	-0.153023	-0.032920	0.485004
O	0.828903	-0.789455	-0.237695
C	1.040067	0.616508	-0.061676
H	-2.073810	-0.829438	-0.038684
H	-2.077014	0.897181	0.329118
H	-1.418825	0.319932	-1.211789
H	-0.153559	-0.246126	1.551103
H	0.953911	1.209723	-0.966484
H	1.865086	0.880260	0.591583



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