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

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ABSTRACT

To analyze vibrational circular dichroism (VCD) spectra the angle between the electric and magnetic dipole transition moments was introduced as robustness index. We demonstrate that VCD for each normal mode can be made *robust* by a suitable translation of the coordinate system origin to a *robust point*. Normal modes differ in how VCD band robustness varies under translations from these respective *robust points*. It is shown that variation in robustness of a VCD band depends on a parameter inversely proportional to the dissymmetry factor *g*. Thus, robustness varies slowly for VCD bands with large dissymmetry factors and *vice versa*.

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 θ 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 θ 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 θ 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 θ 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 θ for the normal mode associated with a fundamental vibrational transition 0–1 is given by the relation:

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

Herein we indicate $\vec{\mu}_{01} = \langle 0|\,\hat{\vec{\mu}}\,|1\rangle$ and $\vec{m}_{10} = \langle 1|\,\hat{\vec{m}}\,|0\rangle$ (tilde indicates complex conjugate and caret indicates operator). Of course the definition of the operators is $\hat{\vec{\mu}} = \sum_j q_j\hat{\vec{r}}_j$ and $\hat{\vec{m}} = \frac{1}{2c}\sum_j \frac{q_j}{m_j}\hat{\vec{r}}_j \times \hat{\vec{p}}_j$ (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]:

$$\Delta\vec{m}_{10} = \vec{m'}_{10} - \vec{m}_{10} = i\frac{\Omega}{2c}\vec{T}\times\vec{\mu}_{01} = i\pi\tilde{\nu}\vec{T}\times\vec{\mu}_{01} \tag{2}$$

In Eq. (2) Ω is in rad/s, and $\tilde{\nu}$ in 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]: $\frac{\hat{p}_j}{m_j} = -\frac{i}{\hbar}\left[\hat{r}_j, \hat{H}\right]$ and applies it to calculate the transition moments $\vec{m}_{10} = \left\langle 1\middle|\hat{\vec{m}}\middle|0\right\rangle$ 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 θ changes to θ'. Then the ratio $(\cos\theta/\cos\theta')$ can be shown (consider Appendix 1) to be:

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

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 θ; 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 $\Delta\vec{M}_{10} = \pi\tilde{\nu}\vec{T}\times\vec{\mu}_{10}$ 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.*:

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

$\vec{T}^*$ 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 T^* has no projection (see Appendix 2 for the proof of this statement and the next equation), *i.e.*:

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

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

$$\vec{T}^* = -\frac{2c}{\Omega}\frac{\vec{\mu}_{01}\times\vec{M}_{10}}{\mu_{01}^2} + k_2\vec{\mu}_{01} = -\frac{\vec{\mu}_{01}\times\vec{M}_{10}}{\pi\tilde{\nu}\mu_{01}^2} + k_2\vec{\mu}_{01} \tag{6}$$

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:

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

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 $g = {}^{4R}\!/\!_{D} = \left(\Delta\varepsilon/\varepsilon\right)$, 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 $\tilde{\nu}$ drops off ($\vec{M}_{10}^*$ is parallel to $\vec{\mu}_{01}$), and thus one obtains:

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

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

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

where the parameter κ is defined by the equation:

$$\kappa^2 = \left(\frac{\Omega}{2c}\frac{\mu_{01}}{M_{10}^*}\right)^2 = \left(\pi\tilde{\nu}\frac{\mu_{01}}{M_{10}^*}\right)^2 = \left(\frac{4\pi\tilde{\nu}}{g}\right)^2 \tag{10}$$

which clearly shows that κ 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 θ' as function of the two variables (τ_x, τ_y); in Figure 1b we plot θ' as function of one variable τ (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 κ the sign of the rotational strength itself, that is:

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

Not only the parameter κ 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 κ, we report in Table 1 the values for the calculated frequencies, for the κ parameter (as derived by the values of $\vec{M}_{10}^*$ and μ_{01} in the next two columns) and for the rotational strengths of all fundamental vibrational transitions in (*R*)-methyloxirane. The values of κ range from *ca.* 7 °/Å to *ca.* 5500°/Å (these values are calculated on the basis of Gaussian 09 program [9]. In Figure 2 we plot θ' 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 κ values (7.7, 5529.7 and 396.3 °/Å, respectively). The three cusps are quite different and the most acute one is the one with largest κ (smallest g); the most obtuse is the one with smallest κ (largest g). For the latter, one can state that Nicu's angle is least affected by translations. This supports considering either the κ-value (small) or the g-value (large) to trust a VCD band. In Table 1 we report also the values for $\vec{T}^*$ (in Å) for $k_2 = 0$, starting from the origin defined in the standard orientation of Gaussian 09 [9] (see Appendix 3).