

# Geometry Change of 1,3-Dicyanobenzene upon Electronic Excitation from a Franck-Condon Fit of Several Fluorescence Emission Spectra<sup>†</sup>

Jascha Martini, Simran Amar, and Michael Schmitt\*

*Institut für Physikalische Chemie I, Heinrich-Heine-Universität, D-40225 Düsseldorf,  
Germany*

E-mail: mschmitt@hhu.de

## Supporting Online Material

### Description of FCFit

FCfit is program for the simulation and fit of vibronic absorption and emission spectra based on the evaluation of relative Franck-Condon (FC) factors and/or Franck-Condon-Herzberg-Teller (FCHT) theory. The program computes the FC integrals of multidimensional, harmonic oscillators mainly based on the recursion formula given in the papers of Doktorov, Malkin, and Man'ko.<sup>1,2</sup> For further theoretical background of the theory as well as similar approaches see also refs.<sup>3-7</sup> A minor correction of a typo in the original publication is given in ref.<sup>8</sup>

The fit of vibronic spectra can greatly be improved if independent information for the geometry change upon electronic excitation is available. This information can be the change

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<sup>†</sup>Dedicated to Henry Mantsch

of the rotational constants upon electronic excitation. While geometry fits to the rotational constants alone are possible and routinely made, using non-linear fits in internal coordinates as basis for the geometries, the combination of rotational constant changes and vibronic intensities allows for determination of much more geometry parameters. In contrast to the separate geometry fits of the two states using rotational constants, in the combined FC fit geometry changes (relative to one of the states, usually the ground state) are determined in the basis of selected normal modes.

## Basic program features

According to the FC principle the probability of a vibronic transition and thus the relative intensity of a vibronic band depends on the overlap integral of the vibrational wave functions of both electronic states. This overlap integral is determined by the relative shift of the two potential energy curves connected by the vibronic transition along the normal coordinates  $Q$  of both states:

$$FC = \left| \int [\Psi'(Q')]^* \Psi''(Q'') dQ' \right|^2 = \langle v' \dots v'_N | v'' \dots v''_N \rangle^2 \quad (\text{S1})$$

where the  $\Psi(Q)$  are the  $N$ -dimensional vibrational wavefunctions. The normal coordinates  $Q'$  of the excited state and  $Q''$  of the ground state are related by the linear orthogonal transformation given by Duschinsky:<sup>9</sup>

$$\mathbf{Q}'' = \mathbf{S}\mathbf{Q}' + \vec{d} \quad (\text{S2})$$

where  $\vec{d}$  is a displacement vector and  $\mathbf{S}$  a rotation matrix, which rotates the coordinate system of one state into that of the other state. This matrix is called the Duschinsky matrix. Using the matrix  $\mathbf{L}$ , which contains the eigenvectors from the diagonalization of the force constant matrix,  $\mathbf{S}$  can be expressed as:

$$\mathbf{S} = (\mathbf{L}'')^T \mathbf{L}' \quad (\text{S3})$$

and  $\vec{d}$  as:

$$\vec{d} = (\mathbf{L}'')^T \mathbf{M}^{1/2} \left( \vec{R}_{eq.}'' - \vec{R}_{eq.}' \right) \quad (\text{S4})$$

where  $\mathbf{M}$  is a diagonal matrix, which contains the square roots of the atomic masses on the diagonal and  $\vec{R}_{eq.}$  is the geometry of the respective state.

Doktorov, Malkin und Man'ko deduced a recursion formula, which allows to compute Franck-Condon integrals considering the Duschinsky effect.<sup>1,2</sup> Starting point of the recursion is the Franck-Condon integral of the electronic origin:

$$\langle 0'' | 0' \rangle = 2^{\frac{N_{vib}}{2}} \left[ \prod_{j=1}^{N_{vib}} \left( \frac{\omega_j''}{\omega_j'} \right)^{\frac{1}{2}} \right] \det \mathbf{Q}^{\frac{1}{2}} \exp \left[ -\frac{1}{2} \delta (1 - \mathbf{P}) \delta \right] \quad (\text{S5})$$

The recursion formula for absorption is:

$$\begin{aligned} & \langle v'' | v', \dots, v_i' + 1, \dots, v_{N_{vib}}' \rangle = \\ & = 2 \sum_{k=1}^{N_{vib}} R_{ki} \left( \frac{v_k''}{v_i' + 1} \right)^{\frac{1}{2}} \langle v_1'', \dots, v_k'' - 1, \dots, v_{N_{vib}}'' | v_1', \dots, v_i', \dots, v_{N_{vib}}' \rangle + \\ & + \sum_{j=1}^{N_{vib}} (2\mathbf{Q} - 1)_{ki} \left( \frac{v_j'}{v_i' + 1} \right)^{\frac{1}{2}} \langle v'' | v', \dots, v_i' - 1, \dots, v_{N_{vib}}' \rangle - \\ & - (\mathbf{R}\delta) \left( \frac{2}{v_i' + 1} \right)^{\frac{1}{2}} \langle v'' | v', \dots, v_i', \dots, v_{N_{vib}}' \rangle \end{aligned} \quad (\text{S6})$$

and for emission:

$$\begin{aligned}
& \langle v''_1, \dots, v''_i + 1, \dots, v''_{N_{vib}} | v' \rangle = \\
& = 2 \sum_{k=1}^{N_{vib}} R_{ik} \left( \frac{v'_i}{v''_k + 1} \right)^{\frac{1}{2}} \langle v''_1, \dots, v''_k, \dots, v''_{N_{vib}} | v'_1, \dots, v'_i - 1, \dots, v'_{N_{vib}} \rangle + \\
& + \sum_{l=1}^{N_{vib}} (2\mathbf{P} - 1)_{kl} \left( \frac{v''_l}{v''_k + 1} \right)^{\frac{1}{2}} \langle v''_1, \dots, v''_l - 1, \dots, v''_{N_{vib}} | v' \rangle + \\
& + (1 - \mathbf{P}\delta) \left( \frac{2}{v''_k + 1} \right)^{\frac{1}{2}} \langle v''_1, \dots, v''_i, \dots, v''_{N_{vib}} | v' \rangle
\end{aligned} \tag{S7}$$

The recursive character of Doktorov's equations suggests to save already computed FC integrals in an appropriate manner for further use. An efficient method is realized using so called Hash tables. The entries in a Hash table are administered using keys. The entries of the Hash tables used in FCfit are the energy and the FC factors of a vibronic transition. A quantum string, describing initial and final state is used as key. This quantum string can be compared to an n-digit number, where n is the number of vibrations of the molecule, sorted by their frequency. The i-th position shows, with how many quanta the i-th mode is excited. E.g. the quantum string "001021" represents the vibrational state of a molecule with the third and sixth mode excited with one quantum and the fifth mode with two quanta. Each vibronic transition can be represented by two quantum strings for the initial and final state, respectively. We use the bracket notation, the bra being the initial state, the ket the final state of the transition. The transition from the vibrationless ground state to the vibrational state of the above example would read then:  $\langle 000000 | 001021 \rangle$ . N.b., that "final" and "initial" refers to the direction of the transition and not to the energetic ordering of states. Using spectroscopic notation this means in absorption  $\langle 001021 \rangle' \leftarrow \langle 000000 \rangle''$  and  $\langle 001021 \rangle'' \leftarrow \langle 000000 \rangle'$  in emission. Thus, the complete description of the transition requires both quantum strings of bra and ket and additionally the information if the transition is in absorption or emission. E.g.  $\langle 001000 | 001000 \rangle$  in emission describes the diagonal transition from the singly excited third mode to the respective ground state mode.

## Calculation of the emission and absorption spectra

The intensities of the transitions between two vibronic states  $m$  and  $n$  are proportional to the square of the transition moment  $M_{mn}$  and to the frequency  $\nu_{mn}$  of the transition for absorption spectra and the fourth power of the frequency  $\nu_{mn}$  for emission spectra, respectively.<sup>1</sup>

$$I_{mn} \propto |M_{mn}|^2 \nu_{mn} \quad (Absorption) \quad (S8)$$

$$I_{mn} \propto |M_{mn}|^2 \nu_{mn}^4 \quad (Emission) \quad (S9)$$

In the present version absorption spectra are calculated only originating from the vibrationless ground state, i.e. a molecular beam experiment is assumed, and no thermal population of vibrational levels of the ground state is taken into account.

## Franck-Condon-Herzberg-Teller theory

Within the frame of the Born-Oppenheimer approximation the vibronic wavefunction is factorized in a vibrational part which depends only on the nuclear coordinates  $Q$  and an electronic part which depends on the electronic coordinates  $q$  and parametrically on the nuclear coordinates:

$$\Phi_{mn}(q, Q) = \Psi_m(q, Q) \nu(Q) \quad (S10)$$

where  $m$  describes the electronic and  $v$  the vibrational quantum number. The transition dipole moment for a transition between an initial electronic state  $m$  and a final electronic state  $n$  is defined as:

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<sup>1</sup>this refers to energy detecting schemes, while for counting schemes (as for example for the nowadays very common CCD detection in optical multichannel analyzers) the intensity depends on the third power of the frequency  $\nu^3$ .<sup>10</sup>

$$M_{mn}(q, Q) = \langle \nu''_{(m)} | \mu_{mn}(Q) | \nu'_{(n)} \rangle \quad (\text{S11})$$

with the electronic transition dipole moment  $\mu_{mn}(Q)$ :

$$\mu_{mn}(Q) = \langle \Psi_m | \mu | \Psi_n \rangle; \quad \mu = \sum_g e r_g \quad (\text{S12})$$

where  $r_g$  is the position vector of the  $g$ th electron. The dependence of the electronic transition dipole moment  $\mu_{mn}$  from the nuclear coordinates can be approximated by expanding  $\mu_{mn}$  in a Taylor series about the equilibrium position at  $Q_0$ . Truncation of the expansion after the second expansion term and inserting into equation 11 yields:

$$M_{mn}(q, Q) = \mu_{mn}(Q_0) \langle \nu''_{(m)} | \nu'_{(n)} \rangle + \sum_i \left( \frac{\delta \mu_{mn}}{\delta Q_i} \right)_{Q_0} \langle \nu''_{(m)} | Q_i | \nu'_{(n)} \rangle \quad (\text{S13})$$

The displacement of the excited state geometry of the state  $n$  along the normal modes  $Q_i$  electronically mixes the wavefunctions of all neighboring electronically excited states  $p$  that are sufficiently close to the excited state. Through these displacements, the excited state gains orbital character from the perturbing state(s). The derivatives of  $\mu_{mn}$  are determined numerically from TDDFT/MRCI calculations of the respective state using the method of symmetric finite differences:

$$\left( \frac{\delta \mu_{mn}}{\delta Q_i} \right)_{Q_0} = \frac{\mu_{mn}(Q_0 + \Delta Q_i) - \mu_{mn}(Q_0 - \Delta Q_i)}{2\Delta Q_i} \quad (\text{S14})$$

The Frank-Condon integrals  $\langle \nu''_{(m)} | \nu'_{(n)} \rangle$  are calculated using the recursive relations of Doktorov [2], which uses the Duschinsky transformation [9] to reduce the integrals over the vibrational ground and vibrational excited state to integrals over the ground state vibrational wave functions only. The integrals  $\langle \nu''_{(m)} | Q_i | \nu'_{(n)} \rangle$  from the HT terms in equation 13 can be calculated from the FC integrals using the following relation:

$$\begin{aligned} \langle \nu''_{(m)} | Q_i | \nu'_{(n)} \rangle = & \sqrt{\frac{\hbar}{2\omega_i}} (\sqrt{\nu_{(n),i} + 1} \langle \nu'_{(m)} | \nu''_{(m),i}, \dots, \nu''_{(n),i} + 1, \dots, \nu''_{(n),i} \rangle \\ & + \sqrt{\nu_{(n),i}} \langle \nu'_{(m)} | \nu''_{(m),i}, \dots, \nu''_{(n),i} - 1, \dots, \nu''_{(n),i} \rangle) \end{aligned} \quad (S15)$$

## Program features

FCFit is capable of computing simulations or fits of vibronic spectra in the FC or FCHT approximation for absorption or emission, using a set of transitions, which can be user-defined. If a simulation is to be performed some of the keys needed are placed in the [General] section, while the same keys are placed in the section [Fit] in case of a fit. Furthermore, the geometry change can also be fit to the change of rotational constants from a rotationally resolved electronic spectrum or to both intensities and rotational constant changes (combined fit). Since from a single spectrum only three rotational constants can be extracted, only two geometry parameters can be determined. This limitation can be overcome if rotational constants of more isotopologues are available. For  $N$  isotopologues a total of  $3N - 1$  geometry parameters can be fit. The fits can be performed with local optimizers as NL2SOL<sup>11</sup> (an extended Levenberg-Marquardt-Algorithm) or PRAXIS<sup>12</sup> (an implementation of the non gradient based method of Brent),<sup>13</sup> or with global optimizers as PGA<sup>14</sup> (a genetic algorithm) or SIMANN<sup>15</sup> (a simulated annealing algorithm). The global minimizer has been extended to allow for intermediate local minimization steps rather than simple cost function evaluations.

## The cost function

In a pure FC fit, the geometry of the excited state is varied, until the weighted sum of the squared errors  $\chi^2$  of the intensities is minimized:

$$\chi_{Int.}^2 = \sum_i w_i (I_i^{calc.} - I_i^{exp.})^2 \quad (S16)$$

Here, the  $I_i^{calc.}$  and  $I_i^{exp.}$  are the  $i$  calculated and experimental intensities, respectively, weighted with individual weight factors  $w_i$ . The reduced standard deviation is calculated via:

$$\sigma_{red} = \sqrt{\frac{\chi^2}{n - p}} \quad (S17)$$

with  $n$  as the number of data points and  $p$  the number of parameters.

For a combined fit of intensities and changes of the rotational constants  $\Delta B_g$ , the total  $\chi^2$  is defined as follows:

$$\chi^2 = \chi_{Int.}^2 + \chi_{Rot.}^2 \quad (S18)$$

with

$$\chi_{Rot.}^2 = \sum_{g=a}^c w_g (\Delta B_g^{calc.} - \Delta B_g^{exp.})^2 \quad (S19)$$

## ***Ab initio* computational prerequisites**

For FC simulations of an absorption or emission spectrum several preliminary *ab initio* calculations are necessary: (i) An optimized geometry for each of the electronic states, connected by the transitions in form of Cartesian coordinates in units of Å. (ii) The second derivative of the energy (Hessian) for both states, calculated at the same level of theory. Since the output of the Hessian matrix differs between the various common *ab initio* program packages two tools are available for conversion of the Hessian into the notation needed for FCfit. Those are: TurboMol2ZmtHess.exe, which expects output from the turbomole program and MolCAS2ZmtHss.exe, which converts MolCAS Hessians to FCfit.

## **Availability**

An executable of the FCfit program for Windows, a detailed manual, and the necessary conversion programs can be downloaded from:

<http://dx.doi.org/10.25838/d5p-33> (Program),

<http://dx.doi.org/10.25838/d5p-34> (Manual), and



<http://dx.doi.org/10.25838/d5p-35> (Example Input).

For time restrictions, no technical help can be offered.

Table S1: SCS-CC2 optimized ground state geometry of 1,3-Dicyanobenzene in Å.

	Cartesian Coordinates		
C	-1.4852238496	-1.0845310473	-0.0003392045
C	-2.3565406780	0.0036864811	-0.0005188583
C	-1.8408266382	1.3076708260	0.0000894958
C	-0.4585575769	1.5238740064	0.0009392780
C	0.4055233516	0.4233892445	0.0011607213
C	-0.1059090487	-0.8822678352	0.0005177037
H	-0.0620614138	2.5297417219	0.0013654472
C	1.8277492078	0.6358702608	0.0020867416
N	2.9909302602	0.8065457040	0.0028691588
H	0.5754647156	-1.7219621569	0.0008088118
H	-1.8811811610	-2.0905884376	-0.0009597141
H	-3.4273990385	-0.1466739885	-0.0012042712
C	-2.7370485133	2.4322723001	-0.0002918263
N	-3.4730275422	3.3490734656	-0.0006974834

Table S2: SCS-CC2 optimized excited state (S1) geometry of 1,3-Dicyanobenzene in Å.

Cartesian Coordinates			
C	-1.4945546329	-1.1085400838	-0.0003421890
C	-2.3936323587	-0.0033510591	-0.0005820764
C	-1.8702225554	1.3329719879	0.0000605325
C	-0.4477211846	1.5516059024	0.0010497784
C	0.4442944941	0.4221846533	0.0012466184
C	-0.0833963206	-0.9124583350	0.0005381404
H	-0.0521413451	2.5570589022	0.0016273797
C	1.8442587061	0.6382114029	0.0020854169
N	3.0114190912	0.8170845840	0.0027737220
H	0.5937743414	-1.7537255213	0.0006698109
H	-1.8902582346	-2.1140757362	-0.0008638166
H	-3.4625350520	-0.1574256027	-0.0012292415
C	-2.7475252505	2.4451507965	-0.0003927694
N	-3.4798676235	3.3714086540	-0.0008153060

Table S3: Dimensionless displacement values with standard deviation  $\sigma$  of the 12 normal modes used in the fit of the 1,3-Dicyanobenzene.

Mode	Displacement	$\sigma$
Q <sub>1</sub>	+0.01642	$\pm$ 0.033549
Q <sub>2</sub>	+0.028429	$\pm$ 0.054316
Q <sub>7</sub>	-0.020391	$\pm$ 0.0018296
Q <sub>10</sub>	-0.038291	$\pm$ 0.0023941
Q <sub>14</sub>	-0.0093164	$\pm$ 0.0077066
Q <sub>20</sub>	+0.0031984	$\pm$ 0.0011586
Q <sub>21</sub>	+0.01451	$\pm$ 0.0218
Q <sub>24</sub>	-0.0075859	$\pm$ 0.0017354
Q <sub>27</sub>	+0.0054897	$\pm$ 0.0077783
Q <sub>29</sub>	+0.0066046	$\pm$ 0.013485
Q <sub>31</sub>	+0.00090465	$\pm$ 0.0053162
Q <sub>36</sub>	+0.015176	$\pm$ 0.016146

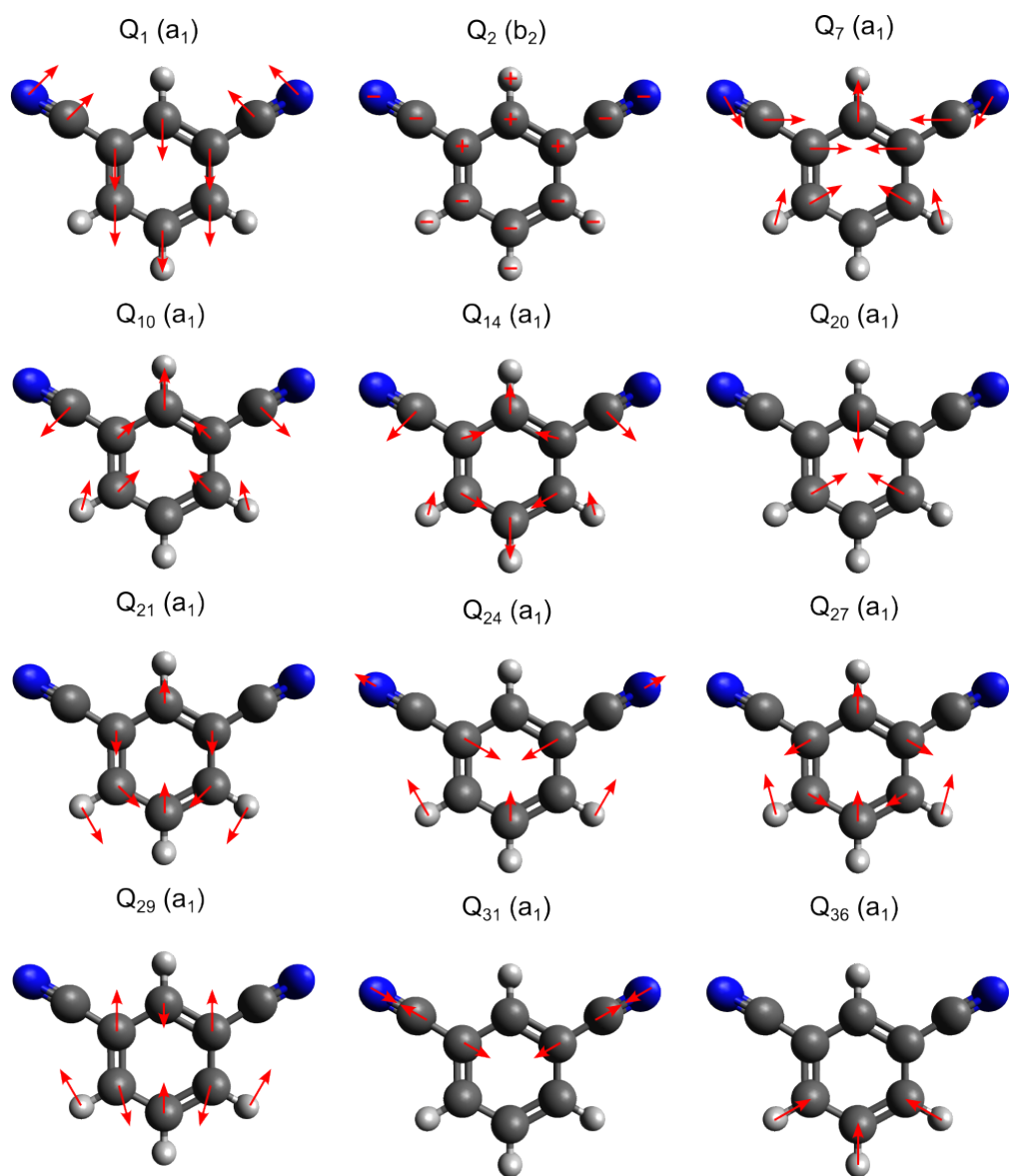


Figure S1: Visual representation of the ground state vibrational modes used in the calculation of the final Fit. All modes with the exception of  $Q_2$  are totally symmetrical.

Table S4: SCS-CC2/cc-pVTZ calculated and experimental wavenumbers of the 36 normal modes of the ground and first electronically excited state of 1,3-Dicyanobenzene along with the coefficients of the Duschinsky matrix, larger than 0.25 for the  $S_1 \leftarrow S_0$  transition.

Mode	$S_0$			$S_1$			Duschinsky-Coefficients
	Sym.	Calc.	Obs.	Sym.	Calc.	Obs.	
$Q_1(S_0)$	a1	114.1	113	b1	106.0		$Q_1(S_1) = -0.99 Q_2(S_0)$
$Q_2(S_0)$	b1	132.1	127	a1	111.2		$Q_2(S_1) = -1.00 Q_1(S_0)$
$Q_3(S_0)$	a2	170.1		a2	132.9		$Q_3(S_1) = +0.98 Q_3(S_0)$
$Q_4(S_0)$	b2	186.5		b2	181.9		$Q_4(S_1) = +1.00 Q_4(S_0)$
$Q_5(S_0)$	a2	370.6		b1	290.6		$Q_5(S_1) = +0.95 Q_6(S_0) + 0.29 Q_9(S_0)$
$Q_6(S_0)$	b1	388.4		a2	302.6		$Q_6(S_1) = +0.97 Q_5(S_0)$
$Q_7(S_0)$	a1	454.3	455	b2	399.4	404	$Q_7(S_1) = +0.99 Q_8(S_0)$
$Q_8(S_0)$	b2	454.8	456	b1	401.0		$Q_8(S_1) = +0.84 Q_9(S_0) - 0.46 Q_{13}(S_0)$
$Q_9(S_0)$	b1	502.5		a1	425.9		$Q_9(S_1) = -0.97 Q_7(S_0)$
$Q_{10}(S_0)$	a1	502.8	510	a1	488.6	497	$Q_{10}(S_1) = +0.97 Q_{10}(S_0)$
$Q_{11}(S_0)$	b2	575.5		a2	508.6		$Q_{11}(S_1) = -0.98 Q_{12}(S_0)$
$Q_{12}(S_0)$	a2	622.1		b1	513.7		$Q_{12}(S_1) = -0.45 Q_9(S_0) - 0.84 Q_{13}(S_0)$
$Q_{13}(S_0)$	b1	694.8		b2	568.8		$Q_{13}(S_1) = -0.96 Q_{11}(S_0)$
$Q_{14}(S_0)$	a1	705.1	703	b1	645.7		$Q_{14}(S_1) = -0.94 Q_{15}(S_0) - 0.28 Q_{17}(S_0)$
$Q_{15}(S_0)$	b1	825.8		a1	659.1	662	$Q_{15}(S_1) = +0.99 Q_{14}(S_0)$
$Q_{16}(S_0)$	b2	898.0	894	a2	708.0		$Q_{16}(S_1) = -1.00 Q_{18}(S_0)$
$Q_{17}(S_0)$	b1	924.7		b1	709.6		$Q_{17}(S_1) = +0.32 Q_{15}(S_0) - 0.93 Q_{17}(S_0)$
$Q_{18}(S_0)$	a2	946.2		b1	787.5		$Q_{18}(S_1) = -0.99 Q_{19}(S_0)$
$Q_{19}(S_0)$	b1	991.7	974	b2	848.1		$Q_{19}(S_1) = -0.98 Q_{15}(S_0)$
$Q_{20}(S_0)$	a1	1007.6	1004	a1	962.2	954	$Q_{20}(S_1) = +1.00 Q_{20}(S_0)$
$Q_{21}(S_0)$	a1	1111.8	1111	a1	1009.2		$Q_{21}(S_1) = +0.98 Q_{21}(S_0)$
$Q_{22}(S_0)$	b2	1160.8		b2	1109.2		$Q_{22}(S_1) = +0.97 Q_{22}(S_0)$
$Q_{23}(S_0)$	b2	1195.8		b2	1176.8		$Q_{23}(S_1) = +0.98 Q_{23}(S_0)$
$Q_{24}(S_0)$	a1	1253.1	1244	a1	1249.2		$Q_{24}(S_1) = +0.99 Q_{24}(S_0)$
$Q_{25}(S_0)$	b2	1314.5		b2	1295.3		$Q_{25}(S_1) = -0.84 Q_{25}(S_0) - 0.41 Q_{26}(S_0)$
$Q_{26}(S_0)$	b2	1362.1		a1	1343.3		$Q_{26}(S_1) = -0.98 Q_{27}(S_0)$
$Q_{27}(S_0)$	a1	1442.8	1427	b2	1426.5		$Q_{27}(S_1) = -0.97 Q_{28}(S_0)$
$Q_{28}(S_0)$	b2	1509.5		a1	1532.6		$Q_{28}(S_1) = -1.00 Q_{29}(S_0)$
$Q_{29}(S_0)$	a1	1614.6	1618	b2	1560.9		$Q_{29}(S_1) = -1.00 Q_{30}(S_0)$
$Q_{30}(S_0)$	b2	1637.7		b2	1814.5		$Q_{30}(S_1) = -0.50 Q_{25}(S_0) + 0.84 Q_{25}(S_0)$
$Q_{31}(S_0)$	a1	2155.3	2150	b2	2091.6		$Q_{31}(S_1) = +0.50 Q_{31}(S_0) - 0.86 Q_{32}(S_0)$
$Q_{32}(S_0)$	b2	2155.9	2158	a1	2097.5		$Q_{32}(S_1) = -0.86 Q_{31}(S_0) - 0.50 Q_{32}(S_0)$
$Q_{33}(S_0)$	a1	3215.3		a1	3225.7		$Q_{33}(S_1) = -0.98 Q_{33}(S_0) + 0.21 Q_{30}(S_0)$
$Q_{34}(S_0)$	b2	3227.0		a1	3238.1		$Q_{34}(S_1) = +0.99 Q_{35}(S_0)$
$Q_{35}(S_0)$	a1	3230.9		b2	3239.6		$Q_{35}(S_1) = +1.00 Q_{34}(S_0)$
$Q_{36}(S_0)$	a1	3237.4	3237	a1	3247.9		$Q_{36}(S_1) = -0.21 Q_{33}(S_0) - 0.97 Q_{36}(S_0)$

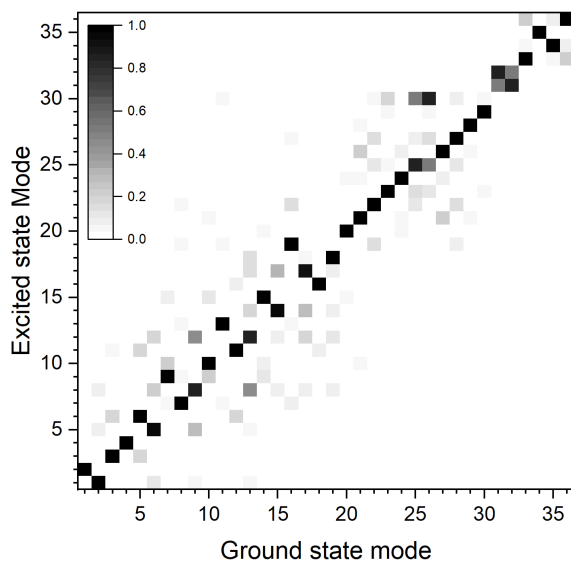


Figure S2: Duschinsky matrix between the ground and first excited state vibrational modes of 1,3-DCB.

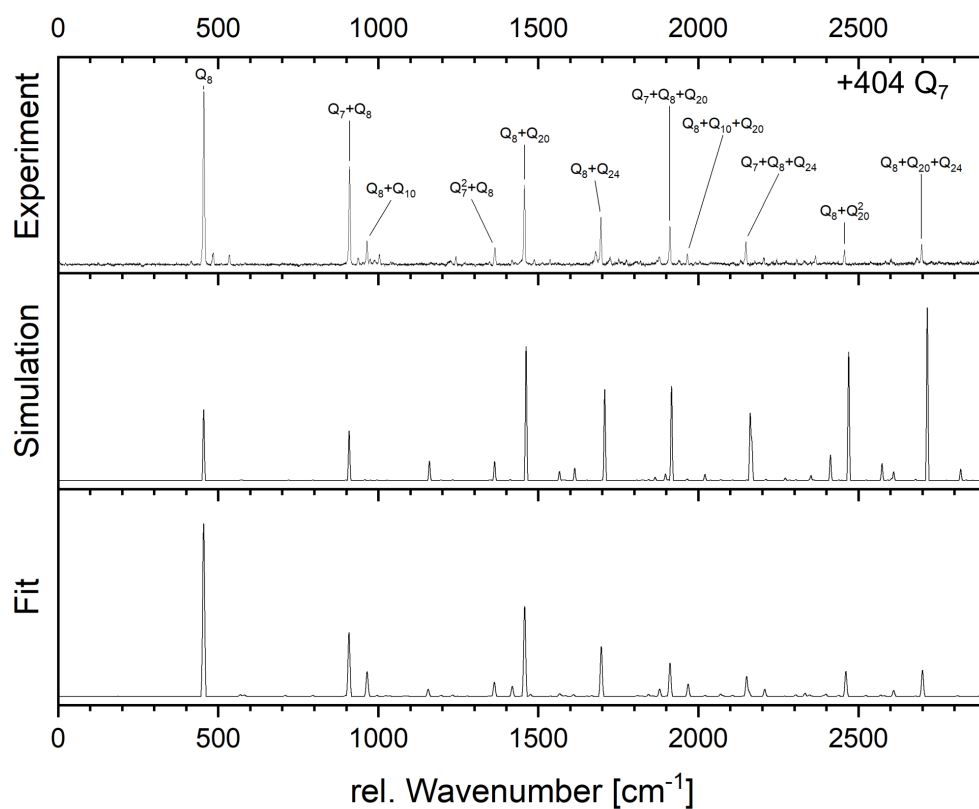


Figure S3: Dispersed fluorescence spectrum of the 0,0+404 excited state mode of 1,3-Dicyanobenzene.

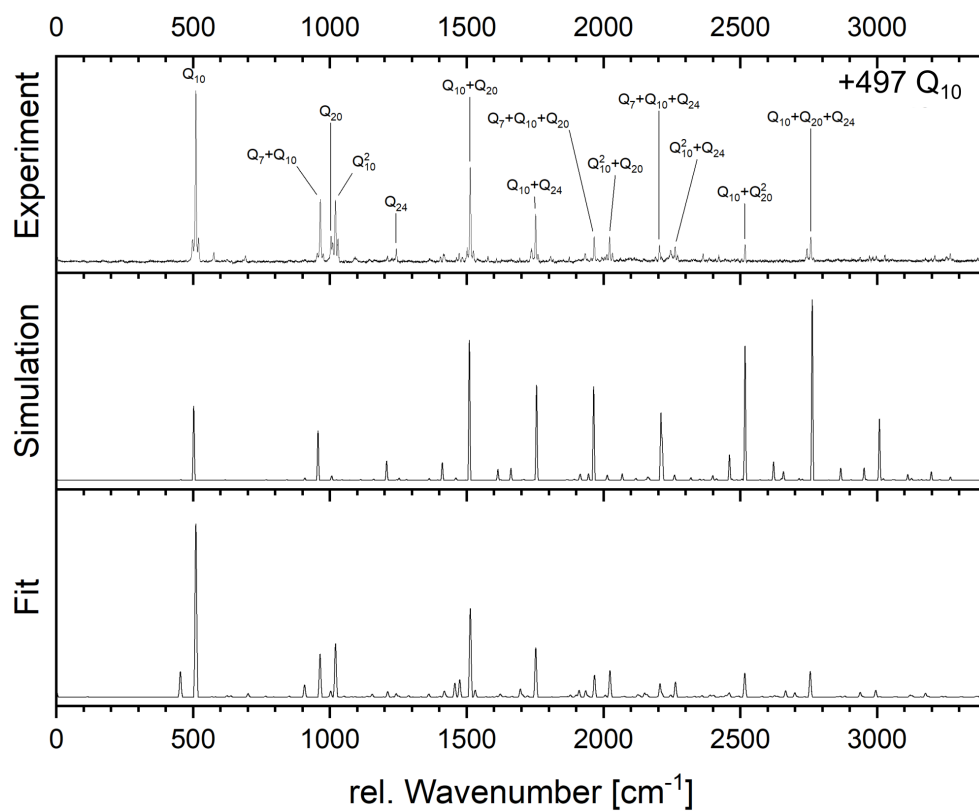


Figure S4: Dispersed fluorescence spectrum of the 0,0+497 excited state mode of 1,3-Dicyanobenzene.

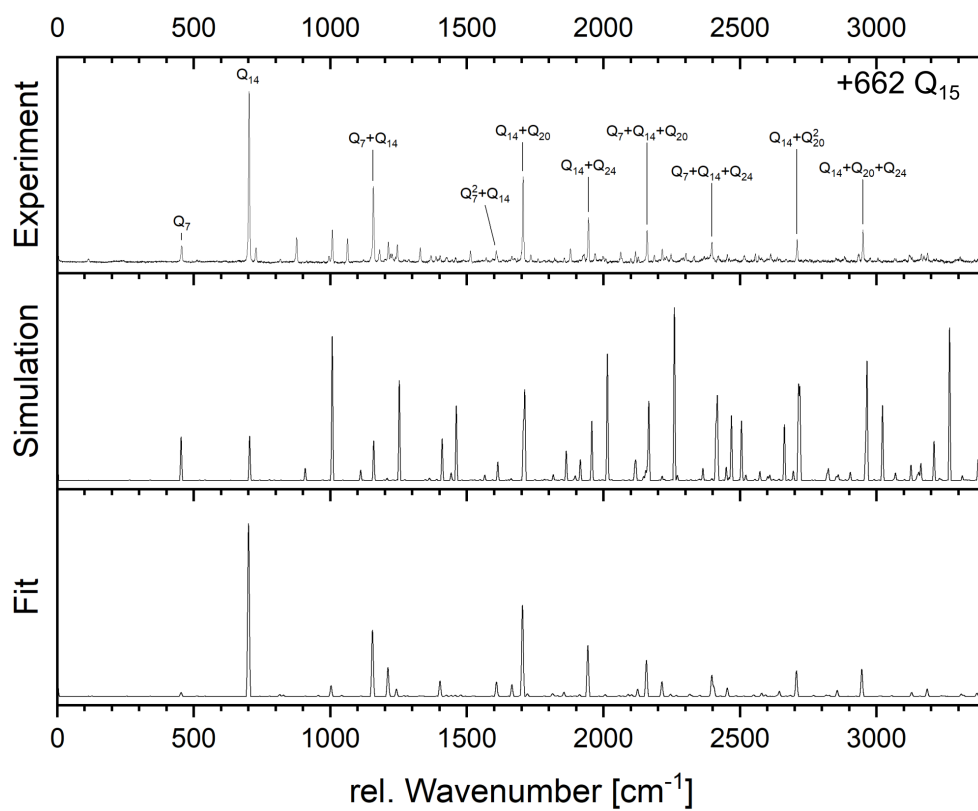


Figure S5: Dispersed fluorescence spectrum of the 0,0+662 excited state mode of 1,3-Dicyanobenzene.



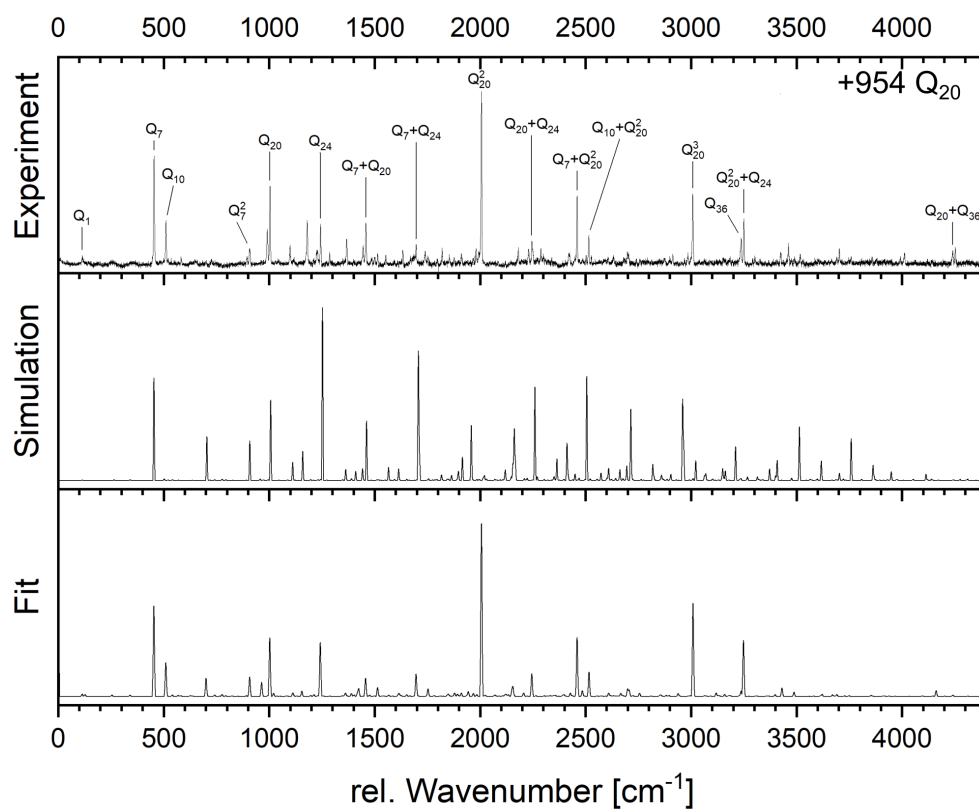


Figure S6: Dispersed fluorescence spectrum of the 0,0+954 excited state mode of 1,3-Dicyanobenzene.

Table S5: Relative intensities of the observed ground state vibrational modes of 1,3-DCB that were assigned in the final fit. Experimental wavenumbers of the overtones & combination modes are derived from the single excited modes.

S <sub>0</sub> Mode	Exp.	0,0	+404	+497	+662	+954
Q <sub>1</sub>	113	0.02				
Q <sub>2</sub>	127	0.02				
Q <sub>7</sub>	455	0.56			0.11	
Q <sub>8</sub>	456		1.00			
Q <sub>10</sub>	510	0.20		1.00		
Q <sub>14</sub>	703	0.05			1.00	
Q <sub>16</sub>	894	0.04				
Q <sub>7</sub> <sup>2</sup>	910	0.10				
Q <sub>7</sub> +Q <sub>8</sub>	911		0.56			
Q <sub>7</sub> +Q <sub>10</sub>	965	0.05		0.37		
Q <sub>8</sub> +Q <sub>10</sub>	966		0.13			
Q <sub>19</sub>	974	0.04				0.45
Q <sub>20</sub>	1004	1.00	0.06	0.16		
Q <sub>21</sub>	1111	0.02				
Q <sub>10</sub> <sup>2</sup>	1120			0.37		
Q <sub>7</sub> +Q <sub>14</sub>	1158				0.45	
Q <sub>10</sub> +Q <sub>14</sub>	1213				0.13	
Q <sub>24</sub>	1244	0.61	0.05	0.09		
Q <sub>7</sub> <sup>3</sup>	1365	0.04				
Q <sub>7</sub> <sup>2</sup> +Q <sub>8</sub>	1366		0.10			
Q <sub>27</sub>	1427	0.09				
Q <sub>7</sub> +Q <sub>20</sub>	1459	0.33				0.24
Q <sub>8</sub> +Q <sub>20</sub>	1460		0.46			

Table S5: Continued

$Q_{10}+Q_{20}$	1514	0.13	0.56	
$Q_7^2+Q_{14}$	1613			0.08
$Q_{29}$	1618	0.03		
$Q_7+Q_{24}$	1699	0.20		0.11
$Q_8+Q_{24}$	1700		0.04	
$Q_{14}+Q_{20}$	1707			0.51
$Q_{10}+Q_{24}$	1754	0.09	0.29	
$Q_7^2+Q_{20}$	1914	0.07		
$Q_7+Q_8+Q_{20}$	1915		0.22	
$Q_{14}+Q_{24}$	1947			0.27
$Q_7+Q_{10}+Q_{20}$	1970		0.16	
$Q_8+Q_{10}+Q_{20}$	1970		0.06	
$Q_{20}^2$	2008	0.21		1.00
$Q_{10}^2+Q_{20}$	2024		0.16	
$Q_{31}$	2150	0.04		
$Q_7+Q_8+Q_{24}$	2155		0.13	
$Q_{32}$	2158	0.03		
$Q_7+Q_{14}+Q_{20}$	2162			0.20
$Q_7+Q_{10}+Q_{24}$	2209		0.11	
$Q_{20}+Q_{24}$	2248	0.29		0.14
$Q_{20}^2+Q_{24}$	2264		0.10	
$Q_7+Q_{14}+Q_{24}$	2402			0.13
$Q_{20}+Q_{27}$	2431	0.04		
$Q_7+Q_{20}^2$	2463	0.06		0.40
$Q_8+Q_{20}^2$	2464		0.09	
$Q_{24}^2$	2488	0.08		

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Table S5: Continued

$Q_{10}+Q_{20}^2$	2518	0.04	0.11	0.17
$Q_{24}+Q_{27}$	2671	0.03		
$Q_7+Q_{20}+Q_{24}$	2703	0.08		
$Q_8+Q_{20}+Q_{24}$	2704		0.12	
$Q_{14}+Q_{20}^2$	2711			0.15
$Q_{10}+Q_{20}+Q_{24}$	2758	0.05	0.15	
$Q_7+Q_{24}^2$	2943	0.04		
$Q_{14}+Q_{20}+Q_{24}$	2951			0.20
$Q_{20}^3$	3012	0.04		0.41
$Q_{36}$	3237	0.04		
$Q_{20}^2+Q_{24}$	3252	0.07		0.25

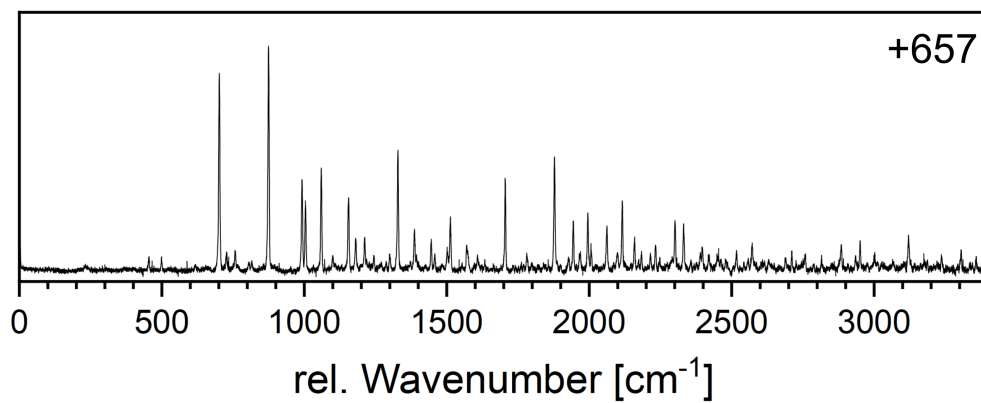


Figure S7: Dispersed fluorescence spectrum of the 0,0+657 excited state mode of 1,3-Dicyanobenzene. This spectrum was not included the final Fit because no valid combination of excitation energy, vibrational mode symmetry & simulation pattern was found.

## References

- (1) Doktorov, E. V.; Malkin, I. A.; Man'ko, V. I. Dynamical symmetry of vibronic transitions in polyatomic molecules and the Franck-Condon principle. *J. Mol. Spec.* **1975**, *56*, 1–20.
- (2) Doktorov, E. V.; Malkin, I. A.; Man'ko, V. I. Dynamical symmetry of vibronic transitions in polyatomic molecules and the Franck-Condon principle. *J. Mol. Spec.* **1977**, *64*, 302–326.
- (3) Sharp, T. E.; Rosenstock, H. M. Franck—Condon Factors for Polyatomic Molecules. *J. Chem. Phys.* **1964**, *41*, 3453–3463.
- (4) Warshel, A.; Karplus, M. Vibrational structure of electronic transitions in conjugated molecules. *Chem. Phys. Letters* **1972**, *17*, 7–14.
- (5) Islampour, R.; Dehestani, M.; Lin, S. A New Expression for Multidimensional Franck-Condon Integrals. *J. Mol. Spec.* **1999**, *194*, 179–184.
- (6) Berger, R.; Fischer, C.; Klessinger, M. Calculation of the Vibronic Fine Structure in Electronic Spectra at Higher Temperatures. 1. Benzene and Pyrazine. *J. Phys. Chem. A* **1998**, *102*, 7157–7167.
- (7) Dods, J.; Gruner, D.; Brumer, P. A genetic algorithm approach to fitting polyatomic spectra via geometry shifts. *Chem. Phys. Letters* **1996**, *261*, 612–619.
- (8) Crompt, B.; Triest, M.; Carrington, J.; Reber, C. A direct-operation time-dependent method for calculating absorption spectra involving multiple electronic states and its application to trans-OsO<sub>2</sub>(oxalate)<sup>22</sup>. *Spectrochim Acta A, special issue entitled Theoretical Spectroscopy: State of the Science* **1999**, *55*, 575–583.
- (9) Duschinsky, F. Zur Deutung der Elektronenspektren mehratomiger Moleküle I. Über das Franck-Condon-Prinzip. *Acta Physicochimica U.R.S.S.* **1937**, *7*, 551–577.

- (10) LeRoy, R. J. Where Is the Intensity Maximum in a Pure Rotational Spectrum? *J. Mol. Spec.* **1998**, *192*, 237–238.
- (11) Dennis, J. E., Jr.; Gay, D. M.; Welsch, R. E. An Adaptive Nonlinear Least-squares Algorithm. *ACM Transactions on Mathematical Software* **1981**, *7*, 348.
- (12) Gegenfurter, K. R. PRAXIS: Brent’s algorithm for function minimization. *Behav. Res. Meth. Instr. & Comp.* **1992**, *24*, 560–564.
- (13) Brent, R. P. *Algorithms for minimisation without derivatives*; Prentice hall: Englewood cliffs, 1973; Chapter 7.
- (14) Levine, D. PGAPack V1.0, PGAPack can be obtained via anonymous ftp from: <ftp://ftp.mcs.anl.gov/pub/pgapack/pgapack.tar.Z>. 1996.
- (15) Goffe, W. L.; Ferrier, G. D.; Rogers, J. Global Optimization of Statistical Functions with Simulated Annealing. *J. Econometr.* **1994**, *60*, 65–100.