Anharmonic Corrections to Vibrational Energies of Molecules: Water and Dideuteriooxirane

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Anharmonic contributions to vibrational energies and absorption and vibrational circular dichroism spectral intensities are discussed for the example of *trans*-2,3-dideuteriooxirane. Higher energy and dipole derivatives are calculated *ab initio* at the Hartree–Fock level in Cartesian coordinates. The combination of variational and perturbational calculations of vibrational energies allows consistent treatment also for the case of Fermi resonances. A cubic energy term can account for the main part of the anharmonic contribution.

Introduction

As a standard procedure in the theoretical treatment of vibrational properties of molecules, the harmonic approximation of the molecular force field is assumed.[1,2] There is a number of examples where this approach cannot be used, for example, nonrigid molecules with rotating bonds or when the transitions to multiple-excited vibrational states are investigated. In most cases, however, the harmonic approximation is the first choice for interpretation of vibrational spectra, measured as either the absorption (IR), vibrational circular dichroism (VCD),[3] Raman scattering, or Raman optical activity (ROA).[4]

For the case of VCD, for example, experimental spectra of middle-sized molecules are with a high level of accuracy simulated by *ab initio* calculations within the harmonic limit. Also, spectra of proteins and nucleic acids can be calculated assuming the harmonicity of the force field, which enables easier transfer of molecular force constants.[3,5] For the case of *trans*-2,3-dideuteriooxirane Stephens claims that "there is no practical advantage to be gained from improvements beyond this (harmonic) level",[6] having in mind the interpretation of the VCD spectrum.

Nevertheless, there is strong evidence of the anharmonic forces in experimental spectra for almost any organic molecule—the bands corresponding to the C–H stretching motion are on the order of 100 cm^{-1} off it compared to predicted harmonic frequencies on best levels of *ab initio* calculations. For the optical activity (VCD, ROA) of bigger molecules' spectra, simulations based on the harmonic approximation are not reliable, since the knowledge of fine splitting of the C–H modes is essential for the determination of the overall spectral shape.

For smaller molecules' force constants of a high order can be calculated, and finally the vibrational levels are determined with sufficient accordance with experimental values.[7-10] For bigger molecules, however, a similar approach would lead to extended calculations, which cannot be performed in real time.

The contact transformation method[1] used also for treatment of molecular anharmonicities is based on the assumption of the dominant role of the harmonic part and nondegeneracy of the basis set functions. It provides formulas which in principle coincide with that of perturbation calculations.[1,11]

Calculation of the vibrational frequencies via the phase integral[12] gives the energies for any potential function; its usage is limited, however, on one-dimensional problems like diatomic molecules. There is also no clear way to obtain spectral intensities by this procedure.

Perturbational Theory

Perturbational theory is often used for the treatment of anharmonicities, using the harmonic Hamiltonian as the starting point, as described elsewhere.[1,2] In the normalization scheme for old (i) and perturbed (i') quantum states $\langle i|i'\rangle = 1$, the corresponding energies are given by

$$E_i' = E_i + V_{ii} + \sum_{n\neq i} V_{in}V_{ni}\Delta E_{in}^{-1}(1 - V_{ii}\Delta E_{in}^{-1}) + \sum_{n\neq i}\sum_{k\neq i} V_{in}V_{nk}V_{ki}\Delta E_{in}^{-1}\Delta E_{ik}^{-1} + O(v^4) \quad (1)$$

where $\Delta E_{in} = E_i - E_n$ and the integrals of the perturbation part are defined as $V_{in} = \langle i\|\mathrm{V}|n\rangle$. The variable v can be thought of as the ratio $|V_{in}/\Delta E_{in}|$.

From eq 1, two main shortcomings of the method are apparent. First, there must be no degeneracy in the harmonic vibrational levels ($\Delta E_{in} \neq 0$), and second, the harmonic terms must be dominant so that $v \ll 1$. But even when these conditions are met, the convergence of (1) is not guaranteed; rather, a semiconvergent character of the expansion is observed. When a perturbational contribution of an nth order reaches its minimal absolute value, the next terms start to grow bigger and oscillate around an average value.[11,13]

For polyatomic molecules the number of harmonic states needed in the summation grows so rapidly that going behind the second-order perturbational term is hardly conceivable. At the same time, variational calculation is prevented as well, except for the smallest molecules, because of the limits of computer memory and speed.

Method Used

In this paper we propose to estimate the cubic and quartic contributions to molecular vibrational energies from Cartesian derivatives, which allows more flexibility than working in normal-mode coordinates. Variational calculation is combined with perturbational calculation for a selected subset of vibrational states, and thus also Fermi resonances and spectral intensities of overtones can be calculated as well as geometry changes.

The Cartesian third energy derivatives were obtained by numerical differentiation of second derivatives, which are part of the Cadpac[14] output. By two-point differentiation some quartic force constants could be also evaluated ($d_{\alpha\beta\gamma\delta}$ where at least two of the indices are equal). The Cadpac program was implemented on an IBM/RS 6000 workstation (32M memory, 4 G harddisk). Thus, the energy derivatives could be determined on the *ab initio* level (HF or MP2). A Cartesian displacement 0.005 au was used for the differentiation. According to our experience, the results are reliable at least in the range of the displacement from 0.001 to 0.01 au. Using Cadpac, the normal-mode coordinates were calculated.

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By a similar procedure, derivatives of atomic axial and atomic polar tensors were calculated. This could be done on the HF level only, since correlated magnetic properties are not implemented in Cadpac.

Another set of programs "S4" was developed for further calculations, implemented on the same computer. The normal-mode third derivatives were calculated from Cartesians by linear transformation. Usually, the coefficients are calculated directly by differentiation according to the normal-mode coordinates,[9] which requires fewer evaluations of second derivatives; nevertheless, this convenience becomes relatively smaller for bigger molecules. The more complicated normal-mode differentiation is not implemented in most quantum programs. Also, for the Cartesian differentiation only one calculation is needed, if an additional isotopic substitution or harmonic force field scaling[2,7] should be done.

The normal-mode fourth energy derivatives (D_{ijkl}) were calculated from the incomplete Cartesian quartic force field. Although the coefficients obtained by this procedure are dependent on the orientation of the molecule in space, major quartic contribution to energies can be calculated, as discussed later. Only the terms of the type "D_{iijj}" need to be calculated, since they contribute to the second-order energy correction.[9,11,15]

Perturbed energies with the cubic and quartic terms were calculated according to eq 1 to second order ($O(v^2)$). Up to pentaexcited molecular states were included in the calculation.

A parallel option included prediagonalization of the harmonic basis set. Higher excited states $|H\rangle$ were taken in the Hamiltonian, if $|\langle L|V|H\rangle/(E_L - E_H)| > \eta$ for some L, where L is either the ground or monoexcited vibrational state. For the diagonalization procedure the Sturm sequence property[16] was used, allowing to select eigenvalues in an interval of interest (typically 0–4000 cm^{-1}). The rest of the higher excited states were used to calculate final corrections to new energies as the second-order perturbation terms.

The "diagonalized" wave functions allowed one to calculate absorption and VCD spectral intensities. The dipole and rotational strengths of a transition $|E\rangle \rightarrow |G\rangle$ are given by[17]

$$D_{GE} = \langle G|\mu|E\rangle\cdot\langle E|\mu|G\rangle \qquad (2)$$

$$R_{GE} = \mathrm{Im}\ \langle G|\mu|E\rangle\cdot\langle E|\mathbf{m}|G\rangle \qquad (3)$$

The transitional dipole vector matrix elements can be evaluated from the expansion of the electronic ground-state moment according to normal-mode coordinates.[1,9] Similar expansion for the magnetic dipole moment is not so straightforward; the electronic part vanishes in the Born–Oppenheimer approximation.[18,19] Here, the magnetic field perturbation theory of Stephens[18] was used, allowing one to express the desired matrix element as

$$\langle G|m_\beta|E\rangle = -2(E_E - E_G)\langle E|\sum_{i,\lambda,\alpha} Q_i M^\lambda{}_{\alpha,\beta}(Q) S^\lambda{}_{\alpha,i}|G\rangle \qquad (4)$$

where **M** is the atomic axial tensor, dependent on coordinates, and **S** is the Cartesian normal-mode transformation matrix. First derivatives of axial and polar tensors were evaluated by numerical differentiation—the atomic axial and atomic polar tensors are parts of the Cadpac output.

Results and Discussion

To test the method, vibrational energies of water molecules were calculated. Calculations of third energy derivatives were performed on various *ab initio* levels, as seen in Table 1. Although there is no resonance in harmonic energies, perturbational and variational terms differ by 10–30%. A basis set of 56 wave functions less than six times excited could be easily included into the Hamiltonian. As expected, the variational corrections are bigger in absolute value and closer to experiment. Surprisingly, the rather primitive 4-31G basis set calculation yields reliable and usable third energy derivatives, within the limit of the deviation 2–10% with respect to the energy term.

TABLE 1: Cubic Corrections to Vibrational Frequencies of H_2O—Basis Set Dependence

	Δ_P/Δ_D[a]					
mode	431G	631G**	6311G**	MP2[b]	δ (%)[c]	exact[d]
1	−23/−33	−27/−36	−25/−34	−20/−30	12.6/7.5	
2	325/316	320/334	311/331	333/355	2.9/4.8	381
3	355/412	342/394	333/382	345/401	2.6/3.2	404

[a] Δ_P and Δ_D are cubic corrections obtained by perturbation and by diagonalization, respectively, in cm^{-1} ($\omega_{anh} = \omega_{harm} - \Delta$). [b] In the 6-311G** basis. [c] Mean square root deviation over the four calculations made.[d] Exact first-order perturbational term, from ref 13.

TABLE 2: Calculated Anharmonicities in Spectral Parameters for H_2O (MP2/6-311G)**

	harmonic	anharmonic	exptl[b]
frequencies (cm^{-1})			
ω_1	1635	1567	1595
ω_2	3816	3680	3657
ω_3	3948	3778	3756
intensities (km/mol)			
I_1	63.9	63.4 (63.9)	53.6
I_2	4.5	3.5 (4.2)	2.2
I_3	59.8	53.7 (58.3)	44.6

[a] For intensities in parentheses only first dipole derivatives were used. [b] Reference 22.

In Table 2 spectral parameters for H_2O are given, as calculated at the MP2/6-311G** level for second, third, and fourth energy derivatives and electric first dipole derivatives. Second dipole derivatives were calculated at the HF level with the same basis set. Substantial improvement of vibrational frequencies is observed, if the anharmonic terms are included. Overall improvement of spectral intensities is also achieved by inclusion of the anharmonic terms. Nevertheless, the dipole strengths are much more sensitive at the level of *ab initio* calculation,[20] and thus the primary error is given by limited accuracy of first dipole derivatives. For the second mode, for example, the harmonic intensity (4.5 km/mol) is 205% of the experimental value, which can be reduced only to 160%, if anharmonicities are included.

As the model molecule, (*S*,*S*)-*trans*-2,3-dideuteriooxirane was chosen so that the results could be compared to the work of Stephens,[6] who calculated harmonic frequencies with a high level of accuracy. Experimental absorption and vibrational CD spectra were measured both in the gas phase and in CCl_4 and CS_2 solutions.[21]

Second energy derivatives, first electric dipole derivatives, and equilibrium geometry were calculated at the MP2/6-311G** level. Stephens'[6] frequencies were conveniently used as the true harmonic limit, when the harmonic parameters were combined with higher energy and dipole derivatives, obtained at the HF level (in 4-31G, 6-31G**, and 6-311G** bases). A total of 570 vibrational states were used in the variational calculation, from the total of 3876 less than five times excited, according to the criterion $\eta > 0.01$.

As seen in Table 3, dramatic improvement of vibrational frequencies is observed, if higher energy derivatives are considered. Unfortunately, energy ordering of the C–D stretching modes (modes 12 and 13) is reversed, which reveals limited accuracy of results. The mode order is conserved if the calculation is performed at the HF/631G** or 431G levels. Nevertheless, the obtained frequency is by 78 cm^{-1} closer to experiment than the harmonic limit. Unlike in the case of water, cubic correction terms are the dominant part of total anharmonic contributions. The square of the diagonal expansion coefficient c_{ii} can be used as a rough estimate of harmonicity of a given vibration, indicating

TABLE 3: Vibrational Energies of the *trans*-2,3-Dideuteriooxirane[a]

				cubic term			total anharmonicity				
mode	ω_{exp}	ω_H	ω_A	Δ_4	Δ_6	Δ_{66}	$\Delta_{66}{}^p$	$\Delta_{66}{}^v$	$\Delta_{66}{}^{p+v}$	Δ_A	$c_{ii}{}^2$
15b	3028	3217	3057	134	121	130	143	96	160	189	79
14a	3015	3212	3052	132	117	128	142	122	160	197	48
13a	2254	2366	2229	108	90	78	79	80	137	112	33
12b	2240	2353	2275	82	71	x	x	50	78	113	75
11a	1397	1439	1379	16	24	38	64	51	60	42	80
10b	1339	1380	1336	7	5	10	52	41	44	41	96
9a	1235	1266	1233	32	24	35	40	23	33	31	89
8a	1112	1147	1115	12	14	23	39	28	32	35	94
7b	1106	1128	1100	10	9	15	35	25	28	22	96
6a	961	973	948	12	17	25	34	21	25	12	91
5b	914	922	902	8	7	11	28	17	20	7	95
4a	885	900	874	19	11	17	31	21	26	15	93
3b	817	820	791	32	32	50	34	19	29	3	93
2a	754	774	765	13	6	10	14	6	9	20	95
1b	673	675	665	3	2	7	16	8	10	2	96

[a] a and b are symmetries of the mode (C_2). ω_{exp} is the experimental frequency (cm^{-1}), ref 21; ω_H is the calculated harmonic from ref 6; and ω_A is the calculated anharmonic frequency (HF/6-311G** force field combined with ω_H). Δ_4, Δ_6, and Δ_{66} are cubic terms obtained by perturbation calculation, for three sets of force constants (4-31G, 6-31G**, and 6-311G**, respectively). $\Delta_{66}{}^p$, $\Delta_{66}{}^v$, and $\Delta_{66}{}^{p+v}$ are calculated anharmonic part, by the perturbational, variational, and combined calculation ($\omega_A = \omega_H - \Delta_{66}{}^{p+v}$), and $\Delta_A = \omega_H - \omega_{exp}$. $c_{ii}{}^2$ is the "harmonicity" of the state, square of the expansion diagonal coefficient as obtained by the variational calculation, in percent; $c_{\mathrm{ground},|0\rangle}{}^2 = 95\%$. x indicates resonance occurred (1380 + 973 = 2353).

TABLE 4: Calculated (HF/4-31G) Quartic (Coordinate System Dependent) Energy Corrections for Three Orientations of *trans*-2,3-Dideuteriooxirane

	$\Delta E^{(1)} + \Delta E^{(2)}$ (cm^{-1})[a]		
state	O1	O2	O3[b]
15b	−27 − 10	−37 − 10	−29 − 10
14a	−27 − 10	−38 − 11	−30 − 10
13a	−22 − 5	−27 − 5	−25 − 5
12b	−22 − 5	−27 − 5	−25 − 5
11a	−60 − 3	−59 − 3	−61 − 3
10b	−68 − 3	−62 − 3	−69 − 3
9a	−26 − 3	−22 − 3	−31 − 2
8a	−37 − 3	−55 − 4	−47 − 3
7b	−46 − 4	−52 − 3	−50 − 3
6a	−37 − 3	−40 − 3	−42 − 3
5b	−49 − 3	−43 − 3	−51 − 3
4a	−29 − 2	−37 − 3	−38 − 2
3b	−21 − 2	−21 − 3	−22 − 2
2a	−26 − 3	−37 − 3	−33 − 2
1b	−32 − 3	−47 − 3	−37 − 3
ground	−28 − 2	−32 − 2	−31 − 2

[a] First- and second-order (perturbational) correction. [b] Molecular orientations—O1: COC in the *xz* plane, $z = C_2$ axis; O2: O1 + rotation around *y* by 45° + rotation around *x* by 45°; O3: HCCD in *xy* plane, C_2 axis in the *xz* plane.

TABLE 5: Spectroscopic Parameters of *trans*-2,3-Dideuteriooxirane[a]

mode	D_{exp}	R_{exp}	D_S	R_S	D_H	R_H	D_A	R_A
15b	53[b]	−11.4	31	23	48	26	57/42	28/22
14a		−8.9	7.4	−24	6.0	−24	5.2/3.4	−17/−12
13a	5.7	12.1	8.6	13	7.2	12	2.8/3.4	4.1/4.3
12b	27	−10	27.4	−11	40	−13	36/32	−12/−10
11a	12	−15	8.4	−8.3	15	−8.6	7.8/7.5	−6.5/−6.4
10b	2.3	−2.5	0.6	−1.3	1.4	−2.0	1.4/1.3	−1.8/−1.9
9a	29.6	24.1	19.7	11	23	12	24/25	11/11
8a		−49	1.9	−6.3	0.0	−0.06	0.2/0.1	−1.6/−1.1
7b	8.6	11.1	6.3	10.1	8.7	9.9	8.5/8.8	9.2/9.5
6a	54	−29	57.1	−28	76	−34	49/51	−27/−27
5b	6.3	−6.9	11.9	−3.7	22	−5.4	19/19	−5.5/−5.9
4a		5	123	8.0	68	12	76/77	7.4/7.2
3b		(+)	39	1.7	32	0.1	35/36	0.6/0.7
2a			114	11.8	97	8.6	116/116	8.7/8.9
1b			0.8	0.0	0.0	−0.1	0.0/0.0	−0.1/−0.2

[a] D_{exp} [esu^2 cm^2 × 10^{43}] and R_{exp} [esu^2 cm^2 × 10^{39}] are experimental dipole and rotational strengths, from ref 21. D_S and R_S are harmonic theoretical strengths, from ref 6. D_H and R_H are calculated harmonic values on the MP2/6-311G** level. D_A and R_A are calculated anharmonic values; numbers after slash sign were calculated using first dipole derivatives only. [b] Sum for transitions 14 and 15.

TABLE 6: Bond Lengths in *trans*-Dideuteriooxirane

		calculated		
bond	experimental[a]	harmonic[b]	anharmonic[b]	diff (%)[b]
C–O	1.435 ± 0.001	1.4299	1.4343	0.31
C–C	1.470 ± 0.001	1.4656	1.4698	0.29
C–D	1.083 ± 0.001	1.0861	1.0891	0.28
C–H	1.083 ± 0.002	1.0861	1.0899	0.35

[a] Reference 20, given in angstroms. [b] Based on MP2/6-311G** calculation + *ab initio* HF/6-311G** third and fourth energy derivatives.

coupling with other vibrational states. As expected, it is close to 100% for the lowest frequency modes.

Working with the incomplete Cartesian quartic force field causes a coordinate system dependence of the results and contributes to the final error of calculated frequencies. In Table 4 quartic perturbational terms for three molecular orientations are presented. As can be seen, the coordinate-dependent part makes a few cm^{-1} of resultant vibrational frequencies and can be neglected in the first approximation. Also, the second-order quartic terms (contribution from five times excited states) are small, at most 8 cm^{-1} for the highest 15th mode, if compared to total anharmonicity (189 cm^{-1} for 15).

In Table 5 the spectroscopic parameters are compared to experiment and to the harmonic limit. On the current level of calculations, we consider the harmonic results superior, since the spectroscopic parameters are much more basis set dependent—especially the rotational strength, explicitly dependent on the gradient of the electronic wave function.[18] But most of the qualitative effects of anharmonicities on spectra can be observed.

As expected, the lower energy modes (1–11) are least affected by anharmonicities; nevertheless, significant contributions appear for the dipole strengths of the 6th and 11th modes, decreased by more than 30%. The decrease is caused mainly by the anharmonicity of energy, as can be judged from the values of $|c_{ii}|^2$ for states 6 and 11 and for the ground state. For the C–H and C–D stretchings (modes 12–15) a bigger influence of the second dipolar derivatives can be observed, as corresponding fundamental vibrational states are more mixed with combinatorial states. For the 15th mode the second derivatives of electric dipole are responsible for an increase of dipolar strength by 36% (42 → 57 10^{43} esu^2 cm^2) and can explain the difference between the experimental and harmonic (D_s) values. Also, the positive bias in the VCD couplet of C–H stretchings, not given by the harmonic limit, is predicted correctly. On the other hand, calculated negative bias of C–D VCD couplet (modes 12 and 13) is unrealistic.

Mainly due to the cubic correction to the harmonic potential, equilibrium positions of atoms may not coincide with the minima of potential energy. The deviation of a nucleus λ is for the molecular ground state equal to $\Delta x^\lambda_\alpha = \sum_i S^\lambda_{\alpha,i}\langle G|Q_i|G\rangle$ and can be easily calculated when the vibrational wave function is available. Changes in bond lengths for the dideuteriooxirane are given in Table 6. Clearly, the anharmonic correction must be included, if the *ab initio* optimized geometry should be compared to experimental results. The anharmonic bond lengths are about 0.3% longer than harmonic, both for bonded hydrogen and bonds between heavy atoms.

In Table 7, the biggest quartic and cubic force constants are listed. Cubic constants can be apparently reliably estimated already at the HF/4-31G level of calculation. Generally, the

TABLE 7: Biggest Cubic and Quartic Force Constants for *trans*-2,3-Dideuteriooxirane, in Dimensionless Normal-Mode Coordinates[a]

	c_{ijk} (cm^{-1})		
i j k	4-31G	6-31G**	6-311G**
12 12 13	−904	−875	−857
13 13 13	−902	−870	−852
14 14 14	−1460	−1413	−1383
14 15 15	−1451	−1404	−1375

	d_{iijj} (cm^{-1})		
i j	4-31G/O1	4-31G/O2	6-311G**
8 14	−245	−255	−258
8 15	−244	−253	−256
12 12	289	279	277
12 13	286	276	273
13 13	283	273	270
14 14	556	569	531
14 15	553	566	529
15 15	552	563	528

[a] The 4-31G results for two molecular orientation, same as in Table 4.

bigger the value of a force constant, the better is the relative accuracy of the calculated value. This approximate "rule" was observed to take place for both cubic and quartic constants, actually also for diagonal and off-diagonal harmonic force constants. For quartics there is a limit of accuracy given by the coordinate system dependence, about 4% for the highest values listed in Table 7.

If the error of harmonic force field competes with the magnitude of further corrections, only limited predictions can be made. As suggested earlier,[7] even the MP2[21] correction may not be sufficient, because of the unbalanced contribution to the derivatives of correlation energy. In most cases, the MP2 method will be probably the first and easiest improvement of SCF methods, shifting the harmonic frequencies by the order of tens of cm^{-1}. If the harmonic term dominates in the molecular Hamiltonian, the influence of cubic and quartic terms may be treated as a perturbation and the energy derivatives can be estimated on a lower level. On average, the HF limit seems to slightly overestimate the anharmonic terms, while the MP2 electron density properties appear smoother than predicted by the SCF theories. Similarly, harmonic frequencies are usually known to be overestimated within the Hartree–Fock limit.

The possibility of neglecting the Cartesian quartic coefficients $d_{\alpha\beta\gamma\delta}$ (no two indices are equal) reminds one of the CNDO model, where two-center integrals are neglected. Since indices with $\alpha \neq \beta \neq \gamma \neq \delta$ must be related to at least two nuclei, it may be expected that they will be less significant than the mononuclear terms.

Scaling of harmonic force field[2,7] should be mentioned here, since it is often used as a tool to cope with anharmonicities. It is justified if it should help to assign experimental frequencies to specific vibrational modes. If it is used to determine the force constants, there is a limit of accuracy because of the anharmonic contribution. Especially the higher frequency modes (C═O, C–D, C–H, N–H stretches) can be coupled to many vibrational states, as the state density grows with the energy. The second-order perturbation term is usually most significant (eq 1) and its sign is determined by the energy difference $\Delta E_{in} = E_i - E_n$. The number of states $|n\rangle$ of higher energy than state $|i\rangle$ is bigger than that of lower states, and thus on average resultant frequencies are lower than the harmonic limits.

Finally, more complete information about the molecular potential energy surface can be obtained, combining the analysis of experimental data with the means of scaling of theoretical force fields and *ab initio* evaluations of the anharmonic terms.

Conclusions

The method described here enables one to calculate second-order anharmonic corrections to vibrational energies of molecules. Fermi resonances with monoexcited vibrational states can be consistently treated when the perturbational and variational calculations are combined. The expression of cubic and quartic force constants in Cartesian coordinates enables a flexible combination of the anharmonic corrections with the harmonic results obtained at a different level of approximation. Also, an isotopic substitution and scaling of the harmonic force field can be made independently on the calculation of anharmonic constants. The infrared absorption and CD spectra can be simulated, including the anharmonic corrections of energies and the contributions of second electric and magnetic dipole derivatives to spectral intensities. Corrections to equilibrium geometries can be obtained.

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