



# On the inversion of geometric parameters from absorption and circular dichroism spectroscopy of molecular dimers

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## ABSTRACT

Absorption spectra of molecular dimers usually exhibit complex line-shapes. In an approximate treatment the excited dimer states are described as a two-level system, leading to two bands separated by twice the electronic coupling element which is responsible for the splitting. The band intensities are related to the relative orientation of the monomer transition dipole-moments. We show, considering absorption and circular dichroism spectra, that extracting geometric parameters using the two-level description can lead to substantial errors when internal monomer vibrations become relevant. The application of sum-rules offers a more accurate approach to invert the data.

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## 1. Introduction

Dimers have been studied as model systems for molecular aggregates ever since the early work of Förster, Kasha, and others [1–3]. The simplest model which aims at the interpretation of dimer UV–Vis spectra rests on the assumption of two degenerate excited states (corresponding to the excitation of one or the other monomer) which are coupled by a matrix element  $J$  containing the interaction between the charge distributions on both monomers [4], i.e. depends on the geometrical arrangement of the monomers. Within this simple two state picture, the splitting of the excited states is equal to twice the value of the coupling element  $J$ . In many cases, dimer absorption spectra exhibit two bands originating from the electronic transitions into these two (one-exciton) states [5–8]. It seems therefore reasonable to estimate the value of the coupling element from the positions of the two band maxima. This goes in hand with the determination of another geometric parameter which is the relative orientation of the monomer transition dipole-moments. The orientation angle  $\gamma$  is then estimated from the relative band intensities. Likewise, one may regard circular dichroism spectra [9] which, in the dimer case, consist of two branches of different sign. This allows a clear identification of transitions into one or the other excited state and the coupling strength can be estimated.

The above considerations, however, neglect line-broadening effects: internal monomer and also monomer–monomer vibrational degrees of freedom lead to an enhanced density of states. Because usually vibrational progressions are not resolved, this is accompanied by a line broadening in the spectra. Of course, even in the ab-

sence of internal nuclear degrees of freedom, electronic transition lines are broadened by the interactions with a bath being a liquid or solid state environment. The purpose of this work is to investigate the influence of line broadening and thus overlapping spectral bands on the inversion of molecular parameters. We will see that line broadening leading to overlapping absorption bands plays a crucial role in arriving at accurate values for the coupling strength  $J$  and also the angle  $\gamma$ , as will be discussed in detail below.

The Letter is organized as follows: in Section 2 we summarize the equations essential for the calculation of dimer absorption and CD-spectra and describe the model Hamiltonians. Also, the simplified two-level description is reviewed. The numerical results are given in Section 3 and a short summary is given in Section 4.

## 2. Theory

### 2.1. Absorption and CD-spectra

The time-dependent formulation of spectroscopy is employed below, where the absorption [10–13] and CD [14–16] spectra are given as (atomic units are employed in what follows)

$$\sigma_s(E_{ph}) \sim \int dt e^{i(E_i+E_{ph})t} c_s(t). \quad (1)$$

Here  $E_{ph}$  is the energy of the incoming photon and  $E_i$  is the energy of the initial state  $|\psi_i\rangle$ , which in our case is the vibrational ground state in the electronic ground state. The time-correlation functions  $c_s(t)$  for dipole transitions differ in the case of absorption ( $s = \text{abs}$ ) and circular dichroism ( $s = \text{cd}$ )

$$c_{\text{abs}}(t) = \langle \vec{\epsilon} \cdot \vec{\mu} \psi_i | U_e(t) \epsilon \cdot \vec{\mu} \psi_i \rangle, \quad (2)$$

$$c_{\text{cd}}(t) = \frac{1}{2i} \{ \langle \vec{\mu} \psi_i | U_e(t) \vec{m} \psi_i \rangle - \langle \vec{m} \psi_i | U_e(t) \vec{\mu} \psi_i \rangle \}. \quad (3)$$

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In the latter equations the polarization vector of the electric field is denoted by  $\vec{\epsilon}$ , and  $U_e(t)$  is the propagator in the excited state  $|e\rangle$  with Hamiltonian  $H_e$ . The electric and magnetic dipole operators are  $\vec{\mu}$  and  $\vec{m}$ , respectively. The magnetic dipole operator of monomer  $n$  is taken as [17]

$$\vec{m}_n = -i \frac{\omega_{eg}}{2c} (\vec{a}_n \times \vec{\mu}_n), \quad (4)$$

where the appearing constant contains the ratio of the mean transition frequency  $\omega_{eg}$  and the velocity of light  $c$ . The two monomer units are separated by a fixed distance  $R$ , and the coordinate system is such that  $\vec{a}_1 = -\vec{R}/2$  and  $\vec{a}_2 = \vec{R}/2$ .

In our numerical calculations presented in Section 3, we multiply the correlation functions by a Gaussian window function  $w(t) = e^{-\beta t^2}$ . This introduces an additional line-broadening [18] which phenomenologically takes the interaction with a bath into account, for more sophisticated treatments see, e.g. Ref. [4]. The energy resolution is obtained as  $\Delta_\epsilon = 8 \ln(2)/\Delta_t$ , which relates the width (full width at half maximum) of a Gaussian in energy ( $\Delta_\epsilon$ ) and time ( $\Delta_t$ ) domain. It should be emphasised that the choice of a Gaussian damping function mimics a Gaussian lineshape which is encountered in the case of an inhomogeneous broadening, for a discussion see, e.g. the book of Mukamel [19]. On the other hand, an exponentially decaying window function leads to a Lorentzian lineshape. The conclusions drawn below are, however, independent of the particular lineshapes for a state-to-state-transition.

## 2.2. Two-level description

We start with a summary of the two-level description for the excited states of a molecular dimer where vibrational degrees of freedom and (static) disorder are not included. Regarding an electronic monomer transition  $M^* \leftarrow M$ , there exist two degenerate (one-exciton) dimer excited states  $M_1^* - M_2$  and  $M_1 - M_2^*$  of energy  $E$  which refer to the localized excitation of monomer (1) and (2), respectively. These configurations are coupled by the Coulomb interaction between charges localized at the two monomers which leads to a coupling matrix element  $J$ . Accordingly, the excited state Hamiltonian is

$$\mathbf{H}_e = \begin{pmatrix} E & J \\ J & E \end{pmatrix}. \quad (5)$$

This Hamiltonian can be diagonalized with the unitary matrix

$$\mathbf{A} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}, \quad (6)$$

leading to eigenvalues of  $E_\pm = E \pm J$ . In what follows, a coordinate system is chosen, such that the monomer electric transition dipole-moments  $\vec{\mu}_n$  are assumed to lie in the  $(x, y)$  plane where the  $y$ -axis bisects the relative angle  $\gamma$  between the two moments. We assume that they are perpendicular to the monomer separation vector  $\vec{R}$ . Note, that this assumption does not alter any of the results presented below. In particular, all conclusions regarding absorption spectra (especially the sum-rules results) remain unaltered. For a non-perpendicular dipole configuration, the absolute magnitude of the magnetic dipole-moments change so that the CD-spectra are identical in shape but of different intensity.

In the case of absorption and upon diagonalization, the correlation function takes the form

$$c_{\text{abs}}(t) = 2 \left\langle \begin{pmatrix} \mu\psi_i \\ 0 \end{pmatrix} | \mathbf{U}_e(t) | \begin{pmatrix} \mu\psi_i \\ \cos(\gamma)\mu\psi_i \end{pmatrix} \right\rangle \\ = \langle \mu\psi_i | \mu\psi_i \rangle \{ e^{-iE_+t} [1 + \cos(\gamma)] + e^{-iE_-t} [1 - \cos(\gamma)] \}, \quad (7)$$

with  $\mu = |\vec{\mu}_1| = |\vec{\mu}_2|$ . Regarding the case of circular dichroism one obtains

$$c_{\text{cd}}(t) = \frac{\omega_{eg}}{2c} R \sin(\gamma) \left\langle \begin{pmatrix} 0 \\ \mu\psi_i \end{pmatrix} | \mathbf{U}_e(t) | \begin{pmatrix} \mu\psi_i \\ 0 \end{pmatrix} \right\rangle \\ = \frac{\omega_{eg}}{4c} R \sin(\gamma) \langle \mu\psi_i | \mu\psi_i \rangle \{ e^{-iE_+t} - e^{-iE_-t} \}. \quad (8)$$

Expressions for the spectra are now readily obtained taking the effect of the window function  $w(t) = e^{-\beta t^2}$  into account. The spectra consist of two terms as ( $s = \text{abs}, \text{cd}$ )

$$\sigma_s(E_{ph}) \sim \sigma_s^+(E_{ph}) + \sigma_s^-(E_{ph}), \quad (9)$$

with the definitions

$$\sigma_{\text{abs}}^\pm(E_{ph}) = e^{-(E_{ph}-E_\pm)^2/4\beta} [1 \pm \cos(\gamma)], \quad (10)$$

$$\sigma_{\text{cd}}^\pm(E_{ph}) = \pm e^{-(E_{ph}-E_\pm)^2/4\beta} [\sin(\gamma)]. \quad (11)$$

The absorption spectrum is the sum of two Gaussians centered at the eigenenergies  $E_\pm$ . Thus, they have a spacing of twice the coupling element:  $E_+ - E_- = 2J$ . If these functions do not overlap, the intensities of the two absorption bands are determined by the orientation angle  $\gamma$ , i.e. they have the weights  $[1 \pm \cos(\gamma)]$ . Then, the value of this geometric parameter can directly be extracted from the band ratio. The case of overlapping bands is more complex. On the other hand, the CD-spectrum depends on  $\gamma$  only via an overall scaling factor of  $\sin(\gamma)$ , so that both bands have the same intensity. For a positive coupling element  $J$ , the bands occurring at lower and higher energies are of negative and positive amplitude, respectively. If they do not show an overlap, the band extrema occur at the identical positions as the ones in the absorption spectrum. Thus, the electronic coupling element may directly be inferred from either the absorption- or the CD-spectrum. The above conclusions apply strictly only if the bands do not overlap. This fact, which is the central aspect of the present work is illustrated below.

## 2.3. Vibrational Hamiltonians

A broadening of the electronic absorption bands, in general, stems from the nuclear degrees of freedom but is also induced by a coupling of the system to its surrounding. We employ a model which treats internal monomer vibrations quantum mechanically [20] whereas the broadening due to system-bath interactions is included phenomenologically, as described in Section 2.1. Neglecting monomer-monomer interactions, the dimer vibrational Hamiltonian in the electronic ground state reads

$$H_g(x_1, x_2) = \sum_{n=1,2} \left( -\frac{1}{2} \frac{\partial^2}{\partial x_n^2} + \frac{\omega^2}{2} x_n^2 \right). \quad (12)$$

Here, harmonic potentials in the monomer coordinates  $x_n$  are included. The excited state configuration  $M_1^* - M_2$  is described by the Hamiltonian

$$H_{1e}(x_1, x_2) = \left\{ -\frac{1}{2} \frac{\partial^2}{\partial x_1^2} + \frac{\omega^2}{2} (x_1 - x_0)^2 + \Delta E \right\} \\ + \left\{ -\frac{1}{2} \frac{\partial^2}{\partial x_2^2} + \frac{\omega^2}{2} x_2^2 \right\}, \quad (13)$$

where the change of geometry is described by the parameter  $x_0$ , and the excitation energy  $\Delta E$  is included. In the numerical calculations we choose the values of  $\omega = 0.175$  eV,  $x_0 = 2.57$  eV<sup>-1/2</sup>,  $\Delta E = 2.35$  eV for the parameters of the model. They were taken from our recent study on aggregates of perylene bisimide dyes [21,22]. We set the value for the orientation angle to  $\gamma = 30^\circ$  [23]. The second excited state vibrational Hamiltonian (configuration  $M_1 - M_2^*$ ) is simply obtained by permutation of the coordinates  $x_1$  and  $x_2$  in

Eq. (13). The Hamiltonian in the excited state then is a matrix of the form

$$\mathbf{H}_e(x_1, x_2) = \begin{pmatrix} H_{1e}(x_1, x_2) & J \\ J & H_{2e}(x_1, x_2) \end{pmatrix}. \quad (14)$$

In the next section we present spectra calculated within the described model. The time-propagation is performed with the split-operator method [24].

### 3. Results

#### 3.1. The conventional method

In Fig. 1, we show absorption and CD-spectra for different values of the coupling element  $J$ , as indicated. The curves in the left and right hand panels differ in their energy resolution  $\Delta_\epsilon$ , as indicated. First, the separation of the two absorption bands is discussed. For the largest value of  $J$ , two bands are detected having extrema separated by a value of twice the coupling element, as is expected from the analysis given in Section 2.2. Decreasing the coupling, shifts the bands closer to each other and already for a value of  $J = 0.15$  eV, they show a substantial overlap. With increasing overlap, the separation of the maxima seen in the absorption spectra becomes more difficult. In fact, no clear maximum structure (originating from excitation of the lower energy state) can then be seen. Rather, the spectrum only exhibits a shoulder. On the other hand, the CD-spectra exhibiting negative and positive branches clearly show characteristics of two separated bands. In Table 1 we compare the coupling elements  $J$  (which are the input parameters in our calculation) to the values ( $J_{cd}, J_{abs}$ ) extracted from the low resolution CD- and absorption spectra displayed in Fig. 1, left panels. As a general trend, the values for  $J_{cd}$  are too large

**Table 1**

Comparison of the input coupling element  $J$  and the orientation angle  $\gamma$  with those obtained from the CD-spectrum (cd), the absorption spectrum (abs), and the sum-rule method (sum).

$J$ (eV)	$J_{cd}$ (eV)	$J_{abs}$ (eV)	$J_{sum}$ (eV)	$\gamma^\circ$	$\gamma_{abs}^\circ$	$\gamma_{sum}^\circ$
0.40	0.41	0.41	0.38	30	31	32
0.20	0.22	0.17	0.18	30	42	34
0.15	0.18	0.12	0.13	30	52	35
0.10	0.15	0.09	0.09	30	74	35

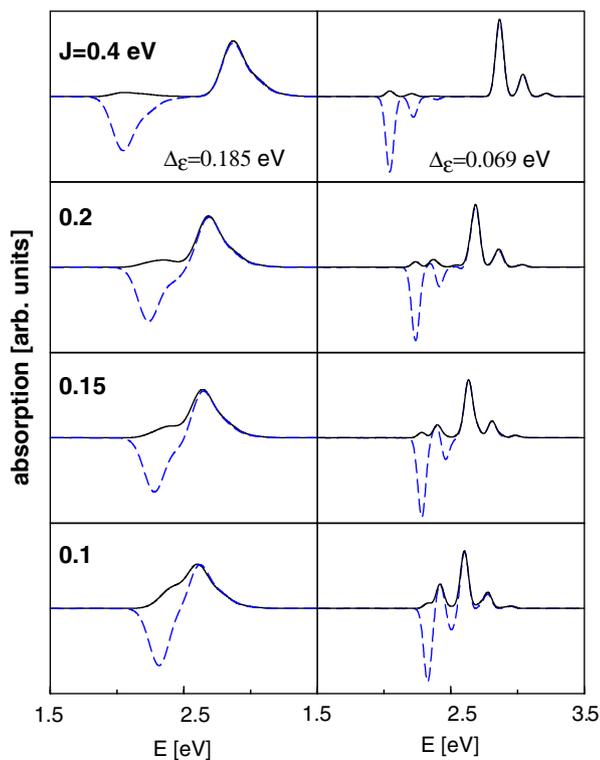
for the coupling strengths regarded here. On the other hand, the values  $J_{abs}$  are (except for the largest coupling) too small.

Increasing the resolution to  $\Delta_\epsilon = 0.069$  eV results in a vibrational progression on each of the two bands. Again, for the largest coupling (upper panel), the separation of the respective vibrational peaks can be used to extract a reliable value of the coupling element. This procedure becomes increasingly difficult with decreasing  $J$  as can be anticipated from the other curves in Fig. 1.

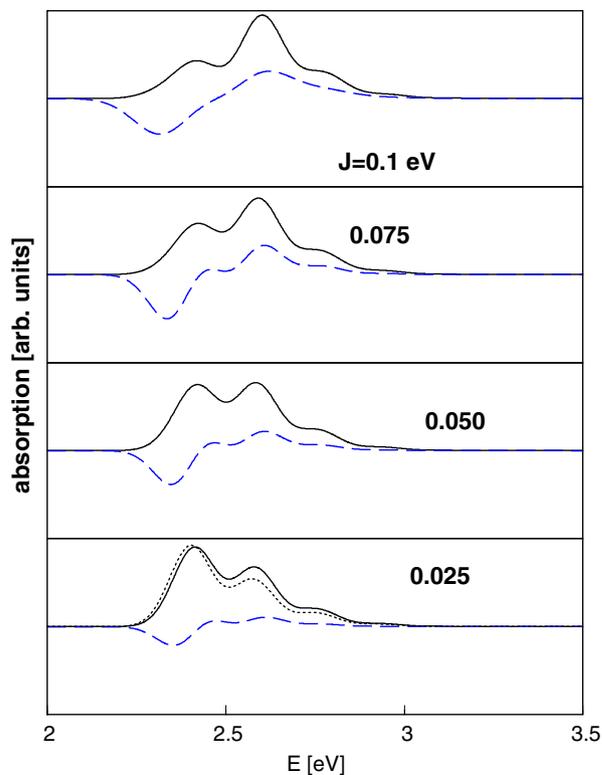
Let us next discuss the relative intensity of the two electronic bands. Within the two-level analysis for non-overlapping bands, and in the case of absorption, the intensity ratio is given by (see Eq. (10))

$$I_r = (1 + \cos(\gamma))/(1 - \cos(\gamma)), \quad (15)$$

which for our choice of  $\gamma = 30^\circ$  leads a factor of  $I_r = 13.9$ . This is in excellent agreement with what is seen in Fig. 1, upper panel. Note that, because the band-shape of the CD-spectrum does not depend on the orientational angle  $\gamma$  the latter cannot be extracted from the extrema of  $\sigma_{cd}$ . It is obvious that, with increasing overlap between the absorption bands, the intensity ratio is modified. In particular, the relative magnitude of the low energy band is enhanced. This is clearly documented in Fig. 2 which contains absorption spectra



**Fig. 1.** Absorption (solid lines) and CD-spectra (dashed lines) calculated for different coupling  $J$ , as indicated. The curves in the right and left hand panels were obtained with spectral resolution of  $\Delta_\epsilon = 0.185$  eV and  $\Delta_\epsilon = 0.069$  eV, respectively.



**Fig. 2.** Absorption (solid lines) and CD-spectra (dashed lines) for different values of the coupling element  $J$ . The absorption spectra evolve into the monomer spectrum (dotted line in the lower panel) in the limit of small coupling.

calculated with a resolution of  $\Delta_\epsilon = 0.139$  eV. Already for a coupling value of  $J = 0.1$  eV, the ratio  $I_r$  assumes a value of two which is about 7 times smaller than the value extracted from the  $J = 0.4$  eV curve. This leads to an angle larger than  $70^\circ$  which differs essentially from the real value, for precise values of the extracted angles, see Table 1. For a smaller coupling two peaks of equal height ( $J = 0.05$  eV) are found and then the peak at lower energy becomes even larger than the next one. Here, however, one has to be careful because for coupling values below  $J = 0.09$  eV, the electronic level splitting (within the two-level approximation) becomes comparable to the vibrational spacing present in our model system. This is seen if comparing the dimer spectra to the monomer spectrum (obtained for  $J = 0$ ) which is included as a dotted line in the lower panel of Fig. 2.

### 3.2. The sum-rule method

From the discussion above it emerges that with the method described above (i.e. using band splitting and relative band intensities to extract  $J$  and  $\gamma$ ) neither absorption nor CD-spectra can be used to obtain accurate numbers for the electronic coupling element and the orientation angle. Therefore we now turn to another method to obtain this information which was recently proposed by one of us [25] and relies on the fact that the moments (e.g. mean, variance, and skewness) of dimer and monomer absorption spectra are not independent but connected via so called sum-rules [20,26,27,25]. For isotropically oriented dimers one then finds the relations [25]

$$z_2^D = z_2^M + J^2 \sin^2 \gamma \quad (16)$$

$$z_3^D = z_3^M + (2z_2^D - z_2^M)J \cos \gamma. \quad (17)$$

Here,

$$z_j = \int (E - \langle E \rangle)^j \sigma_{\text{abs}}(E) dE \quad (18)$$

is the  $j$ th central moment of the (normalized) absorption spectrum and  $\langle E \rangle$  denotes the mean. By  $z_j^M$  and  $z_j^D$  monomer and dimer quantities are distinguished. As shown in Ref. [25] the relations Eqs. (16) and (17) can be solved for the parameters  $\gamma$  and  $J$  (up to the sign). The sign of  $J$  can be fixed by using the CD-spectrum, see the discussion at the end of Section 2.2. Thus it is sufficient to determine the second and third moments of the dimer and the monomer to extract the coupling strength  $J$  and the angle  $\gamma$ . This requires only four one-dimensional integrals to be evaluated.

The values of the coupling strength  $J_{\text{sum}}$  and the angle  $\gamma_{\text{sum}}$  obtained by using the sum-rules-method are presented in Table 1. Although all values  $J_{\text{sum}}$  are slightly smaller than the true values  $J$  the agreement between  $J_{\text{sum}}$  and  $J$  is quite good in all cases. Compared to the values  $J_{\text{cd}}$  and  $J_{\text{abs}}$  obtained from the naive approach presented above the agreement with the true value is equally good, if not even better. However, the strength of the sum-rules-method becomes fully apparent when considering the angle  $\gamma_{\text{sum}}$ . Here, contrary to  $\gamma_{\text{abs}}$  there is good agreement with the true angle  $\gamma = 30^\circ$ , even in those cases where  $\gamma_{\text{abs}}$  is totally wrong. This demonstrates that it is favorable to use the sum-rules method instead of a naive estimate of the band intensities.

Although the deviations of  $J_{\text{sum}}$  and  $\gamma_{\text{sum}}$  from the true values  $J$  and  $\gamma$  is reasonably small, it is worth to consider the origin of this discrepancy in more detail. To do so, one has to remember that in the original derivation of the sum-rules [20,26,27,25] internal vibrations of the monomers have been fully taken into account, but the influence of finite resolution was not included. However in the theoretical spectra used above, the broadening of the stick spectra caused by finite resolution is comparable with the vibrational spacing. And this, in turn, leads to the mentioned deviations.

## 4. Conclusions

In this Letter we have demonstrated by model calculations that in order to extract geometric properties of molecular dimers from absorption and CD-spectra one cannot ignore effects of line-broadening being due to internal vibrational degrees of freedom or a coupling to a bath. The usual way of extracting electronic coupling elements and orientational angles directly from the dimer absorption or CD-lineshapes can lead to substantial errors. On the other hand, a method based on sum-rules yields much more accurate values for the geometric parameters.

The analysis of the failure of the naive approach to extract the geometric parameters was based on a simple model where one internal vibrational mode of each monomer was included explicitly and a Gaussian line-broadening was incorporated phenomenologically. Although this seems to be quite restrictive, such a model, in general, reproduces experimental spectra quite well [6,28,21].

However, one should keep in mind that the convolution (with the same function for all coupling strength  $J$ ) has no a priori justification. Indeed, when the broadening of the spectra is mainly due to internal vibrations or static disorder in the transition energies of the monomers one expects a narrowing of the convoluting function by a factor  $1/\sqrt{2}$  [28–30] in the case when the coupling energy  $J$  becomes much greater than the width of the monomer spectrum. Furthermore the high energy side narrows slower than the low energy side with increasing  $J$  leading to a further asymmetry in the width of the two bands similar to the J- and H-band of longer aggregates [31]. Nevertheless, the conclusions drawn in Section 3.1 remain qualitatively unaltered, since the convoluting function could have been chosen quite arbitrarily as long as it smears out the ‘stick’ spectra resulting from the single vibrational mode included in the model.

To extract the geometrical parameters from experimental spectra the sum-rule method seem ideally suited, since it only needs the evaluation of simple one-dimensional integrals. For our dimer model with internal vibrational monomer modes the sum-rules are exact if no line broadening is present. That the derived parameters employing the sum rules are in excellent agreement with the exact ones is due to the fact that the monomer vibrational progression is well resolved. As has already been demonstrated, for measured spectra in solution [25], the sum-rules method gives results in accordance with fits based on the method of Section 2.2. Furthermore the sum-rule method is even valid if the influence of additional internal vibrational modes becomes apparent, as it is the case in high-resolution spectra, where fitting procedures become more and more complicated by the increasing number of resolved vibrational modes which have to be taken into account in the calculations.

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