

Theory of Molecular Vibrational Zeeman Effects as Measured with Circular Dichroism

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We present a general theory that enables the first nonempirical computation of molecular vibrational Zeeman effects as are detectable with magnetic vibrational circular dichroism spectroscopy (MVCD). In this method, the second derivatives of the molecular magnetic moment appear to be essential to determine the observable MVCD intensities. Using a quasiharmonic approximation, computations based on our method allowed a band-to-band comparison of simulated to measured spectra. Given this new possibility of its reliable interpretation, MVCD spectroscopy may develop as a useful tool to yield detailed information on molecular vibrational states and structure, including achiral systems.

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Introduction.—Circular dichroism (CD) (differential absorption of left- and right-circularly polarized light) is an established method to study properties of chiral molecules. For any molecule placed in a static magnetic field, the Faraday effect also gives rise to measurable CD resulting from Zeeman perturbations. However, although magnetic circular dichroism (MCD) of molecular electronic transitions is relatively widely used for achiral molecules [1], its theory established [2,3], and intensity simulations implemented in major quantum-chemical programs [4–10], measurement and interpretation of magnetic vibrational circular dichroism (MVCD) is rarer. First observed in 1981 [11], the phenomenon was described at a qualitative level, but the spectral shapes were never directly linked to the structure. We find filling this gap important for new uses of this technique, e.g., in detecting isotopic species indistinguishable by electronic methods [12], but also for general exploration of molecular properties and their interaction with light, such as in optoelectrical components. As a longer-range motivation, the vibrational Zeeman effect, similarly as for the rotational one, may help to identify organic molecules in interstellar magnetic fields [13].

It should be noted that we here investigate only pure vibrational molecular states, relevant for studies of solutions and other condensed phase samples. The present study does not concern rotationally resolved MVCD of gas phase molecules [14–18], where the intensities are largely determined by the Zeeman splitting of rotational molecular levels [19,20]. Similarly, systems with low-lying excited electronic states are not included, since these might require a formalism beyond the Born-Oppenheimer approximation [21].

Although the measurement of rotational Zeeman splitting via MVCD and vibrationally induced MVCD can be performed with the same instruments [22], molecular vibrational states can develop measurable MVCD independent of

rotations. While all molecules, in principle, exhibit MVCD spectra, high-symmetry molecules tend to provide the largest intensities (differential absorbances), with many examples having been reported for closed-shell organic molecules, including haloforms [23,24], 1,3,5-tri-substituted benzenes [25,26], porphyrins [27], and C₆₀ fullerene [28].

Previous theoretical models were able to explain the experimental observations on an empirical, qualitative level [26,29]. Spectral band shapes were characterized as MVCD “A terms” and “B terms,” dominated by first-order Zeeman splitting and off-diagonal magnetic-field-induced mixing, respectively. Typically, an A-term band resembles a couplet (derivative shape, positive and negative intensity of the same magnitude), while B terms are single signed, with the same shape as the absorption [3,30]. An alternative vibronic model was proposed by Nafie to explain B-term MVCD and applied to cases where low-lying excited magnetic states could interact with ground state vibrations [31]. Our method is not designed for those unique, open-shell situations. In the present study, we investigate the full coupling of all vibrational states as perturbed by the magnetic field and take advantage of the efficient implementation of algorithms for obtaining magnetic dipole derivatives using the density functional theory (DFT) [32], thereby enabling the first MVCD simulations devoid of any empirical parameters, even for relatively large molecules.

Theory: Molecular vibrational states in a static magnetic field.—As in all MVCD experiments available so far, we consider a magnetic field **B** oriented along the direction of light propagation (*z* axis; see Fig. 1). Then the absorption probability for right (*R*)- and left (*L*)-circularly polarized light (RCPL and LCPL, or + and -, respectively) and a vibrational transition $n \rightarrow j$ is [3,33]

$$A_{nj,R/L} = \kappa |\mu_{nj,\pm}|^2, \quad (1)$$

$$m_{\alpha}(Q, P) = m_{0\alpha} + \sum_I M_{\alpha I} P_I + \sum_{I, J} M_{\alpha IJ} P_I Q_J, \quad (7)$$

where \mathbf{m}_0 is the equilibrium magnetic dipole moment (zero for diamagnetic molecules), $M_{\alpha I} = (\partial m_{\alpha} / \partial P_I)|_0$ is the atomic axial tensor (AAT, transformed to the normal modes), P_I is the momentum conjugated to the normal mode coordinate Q_I , and $M_{\alpha IJ} = (\partial M_{\alpha I} / \partial Q_J)|_0$. Note also that $(\partial m_{\alpha} / \partial Q_I) = 0$ in the Born-Oppenheimer approximation [43,44].

Within the harmonic approximation, the general molecular vibrational wave functions in (4b) are replaced by harmonic oscillator eigenfunctions. These provide strong selection rules enabling the simplification of simulations and a better understanding of the origins of Zeeman and MVCD phenomena. As argued in Supplemental Material [34], the AAT derivatives, which are conventionally the “anharmonic” part of Eq. (7), appear essential and dominant for MVCD simulations within the otherwise harmonic approach. Introducing normal mode angular frequencies ω_J , $E_{JK}/\hbar = \omega_J - \omega_K$ and utilizing harmonic oscillator matrix elements for P_J and Q_J for a $0 \rightarrow 1$ fundamental transition of mode J , we get (see theoretical remarks in Supplemental Material [34] for a fuller development)

$$\mathcal{B}_{0 \rightarrow 1_J} \cong \frac{\hbar}{4} \sum_{\alpha, \beta, \gamma} \varepsilon_{\alpha\beta\gamma} \sum_{K \neq J} \frac{\Pi_{\alpha, \gamma} \Pi_{\beta, K} (M_{\gamma K, J} / \omega_J - M_{\gamma J, K} / \omega_K)}{\omega_J - \omega_K}. \quad (8)$$

The validity of this approach was also tested by the replication of experimental results for the examples described below. Going beyond the harmonic limit, e.g., using a limited vibrational configuration interaction formalism [42,46,47], is straightforward; however, the general anharmonic problem goes beyond the scope of this work. Given the experimental dominance of the MVCD for fundamental transitions, we may expect that anharmonic effects including rovibrational interaction and Coriolis coupling will play a minor role for MVCD, just as they do for natural VCD.

Formula (8) also shows that MVCD is primarily found for the fundamental transitions, similarly as for infrared absorption and Raman, which has been observed experimentally in many studies [23,24]. Second, it singles out the dominant contribution of AAT derivatives for MVCD; i.e., two modes (K and J) need to be coupled to produce the effect. Intuitively, the modes provide both the nuclear and electronic charge shift (dipole moment change) and its rotation needed for vibrational magnetic moment (cf. Scheme S1 in Supplemental Material [34]). Finally, it is clear that vibrational states close in energy ($\omega_J \sim \omega_K$) have the largest contribution, and consequently A terms, for which $\omega_J = \omega_K$, will dominate the spectra.

Molecular geometries, vibrational frequencies, and intensity tensors were calculated at the DFT level as summarized in Table S1 [34].

Results and discussion.—What does MVCD say about molecules? A simple example of its use is presented in Fig. 2 for a comparison of sym-triazine and 1,3,5-trichlorobenzene spectra. For these molecules, the 1600 and 1440 cm^{-1} bands in each molecule arise from similar normal modes and yield similar IR spectra (except for weaker anharmonic transitions evident at ~ 1400 – 1360 cm^{-1} for 1,3,5-trichlorobenzene). The stronger band at 1600 cm^{-1} is more due to C = C or C-N stretching, and the weaker 1440 cm^{-1} band has a larger C-H bending contribution (see Fig. S2, Supplemental Material [34]). The MVCD signal discriminates between the two molecules, in that triazine has two couplets of the same sign (“−+” from higher to lower frequency), but the lower-frequency couplet is reversed (“+−”) for 1,3,5-trichlorobenzene. The involved modes are rather similar for the two molecules, but the 1440 cm^{-1} band for triazine has much less C or N motion (Fig. S2), which causes different signs of the AAT derivatives and the MVCD sign inversion. The calculation thus determines the observed sign pattern variation between the two molecules correctly and reproduces the overall MVCD intensity. Calculated wave

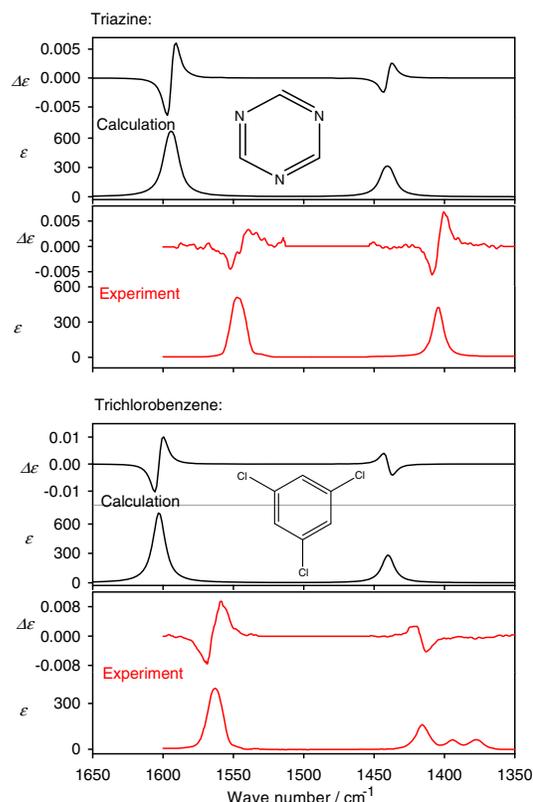


FIG. 2. Sym-triazine and 1,3,5-trichlorobenzene, MVCD and absorption, comparing calculated (above, black) and experimental (below, red) spectra. The experimental data are reproduced from Ref. [25].

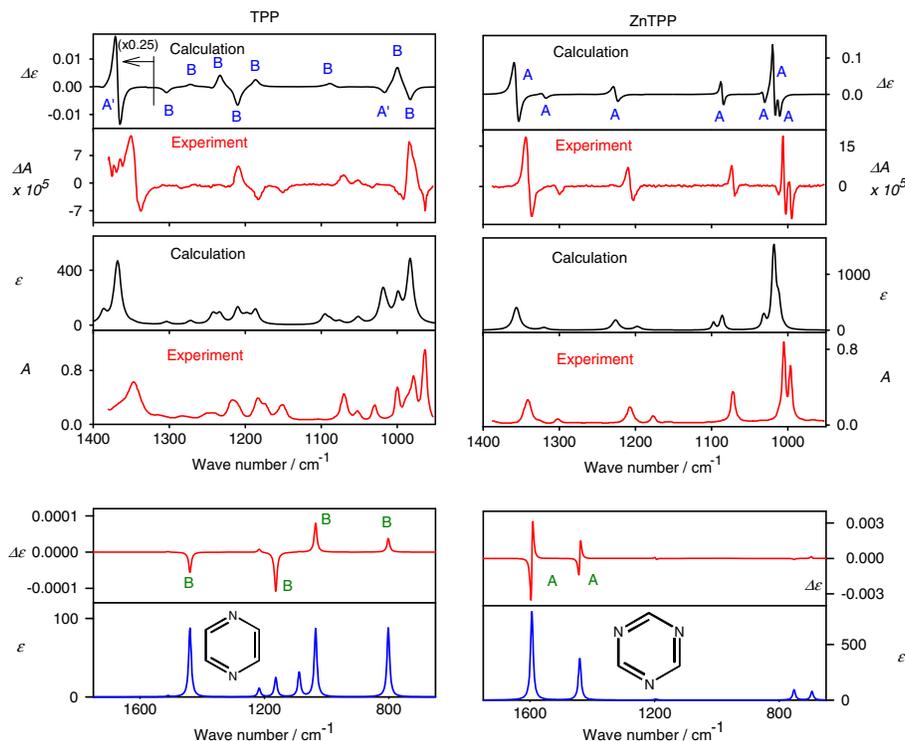


FIG. 3. Systems of different symmetry: (Top) Calculated and experimental MVCD and absorption spectra of tetraphenylporphine (TPP, D_{2h}) and ZnTPP (D_{4h}); the experimental data are reproduced from Ref. [27]. (Bottom) Pyrazine (D_{2h}) and triazine (D_{3h}). Large A and B terms are indicated. Although conventional A terms appear only for molecules having degeneracy (ZnTPP and triazine), in TPP near degeneracy can lead to pseudo-A terms, marked by A' (designated for multiple transitions separated by less than 2 cm^{-1}).

numbers are $\sim 20\text{--}40\text{ cm}^{-1}$ higher than observed experimentally, which is usual for the combination of DFT computations and the harmonic approximation. The relative intensities of the 1570 and 1420 cm^{-1} bands in trichlorobenzene are in good agreement between calculation and experiment, but the corresponding triazine relative intensities are less so, most probably because of a DFT error.

For an example of symmetry effects, a comparison of tetraphenylporphine and its zinc derivative (Fig. 3, top; selected TPP and ZnTPP modes are shown in Supplemental Material [34], Figs. S3 and S4) shows that the theory confirms the experimental observations [27,28] that high molecular symmetry and degenerate molecular states are favorable but not necessary conditions for observing MVCD. The lower (D_{2h} for the porphyrin core) symmetry of TPP and higher (D_{4h}) one of ZnTPP both provide easily measurable MVCD, with the ZnTPP giving sharp experimental MVCD features composed of several coupletlike A terms. TPP has a weaker MVCD spectrum less dominated by well-defined couplets, and B terms prevail, although for near degenerate states pseudo-A terms result in couplet shapes that obscure the differences.

The situation is clearer for the stronger symmetry difference between triazine (D_{3h}) and pyrazine (D_{2h}) (Fig. 3, bottom). The pyrazine MVCD band intensities

are more than 10 times smaller than for triazine, and only B terms are computed. Further examples simulating the effects of lower symmetry on MVCD for substituted triazines (Fig. S5) and MVCD of a larger, very high symmetry molecule, such as C_{60} (I_h , Fig. S6) are provided in Supplemental Material [34].

The simulated absorption and MVCD intensities seem to correspond well to the experimental molar absorptivity (ϵ , $\Delta\epsilon$; cf. Fig. 2). Also, if we compare g factors (ratios of $\Delta A/A$, Table S2 [34]), we can see a very good correlation of calculated and experimental parameters at the usual level achieved for other chiroptical molecular properties [48–50]. By comparing the simulated spectra of porphine and TPP (Figs. S7 and S8 [34]), we can also see in more detail how MVCD reflects structural differences in similar molecules. For example, the large “ \pm ” $1075/1073\text{ cm}^{-1}$ porphine signal is much weaker in TPP, although nearly the same vibrational modes are involved.

At present, the MVCD technique interpreted through *ab initio* computations appears generally applicable to all molecules that can be studied by other vibrational techniques. The necessity to calculate the AAT derivatives makes the computational cost somewhat higher than for natural VCD, but this obstacle is not prohibitive and can be overcome, for example, by the tensor transfer techniques

[51]. Explorations of nonfundamental transitions may be problematic because of the need to solve the general vibrational problem. A big challenge for the future, as for all chiroptical methods, is to make the technique more sensitive.

Conclusions.—We have derived expressions that are usable for routine computations of the MVCD spectra of diamagnetic molecules in a solution and helped us to better understand the vibrational Zeeman effect. The principal spectral features could be simulated using the density functional theory, harmonic force field, first derivatives of the electric dipole moments (atomic polar tensor), and the “anharmonic” derivatives of the atomic axial tensors. For the selected molecular examples, the theoretical MVCD spectral shapes are in good agreement with the experimental ones. The results show that the MVCD technique can be used to discriminate and assign individual vibrational transitions, often not resolved in absorption spectra, and thus can be useful in molecular structural studies. Contrary to previous expectations, our new results show that, while molecules with high symmetry and degenerate vibrational states often have more intense spectra, this is not a necessary condition for detecting MVCD, which is, in principle, a property of any system.

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