Anharmonic mid–infrared vibrational spectra
of benzoic acid monomer and dimer

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Abstract

Anharmonic vibrational calculations for the benzoic acid monomer and dimer in the mid–IR regime ($500 \ldots 1800$ cm^{-1}) are reported. Harmonic frequencies and intensities are obtained at the DFT/B3LYP level of theory employing D95(d,p) and cc-pVTZ basis sets. Anharmonic corrections obtained from standard perturbation theory lead to red shifts of $1 \ldots 3$ %. In almost all cases, the resulting frequencies deviate by less than 1 % from previous measurements [J. Chem. Phys. **119**, 11180 (2003)]. Calculated intensities are in qualitative agreement with the absorption experiment, with the cc-pVTZ values being superior to the D95(d,p) ones for a few modes of the dimer. The antisymmetric out-of-plane bending mode of the dimer, which is strongly blue–shifted with respect to the monomer frequency, represents a remarkable exception: The harmonic frequencies obtained for the two basis sets differ notably from each other, and the anharmonically corrected frequencies deviate from the experimental value by 8 % (D95(d,p)) or 3 % (cc-pVTZ). Non-perturbative calculations in reduced dimensionality reveal that the relatively small total anharmonic shift (few tens of cm^{-1}) comprises of partly much larger contributions (few hundreds of cm^{-1}) which are mostly canceling each other. Many of the individual anharmonic couplings are beyond the validity of second order perturbation theory based on cubic and semi–diagonal quartic force constants only. This emphasizes the need for high–dimensional, non–perturbative anharmonic calculations at high quantum chemical level when accurate frequencies of H–atom vibrations in double hydrogen bonds is sought for.

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I. INTRODUCTION

Complexes dominated by hydrogen bonds play a central role in many fields of chemistry. In particular, double hydrogen bonds are of paramount importance in biochemistry because of their abundance in nucleic acid base pairs holding together the double stranded helices in DNA. Carboxylic acid dimers provide the simplest model systems to study doubly hydrogen bonded systems where the cyclic arrangement of these dimers gives rise to a symmetric double proton transfer mediated by concerted tunneling [1, 2, 3]. Vibrational spectroscopy of these complexes has proven especially useful in elucidating structure and dynamics of these complexes. In particular, there has been an increasing interest in gas phase vibrational spectroscopy of these aggregates in recent years. Due to the availability of double resonance spectroscopy (ion dip technique), the benzoic acid dimer has received considerable attention in recent years [4, 5, 6]. It is well known that the strongest effects of the intermolecular bonding can be found in the region of the OH stretching frequency (≥ 2500 cm^{-1}). In addition to a considerable frequency shift with respect to the monomeric vibration, very broad structures have been observed in the spectra of carboxylic acid dimers, extending over several hundreds of cm^{-1} [4, 7]. Similar features were also found for related dimers such as $CH_3NO_2^-\cdot H_2O$ and $CH_3CO_2^-\cdot H_2O$ [8]. However, also the mid—infrared (IR) spectrum (500–2500 cm^{-1}) is providing a wealth of information on strongly hydrogen bonded systems in the gas phase as has been demonstrated in spectroscopic studies of the protonated water dimer [9, 10] and dimers of ethers [11] or even nucleobases [12]. In a recent study of the benzoic acid monomer and dimer, an inspection of a larger portion of the mid–infrared spectrum has been carried out [6]. Also in that frequency regime, quite a few resonances of the dimer spectrum were found to be distinctly different from those of the monomer. The extreme case is the strong blue shift of the COH out-of-plane bending vibration from 571 cm^{-1} in the monomer to 962 cm^{-1} in the dimer which is essentially caused by an effective stiffening of the bending motion due to hydrogen bonding. Note that also in an argon matrix an almost identical value (960 cm^{-1}) was found [13].

With the availability of powerful computers and the advent of efficient density functional theory (DFT) methods implemented in standard codes, structure and dynamics of systems containing a few tens of atoms (or even more) are now within reach. Vibrational spectra of small molecules of biological or pharmaceutical relevance are routinely treated combing

DFT electronic structure calculations with a harmonic analysis [14]. Due to deficiencies of the quantum chemical calculations and/or due to the neglect of anharmonic effects, these frequencies are typically a few percent higher than the observed ones. However, using empirical scaling factors, satisfactory quantitative agreement with experimental vibrational spectra in the mid–IR regime can be achieved in many cases [15]. Nonetheless, pronounced discrepancies are occasionally found, e. g., for vibrational modes where the contributing atoms are directly involved in a hydrogen bond. For the case of the benzoic acid monomer and dimer to be studied here, the situation is as follows [6]: Employing DFT (B3LYP) calculations with a basis set of moderate size (D95(d,p)), almost all of the observed mid–IR vibrational frequencies can be reproduced within the harmonic approximation (using an empirical scaling factor of 98 %). However, the COH bending vibrations of the dimer exhibit a peculiarity. While the in-plane vibration can be reproduced by that approach very well, the theoretical value for the (antisymmetric) out-of-plane bending mode is 7 % higher than the observed one [6]. A similar situation was also found for the formic acid dimer [5]. The main goal of the present work is a quantitative explanation of this discrepancy. In particular, the question has to be answered whether this is due to insufficient quality of the quantum chemical treatment or due to the use of the harmonic approximation for the molecular vibrations (or both). At least for the case of the OH stretch spectra of carboxylic acid dimers, the importance of anharmonic effects has been demonstrated. Theoretical models involving strong anharmonic coupling to several other vibrational modes can qualitatively reproduce the unusual features of the measured spectra in the 3000 cm^{-1} region [4, 5]. Similarly, large anharmonic coupling constants were found in a far–infrared study of the acetic acid dimer as well [16]. However, these investigations already show the principle problem encountered in simulations of anharmonic vibrational spectra of medium–sized to large molecular systems. On the one hand there are highly developed, very precise methods based on variational calculus which are, however, essentially limited to few degrees of freedom only [17]. On the other hand, the standard perturbation based approach to anharmonic vibrations is computationally less demanding but its range of validity is not quite clear [18, 19, 20, 21, 22]. The recently developed vibrational self–consistent–field techniques [23] and its extensions [24, 25, 26] appear to provide a promising compromise.

In the present work we focus on a quantitative assessment of anharmonic effects on the COH out-of-plane vibrational frequency of benzoic acid. By comparison of monomer and

dimer vibrations we aim at shedding some light on the effect of the strong double hydrogen bond. For this purpose we calculate anharmonic vibrational frequencies following a mixed strategy. First, perturbative calculations are carried out in full dimensionality. Based on these results, we then concentrate on the most important anharmonic couplings which are treated in a non-perturbative manner but in reduced dimensionality. The remainder of the paper is organized as follows. Sec. II explains the methods used for the calculation of electronic structure and of harmonic and anharmonic vibrational frequencies. The results of perturbative and non–perturbative vibrational analysis of the benzoic acid monomer and dimer are discussed in Sec. III. Finally, our conclusions are presented in Sec. IV.

II.   METHODS

A.   Electronic structure calculations

Quantum chemical calculations were performed for the benzoic acid monomer and dimer within the framework of density functional theory (DFT) using Becke's three parameter Lee–Yang–Pair (B3LYP) functional [27], as implemented in the Gaussian software [28]. Both Dunning's D95(d,p) [29] and the correlation consistent cc-pVTZ basis set [30] were used comprising 174 or 354 basis functions for each of the benzoic acid moieties, respectively. Normal mode vibrational amplitudes, harmonic frequencies, and infrared intensities of molecular vibration were calculated based on an analytic evaluation of the Hessian matrix. For the monomer the geometry is planar (C_s symmetry); for the dimer a planar structure with cyclic arrangement of the hydrogen bonds (C_{2h} symmetry) was obtained. These structures were found to be global minima on their potential energy surfaces; no imaginary frequencies were found in the vibrational analysis.

While it would be desirable to check the accuracy of the density functional theory against high–level wave-function (WV) based electronic structure calculations, the numerical effort, especially for the benzoic acid dimer, is exceedingly high. However, for the closely related formic acid monomer and dimer a systematic study of optimized geometries and harmonic frequencies was conducted comparing DFT and WV based methods for several basis sets [5]. With the largest basis set considered there (aug-cc-pVTZ), B3LYP and MP2 calculations yield very good agreement for all vibrational modes of the formic acid monomer. While

the high frequency modes (CH, OH stretching) of the formic acid dimer differ by up to 5 %, the mid–IR vibrational modes were found to differ by less than 1 %. For example, the calculated harmonic frequencies for the out-of-plane COH bending mode are 995 cm^{-1} and 1002 cm^{-1} for the MP2 and B3LYP method, respectively [5]. Moreover, no tendency towards a reduction of the deviation from the experimental value of 917 cm^{-1} can be deduced for increasing basis set. Similarly, a discrepancy of 6 % was found for the COH bending wavenumber of the benzoic acid dimer employing a mixed basis set similar to the D95(d,p) basis used in this work, while larger basis sets were not considered in Ref. [5]. Hence, we conclude that for carboxylic acid dimer COH bending modes it is not immediately clear whether the quantum chemical method or anharmonic effects are mainly responsible for the mismatch between theory and experiment found in previous works [5, 6].

B. Perturbation theory

The standard approach to the calculation of anharmonic vibrational frequencies of a polyatomic molecule rests on an expansion of the potential energy hypersurface in terms of normal coordinates. The contribution of the anharmonic terms is then treated as a perturbation acting on the harmonic normal mode Hamiltonian. Vibrational energy levels characterized by a set of quantum numbers $\{n_i\}$ can be expressed as [18, 19, 20, 21, 22]

$$\frac{E}{hc} = \sum_{r=1}^{3N-6} \omega_r \left(n_r + \frac{1}{2}\right) + \sum_{r \geq s} \chi_{rs} \left(n_r + \frac{1}{2}\right) \left(n_s + \frac{1}{2}\right) \tag{1}$$

where ω_r are the harmonic frequencies of vibration (in units of wavenumbers). Neglecting Coriolis effects, the diagonal and off–diagonal anharmonic constants χ are obtained from

$$\begin{aligned}
\chi_{rr} &= \frac{1}{16}\phi_{rrrr} - \frac{1}{16}\sum_{s=1}^{3N-6} \phi_{rrs}^2 \frac{8\omega_r^2 - 3\omega_s^2}{\omega_s(4\omega_r^2 - \omega_s^2)} \\
\chi_{rs} &= \frac{1}{4}\phi_{rrss} - \frac{1}{4}\sum_{t=1}^{3N-6} \frac{\phi_{rrt}\phi_{tss}}{\omega_t} \\
&\quad - \frac{1}{2}\sum_{t=1}^{3N-6} \frac{\phi_{rst}^2 \omega_t(\omega_t^2 - \omega_r^2 - \omega_s^2)}{\Delta_{rst}}, \qquad r \neq s \\
\Delta_{rst} &= (\omega_r + \omega_s + \omega_t)(\omega_r - \omega_s - \omega_t) \\
&\quad \times (-\omega_r + \omega_s - \omega_t)(-\omega_r - \omega_s + \omega_t)
\end{aligned} \tag{2}$$

where ϕ_{rst} and ϕ_{rrss} stand for mixed third and fourth derivatives of the potential energy function with respect to the normal coordinates of vibration. The above formulae have

been implemented in the Gaussian 03 software thus making anharmonic calculations easily available to a wider range of the quantum chemical community [28]. While second derivatives are obtained analytically in Gaussian, third and fourth order terms are computed from finite differences with the effort scaling linearly with the number of normal modes [21, 22, 31]. We note that for several small molecules the quality of the computed anharmonic corrections has been shown to be not very sensitive to the choice of the quantum chemical method or the size of the basis set [22]. This finding opens the way for the efficient calculation of anharmonic vibrations where only harmonic frequencies are obtained from a high–level computations while cheaper models are sufficient to estimate the anharmonic corrections.

In applying the above procedure, one has to keep in mind that this approach rests on two assumptions: (1) In the vicinity of a minimum, the potential energy function can be expressed in terms of a Taylor series which is truncated to yield a fourth order polynomial. (2) The above formulae rest on first and second order perturbation theory (PT2) for the treatment of the quartic and cubic force constants, respectively. It is noted that the restriction to first order for the quartic contribution implies that only diagonal (ϕ_{rrrr}) and semi–diagonal (ϕ_{rrss}) derivatives are taken into account. While higher order treatments were explored for one–dimensional anharmonic oscillators [32, 33], no such approaches can be found in the literature for the multi–dimensional case of polyatomic molecular vibration.

However, it is not *a priori* clear whether these two assumptions are justified: As will be discussed below, some of the two– and three–dimensional slices of the potential energy function are more complicated functions of the respective normal coordinates. Moreover, the use of second order perturbation theory (PT2) is questionable in cases where the anharmonic effects are becoming large. In Sec. III B we are going to present examples where either one (or both) of the two assumptions are not valid.

C.   Non-perturbative calculations

As an alternative we pursue non-perturbative anharmonic vibrational analysis. While variational treatments or the vibrational self–consistent–field approach can treat approximately up to ten degrees of freedom, for systems of the size considered here (15 or 30 atoms), studies in full dimensionality are clearly out of the range of today's computational means. Nevertheless, low–dimensional calculations for suitably chosen vibrational modes are instru-

mental in gaining a deeper understanding of the anharmonic coupling mechanisms. In the present work we proceed as follows: On the basis of the harmonic vibrational analysis of benzoic acid monomer and dimer, one–, two–, and three–dimensional scans of the potential energy are performed with single point energy calculations with the equilibrium structure displaced along a single normal coordinate (1D) or along the linear combination of two or three of those coordinates (2D, 3D). The respective grid representations have a spacing of 0.1 Å for hydrogen stretching vibrations, 0.2 Å for the remaining intramolecular vibrations, and 0.5 Å for the intermolecular vibrations of the dimer.

Eigenvalues and eigenfunctions corresponding to bound states are then obtained by propagating the nuclear Schrödinger equation in imaginary time where an expansion of the evolution operator in terms of Chebychev polynomials was used. The Hamiltonian is represented on an equidistant grid thus allowing the kinetic energy to be calculated by fast Fourier transforms [34, 35]. Vibrationally excited states were also obtained by this relaxation method, where the contribution of lower states have to be projected out at each evaluation of the Hamiltonian. The differences of ground and excited state energies yield fundamental frequencies. These calculations can be used to investigate the quality of the perturbation–based results: First, a comparison of the potential energy surfaces with low–order polynomials directly allows to judge the validity of the truncated polynomial expansion. Second, through a comparison of the non-perturbative results with corresponding one–, two–, and three–dimensional perturbative calculations, the validity of the perturbation treatment (PT2) can be critically assessed.

III. RESULTS AND DISCUSSION

A. Perturbative anharmonic vibrational analysis

Monomer. Due to computational restrictions owing to the size of the molecules under investigation, we follow the above–mentioned mixed strategy of Ref. [22] throughout this work. We are employing a very large basis set for the computation of the harmonic frequencies while anharmonic corrections have to be estimated from cheaper calculations. First, infrared intensities and harmonic frequencies are calculated for the benzoic acid monomer (C_s symmetry) at the DFT (B3LYP) level of theory using the D95(d,p) [29] and the much

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larger cc-pVTZ [30] basis set. In addition, anharmonic contributions based on the perturbation formulae (1,2) are computed only for the smaller D95(d,p) basis set in full dimensionality and are used to correct both the D95(d,p) and the cc-pVTZ results. Our results given in Tab. I include only those vibrational modes that were observed in the previous gas phase infrared absorption spectroscopic study covering the mid–IR regime $500 \ldots 1800$ cm^{-1} [6]. Complete tables of force constants and frequencies are available from the authors [36]. Note that throughout the scope of this work normal modes are numbered according to ascending D95(d,p) frequencies. The harmonic vibrational frequencies are found to be lowered by $1 \ldots 3$ % owing to the effect of anharmonicity. This leads to excellent agreement with the experimental absorption spectrum of Ref. [6] with deviations in the frequencies rarely exceeding 1 %, in almost all cases even significantly below, see Fig. 1(a). Moreover, on grounds of the comparison with experiment, neither frequencies nor intensities provide clear preference for one of the basis sets used here. This indicates that the empirical scaling of the harmonic frequencies for the benzoic acid monomer used, e. g. in Refs. [6, 15], mainly reflects the effect of anharmonicity rather than deficiencies of the quantum–chemical method.

Dimer. Upon dimerization the number of intramolecular vibrational modes is doubled with the A' modes of the monomer (C_s symmetry) correlating with A_g and B_u modes of the dimer (C_{2h} symmetry) and A" correlating with A_u and B_g. In most cases, the dimer modes are best described as either symmetric (*gerade*) or anti-symmetric (*ungerade*) combinations of two monomeric vibrations where only the latter ones are infrared–active. Our results are summarized in Tab. II and in Fig. 1 (b): The frequency shifts with respect to the corresponding monomeric frequencies are largely different: While most frequencies are shifted by less than 10 cm^{-1} (modes 25, 27, 32, 44, 48, 53, 60, 63, 65, 67, 70), the modes involving atoms participating in the double hydrogen bond exhibit shifts of a few 10 cm^{-1} (modes 20, 24, 30, 49, 56, 58, 61, 72). For those modes also the splitting of *gerade* and *ungerade* modes is appreciable while in the other cases the splitting is often less than 1 cm^{-1}. Out of the vibrational modes in the mid IR frequency regime considered here, the out-of-plane C-O-H bending mode experiences the largest effect of dimerization: Using the D95(d,p) basis set, the harmonic wavenumber is shifted (and split) from 594 cm^{-1} (ν_8, A") in the monomer to 1003 cm^{-1} (ν_{39}, B_g) and 1050 cm^{-1} (ν_{46}, A_u) in the dimer. While all other frequencies do not change substantially upon increasing the basis size from D95(d,p)

to cc-pVTZ, the latter case represents a remarkable exception: For the larger basis set (cc-pVTZ) there are two intensely absorbing normal modes containing notable contribution of COH out-of-plane bending with frequencies of 1005 and 1008 cm^{-1} (both of A$_u$ symmetry) thus being substantially lower than the corresponding result (1050 cm^{-1}) for the smaller basis set (D95(d,p)). Note that this is in contrast to the detailed investigation of the formic acid dimer in Ref. [5], where no pronounced dependence of the COH bending frequency on the basis set was found. This appears to indicate that the calculations are sensitive to the coupling between COH bending motion and ring CCH bending also present in the 1005 and 1008 cm^{-1} modes of the dimer.

Because of the enormous computational effort, anharmonic corrections in full dimensionality using Eqs. (1,2) can only be evaluated for the D95(d,p) basis set. These corrections are used for both basis sets. As indicated in Tab. II, the anharmonic effects again lower the vibrational frequencies by about $1 \dots 3$ %. As in the case of the monomer, the agreement with measured gas phase frequencies [6] is excellent in almost all cases, with deviations being below 1 %. While the frequencies obtained for the two basis sets are in almost all cases very close to each other, the cc-pVTZ intensities are in some cases closer to the experimental ones, see Fig. 1 (b). However, there is a huge discrepancy for the frequency of the antisymmetric out-of-plane C-O-H bending mode (ν_{46}, A$_u$). The anharmonically corrected D95(d,p) value (1037 cm^{-1}) differs by 8 % from the measured gas phase value (962 cm^{-1}) [6]. Also for the much larger cc-pVTZ basis, the anharmonic values of 992/995 cm^{-1} are still 3% higher than the measured one. Furthermore, similar findings were also made in previous work on the benzoic acid dimer, where an unusual discrepancy of measured and calculated values for the out-of-plane COH bending wavenumber was published in Ref. [5]. Although the present results indicate that the deviations found in previous works are partly an effect of the basis size, the remaining discrepancy may still be due to anharmonic effects. Hence, we shall present a more detailed study of anharmonic couplings of the ν_8 mode of the monomer and the ν_{46} mode of the dimer in the following section.

B. Non-perturbative vibrational analysis of uncoupled modes

Monomer. As a first step towards a non-perturbative anharmonic vibrational analysis, we present results for anharmonicity arising from calculations for uncoupled normal

modes. We restrict ourselves to those vibrational modes featuring a notable amplitude of the acid group hydrogen atom. Our calculated B3LYP/D95(d,p) frequencies of benzoic acid monomer are summarized in Tab. III. The anharmonic frequencies obtained from bound state calculations based on one–dimensional scans of the potential energy surface, see Sec. II C. Note that the table includes only those modes where the contribution of anharmonicity exceeds 10 cm^{-1}. The largest anharmonic effect is found for the COH out-of-plane bending frequency (ν_8) which is shifted by 173 cm^{-1} to the blue while the umbrella mode (ν_{12}) which involves similar H atom motion as the ν_8 mode is blue–shifted by only 12 cm^{-1} due to the much smaller amplitude. The OH stretching frequency (ν_{39}) is shifted by 168 cm^{-1} to the red. The vibrational amplitudes for these three modes are depicted in Fig. 2 with corresponding potential energy curves shown in Fig. 3. While the anharmonic potential of the OH stretching mode resembles a Morse oscillator, the potential for the COH bending mode is steeper than a harmonic potential in a symmetric fashion. Other modes involving notable acid group H atom movement are the in-plane COH bend (ν_{25}) with a blue shift of 14 cm^{-1} as well as the intramolecular torsion (ν_1) with a blue shift of 19 cm^{-1}. Furthermore, significant anharmonic effects are found for modes that involve motion of the hydrogen atoms in the benzoic moiety (not included in the table): Various CH stretching frequencies are found to be shifted by $\pm(50 \ldots 70)$ cm^{-1}, while the CCH bending frequencies are typically shifted by $\pm(10 \ldots 20)$ cm^{-1}.

Dimer. The results of an analogous B3LYP/D95(d,p) vibrational analysis for the dimer are given in Tab. IV. As discussed in Sec. III A, the modes involving motions of the acid group are strongly affected by the double hydrogen bond. Both the frequency shifts with respect to the monomer values and the splittings of *gerade* and *ungerade* mode frequencies are particularly large. Our results are summarized in Tab. IV. The harmonic frequencies of the symmetric (ν_{73}, A_g) and antisymmetric (ν_{74}, B_u) OH stretching modes are strongly red shifted by 836 and 712 cm^{-1} with respect to the monomeric vibration. The anharmonicity leads to an additional red shift of 229 cm^{-1} (ν_{73}) and a blue shift of 113 cm^{-1} (ν_{74}) thus further increasing the difference between symmetric and anti-symmetric vibration frequencies. While the OH stretching frequency is discussed extensively in the literature [4, 5, 8], the OH bending frequency has received relatively little attention: Within the harmonic approach, the symmetric (ν_{39}, B_g) and antisymmetric (ν_{46}, A_u) out-of-plane bending motions are strongly blue shifted (409 and 456 cm^{-1}, resp.) with respect to the monomer

vibration. The diagonal anharmonicity further shifts these frequencies by 44 and 39 cm^{-1} towards higher values. Apart from these outstanding cases, the effect of anharmonicity is much weaker for the dimer than for the monomer. For example, the in-plane COH bending mode which is blue–shifted upon dimerization by a little more than 100 cm^{-1} becomes essentially harmonic. The same is true for the CCH bending modes (≤ 6 cm^{-1}) and also the anharmonic effect on the CH stretching vibrations is reduced by one half.

Comparison with perturbation theory. Finally, we compare the fundamental frequencies obtained from numerically exact results of the Schrödinger equation with those obtained from perturbation theory, see Eq. (1,2). The first question of interest is how precisely the one–dimensional potential scans can be reproduced by the truncated Taylor expansion around the optimized geometry. In all cases discussed above (monomer and dimer), the quartic polynomials provide a reasonably good approximation, at least within the energy range of the fundamentally excited states, see Fig. 3 for the ν_8, ν_{12}, and ν_{39} mode of the benzoic acid monomer. Based on this finding, the use of second order perturbation theory can be validated. For one–dimensional calculations of the anharmonic shifts of fundamental excitation frequencies, Eqs. (1,2) yield

$$\Delta\nu_r^{1D} = 2\left(\phi_{rrrr} - \frac{5}{48}\frac{\phi_{rrr}^2}{\omega_r}\right) \tag{3}$$

Note that the cubic constants ϕ_{rrr} vanish for all modes except those of A' symmetry (monomer, C_s) and A_g symmetry (dimer, C_{2h}). The anharmonic shifts are also included in Tabs. III and IV. For the cases with small relative corrections, the numerically exact results are fairly well reproduced by perturbation theory. This includes the out-of-plane COH bending modes of the dimer (ν_{39}, ν_{46}) as well as the OH stretching modes of both monomer (ν_{39}) and dimer (ν_{73}, ν_{74}), where the anharmonic shifts reach up to nearly 10 %. However, major discrepancies are found for modes with strong anharmonic effects: Apart from the low frequency intramolecular and intermolecular torsional modes of monomer (ν_1) and dimer (ν_2), respectively, the very large blue shift of about 30 % (173 cm^{-1}) of the out-of-plane COH bending mode of the monomer (ν_8) is strongly overestimated (339 cm^{-1}) in standard perturbation theory. Obviously, these cases are beyond the regime of PT2 treatment.

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C. Non-perturbative vibrational analysis of anharmonic coupling

Based on the frequencies obtained from the one–dimensional bound state calculations, we now proceed to explore the effect of anharmonic coupling at the B3LYP/D95(d,p) level. Here we restrict ourselves to the out–of–plane bending vibration (ν_8) of the benzoic acid monomer and the antisymmetric (IR–active) combination (ν_{46}) for the dimer. As has been mentioned above, this mode has been found to be strongly affected by the dimerization. Moreover, it is strongly anharmonic. In order to study anharmonically coupled vibrations, we perform 2–dimensional scans of the potential energy surface spanned by pairs of normal modes and solve the stationary Schrödinger equation numerically using the propagation in imaginary time.

Monomer. Our results for the benzoic acid monomer are summarized in Tab. V. Note that only those cases are listed where the fundamental frequencies obtained in the two–dimensional pictures differ by at least 3 cm^{-1} from the results of the corresponding one–dimensional calculations. With the exception of the coupling to the umbrella mode (ν_{12}) and the OH stretching mode (ν_{39}), all other couplings lead to shifts of the COH out-of-plane bending mode (ν_8) by $4 \ldots 18$ cm^{-1} towards higher frequencies. An unusual case of strong coupling arises for modes ν_8 and ν_{12}, the latter of which involves some COH out-of-plane bending, too, see Fig. 2 (b). The tilted shape of the isoenergy contours shown in Fig. 4 (a) is due to the addition or subtraction of the acid group H atom out-of-plane amplitude connected with the two modes. Note that this is the only case where the nodal lines of the vibrational wavefunctions are not essentially parallel to the normal coordinate axes thereby not allowing an unambiguous identification of the vibrationally excited states to either one of the participating modes. The resulting anharmonic wavenumbers are 713 and 813 cm^{-1}, where we choose the latter one which is due to an in-phase combination of the H atom motions and, hence, bears much higher IR absorption. The largest anharmonic coupling effect, however, is found for the OH stretching mode ν_{39}. Within our two–dimensional picture, this coupling reduces the COH out-of-plane bending frequency by 200 cm^{-1}. The reason for this peculiarity becomes obvious from Fig. 4 (ab). Both the strong diagonal anharmonicity of ν_8 as well as the large coupling to ν_{39} is due to the definition of normal coordinates as rectilinear coordinates which do not represent the curvilinear nature of the large amplitude bending motion of the H atom appropriately. Finally, there are also anharmonic couplings

to the remaining 26 modes not listed in Tab. V because the effect on the COH bending frequency is below ± 3 cm^{-1} in each of those cases. Since these shifts are in almost all cases towards higher frequencies, the resulting effect is a blue shift of 56 cm^{-1} if one assumes simple additivity of the pairwise couplings. The strong mixing of modes ν_8 and ν_{12} together with the strong coupling of each of those modes to the OH stretching mode ν_{39} lead us to investigate the presence of possible three–mode coupling effects, too. A bound state calculation for a three–dimensional potential energy surface yields a red shift of the COH bending mode (ν_8) by 168 cm^{-1} which, however, does not substantially differ from the sum of the two–mode couplings to the ν_{12} (+46 cm^{-1}) and ν_{39} (–200 cm^{-1}) modes. It is noted that the same calculation shows that the umbrella mode (ν_{12}) is practically unshifted with respect to the one–dimensional calculation which is not expected on the basis of the pairwise couplings to the ν_8 (–25 cm^{-1}) and to the ν_{39} (–13 cm^{-1}) modes. An inspection of the corresponding potential energy functions reveals that the strong coupling of ν_8 and ν_{12} (see Fig. 4 a) is not present in the three–dimensional calculation but is rather a peculiarity for the case of vanishing displacement of the OH stretching mode (ν_{39}) only.

Dimer. Results of an analogous analysis of anharmonic coupling effects on the anti-symmetric COH out-of-plane bending mode (ν_{46}) of the benzoic acid dimer are collected in Tab. VI. Again, only modes are included where the coupling shifts the frequencies by at least 3 cm $^{-1}$. Because of the reduced vibrational amplitudes of the atoms participating in the double hydrogen bond, there are much fewer and weaker anharmonic couplings for the dimer than for the monomer. Among the few cases of relatively strong coupling, there is a significant Davydov–type coupling with the symmetric COH bending mode (ν_{39}). The corresponding isoenergy contours are slightly diamonds–shaped, see Fig. 5 (a). This leads to an increase (blue shift) of the fundamental frequency of the antisymmetric mode (ν_{46}) by 31 cm^{-1}. Moreover, there are strong couplings to the symmetric (ν_{73}) and antisymmetric (ν_{74}) OH stretching modes. Within our two–dimensional calculations these interactions give rise to red shifts of the ν_{46} frequency by 43 or 54 cm^{-1}, respectively. The corresponding potential energy surfaces are shown in Fig. 5 (b,c). Although the potential surface spanned by the ν_{46} and ν_{73} normal coordinate is qualitatively similar to that for the monomer as depicted in Fig. 4 (b), the amplitude of the COH bending is much reduced thus rendering its curvilinear nature less important. Due to the different symmetry, the potential energy surface spanned by ν_{46} and ν_{74} normal coordinates is qualitatively different with slightly rectangular–shaped

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contours. In addition, there are notable couplings to two other intramolecular modes (ν_6, ν_{58}) as well as to the intermolecular stretching mode (ν_8) each of which does not exceed 10 cm^{-1}. Finally, the anharmonic couplings to the remaining 66 modes not listed here are again in almost all cases towards higher frequencies, so that the resulting effect is a blue shift of 72 cm^{-1} assuming simple additivity.

Following a similar argument as for the case of the coupling of the ν_8, ν_{12}, and ν_{39} modes of the monomer, the strong coupling between the antisymmetric COH bending mode ν_{46} of the dimer and each of the three modes ν_{39}, ν_{73}, and ν_{74} motivates three–dimensional calculations. The anharmonic coupling to the two OH stretching modes results in a red shift of the ν_{46} mode by 41 cm^{-1} which is quite different from the sum of the above pairwise couplings to modes ν_{73} (–43 cm^{-1}) and ν_{74} (–54 cm^{-1}). Also the three–mode–coupling to modes ν_{39} and ν_{73} yielding –16 cm^{-1} and to modes ν_{39} and ν_{74} yielding –42 cm^{-1} differ substantially from the pairwise picture.

Comparison with perturbation theory. As in the case of the one-dimensional calculations discussed above, we want to compare our results with those obtained from the standard perturbation approach. First of all, the polynomial expansion underlying Eq. (2) is reviewed. While in almost all cases the two–dimensional scans of the potential energy surface are reproduced very well, there are a few remarkable exceptions for the above mentioned cases of strong coupling: The curved shape of the potential well spanned by the COH bending (ν_8) and OH stretching (ν_{39}) mode of the monomer is not even qualitatively approximated by a quartic expansion, see dashed contours in Fig. 4 (b). Although to a lesser extent, the same is true for the potential function spanned by ν_{46}, ν_{73} of the dimer, see Fig. 5 (b). Also the tilted shape of the contours of the potential surface spanned by the COH bending (ν_8) and the umbrella (ν_{12}) normal coordinates of the monomer (Fig. 4 a) cannot be reproduced by diagonal and semi-diagonal quartic terms only. However, inclusion of the (rather large) force constant $\phi_{8,8,8,12}$ would lead to very good agreement. In contrast, the dimer potentials in the (ν_{39}, ν_{46}) and (ν_{46}, ν_{74}) planes are well reproduced by (relatively large) positive and negative semi-diagonal quartic force constants.

Next, we compare our numerically exact solutions of the time–independent Schrödinger equation with those obtained from perturbation theory of Eqs. (1,2). The shift of the

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fundamental excitation frequencies ν_r due to anharmonic coupling to mode ν_s is given by

$$\Delta\nu_r^{2D} = \frac{1}{8}\left(\phi_{rrss} - \frac{\phi_{rrr}\phi_{rss}}{\omega_r} - \frac{\phi_{rrs}}{\omega_s}\left[\phi_{sss} + \phi_{rrs}\frac{8\omega_r^2 - 3\omega_s^2}{4\omega_r^2 - \omega_s^2}\right]\right) \tag{4}$$

These values are included for comparison in Tabs. V and VI. In addition to those cases where the truncated Taylor expansion fails (e. g. coupling of the ν_8 mode to ν_{12} and ν_{39} of the monomer, ...) also most of the other anharmonic couplings are not reproduced correctly by perturbation theory, apparently regardless of the relative size of the shifts. The failure of the second order approach is much more pronounced than in the case of the one–dimensional data compiled in Tabs III and IV where large deviations are limited to the cases of unusually strong anharmonic effects.

IV. CONCLUSIONS

An anharmonic vibrational analysis of benzoic acid monomer and dimer has been carried out at the DFT/B3LYP level of theory employing D95(d,p) and cc-pVTZ basis sets. The standard second order perturbation (PT2) approach yields very good agreement with measured absorption spectra in the mid–infrared regime ($500\ldots1800$ cm^{-1}) [6]. The frequencies rarely deviate by more than 1 %, in most cases even considerably less. Although these results are certainly better than expected, they may be to some extent caused by error cancelations in the computational approach, at least for the spectral region considered here. The infrared intensities are reproduced qualitatively where the absorption patterns are notably better for the larger of the two basis sets (cc-pVTZ). The total effect of anharmonic coupling leads to red shifts of the fundamental excitation frequencies by about $1\ldots3$ %. This is approximately in accord with the common practice of empirically scaling harmonic frequencies in order to match experimental spectra. Of particular interest is the out-of-plane COH bending mode of the monomer (ν_8) which exhibits an extreme blue shift upon dimerization (ν_{39}, ν_{46}) which has motivated the present non–perturbative studies of anharmonic effects in reduced dimensionality. The results of our one–, two–, and three–dimensional studies show two peculiarities: (1) The relatively small total anharmonic shift of the monomer COH bending frequency (ν_8) of 20 cm^{-1} comprise of many individual shifts which are of the order of a few hundreds of cm^{-1} and which are canceling each other for the most part. Although the total anharmonic effects for the dimer are in general much less

pronounced, it is again found that – due to similar cancelation effects as for the monomer – the total anharmonic frequency shift of 13 cm for the ν_{46} mode is much smaller than some of its constituents. (2) Within the low–dimensional pictures it has been shown that the conditions for the standard PT2 perturbative approach are not always fulfilled. In some cases, the underlying truncation of the Taylor series containing only cubic and semi–diagonal quartic force constants is inappropriate, in other cases the second order treatment is insufficient.

Given these findings, the results of anharmonic calculations for the COH out-of-plane vibrational mode have to be considered critically: The strong diagonal anharmonic shift of the ν_8 mode ($+173$ cm^{-1}) of the monomer is almost compensated by the (combined) anharmonic coupling (-168 cm^{-1}) to the umbrella mode ν_{12} and the OH stretching vibration ν_{39} thus suggesting a rather small anharmonic effect. However, the nearly perfect match of the theoretical (PT2) values of 574 cm^{-1} (D95(d,p)) or 575 cm^{-1} (cc-pVTZ) and the experimental value of 571 cm^{-1} could be partially accidental. The antisymmetric mode COH bending mode (ν_{46}) of the dimer is the only case where our harmonic results obtained for the two basis sets deviate by more than 1 % from each other. Moreover, the 8 % or 3 % difference between anharmonic (PT2) values of 1037 cm^{-1} (D95(d,p)) or 992/995 cm^{-1} (cc-pVTZ) and the experimental value of 962 cm^{-1} represents the largest discrepancy within the mid–IR regime considered here. At present, this cannot be explained satisfactorily by our non–perturbative results either: We have identified strong anharmonic coupling to three modes (symmetric COH bending ν_{39} as well as the two OH stretching modes ν_{73}, ν_{74}). The shifts obtained from non–perturbative calculations of anharmonic coupling to any pair of these modes deviate substantially from the sum of the respective pairwise calculations. Hence, it is anticipated that (at least) four–dimensional calculations are required to finally clarify the question of the anharmonic effect on the ν_{46} vibrational mode of the benzoic acid dimer. Moreover, in order to ensure convergence of the electronic structure calculations for this particular vibrational frequency, even larger basis sets and/or higher quantum chemical methods may be required. However, either of these approaches are currently beyond the available computational means.

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TABLE I: Theoretical (B3LYP) infrared intensities (in km/mol), harmonic and anharmonic frequencies (in cm^{-1}) for two different basis sets (D95(d,p) and cc-pVTZ) versus observed frequencies [6] for vibrational normal modes of the benzoic acid monomer (C_s). In both cases, anharmonic corrections are based on second order perturbation, see Eq. (1), for the smaller of the two basis sets (D95(d,p))

Mode		D95(d,p)			cc-pVTZ			Obs.	Description
		Int.	Harm.	Anh.	Int.	Harm.	Anh.		
8	A"	71	594	574	61	595	575	571	C-O-H b
10	A'	50	630	623	49	640	633	631	rg C-C-C b
11	A"	6	700	685	10	710	695	688	rg C-C-H b
12	A"	151	726	710	118	732	716	710	rg C-C-H b (u)
13	A'	9	771	761	9	777	767	767	C-O-H b, rg def
20	A'	15	1039	1025	17	1050	1036	1026	rg C-C-H b
21	A'	64	1090	1068	107	1094	1072	1063	rg C-C-H b
22	A'	58	1117	1099	43	1118	1100	1084	rg C-C-H b
24	A'	95	1186	1172	159	1191	1177	1173	C-C-H b, C-O-H b
25	A'	148	1208	1180	62	1212	1184	1187	C-C-H b, C-O-H b
28	A'	130	1381	1343	113	1372	1334	1347	C-C-H b, C-O-H b
29	A'	18	1474	1452	16	1488	1466	1455	C-C s, rg def
31	A'	5	1628	1592	5	1625	1589	1591	C-C s, rg def
32	A'	18	1649	1612	17	1646	1609	1609	C-C s, rg def
33	A'	348	1804	1770	331	1792	1758	1752	C=O s, C-O-H b

b = bend, s = stretch, rg = ring, def = deformation, u = umbrella

TABLE II: Same as Tab. I but for the cyclic benzoic acid dimer (C_{2h}). Bracketed numbers in the last column indicate the index of the corresponding monomeric mode of vibration.

Mode		D95(d,p)			cc-pVTZ			Obs.	Description
		Int.	Harm.	Anh.	Int.	Harm.	Anh.		
20	B_u	131	554	555	114	553	554	540	acid groups rocking (7)
24	B_u	44	673	668	45	683	678	664	acid groups scissor (10)
25	A_u	15	695	683	20	706	694	682	rg C-C-H b (11)
27	A_u	163	720	711	133	728	719	708	rg C-C-H b (u) (12)
30	B_u	22	815	808	25	822	815	797	acid groups scissor, rg def (13)
32	A_u	17	820	806	8	831	817	810	rg C-C-H b (14)
44	B_u	24	1040	1023	22	1050	1033	1022	rg C-C-H b (20)
46	A_u	222	1050	1037	104	1005	992	962	rg C-C-H b, C-O-H b (8)
					55	1008	995		
48	B_u	24	1096	1068	20	1104	1076	1066	rg C-C-H b (21)
49	B_u	8	1150	1128	13	1152	1130	1126	rg C-C-H b (22)
53	B_u	48	1191	1180	59	1202	1191	1176	rg C-C-H b (24)
56	B_u	138	1328	1304	556	1324	1300	1297	C-C-H b, C-O-H b (25/26)
58	B_u	682	1353	1324	276	1349	1320	1322	C-C-H b, C-O-H b (25/26)
61	B_u	76	1471	1436	155	1467	1432	1432	C-C-H b, C-O-H b (28)
63	B_u	201	1477	1444	69	1488	1455	1453	C-C-H b, C-O-H b (29)
65	B_u	51	1521	1490	9	1532	1501	1498	C-C-H b, C-O-H b (30)
67	B_u	52	1627	1588	50	1624	1585	1591	C-C s, rg def (31)
70	B_u	60	1649	1608	53	1646	1605	1618	C-C s, rg def (32)
72	B_u	956	1745	1704	900	1733	1692	1709	C=O s stretch, C-O-H b (33)

b = bend, s = stretch, rg = ring, def = deformation, u = umbrella

TABLE III: One–dimensional vibrational analysis of benzoic acid monomer (C_s). Harmonic and anharmonic frequencies (in cm^{-1}) are calculated using B3LYP/D95(d,p) density functional method (anharmonic frequency shifts in brackets). Results from corresponding one-dimensional perturbation calculations (3) are included for comparison ($\Delta\nu_r^{1D}$).

Mode		Harm.	Anharm.		$\Delta\nu_r^{1D}$	Description
1	A"	67	86	(+19)	+31	C-C-C-OOH t
8	A"	594	767	(+173)	+339	C-O-H b
12	A"	726	738	(+12)	+14	rg C-C-H b (u)
25	A'	1208	1222	(+14)	+15	rg C-C-H b, C-O-H b
39	A'	3785	3617	(−168)	−183	O-H s

rg = ring, b = bend, s = stretch, t = torsion, u = umbrella

TABLE IV: Same as Tab. III but for the cyclic benzoic acid dimer (C_{2h})

Mode		Harm.	Anharm.		$\Delta\nu_r^{1D}$	Description
2	A_u	32	55	(+23)	+65	inter-mol. twist
39	B_g	1003	1047	(+44)	+53	C-O-H b
46	A_u	1050	1089	(+39)	+48	C-O-H b
73	A_g	2949	2720	(−229)	−210	O-H s
74	B_u	3073	3186	(+113)	+123	O-H s

b = bend, s = stretch

TABLE V: Anharmonic coupling in the benzoic acid monomer (C_s) at B3LYP/D95(d,p) level of theory. Results of two– and three–dimensional calculations for interaction of modes ν_s with COH out-of-plane bending mode (ν_8, A"). Shifts with respect to the one-dimensional anharmonic result (767 cm^{-1}) are given in brackets. Results from corresponding two-dimensional perturbation calculations (4) are included for comparison ($\Delta\nu_8^{2D}$). Only modes with a coupling of at least 3 cm^{-1} are included.

Mode		ν_s	ν_8		$\Delta\nu_8^{2D}$	Description
2	A"	173	774	(+7)	+23	C-C-C(OOH) b
3	A'	219	771	(+4)	+4	C-C-C(OOH) b
6	A"	444	785	(+18)	+37	rg C-C-C b, C-O-H b
7	A'	497	771	(+4)	+4	C-C-O(H) b
10	A'	637	773	(+6)	+8	O-C-O b, rg d
11	A"	695	783	(+16)	+10	rg C-C-H b
12	A"	713	813	(+46)	+28	rg C-C-H b (u)
13	A'	774	771	(+4)	+4	O-C-O b, C-C(OOH) s, rg d
14	A"	831	764	(−3)	+4	rg C-C-H, C-C-C(OOH) b
24	A'	1197	773	(+6)	+25	rg C-C-H b, C-O-H b
25	A'	1235	780	(+13)	+17	rg C-C-H b, C-O-H b
28	A'	1384	771	(+4)	+2	C-O(H) s, C-O-H b
39	A'	3602	567	(−200)	−398	O-H s
				(+56)		all other modes (sum)
12/39	A"/A'	738/3656	599	(−168)		

rg = ring, b = bend, s = stretch, d = deformation, u = umbrella

TABLE VI: Same as Tab. V but for the antisymmetric COH out-of-plane bending mode (ν_{46}, A_u) of the cyclic benzoic acid dimer (C_{2h}). Shifts with respect to the one-dimensional anharmonic result (1089 cm^{-1}) are given in brackets.

Mode		ν_s	ν_{46}		$\Delta\nu_{46}^{2D}$	Description
6	A_u	108	1093	(+4)	+8	C-C-C-OOH t
8	A_g	119	1081	(−8)	−10	inter-molecular stretch
16	A_g	442	1086	(−3)	−2	rg C-C-C b, C-C(OOH) s
39	B_g	1077	1120	(+31)	+51	C-O-H b
58	B_u	1356	1094	(+5)	+4	rg C-C-H b, C-O-H b
73	A_g	2551	1048	(−43)	−79	O-H s
74	B_u	2675	1048	(−54)	−61	O-H s
				(+72)		all other modes (sum)
73/74	A_g / B_u	2551/2675	1048	(−41)		
39/73	B_g / A_g	1029/2785	1073	(−16)		
39/74	B_g / B_u	1004/3057	1047	(−42)		

rg = ring, b = bend, s = stretch, t = torsion

FIG. 1: Experimental vs. calculated mid–IR spectra of benzoic acid at various levels of theory. Computed lines are convoluted with Gaussians of 1 % FWHM to match the resolution of the measurements [6]. (a) Monomer. (b) Dimer

FIG. 2: (Color online) Displacement vectors for selected normal modes of the benzoic acid monomer. (a) COH out-of-plane bending vibration (ν_8, A''). (b) Umbrella vibration (ν_{12}, A''). (c) OH stretching vibration (ν_{39}, A').

FIG. 3: (Color online) Potential energy curves along selected normal modes of the benzoic acid monomer (ν_8, ν_{12}, and ν_{39}) see also Fig. 2. Full curves: B3LYP/D95(d,p) results. Dashed and dotted curves: Quadratic and quartic approximation, respectively.

FIG. 4: (Color online) Two–dimensional potential energy surfaces (in cm^{-1}) of benzoic acid monomer. COH bending (ν_8) vs. (a) umbrella mode (ν_{12}) and (b) OH stretching mode (ν_{39}). Thick contours: B3LYP/D95(d,p) results. Thin contours: Quartic approximation. The contour spacing is 1000 cm^{-1}.

FIG. 5: (Color online) Same as Fig. 4 but for benzoic acid dimer. Antisymmetric COH bending (ν_{46}) vs (a) symmetric COH bending mode (ν_{39}), (b) symmetric OH stretching mode (ν_{73}), and (c) antisymmetric OH stretching mode (ν_{74})

Figure 2a, Antony et al., Journal of Chemical Physics
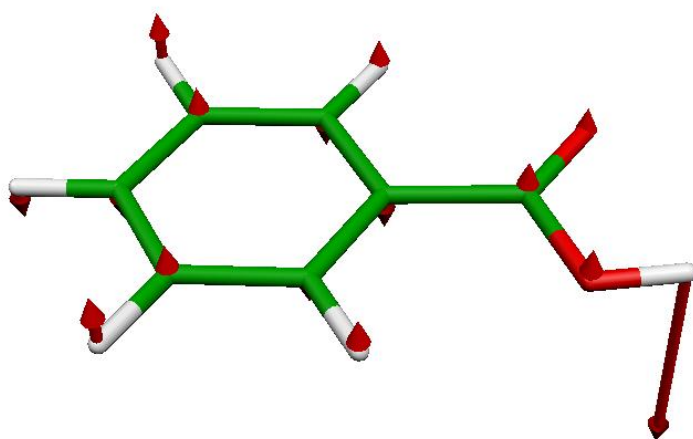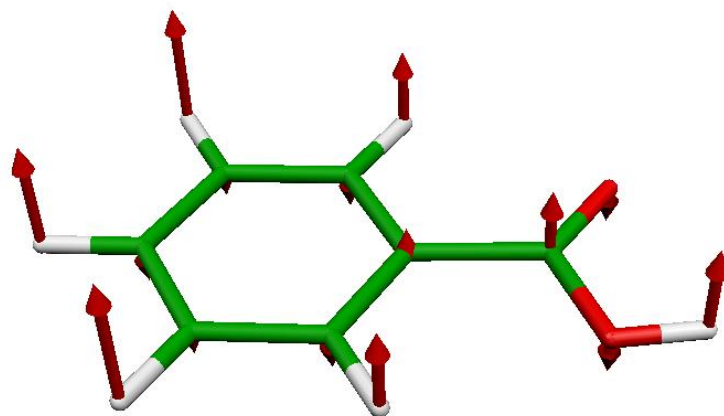
Figure 2c, Antony et al., Journal of Chemical Physics

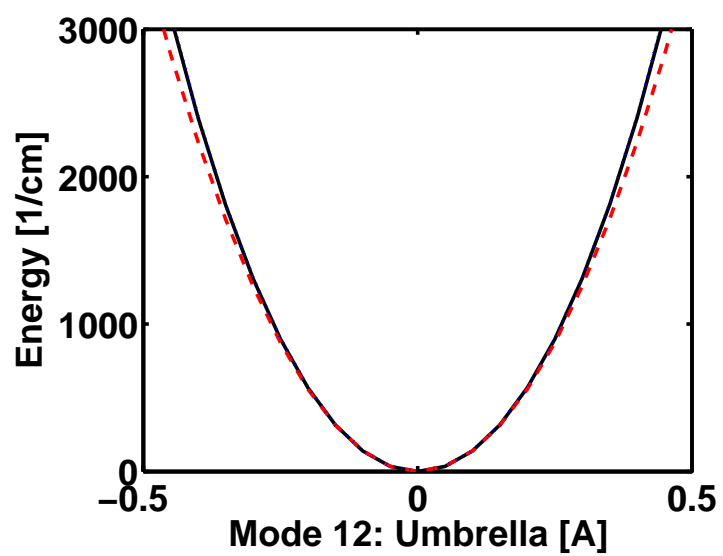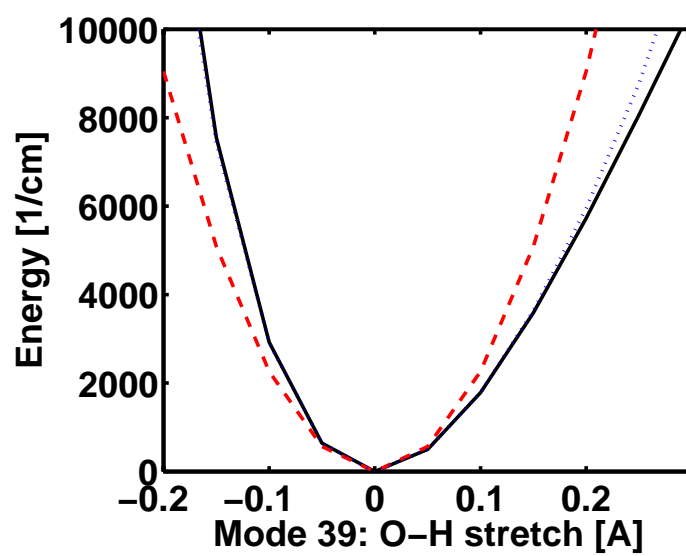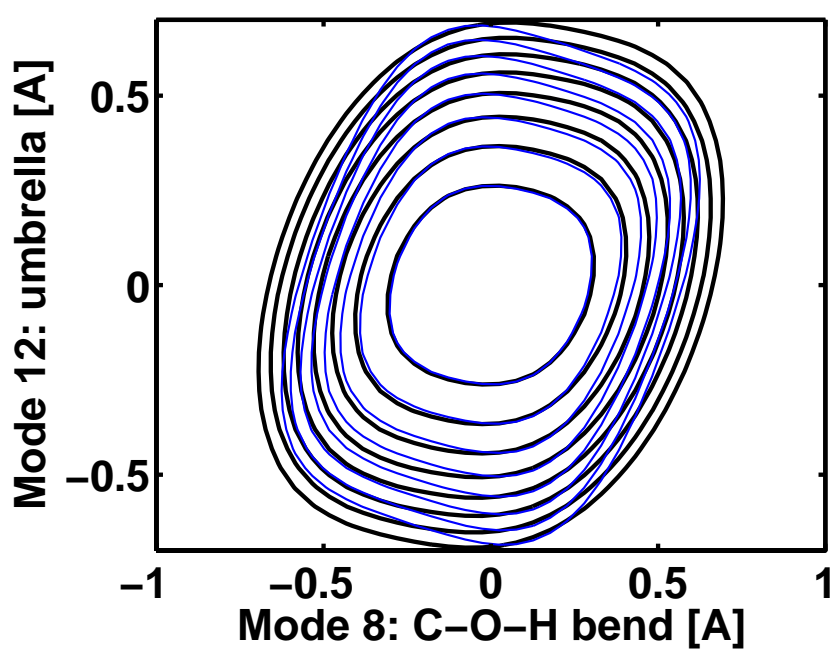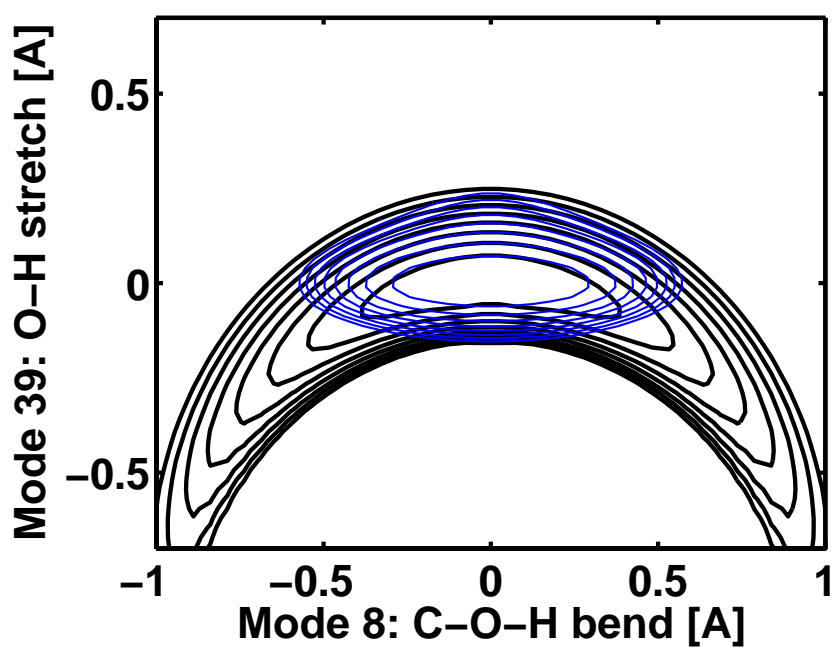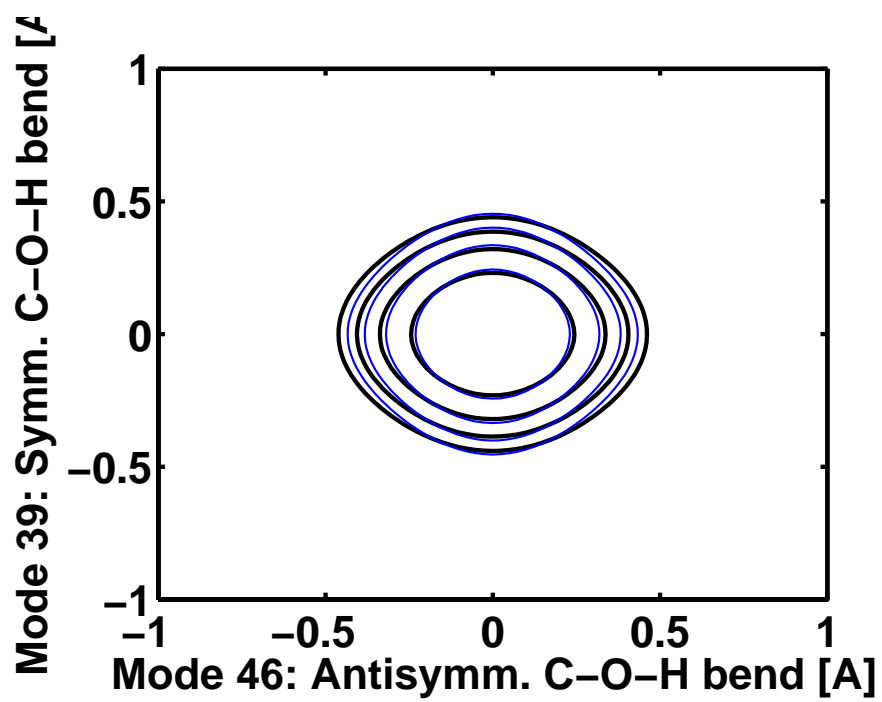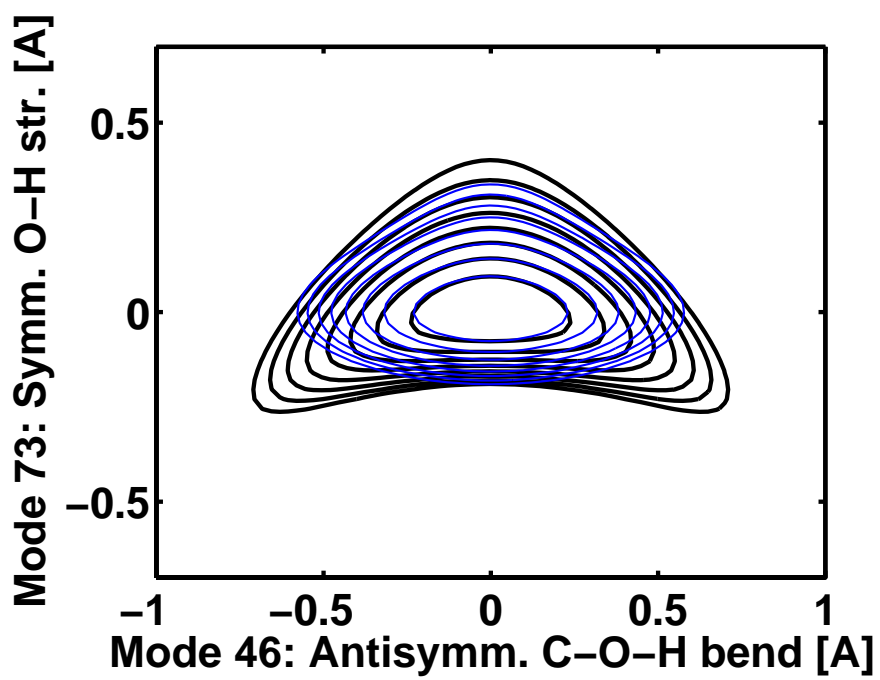Figure 5c, Antony et al., Journal of Chemical Physics