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Transferability of anharmonic force fields in simulations of molecular vibrations

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Accurate simulations of vibrational molecular spectra require precise molecular force fields, at least with cubic and quartic anharmonic corrections beyond the harmonic limits. Generation of such force field terms becomes computationally prohibitive for larger molecules. In this work, an alternate possibility is explored, where approximate anharmonic force field components are obtained from molecular fragments. Transferability properties of the cubic and incomplete quartic fields are discussed and tested on model oligoproline molecules. Automatic transfer schemes including cubic, two and three atomic quartic force constants are developed and implemented. The results indicate that the main vibrational interactions in molecules are local and the anharmonic constants are mostly well amendable to the transfer. Exact anharmonic normal mode force fields of larger molecules compared very well to those obtained from smaller molecular parts. The most important changes in vibrational spectra caused by the anharmonic interactions could be reproduced with two and three atomic force field terms. The transfer scheme thus provides molecular anharmonic force fields without a significant loss of accuracy and brings significant savings of computer time and memory needed to generate molecular vibrational energies and spectra. © *2010 American Institute of Physics*. [doi:10.1063/1.3464759]

I. INTRODUCTION

Studies of molecular structure and dynamics by the vibrational spectroscopy have been significantly enhanced by the possibility to accurately simulate spectral frequencies, intensities, and actual band shapes. For example, combination of the computations with polarized spectroscopic experiments, such as vibrational circular dichroism[1] or Raman optical activity,[2] revealed details about conformations of peptide[3] or nucleic acid[4] strands. Accurate conformational equilibria were obtained from comparison of the calculated and experimental spectra for small molecules.[5] *Ab initio* wave function and density functional methods[6] established as the most versatile tools for spectral simulations, as they require minimum of *ad hoc* input parameters and, at least in principle, provide exact results. Usually, the harmonic approximation is used to approximate molecular nuclear potential;[7] therefore, second energy derivatives (Hessian) have to be computed. Contemporary quantum-chemical software packages provide efficient ways for the Hessian generation, such as the analytical coupled-perturbed computational schemes.[8]

Even for larger molecules, accurate vibrational energies and spectral profiles can be obtained utilizing a short-range (springlike) character of the most important interatomic interactions.[9] In such cases molecular Hessians can be gained from smaller molecular fragments. The spectral intensity parameters are transferable even more easily as they are functions of one atom only.[10] The Cartesian coordinate transfer (CCT) procedure[10,11] respects the local character of the vibrations (unlike approaches based on the normal mode treatment)[12] and is prone to easy computer implementation (unlike internal coordinate-based schemes).[13] Alternatively, internal coordinate force constants[13] or scaling factors of computed force fields[14] can be transferred.

With the increasing precision of the quantum-chemical methods the harmonic limit, however, becomes a bottleneck in many application, such as vibrational averaging of optical rotatory dispersion,[15] nuclear magnetic resonance parameters,[16] or infrared and Raman spectroscopies.[17] The harmonic limit can be overcome by various computational schemes including vibrational configuration interaction (VCI)[18] based on the harmonic oscillator wave functions, vibrational self-consistent field (VSCF),[19,20] many-body perturbation theory (PT),[21] which can also be partially adapted for degenerate states,[22] contact transformation,[23] and vibrational coupled-cluster calculus.[24]

Another restriction in calculations of vibrational spectra of molecules, which is not addressed in the present study, is the accurate representation of the molecular potential energy surface. Nevertheless, it is important to realize that the accuracy of the electronic and vibrational computations should be comparable. Modern quantum chemical methods provide means for simulations of the nuclear potential for small molecules quite far from the equilibrium, which enables reliable

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estimation of highly excited vibrational states.[25] For such cases, the limited Taylor expansion of the potential used below is not adequate.

The partial corrections of the harmonic force field, nevertheless, even when calculated with a limited precision, can still significantly improve the harmonic vibrational transition frequencies for larger molecules, often by several hundreds of cm^{-1}.[26,27] The additional cubic and quartic terms needed for this approach can be obtained relatively easily by a numerical differentiation of harmonic force fields.[28] Analytical implementations[29] are still relatively rare. In any case, as the number of the constants and required computational time grow sharply with the number of atoms, their direct computations become unreasonable for sizable systems. Thus the CCT techniques,[10] where the anharmonic force field parameters are estimated in smaller molecular fragments and transferred onto a target system, appear as a more efficient alternative, also allowing one to explore the locality of vibrational interactions. As a result, a much smaller number of constants needs to be calculated on a higher level of approximation than by the direct methods. Our results shown below confirm that the force fields thus obtained do provide significant improvements of the vibrational spectra of sizable molecules if compared with the harmonic limit, with accuracy comparable to full *ab initio* computations.

II. THEORY

A. The vibrational model

We restrict ourselves to a model nuclear potential V expanded to Taylor series[7] up to fourth powers in dimensionless normal mode coordinates q_I,

$$V(q_1, \ldots ,q_M) = \frac{\hbar}{2}\sum_{I=1}^{M} \omega_I q_I^2 + \frac{1}{6}\sum_{I=1}^{M}\sum_{J=1}^{M}\sum_{K=1}^{M} C_{IJK}q_I q_J q_K + \frac{1}{24}\sum_{I=1}^{M}\sum_{J=1}^{M}\sum_{K=1}^{M}\sum_{L=1}^{M} D_{IJKL}q_I q_J q_K q_L, \tag{1}$$

where $M=3N-6$, N is number of atoms, and $\omega_I = f_{II}$ is the normal mode frequency. The dimensionless coordinates are related to the classical normal mode coordinates Q_I as $Q_I = \sqrt{\hbar/\omega_I}q_I$; $\hbar$ is the reduced Planck constant. The cubic ($\mathbf{C}$) and quartic ($\mathbf{D}$) normal mode force constants are calculated from the Cartesian ones ($\mathbf{c},\mathbf{d}$) by linear transformations, such as $C_{IJK}=\sum_{i=1}^{3N}\sum_{j=1}^{3N}\sum_{k=1}^{3N} c_{ijk}S_{iI}S_{jJ}S_{kK}$, where $\mathbf{S}$ is the Cartesian-normal mode transformation matrix.[7] For the purpose of this study, we take for granted that only semidiagonal normal mode quartic constants (D_{IIJK}, etc.) are needed for sufficiently accurate frequencies[28] as the one, two, and three mode interactions dominate the anharmonic coupling.[20,30] This restriction is computationally convenient; however, it is not essential, and does not affect the transfer and force field properties discussed further on. Note that for the dimensionless coordinates all normal mode force field constants have the same units of energy and can be expressed, for spectroscopic convenience, in cm^{-1}.

B. Transferability of the quartic constants

The Cartesian cubic force field constants were calculated numerically as

$$c_{ijk} = \frac{f_{jk}(x_i+\Delta) - f_{jk}(x_i-\Delta)}{2\Delta}, \tag{2}$$

where Δ is the differentiation step, $f_{jk}(x_i+\Delta)$ and $f_{jk}(x_i-\Delta)$ are the harmonic force field (FF) components at a geometry where the equilibrium i-coordinate is shifted by Δ and $-\Delta$, respectively. Note that for a molecule with N atoms ($3N$ Cartesian coordinates), $6N+1$ evaluations of harmonic FFs are needed. For the quartic part, only semidiagonal quartic constants (at least two indices are the same) can be obtained by such two-step differentiation,[22,31] according to the formula

$$d_{iijk} = \frac{f_{jk}(x_i+\Delta) + f_{jk}(x_i-\Delta) - 2f_{jk}(0)}{\Delta^2}. \tag{3}$$

However, the semidiagonal quartic constants are not suitable for the transfer including rotations, which are typically determined by an overlap between covalent bonds in the smaller and larger molecule.[10] Using explicit indices containing the atomic and coordinate symbols (e.g., $i \rightarrow \lambda\alpha$, $\lambda = 1, \ldots ,N$, $\alpha = x,y,z$), for the rotated, $\mathbf{d}'$, and old, $\mathbf{d}$, quartic constants we get

$$d'^{\lambda\mu\nu\omega}_{\alpha'\beta'\gamma'\delta'} = \sum_{\alpha}\sum_{\beta}\sum_{\gamma}\sum_{\delta} U_{\alpha'\alpha}U_{\beta'\beta'}U_{\gamma'\gamma}U_{\delta'\delta}d'^{\lambda\mu\nu\omega}_{\alpha\beta\gamma\delta}, \tag{4}$$

where $\mathbf{U}$ is the unitary 3×3 rotation matrix, the upper index (λ) denotes the atom, while the lower ones (α, β, γ, and δ) correspond to x, y, or z coordinates. Thus an incomplete semidiagonal $iijk$ set of force constants generally produces also off-diagonal $ijkl$ ones. Vice versa, to obtain exact semidiagonal rotated set, a complete quartic force field needs to be evaluated at the beginning. Such evaluation is computationally very demanding as, depending on the implementation, about $(6N)^2$ harmonic FF evaluations are needed for a complete Cartesian quartic field calculated, for example, using

$$d_{ijkl} = \frac{f_{kl}(x_i+\Delta,x_j+\Delta) - f_{kl}(x_i+\Delta,x_j-\Delta) - f_{kl}(x_i-\Delta,x_j+\Delta) + f_{kl}(x_i-\Delta,x_j-\Delta)}{(2\Delta)^2}. \tag{5}$$

In addition, vibrational energies computed with the incomplete $iijk$ part are dependent on molecular orientation, which is even less acceptable than their lengthy evaluation. To avoid the orientation dependence while conserving the computational time linearly proportional to the number of atoms, off-diagonal quartic force field could also be obtained directly by Eq. (3), but using the normal mode coordinates. However, this procedure would prevent to exploit the locality.

Therefore, in this work, we utilize the observation that the most important quartic corrections stem from one, two, and three atomic interactions. Since only three different spatial coordinates are possible, quartic constants $d^{\lambda\lambda\lambda\lambda}_{\alpha\beta\gamma\delta}$ associated with one atom only are always semidiagonal and can easily be obtained, for example, by Eq. (3). Two ($d^{\lambda\lambda\mu\mu}_{\alpha\beta\gamma\delta}$ and $d^{\lambda\mu\mu\mu}_{\alpha\beta\gamma\delta}$) and three ($d^{\lambda\lambda\mu\nu}_{\alpha\beta\gamma\delta}$) atom constants that are not semidiagonal any more and can be obtained, for example, by the formula analogous to Eq. (5),

$$d^{\lambda\lambda\mu\nu}_{\alpha\beta\gamma\delta}=\frac{f^{\mu\nu}_{\gamma\delta}(x_{\lambda\alpha}+\Delta,x_{\lambda\beta}+\Delta)-f^{\mu\nu}_{\gamma\delta}(x_{\lambda\alpha}+\Delta,x_{\lambda\beta}-\Delta)-f^{\mu\nu}_{\gamma\delta}(x_{\lambda\alpha}-\Delta,x_{\lambda\beta}+\Delta)+f^{\mu\nu}_{\gamma\delta}(x_{\lambda\alpha}-\Delta,x_{\lambda\beta}-\Delta)}{(2\Delta)^2}. \tag{6}$$

Indeed, this evaluation only requires about $36N$ computations of harmonic FFs only, depending on computational details, such as exploration of the symmetry of the indices. The computational time is thus linearly dependent on the number of atoms so that it does not represent excessive computational burden in comparison with the cubic force field evaluation. Additionally, normal mode force field thus obtained is not dependent on the molecular orientation any more.

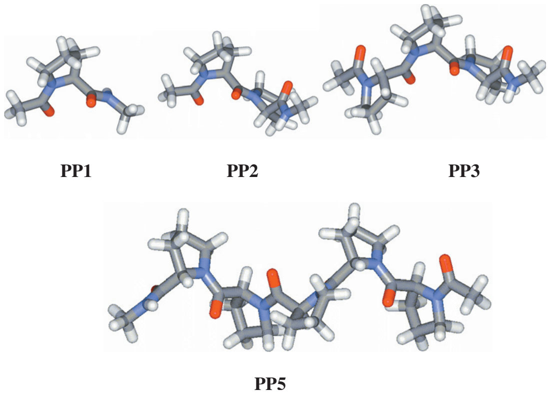
III. COMPUTATIONS

Oligoproline molecules containing one to five proline residues (PP1, PP2, PP3, and PP5, i.e., with two to six amide groups) were chosen as model systems (Fig. 1). The hydrophilic amide and hydrophobic proline parts well represent typical biological molecules of spectroscopic interest; the polyproline II conformation of the peptide main chain can often be encountered with other amino acid sequences and constitutes a large part of the so called random coil peptide structures.[32,33]

Starting geometries were generated by the MCM95 (Ref. 34) graphical software. The conformation of the main polyproline chain was kept fixed by restraints to the main chain torsion angles ($\omega=180°$, $\varphi=-75°$, and $\psi=147°$) so that it corresponded to the most frequent polyproline II conformation.[35] All other coordinates including the five-membered proline ring puckering[32,36] were relaxed. *Ab initio* geometry optimizations with these constraints and corresponding harmonic force fields were performed with the GAUSSIAN suite of programs.[37] By default, the HF/6-31G method was used for the electronic computations. This level of approximation is obviously too crude to provide very accurate results, but it is efficient and provides us with realistic anharmonic force fields of sizable molecules. For PP3, complete cubic and semidiagonal quartic force fields were also obtained with the 6-31G* basis, and a limited number of (26 244 cubic and 26 244 quartic) constants was calculated with the 6-31G, 6-31G*, 6-311G**, and 6-311++G** basis sets. The 6-311G(d,p) basis was additionally used to calculate some normal mode constants of PP2. The larger basis set calculations, however, did not lead to any qualitative change of the anharmonic constants behavior, e.g., their locality, and are therefore not discussed in detail.

For PP3, the harmonic force field was also calculated at the B3LYP (Ref. 38)/6-311++G**/CPCM (Ref. 39) (H_2O) level, as specified below, for the sake of comparison with experiment. With the PMZ and S4 programs[26,40] we generated the input geometries for the displaced coordinates and calculated the cubic and quartic constants and anharmonic vibrational frequencies. Cartesian displacements of 0.025 Å were used for all the numerical differentiations; similarly, the normal mode differentiation step corresponded approximately to 0.025–0.050 Å Cartesian displacements. VSCF, second order perturbation (PT2), and a control VCI (not shown) computations were performed as described in detail elsewhere.[17,22,26,40] The PT2 computations for PP5 and PP3 were performed with the degeneracy correction[22] and cubic and quartic normal mode constants bigger than 100 cm^{-1} (in dimensionless normal mode coordinates)[7] only. This restriction produced, respectively, 169 477 and 98 622 harmonic oscillator states that were used for corrected energies of the ground and fundamental vibrational states. Statistical analyses of the anharmonic force fields were performed within the MYSQL database server environment.[41]

To test the transfer properties, shorter peptides


PP1 PP2 PP3

PP5

FIG. 1. Model molecules: N-methylacetylproline (PP1), proline dimer (PP2), trimer (PP3), and pentamer (PP5).

TABLE I. Average and maximum error of fundamental VSCF frequencies in PP3 as a function of the distance cutoff in the anharmonic vibrational potential.

Cutoff (Å)	$\lvert\Delta\rvert_{\mathrm{avg}}$ (cm^{-1})	$\lvert\Delta\rvert_{\mathrm{max}}$ (cm^{-1})
5	0.50	7.23
7	0.22	6.77
9	0.07	1.85
11	0.02	0.34
13	0.01	0.17

("fragments") were created from the longer ones. For example, two PP2 structures were obtained from PP3, so that the middle proline residue was conserved in both fragments. The fragments were optimized by an energy minimization in the normal mode coordinates,[42] with fixed modes within the i300(imaginary), … ,300 cm^{-1} interval of wavenumbers. This procedure ensured for a complete relaxation of the higher-frequency modes, most important for the vibrational spectroscopy, under a minimal change of geometry. Then the Cartesian cubic, two and three atomic quartic [cf. Eq. (6)] force constants were calculated by the GAUSSIAN, PMZ, and S4 programs, and transferred to the large peptide by the CCT[43] software. The transfer was based on a local overlap of atoms and bonds in the shorter and larger fragment.[10]

IV. RESULTS AND DISCUSSION

A. Locality of the vibrational interactions

It is well known that short-distance springlike bonding interactions are responsible for the primary vibrational properties of molecules,[9] whereas electrostatic forces, such as the dipolar coupling,[44] and other factors contribute much less. This can be documented for PP3 in Table I, where the average and maximum error of fundamental VSCF frequencies is listed as a function of the distance cutoff=$\max(r_{ij}, r_{ik}, \ldots)$, where r_{ij}, etc., are distances between atoms contained in the force constants, used for both Cartesian cubic and quartic constants. Already for the cutoff of 5 Å the average frequency error is smaller than 1 cm^{-1} so that the vibrational frequencies of most modes are reproduced within the usual experimental accuracy achieved for peptides in solutions.[1,11,17] The maximal error, however, is still quite large (7.23 cm^{-1} for 5 Å), mostly due to the delocalized lower-frequency modes. Also this error becomes smaller than 1 cm^{-1} for the cutoff distances bigger than 10 Å. The cubic and quartic interactions in molecules thus vanish for larger separations similarly as the harmonic ones.[9,45]

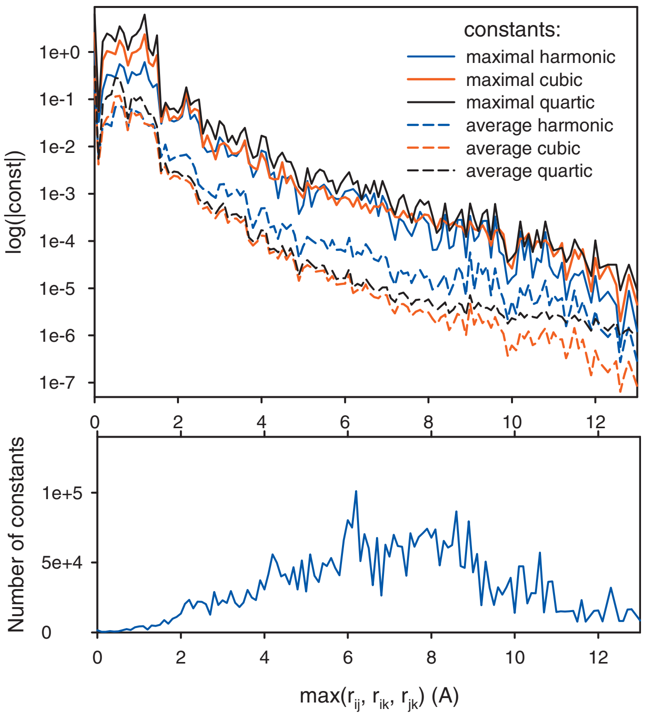


FIG. 2. Calculated dependence of PP3 Cartesian harmonic (f_{ij}), cubic (c_{ijk}), and quartic (d_{iijk}) constants (logarithmic scale for constants in atomic units) on the maximum atomic distances (top), and distribution of the cubic and $iijk$ quartic constants (number per 1 Å distance interval, bottom).

The distance dependence can also be illustrated in Fig. 2, where the average and maximal harmonic, cubic, and quartic Cartesian constants in PP3 as dependent on the largest interatomic distance are plotted. A very similar graph was obtained for PP5 and is not shown. Similarly, the trial basis set variations (6-31G, 6-31G*, 6-311G**, and 6-311++G**) for PP3 did not change the basic behavior of the constants. From Fig. 2, we see that with some variations all the force field constants rapidly faint at large distances. As may be expected, the constants of atoms connected by chemical bonds [approximately for $\max(r) < 1.5$ Å] are by an order of magnitude larger than the more distant ones. The distribution of the cubic and semidiagonal quartic constants in this molecule (bottom panel at Fig. 2) brings us to the conclusion that their overwhelming majority is quite small. As the smallest constants ($\sim < 10^{-5}$) are severely affected by the accuracy of the calculated Hessians and the numerical differentiation, we found it important to use the same hardware and software (operation system, etc.) in order to reproduce them accurately. Although occasional errors can be easily identified, e.g., by a check of invariance under index permutations, all the presented results were obtained in a consistent way to ensure maximum accuracy, even though the effect on calculated molecular vibrational frequencies is quite negligible (cf. Table I).

B. Dependence of the force constants on the number of involved atoms

The harmonic, cubic, and quartic constants connect up to two, three, and four atoms, respectively. Their magnitude decreases with the increasing atom number, which has favorable consequences for the transfer and efficient calculation of vibrational energies. The dependence can be documented for the PP5 peptide in Table II, where the average and maximal harmonic and anharmonic force constants are sorted according to the number of connected atoms. The average two atomic constants are much smaller than the monatomic ones. However, the maximal two and monatomic constants are about the same. The three atomic maximal cubic and quartic constants are, respectively, 52 and 100 times smaller than the two atomic ones. The number of the involved atoms thus

TABLE II. Dependence of the average and maximal harmonic (f), cubic (c), and quartic (d) force constants on the number of involved atoms (in atomic units, for the PP5 molecule, calculated with HF/6-31G).

No. of atoms	$\langle\lvert f\rvert\rangle$	$\lvert f\rvert_{\max}$	$\langle\lvert c\rvert\rangle$	$\lvert c\rvert_{\max}$	$\langle\lvert d\rvert\rangle$	$\lvert d\rvert_{\max}$
1	0.222 36	1.049	0.276 48	2.718	0.490 36	7.023
2	0.003 15	0.664	0.004 84	2.547	0.009 56	6.854
3	⋯	⋯	0.000 03	0.049	0.000 05	0.068

seems to be a much more important parameter in the vibrational interactions than a particular (quadratic, cubic, and quartic) form of the vibrational potential.

As expected, the four atomic quartic constants that could be evaluated for the smaller PP1 molecule only are smaller than all the other ones (Table III). The maximal four atomic constant (0.029, cf. Table III) is, however, only about three times smaller than the three atomic constant (0.085), which contrasts with the two/three atomic constant ratio of 84 (=7.15/0.085). A closer inspection reveals that the relatively high values of the four atomic constants are adopted exclusively in the vicinity of the carbonyl (C═O) moiety. The out of plane carbonyl carbon motion, similarly as the out of plane amide nitrogen deviation,[46] is strongly anharmonic, and, because of the planar symmetry, the quartic interaction is most probably the next most important term after the harmonic part. The out of plane deviations of atoms connected in aromatic or π-electron conjugated planar systems are in general associated with strongly anharmonic potentials.[26,46,47] Nevertheless, even in the amide moiety, the four atomic term is much smaller than the two atomic one and supposedly has a minor effect on the vibrational properties. Indeed, the average four atomic constant is eight times smaller than the three atomic, and 63 times smaller that of the two atomic average.

TABLE III. Complete HF/6-31G quartic FF of PP1, dependence of average and maximum constants (in atomic units) on the number of involved atoms.

Number of involved atoms	No. of constants	$\langle\lvert d\rvert\rangle$	$\lvert d\rvert_{\max}$
1	390	0.559 99	7.345
2, *iiij* type	19 500	0.029 61	7.218
2, *iijj* type	152 100	0.002 50	7.149
3	280 800	0.000 32	0.085
4	1 210 950	0.000 04	0.029

TABLE IV. Selected PP1 normal mode quartic constants D_{IIJK} (cm^{-1}) calculated with (complete) Cartesian quartic force field including one, two and three atomic constants.

IIJK	One at.	Two at.	Three at.	Exact
6 6 6 6	−432	34	83	92
6 6 6 8	−146	−22	−31	−33
22 22 51 62	34	49	48	49
24 24 24 24	−17	29	30	33
42 42 61 61	−116	−192	−192	−190
56 56 72 72	−184	−333	−334	−333
58 58 58 58	19	103	102	101
59 59 59 59	645	845	846	847
59 59 59 64	151	235	237	239
72 72 72 70	−13	−18	−18	−18
72 72 72 72	1014	1357	1357	1361

In Table IV we can follow the significance of the one, two, three and four atomic Cartesian quartic constants for selected normal mode constants. Larger constants were selected to separate the influence of the number of involved atoms from a numerical error (~1 cm^{-1}). Complete Cartesian field, with no cutoffs, was used. For the low-energy and rather delocalized modes (6 and 8) the polyatomic interactions are more important. For most of other modes, the two atomic constants already yield the normal mode constants with a reasonable accuracy. For example, the two atomic $D_{24\ 24\ 24\ 24}$ constant (29 cm^{-1}, Table IV) is only partially improved (to 30 cm^{-1}, the exact value is 33 cm^{-1}) by the three atomic calculation. For the highest-frequency C═O stretching (number 58) and C—H and N—H stretching (59–72) modes the two and three atomic constants are almost identical, and the minor differences from the exact values can be attributed to the limited numerical accuracy. Note also that for the hydrogen vibrations (modes 59 and 72) even the monatomic Cartesian quartic constants generate most of the normal mode quartic forces. The behavior of the diagonal constants is similar as that of those having different indices.

In Fig. 3, resultant PT2 anharmonic energies of PP1 ground state and transition energies of selected modes are plotted as calculated with the one, two, three, and four atomic quartic constants. The three atomic constants appear sufficient to reasonably reproduce most of the anharmonic corrections. Interestingly, for the C—H stretching motion (modes 68–71 in Fig. 3), the anharmonic part is dominated by the cubic potential, while for the N—H stretching the cubic contribution (red bars in Fig. 3) is negligible. In accord with the discussion to Table IV above, the one atomic constants are insufficient for the lowest-energy modes (1–5, Fig. 3), whereas they reasonably well represent the quartic energy perturbation for all the hydrogen stretching motions. The ground-state anharmonic vibrational energy correction (~800 cm^{-1}=2.2 kcal/mol) is relatively minor in comparison with the total zero-point vibrational energy (ZPE) of ~150 kcal/mol; nevertheless, it may be important, for example, for accurate conformational studies. We can see that the anharmonic part of ZPE in PP1 is composed approximately to the same extent by both the cubic and quartic contributions.

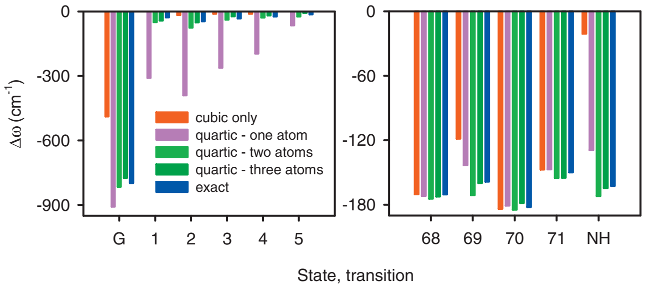


FIG. 3. Anharmonic corrections to the PP1 energy of the ground state and five lowest and five highest-energy transition energies, calculated with the PT2 method without the quartic contribution, and with one, two, three, and four atomic Cartesian quartic constants.

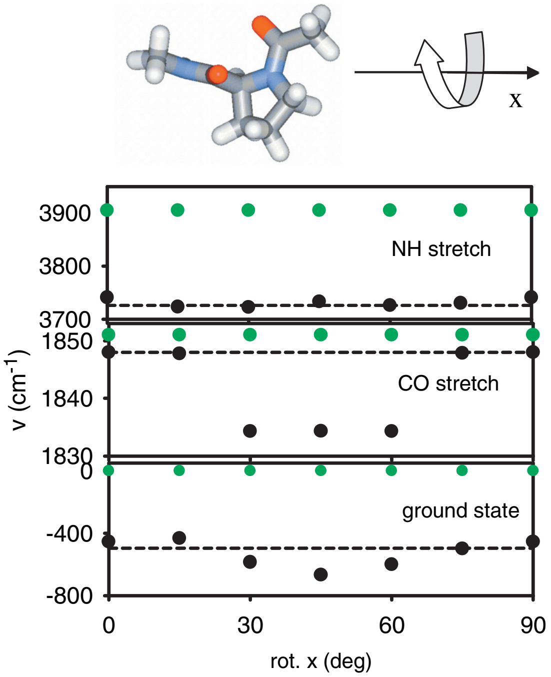


FIG. 4. The dependence of selected PP1 frequencies on molecular orientation: (green circles) harmonic and (black circles) PT2 anharmonic frequencies calculated with the incomplete quartic force field. The accurate anharmonic limit is marked by the dashed lines.

C. The orientation dependence of the incomplete quartic force field

The extent to which the molecular frequencies are influenced by the incomplete semidiagonal Cartesian quartic force field (*iijk*) can be seen in Fig. 4, where the PP1 ground state energy, and C═O and N═H stretching frequencies are plotted as a function of an angle corresponding to the rotation of the molecule around a fixed spatial direction. The transition frequencies vary within an interval of up to ~70 cm^{-1}, the ground state energy changes even by more than 200 cm^{-1} depending on the molecular orientation. In particular, the anharmonic downshift for the C═O stretching mode is significantly overestimated for some molecular orientations (rotations within 30°–60°). Thus although the semidiagonal constants can be obtained relatively easily [cf. Eq. (3)], the error associated with their usage is in general unacceptable. For rough estimations, they can be perhaps used for computational convenience to calculate the magnitude of the hydrogen stretching quartic anharmonic corrections, since these are large (~170 cm^{-1}, Fig. 4) and dominated by the monatomic constants (Fig. 3) that are always semidiagonal, and thus independent on molecular orientation.

This can be also seen in Fig. 5. For two PP1 orientations (corresponding to the X-rotation by 0° and 45°, see Fig. 4) diagonal and *IIJK* semidiagonal normal mode constants were computed from the semidiagonal Cartesian quartic force field and compared to the exact results. The constants corresponding to the higher-frequency modes (green) are indeed reproduced reasonably well, while the approximation is quite unreasonable for the lowest-frequency delocalized modes (black circles). Medium frequency mode constants (300–1800 cm^{-1}, red circles in Fig. 5) are rather small, but some of them are also very dependent on the orientation if calculated from the incomplete force field. Thus the dependence of the incomplete quartic force field on molecular rotation reveals interesting information about locality and transferability of the anharmonic properties.

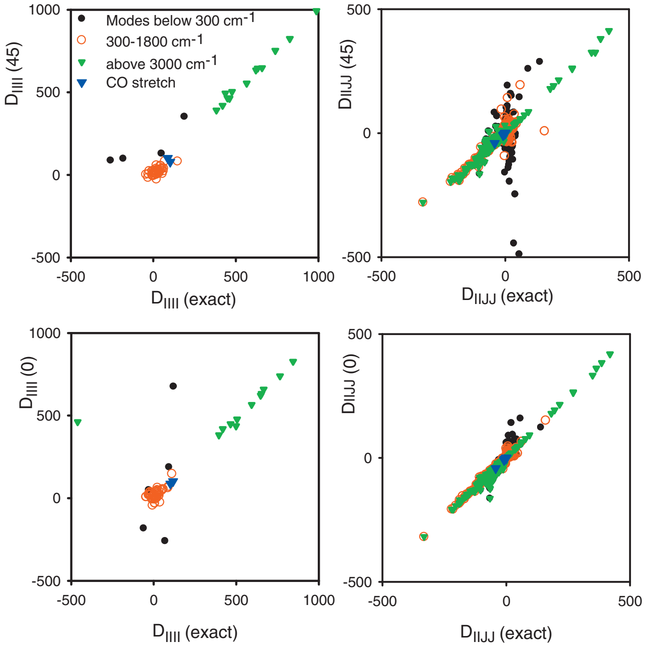


FIG. 5. Diagonal (left) and semidiagonal (right) normal mode quartic constants of PP1 calculated for 45° (top) and 0° (bottom) orientations from the incomplete (d_{iijk}) Cartesian quartic force field, plotted against the exact values.

D. The transfer of anharmonic force fields

The accuracy with which the transferred anharmonic force field from the PP1 fragment can reproduce the exact quartic constants of the larger PP2 molecule can be seen in Fig. 6, where the exact normal mode diagonal quartic force constants are compared to those obtained from two PP1 fragments. For most normal modes the force field obtained by the transfer reasonably well approximates the exact values. On average, as expected, the three atomic Cartesian quartic constants give better agreement than the two atomic ones, although the difference is quite minor [cf. the correlation coefficients (cc's) in Fig. 6]. The largest constants usually associated with the hydrogen-stretching motion (note the logarithmic scale in Fig. 6) are reproduced most accurately.

The diagonal quartic constants for modes 6, 9, 82, 113, and 114 of PP2 are compared separately as calculated in the 6-31G and 6-311G(d,p) basis sets in Fig. 7. The basis set variation does not affect general trends, e.g., the two atomic transfers are slightly less accurate or equivalent to the case when the three atomic constants are used, and the C—H stretching modes (113, 114) are almost independent on the three atomic interactions. Larger variation is exhibited by the smallest constants, of modes 9 and 82. Note, however, that the basis set dependence may also reflect small geometrical changes during the partial normal mode optimization procedure.

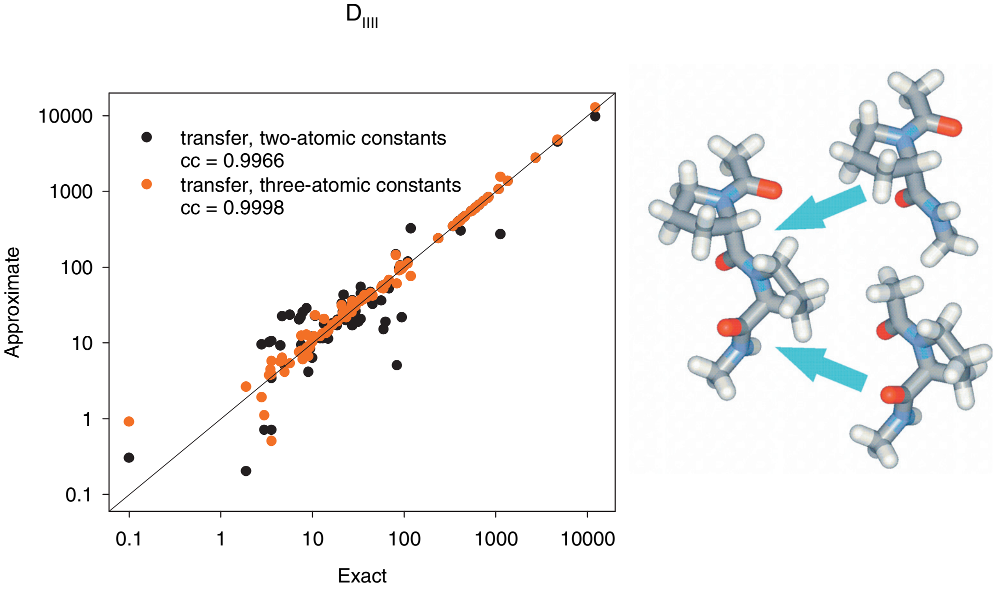


FIG. 6. Comparison of exact diagonal quartic normal mode constants in PP2 calculated at the HF/6-31G level with those obtained by the transfer from the two smaller (PP1) molecules, using the complete two (black circles) and three atomic (red circles) Cartesian quartic force field. cc's for the two and three atomic constants are listed in the graph; respective correlation coefficients for the logarithmic values ($\log|D_{IIII}|$) are 0.947 and 0.985, root mean square deviations are 277 and 66 cm^{-1}.

Similarly as for PP2, the PP5 cubic and quartic force field was constructed from four larger PP2 fragments containing two proline side chain residues. The harmonic force field was not transferred. Unlike for PP2 (Fig. 6) the PP5 fragmentation with overlapping segments minimized the end effects and provided cubic and three atomic quartic force constants much closer to the exact values (correlation coefficients of 0.9995 and 0.9998, respectively, Fig. 8). Results with the two atomic quartic constants were almost the same (with cc=0.9997) as for the three atomics, and are not shown. Alternate correlation coefficients for the logarithms of the constants (listed in captions of Figs. 6 and 8) are lower than the ordinary ones, which reflect the fact that large constants are calculated with smaller relative error.

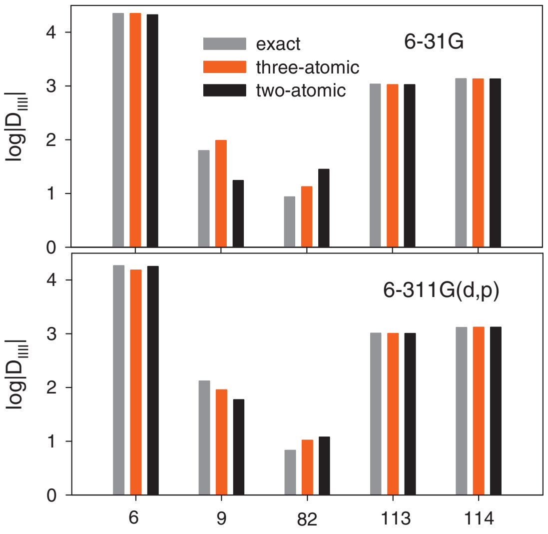


FIG. 7. Selected diagonal quartic normal mode constants in PP2 for the transfer described in Fig. 6 as calculated at the HF level with the 6-31G and 6-311G(d,p) basis sets.

The harmonic absorption spectra, and spectra obtained with exact and transferred cubic and quartic constants are plotted at the bottom of Fig. 8. The transfer does results in some deviations from the exact spectral curve. For example, the NH stretching band is calculated at 3729 and 3707 cm^{-1} with and without the transfer, and the absorption profiles of the CH stretching vibrations within 3000–3220 cm^{-1} are different. However, these differences are quite minor in comparison with the overall benefit achieved by adding of the anharmonic corrections to the harmonic spectrum. Even smaller differences in the two anharmonic approaches appear in the region of wavenumbers below 2000 cm^{-1}. For example, the amide II band calculated at the HF/6-31G harmonic level at 1721 cm^{-1} shifts to 1684 and 1687 cm^{-1} in the exact and transfer anharmonic scheme, respectively.

Finally, we present an application of the transfer technique where different electronic levels used in the harmonic and anharmonic force field calculations are combined. The PP3 molecule was optimized by the restrained ($i300,\ldots,300\ \mathrm{cm}^{-1}$) normal mode method, and the harmonic force field was obtained using the B3LYP/6-311++G** approximation and the CPCM solvent correction.[39] The HF/6-31G cubic and three atomic quartic force constants were transferred from two PP2 fragments. In Fig. 9 the resultant harmonic and anharmonic (PT2) Raman spectra are compared to experimental backscattered signal of L-Pro trimer and monomer in aqueous solutions. Experimental spectra of the PP3 model are not available to us; nevertheless, because of the weak dependence of the Raman signal on the length of the oligoproline chain,[48] the experimental and calculated frequencies of the main groups of vibrational transitions are supposedly well comparable.

From Fig. 9, it is clear that the anharmonic correction most significantly improves the higher-frequency region. The highest-frequency CH stretching band calculated at

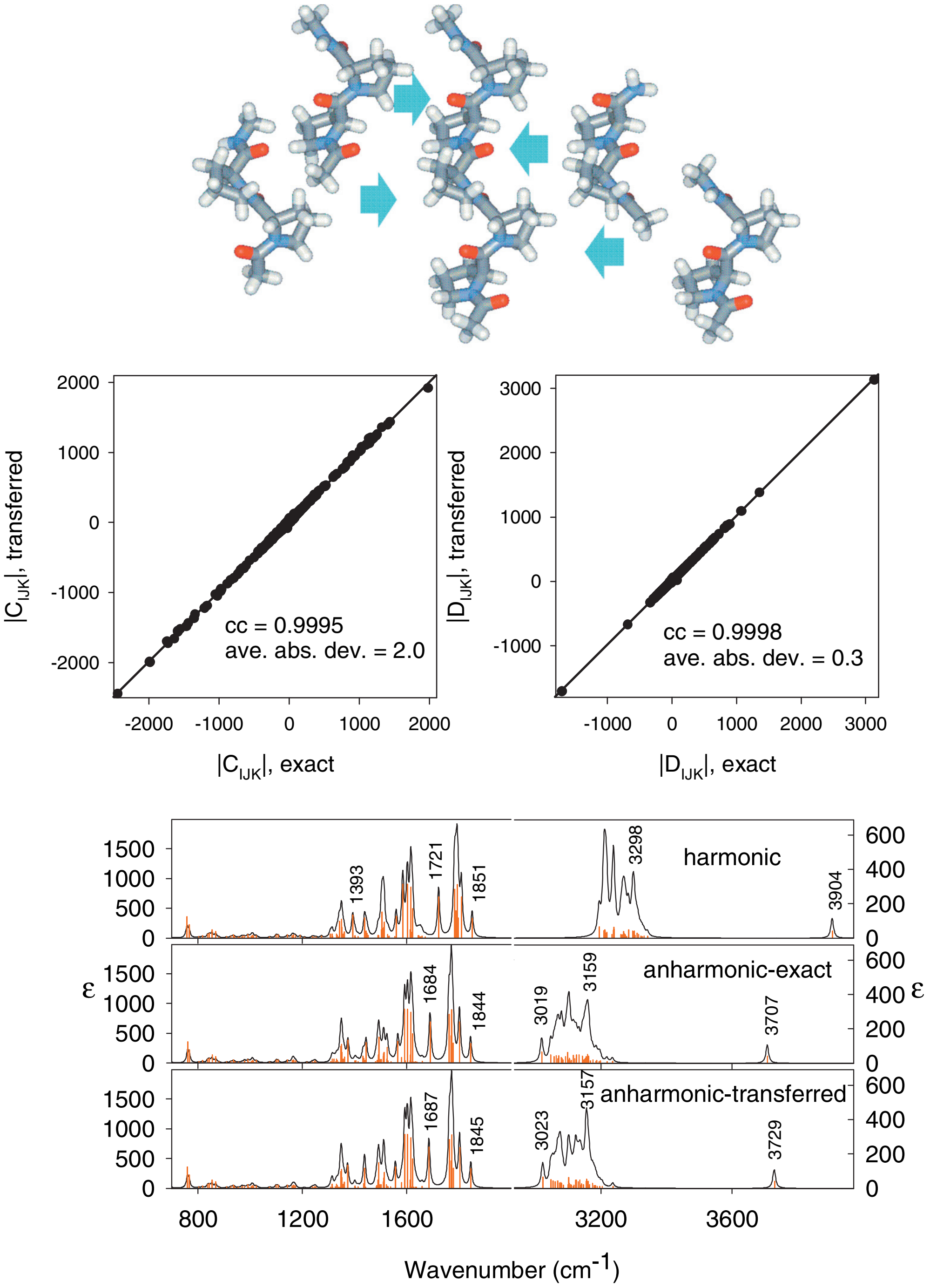


FIG. 8. Construction of PP5 anharmonic force field from four smaller PP2 fragments. Comparison of the largest exact and transferred cubic (C_{IJK}) and quartic (D_{IIJK}) normal mode constants (in the middle, with correlation coefficients and average absolute deviations; corresponding logarithmic correlation coefficients are 0.9989 and 0.9993) and resultant harmonic and anharmonic absorption spectra (bottom, obtained by PT2).

3116 cm^{-1} with the harmonic force field is downshifted to 2930 cm^{-1} with the correction, which is reasonably close to the experiment (2995 cm^{-1}). An analogous improvement can be observed for the NH stretching ($3623 \rightarrow 3489 \rightarrow 3420$ cm^{-1}). It is also interesting that the anharmonic forces improve the experimental profile even at relatively low frequencies: the intensity at 1266 cm^{-1} (harmonic) diminishes and shifts up (to 1282 cm^{-1} for the PT2 calculation), which better corresponds to the experimental signal at 1280 cm^{-1}. The results are consistent with a previous analysis of the N-methylacetamide force field[46] and confirm the possibility to combine the harmonic and anharmonic force field terms obtained at different approximation levels, at least for the higher-frequency vibrational motions. It should be noted that the intensity anharmonicity (second and higher dipole derivatives) were ignored in the current approach, which may account for some discrepancies with experiment.

V. CONCLUSIONS

The computations confirmed the possibility and a significant computational advantage of the transfer of cubic and

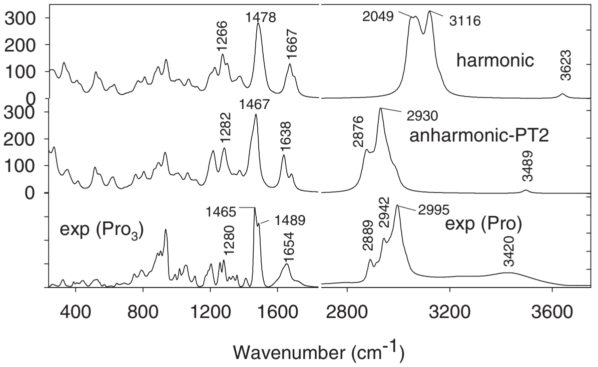


FIG. 9. (From top to bottom) Raman spectra of PP3 calculated at the harmonic approximation (B3LYP/6-311++G**/CPCM(H_2O), spectra obtained with the same harmonic force field and HF/6-31G anharmonic force constants transferred from PP2, and experimental spectra of proline trimer (Ref. 48) (240–1840 cm^{-1}) and monomer (Ref. 36) (2600–3700 cm^{-1}).

quartic anharmonic force fields to larger molecules. Both harmonic and anharmonic vibrational interactions between atoms quickly become weaker when more or distant atoms are involved. The orientation dependence of the incomplete Cartesian quartic force field could be overcome by the restriction to constants connecting two or three atoms. This limitation, however, did not significantly affect the accuracy of calculated vibrational energies. The quartic part of the potential can thus be calculated approximately with the same computational effort as the cubic one. In the presented implementation the cubic and quartic terms were obtained by numerical differentiation of harmonic force fields, so that computational times in both cases depended similarly on the molecular size. The results on the polyproline model systems suggest that the improvement of the anharmonic molecular force fields via the transfer can be particularly useful for vibrational spectroscopy of biopolymers. Spectroscopic accuracy of several cm^{-1} was achieved with the transferred anharmonic dimer force fields for the proline pentamer if compared to direct anharmonic calculation; the overall error (~60 cm^{-1}) was limited by the underlying electronic quantum-chemical calculation. Another convenience of the transfer algorithm could be documented on the combination of the harmonic and anharmonic trimer fields calculated at different levels, which provided better agreement of the calculated Raman spectrum with experiment if compared to the harmonic case.

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