Accurate Anharmonic Vibrational Frequencies for Uracil: The Performance of Composite Schemes and Hybrid CC/DFT Model

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ABSTRACT: The vibrational spectrum (frequencies as well as intensities) of uracil has been investigated at a high level of theory. The harmonic force field has been evaluated at the coupled-cluster (CC) level in conjunction with a triple-ζ basis set. Extrapolation to the basis set limit as well as inclusion of core-correlation and diffuse-function corrections have been considered by means of the second-order Møller–Plesset perturbation theory. To go beyond the harmonic approximation, a hybrid CC/DFT approach has been employed, which will be proved to provide state-of-the-art results. As the spectroscopic investigation of uracil is hampered by numerous Fermi resonances, models for explicitly taking them into account have been implemented and applied. On general grounds, the computational procedure presented is able to provide the proper accuracy to support experimental investigations of large molecules of biological interest.

INTRODUCTION

Nowadays, spectroscopic techniques represent the most reliable and flexible approaches for the investigation of structural and dynamical properties of molecular and supra-molecular systems, either isolated or in condensed phases. However, interpretation of spectra is seldom straightforward, and integrated experimental/computational investigations are becoming more and more popular, thanks to the improved reliability and effectiveness of quantum mechanical (QM) computations.[1,2] For small molecules, the most refined QM methods provide such accurate results that any disagreement between computational data and experimental findings casts serious doubts on the reliability of the latter.[3,4] With regard to the topic of the present work, as a significant example, we mention the new IR spectrum assignment for the vinyl radical based on anharmonic force field computations[5-7] that was eventually confirmed by new purposely tailored experiments.[8]

For polyatomic molecules, effective computational solutions of the vibrational problem and simulation of IR and Raman spectra are among the most important tasks of contemporary computational chemistry.[9] While theoretical evaluations of vibrational frequencies and IR/Raman intensities within the harmonic approximation have become a routine tool for assisting the interpretation of spectroscopic experiments, in the past decade great effort has been made to go beyond the harmonic approximation and perform anharmonic computations by means of perturbative[10-23] or variational approaches.[24-32] An effective approach is obtained when the vibrational second-order perturbation theory (VPT2)[10-14,23] is applied to a fourth-order representation of the potential energy surface (PES). In particular, Density Functional Theory (DFT) using hybrid (especially B3LYP[7,33-37]) or double-hybrid (especially B2PLYP[38-40]) functionals in conjunction with medium-sized basis sets is known to provide rather accurate results and can be exploited for large systems. Further improvements in accuracy can be obtained by computing the harmonic part of the force field at a more refined level, with the coupled cluster (CC) method providing the most effective route, at least in the absence of strong multireference character.[33,37,41-44] The inclusion of the CCSD(T) harmonic part in a DFT anharmonic force field leads to the definition of hybrid CC/DFT approaches,[37,43,44] which nowadays represent the method of choice for computing accurate vibrational spectra of semirigid systems.

The present work is part of a comprehensive research project aimed at extending composite schemes to the accurate prediction of molecular and spectroscopic properties for small- to medium-sized molecules. On this topic, we are particularly interested in building blocks of biomolecules in view of their relevance in several fields ranging from prebiotic systems to biosensors. Characterization of isolated molecules in the gas phase is a mandatory prerequisite for the subsequent analysis of the role of different effects (e.g., hydrogen bonding, environmental effects, etc.) in determining the overall behavior of these systems. However, from an experimental point of view, the structural characterization of the simplest building blocks of biomolecules (e.g., amino acids or nucleic acid bases) in the gas phase is not straightforward at all. In the field of vibrational spectroscopy, interpretation of spectra suffers from the overlapping of several bands and from the presence of strong resonances. In the case of uracil, the simplest nucleobase (see Figure 1), encouraging results have already been obtained for the molecular parameters and spectroscopic properties related to rotational spectroscopy by means of a composite QM scheme.[45] On the other hand, such an accurate approach can be used to benchmark less accurate but computationally cheap methods rooted in the density functional theory as well as to set up hybrid CC/DFT models.
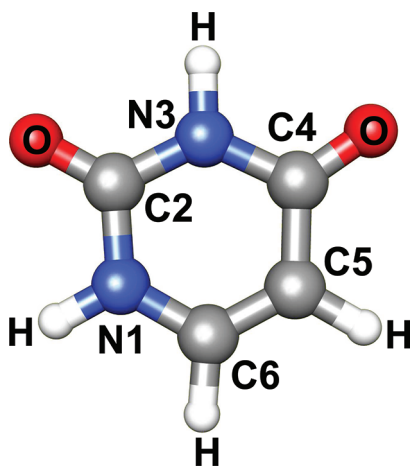
Figure 1. Molecular structure of uracil: atoms labeling.

Moving to the topic of the present work, vibrational spectra of uracil have been investigated in several theoretical and experimental works. The IR and Raman spectra of gaseous,[46] dissolved,[47,48] polycrystalline,[49−51] and matrix-isolated[52−60] uracil were recorded. A number of semiempirical and ab initio quantum mechanical approaches were also used to compute and analyze the vibrational spectra (see refs 61 and 62 and references therein). However, a number of unresolved questions are still open, and they mostly concern the intensities of the C−O stretching vibrations and the assignment of some other bands. As a consequence, there are still significant doubts on the interpretation of the vibrational spectrum of isolated uracil, the main problem being the large number of overtones and combination bands having intensities comparable to those of some fundamentals. This is mainly due to Darling−Dennison and Fermi resonances, which need to be properly taken into account in order to reliably reproduce the uracil IR spectrum. This implies that one should calculate the latter at the anharmonic level by means of an accurate quantum chemical approach, also including Fermi and Darling−Dennison resonances.

The paper is organized as follows. In the next section, the methodology used is explained together with the corresponding quantum-chemical details. Thereafter, the results are reported and discussed with particular emphasis on the proper account of interactions in the anharmonic frequency calculations. Harmonic frequencies and intensities are also reported and discussed.

■ METHODOLOGY AND COMPUTATIONAL DETAILS

Coupled-Cluster Computations. The best-estimated harmonic force field for uracil in its electronic ground state has been evaluated by means of a composite scheme to account for electron-correlation and basis-set effects. This approach is based on the assumption of the additivity for various contributions. The second-order Møller−Plesset perturbation theory (MP2)[63] and CC singles and doubles approximation augmented by a perturbative treatment of triple excitations [CCSD(T)][64] have been employed. Correlation-consistent basis sets, (aug)-cc-p(C)VnZ (n = T,Q),[65−67] have been used in conjunction with the above-mentioned methods.

The harmonic force field has been computed at the MP2 and CCSD(T) levels employing different basis sets.[68] Following the procedure introduced in ref 17, the harmonic frequencies, ω,

have been extrapolated to the complete basis set (CBS) limit starting from the results obtained at the MP2/cc-pVTZ and MP2/cc-pVQZ levels. More precisely, the extrapolated correlation contribution has been added to the HF-SCF CBS limit, which is assumed to be reached at the HF/cc-pVQZ level. The latter assumption seems to be reasonable, as in most cases the differences in frequency between the HF/cc-pVTZ and HF/cc-pVQZ levels are smaller than 1 cm^{-1} and always much smaller than 0.5% in relative terms. Corrections due to core−valence (CV) correlation and effects due to diffuse functions (aug) in the basis set have then been evaluated at the MP2/cc-pCVTZ ($\Delta\omega(CV) = \omega(MP2/cc\text{-}pCVTZ,all) - \omega(MP2/cc\text{-}pCVTZ,fc)$) and MP2/aug-cc-pVTZ levels ($\Delta\omega(aug) = \omega(MP2/aug\text{-}cc\text{-}pVTZ,fc) - \omega(MP2/cc\text{-}pVTZ,fc)$), respectively. The latter correction has been introduced, as diffuse functions are required to properly describe electronegative atoms and thus to recover the limitations that are inherent in the extrapolation of the cc-pVTZ and cc-pVQZ basis sets to the CBS limit. In the expressions given in parentheses, "fc" and "all" stand for frozen-core approximation and all electrons (also 1s electrons of C, N, and O) correlated, respectively. Higher-order electron-correlation energy contributions ($\Delta\omega((T))$) have also been considered. The corresponding corrections have been derived by comparing the harmonic frequencies at the MP2 and CCSD(T) levels, both in the cc-pVTZ basis set. Inclusion of all terms

$$\omega(best) = \omega(CBS(T,Q)) + \Delta\omega(CV) + \Delta\omega(aug) + \Delta\omega((T)) \qquad (1)$$

finally provides the best estimated harmonic frequencies.

An analogous composite scheme has also been used to determine best estimates for the infrared intensities, $I(best)$, within the harmonic approximation. As extrapolation schemes have not been formulated yet for such a property and diffuse functions are known to be important to correctly describe dipole moment derivatives, eq 1 has been rearranged as follows:

$$I(best) = I(MP2/augVTZ) + \Delta I(CV) + \Delta I(QZ - TZ) + \Delta I((T)) \qquad (2)$$

where $\Delta I(QZ - TZ)$ is the correction due to the MP2/cc-pVQZ − MP2/cc-pVTZ difference.

The CFOUR program package[69] has been employed for all computations mentioned in this section.

Density Functional Theory Computations. Density Functional Theory has been employed to compute harmonic and anharmonic force fields. Within the DFT approach, the standard B3LYP functional[70] has been used in conjunction with the aug-N07D[71] and aug-cc-pVTZ[65,66] basis sets. Recently, the original polarized double-ζ basis set N07D[71−74] has been modified by consistent inclusion of diffuse s functions and then further augmented by one set of diffuse d functions on C and N atoms (already present on O). On general grounds, the DFT/N07D approach has been developed for spectroscopic studies of medium-to-large molecular systems and provides an excellent compromise between reliability and computational effort.[7,37,39,75,76] The two different basis sets employed allow us to monitor basis set effects as well as the performance of the newly developed aug-N07D set. Harmonic and anharmonic force fields have been computed starting from equilibrium structures optimized using tight convergence criteria.

As concerns anharmonic force fields, the third and semidiagonal fourth force constants have been obtained by numerical

Table 1. Harmonic Vibrational Frequencies (cm^{-1}) of Uracil

assignment	B3LYP/aug-N07D	B3LYP/aug-cc-pVTZ	MP2/cc-pVTZ	MP2/cc-pVQZ	CBS	ΔCV	Δaug	Δ(T)	best[a] estimate
ν(N1−H)	3640.9	3634.4	3669.4	3666.4	3665.8	5.3	−14.9	−3.4	3652.7
ν(N3−H)	3596.4	3589.5	3616.4	3612.9	3612.3	5.4	−15.6	−0.0	3602.2
ν(C5−H)	3248.7	3243.9	3292.0	3289.2	3287.6	6.1	−10.5	−30.5	3252.8
ν(C6−H)	3207.7	3200.6	3246.5	3246.8	3245.9	5.9	−6.9	−27.5	3217.5
ν(C2=O)	1798.9	1792.7	1828.6	1818.3	1815.6	4.6	−24.3	−5.9	1790.0
ν(C4=O)	1764.3	1760.2	1790.4	1780.8	1779.1	5.0	−21.6	−1.0	1761.5
ν(C5=C6)	1674.0	1672.3	1686.2	1684.2	1684.8	6.0	−8.3	−5.0	1677.5
δ(N1−H)	1499.7	1497.8	1513.4	1513.5	1513.8	4.4	−4.9	−7.9	1505.4
δ(C6−H)	1403.5	1405.5	1427.2	1428.6	1428.7	4.3	−3.8	−2.1	1427.2
δ(N3−H)	1417.8	1422.3	1413.3	1413.8	1414.8	4.0	−3.9	−0.8	1414.0
δ(C5−H)	1383.2	1382.5	1389.2	1389.6	1390.1	3.2	−0.4	1.0	1394.0
ν(ring)	1229.0	1227.9	1246.8	1247.3	1248.6	5.0	−1.6	−3.9	1248.2
ν(ring)	1195.7	1192.5	1212.2	1212.4	1212.3	3.5	−2.5	−8.0	1205.3
ν(ring)	1086.8	1097.2	1095.3	1094.7	1094.3	3.5	−4.1	−9.5	1084.2
ν(ring)	992.8	993.7	992.7	994.7	995.1	3.3	−0.9	−0.9	995.4
ν(ring)	973.4	985.9	968.9	969.7	970.5	3.9	2.2	−9.0	967.7
ν(ring)	770.6	769.7	774.9	776.5	777.6	2.9	−1.5	−6.2	772.8
δ(ring)	557.5	574.0	562.2	564.5	565.6	3.9	3.2	−27.5	545.3
δ(ring)	542.4	543.6	538.1	539.4	540.3	2.5	−2.0	−0.0	540.8
δ(ring)	521.4	522.5	515.4	516.6	516.9	2.2	−1.0	−1.0	517.2
δ(C=O)	386.9	387.7	385.7	386.7	386.8	1.7	−1.5	0.4	387.4
γ(C6−H)	965.3	964.0	977.0	978.3	978.6	3.3	−1.0	−7.6	973.3
γ(C5−H)	823.5	828.2	817.8	816.6	815.7	3.6	3.1	−8.8	813.6
γ(C2=O)	767.0	771.8	762.8	764.5	765.9	4.8	−1.9	−3.5	765.2
γ(C4=O)	730.5	734.3	735.2	734.2	733.8	2.5	−0.4	−8.2	727.6
γ(N3−H)	675.8	687.9	691.6	690.5	690.1	2.6	−3.5	−18.8	670.3
γ(N1−H)	559.3	559.9	559.0	559.9	559.8	2.3	−2.1	−1.2	558.7
γ(ring)	399.3	404.5	394.8	395.7	395.9	2.8	−11.5	−11.5	387.9
γ(ring)	168.5	169.8	163.2	163.7	164.1	1.1	−0.3	−5.8	159.1
γ(ring)	154.1	152.4	146.4	147.0	146.9	1.4	−1.5	−6.4	140.4

[a] From eq 1.

differentiation of the analytical second derivatives. The semidiagonal quartic force fields[77] have then been used to compute spectroscopic parameters and, in particular, anharmonic frequencies by means of the fully automated generalized second-order vibrational perturbation (GVPT2) approach,[10,11] as implemented in the Gaussian package.[13,14,23] As in perturbative treatments nearly resonant contributions should be removed, in the present work two possible approaches to defining Fermi and Darling−Dennison resonances have been followed. First, an automatic procedure (GVPT2, Fermi: auto) based on the criteria proposed by Martin et al.,[15] which are known to provide accurate results,[35,61] has been used to remove potentially divergent terms. In the current version of the code, an *ad hoc* procedure (GVPT2, Fermi: INP) to directly specify resonant terms has been also implemented. The latter allows us to directly compare with other theoretical approaches as well as to test the influence of any specific interaction on the overall results. In both cases, in a second step, all resonant terms are then treated variationally.[11,13] Finally, simple removal of resonant terms leads to the so-called deperturbed model, DVPT2.

All DFT computations have been performed employing the Gaussian suite of programs for quantum chemistry.[78]

The Hybrid CC/DFT Approach. A hybrid CCSD(T)/DFT approach[33,37,41−44] has also been used to evaluate anharmonic frequencies. This model is based on the assumption that the differences between CCSD(T) and B3LYP anharmonic frequencies are solely due to the harmonic terms. In this way, prohibitively expensive computations of cubic and quartic force constants at the CCSD(T) level are avoided, and the hybrid CCSD(T)/DFT scheme therefore provides a viable route to extend accurate predictions of anharmonic frequencies to relatively large systems. In the present case, two possible approaches have been implemented. In the simplest one, the hybrid frequencies have been computed by means of *a posteriori* DFT corrections to the best-estimated harmonic frequencies: $\nu_{CC/DFT} = \omega(\text{best}) + \Delta\nu_{DFT}$. Such an approximation has already been validated for several closed- and open-shell systems (see, for instance, ref 37). On the other hand, in the second approach, the best-estimated harmonic frequencies are directly introduced into the GVPT2 computations along with the 3rd and 4th force constants obtained at the DFT level. It should be noted that the latter scheme can significantly improve the quality of the results when the discrepancy between harmonic frequencies computed at the DFT level and best estimates leads to an incorrect definition of Fermi resonances through automatic procedures.[37,39] However, a more general way to overcome such inconsistencies relies on generalized treatment that completely avoids divergent terms.[79]

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Table 2. Anharmonic Vibrational Frequencies (cm^{-1}) of Uracil from the CCSD(T)/B3LYP Hybrid Force Field[a]

symmetry/mode		assignment	harmonic best estimate	DVPT2	GVPT2 Fermi: DFT[d]	Fermi: CC[e]	Fermi: DFT+INP[f]	Fermi: CC+INP[f]	B3LYP/6-31+G(d,p)[c] (Ten et al.)	experiment[b] frequency	intensity
A′	ω_1	$\nu(\text{N1}-\text{H})$	3652.7	3484	3484	3485	3484	3485	3480	3485	166
A′	ω_2	$\nu(\text{N3}-\text{H})$	3602.2	3436	3436	3436	3436*	3436*	3436	3435	100
A′	ω_3	$\nu(\text{C5}-\text{H})$	3252.8	3117	3117	3117	3117	3117	3140		4
A′	ω_4	$\nu(\text{C6}-\text{H})$	3217.5	3084	3072*	3072*	3083*	3072*	3082		
A′	ω_5	$\nu(\text{C2}=\text{O})$	1790.0	1760	1762*	1762	1771*	1761*	1776	1764	680
A′	ω_6	$\nu(\text{C4}=\text{O})$	1761.5	1735	1744*	1737*	1760*	1733*	1762	1706	291
A′	ω_7	$\nu(\text{C5}=\text{C6})$	1677.5	1644	1644	1644	1644	1643	1643	1643	33
A′	ω_8	$\delta(\text{N1}-\text{H})$	1505.4	1465	1461*	1465	1484*	1466*	1461	1472	83
A′	ω_9	$\delta(\text{C6}-\text{H})$	1427.2	1382	1386*	1385	1392*	1388*	1394	1400	56
A′	ω_{10}	$\delta(\text{N3}-\text{H})$	1414.0	1394	1391*	1386*	1384*	1384*	1374	1389	21
A′	ω_{11}	$\delta(\text{C5}-\text{H})$	1394.0	1360	1360*	1353	1361*	1355*	1353	1359	13
A′	ω_{12}	$\nu(\text{ring})$	1248.2	1220	1223*	1221	1226*	1221*	1210	1217	4
A′	ω_{13}	$\nu(\text{ring})$	1205.3	1176	1176	1176	1176	1176	1171	1185	109
A′	ω_{14}	$\nu(\text{ring})$	1084.2	1063	1061*	1061*	1064*	1061*	1073	1075	14
A′	ω_{15}	$\nu(\text{ring})$	995.4	980	981*	978	995*	978*	961	980	
A′	ω_{16}	$\nu(\text{ring})$	967.7	940	940	940	940	940	947	958	7
A′	ω_{17}	$\nu(\text{ring})$	772.8	756	756	752*	756	751*	756	759	
A′	ω_{18}	$\delta(\text{ring})$	545.3	552	549*	555*	545*	549*	550	562	17
A′	ω_{19}	$\delta(\text{ring})$	540.8	533	533	530	529	530	534	537	7
A′	ω_{20}	$\delta(\text{ring})$	517.2	511	511	510	511	510	515	516	23
A′	ω_{21}	$\delta(\text{C}=\text{O})$	387.4	383	383	384	383*	386*	385	391	33
A″	ω_{22}	$\gamma(\text{C6}-\text{H})$	973.3	955	955	954	955*	954*	950	987	2
A″	ω_{23}	$\gamma(\text{C5}-\text{H})$	813.6	793	793	793	793	793	803	804	175
A″	ω_{24}	$\gamma(\text{C2}=\text{O})$	765.2	746	746	746	746	746	749	757	125
A″	ω_{25}	$\gamma(\text{C4}=\text{O})$	727.6	711	711	711	711*	711*	715	718	14
A″	ω_{26}	$\gamma(\text{N3}-\text{H})$	670.3	654	654*	654	660*	654*	666	662	100
A″	ω_{27}	$\gamma(\text{N1}-\text{H})$	558.7	546	546	549	546	555	567	551	25
A″	ω_{28}	$\gamma(\text{ring})$	387.9	387	387	387	387	384	398	411	
A″	ω_{29}	$\gamma(\text{ring})$	159.1	155	155	155	155	155	167	185	
A″	ω_{30}	$\gamma(\text{ring})$	140.4	133	133	132	133	132	155		
MAE[g]				9	10	10	11	9	10	9	

[a] The asterisks denote the modes explicitly considered in the variational treatment of Fermi resonances. See text. [b] Refs 58−60. [c] Ref 62: Anharmonic frequencies and intensities at the B3LYP/6-31+G(d,p) level with Fermi resonances accounted for. [d] Fermi resonances identified through automatic procedure using harmonic frequencies and anharmonic force constants computed at the DFT level. [e] Fermi resonances identified through automatic procedure using harmonic frequencies computed at the CC level and anharmonic force constants computed at the DFT level. [f] All Fermi resonances reported in Ten at al.[62] have been considered. [g] MAE stands for Mean Absolute Error. See text.

■ RESULTS AND DISCUSSION

Harmonic Vibrational Frequencies. Harmonic vibrational frequencies, as obtained from the composite scheme described in the Methodology and Computational Details section, are collected in Table 1. From this table, we first note that the MP2/cc-pVQZ level of theory already provides results close to the CBS limit, the differences being in most cases smaller than 1 cm^{-1}; this is mostly related to the fact that the correlation contributions are already well converged at the MP2/cc-pVQZ level of theory. While core-correlation corrections are quite small, i.e., they range from 1 to 6 cm^{-1}, and tend to enlarge when the frequency value increases, the effects due to the inclusion of diffuse functions in the basis set are contradictory, as they range from being negligible (<1 cm^{-1}) to being large (>20 cm^{-1} in absolute value terms). While CV corrections are always positive, those related to the

diffuse functions are in most cases negative. As concerns the effect of higher-order electron-correlation corrections, for which the inclusion of triples is expected to be the most relevant contribution, we note that they are rather large and mostly negative. The particularly large corrections observed for a few cases when accounting for the $\Delta\omega(\text{aug})$ and $\Delta\omega((\text{T}))$ contributions deserve to be discussed a little bit more in detail. For the former, as already noticed for the molecular structure (see ref 45), diffuse functions in the basis set are important for correctly describing the oxygen atoms; in fact, large $\Delta\omega(\text{aug})$ corrections are observed for the two C−O stretchings. As mentioned above, the inclusion of such corrections is expected to recover the limitations of our extrapolation based on the cc-pVTZ and cc-pVQZ basis sets. Less straightforward is how to understand the large effect due to higher excitations observed for the two C−H stretchings, two N−H out-of-plane vibrations, and one ring

Table 3. Combination Bands and Overtones (cm^{-1}) of Uracil from the CCSD(T)/B3LYP Hybrid Force Field^a

| assignment | DVPT2 | GVPT2 | | | | B3LYP/6-31+G(d,p)^b (Ten et al.) | Experiment^f |
		Fermi: DFT^c	Fermi: CC^d	Fermi: DFT+INP^e	Fermi: CC+INP^e		
$\omega_{28} + \omega_{29}$	544	544	543	544	542	569	557
$\omega_{19} + \omega_{30}$	667	667	669	665*	669*	691	682
$\omega_{18} + \omega_{30}$	672	672	685	667*	685*	707	685
$\omega_{27} + \omega_{28}$	947	947	936	947*	936*	984	963
$2\omega_{19}$	1065	1067*	1069*	1053*	1069*	1069	1070
$2\omega_{27}$	1126	1126	1110*	1126	1110*	1141	1102
$\omega_{23} + \omega_{28}$	1180	1180	1179	1180	1179	1197	1192
$\omega_{24} + \omega_{27}$	1304	1304	1294	1304	1294	1317	1283
$2\omega_{26}$	1297	1297	1298	1311	1303	1325	1314
$\omega_{25} + \omega_{26}$	1369	1368*	1370*	1374*	1370*	1382	1366
$\omega_{14} + \omega_{21}$	1445	1445	1445	1445*	1445*	1448	1461
$2\omega_{17}$	1510	1510	1519	1510	1518	1519	1525
$\omega_{16} + \omega_{17}$	1695	1695	1700	1695*	1699*	1698	1699
$\omega_{13} + \omega_{19}$	1703	1703	1710*	1697*	1710*	1705	1707
$\omega_{12} + \omega_{20}$	1729	1729	1729*	1732*	1727*	1720	1720
$\omega_{12} + \omega_{19}$	1753	1749*	1757	1758*	1757*	1739	1733
$\omega_{22} + \omega_{23}$	1746	1746	1745	1746*	1745*	1750	1758
$\omega_{12} + \omega_{18}$	1760	1760	1774	1757*	1773*	1753	1762
$\omega_7 + \omega_{11}$	2998	2998	2998	2999	2998	2984	2970
$2\omega_6$	3456	3456	3431	3481	3442	3470	3477
MAE^g	13	13	13	14	12	12	
MAE(all)^h	11	11	11	12	11	12	

^{a} The asterisks denote the modes explicitly considered in the variational treatment of Fermi resonances. See text. ^{b} Ref 62: Anharmonic frequencies and intensities at the B3LYP/6-31+G(d,p) level with Fermi resonances accounted for. ^{c} Fermi resonances identified through automatic procedure using harmonic frequencies and anharmonic force constants computed at the DFT level. ^{d} Fermi resonances identified through automatic procedure using harmonic frequencies computed at the CC level and anharmonic force constants computed at the DFT level. ^{e} All Fermi resonances reported in Ten at al.^{62} have been considered. ^{f} Refs 58−60. ^{g} MAE stands for Mean Absolute Error. See text. ^{h} MAE computed considering fundamentals, overtones, and combination bands. See text.

deformation of A′ symmetry. For instance, in the case of the C−H stretchings, such an effect might be related to the significant coupling between the two vibrational modes, which probably requires an improved correlation treatment. Finally, a brief discussion on the accuracy of the best estimated harmonic frequencies is warranted. First of all, we need to point out the role of higher-order effects in the correlation treatment beyond CCSD(T). From the literature available (see for example refs 80 and 81), the full CC singles, doubles, and triples method (CCSDT) is expected to provide no improvements with respect to CCSD(T). The corrections due to quadruple excitations seem to be non-negligible and opposite in sign with respect to core-correlation effects.[81,82] On the other hand, for these contributions, the literature available is very limited and mostly related to diatomics, while the importance of taking into account the effects of core correlation is well recognized.[81−83] On the basis of the approximations made, the estimates for neglected contributions (mainly due to higher excitations beyond CCSDT: −0.1% to −0.3%, in relative terms), the corrections included as well as the literature on this topic (see, for example, refs 17 and 81), we expect that the accuracy obtained is a few wavenumbers: from 4 cm^{-1} to 11 cm^{-1}, where the latter value essentially applies to the larger frequency values.

A comparison of best-estimated harmonic frequencies with DFT results (Table 1) confirms the overall good accuracy of the latter in the present case. In fact, such a comparison shows a mean absolute error (MAE), with respect to best-estimated values, of about 7 cm^{-1} and 11 cm^{-1} for the B3LYP/aug-N07D and B3LYP/aug-cc-pVTZ levels of theory, respectively. The MAEs point out that the B3LYP/aug-N07D level of theory performs a little bit better than the B3LYP/aug-cc-pVTZ one, despite the significantly lower computational cost (232 vs 460 basis sets, respectively). Although this can be due to error compensation, the observed trend is quite general and suggests the B3LYP/augN07D level as the method of choice for spectroscopic investigations of large molecules, provided that DFT does not fail in describing the system under consideration.[39,84]

In the literature, some previous theoretical and experimental data are available for comparison. While the comparison to experiment is meaningful only once anharmonic corrections are accounted for (we therefore postpone such a comparison to the next section), a brief comment is deserved for what concerns theory. Among the literature papers available, we mention the works carried out by Barone et al.[61] and Ten et al.[62] Within the B3LYP approach, the former allows us to point out the improvement in the performance obtained by the aug-N07D set with respect to the 6-31G(d) basis set augmented by diffuse functions only on oxygen atoms. In fact, the discrepancies with respect to the best estimates decrease by a few (2−5) to somewhat greater (up to ∼20) wavenumbers. As concerns ref 62, rather good agreement between the B3LYP/6-31+G(d,p) harmonic frequencies

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and our best estimated values is observed, further confirming the good performance of B3LYP for this specific molecule.

Anharmonic Vibrational Frequencies. Going beyond the harmonic approximation, as already mentioned in the Introduction, the GVPT2 model applied to anharmonic DFT force fields (in particular with Becke-family hybrid functionals) with the proper treatment of Fermi and Darling–Dennison resonances[15] is known to provide accurate results for semirigid systems.[35,61] As the use of a hybrid CC/DFT scheme improves the accuracy, we limit our discussion to the results obtained by means of the two hybrid models described in the Methodology and Computational Details section, with anharmonic corrections computed at the B3LYP/aug-N07D level. The anharmonic frequencies evaluated with the different models for taking into account resonances are compared in Tables 2 and 3 for fundamental transitions and for overtones and combinational bands, respectively; for comparison purposes, the deperturbed values are also given. In particular, as uracil is known to be a difficult case due to the presence of strong Fermi resonances, such a comparison provides us with additional insights into the performance of the DVPT2 scheme with respect to GVPT2. For GVPT2 calculations, two cases have been actually considered: that where all of the Fermi resonances included in the work by Ten et. al[62] have been considered (Fermi: INP) and that in which Fermi interactions are taken into account through an automatic procedure with the harmonic frequencies evaluated either at the DFT level or from the composite scheme (Fermi: DFT and Fermi: CC, respectively). We first note that all schemes provide very similar results. In Tables 2 and 3, our results are also compared to the available experimental[58−60] and theoretical[62] data. On average, the hybrid CC/DFT approach leads to discrepancies, with respect to experimental results, of about 10 cm^{-1} and 13 cm^{-1} (with the largest discrepancies being ~38 cm^{-1} and 29 cm^{-1}) for fundamentals and for overtones and combination bands, respectively. As concerns the results of ref 62, we note that the B3LYP/6-31+G(d,p) level of theory with the proper account of Fermi resonances shows good agreement with experimental results but a worse one than that noted for our hybrid CC/DFT approach. In fact, even though a MAE of ~12 cm^{-1} is observed, larger discrepancies (the maximum discrepancy is 56 cm^{-1}) are evident. As the B3LYP/6-31+G(d,p) anharmonic corrections can be considered as good as ours (B3LYP/aug-N07D) and Ten et al.[62] correctly accounted for all Fermi interactions, the slight improvement obtained should be mainly ascribed to the hybrid approach used, which includes accurate estimates for harmonic frequencies. Anyway, it is worth noting that the present system seems to be a fortunate case, as usually the performance of DFT at the harmonic level with respect to highly correlated methods is definitely worse.[33,37,39,42,43]

As we claim for our anharmonic frequencies an overall accuracy of about 11 cm^{-1}, we can consider ours state-of-the-art results. For such a challenging case, systematic strategies to further reduce MAE below 10 cm^{-1} are not yet available. Additionally, it should be noted that in many cases the accuracy of experimental data (in particular for the lower intensity transitions) is not sufficient to justify the effort to reach a 1 cm^{-1} agreement between theory and experimental results. It is worth noting that the largest discrepancies are found for the 1700−1800 cm^{-1} frequency range, where several intense transitions due to the Fermi interaction involving C−O stretching vibrations are exhibited. In fact, both ours and Ten et al.'s investigations predict a number of vibrational transitions in this zone, a few of them with similar intensity.[62] Therefore, the proper assignment is cumbersome because of different possible interactions (see modes involved in Fermi resonances). The direct comparison between the computational simulated IR spectra and the experimental counterpart would be more meaningful. For uracil, such an attempt has been carried by Ten et al,[62] but the analysis was hampered by the lack of experimental data in the proper numerical form as well as by the limited experimental resolution.

As the vibrational spectrum of uracil is dominated by a large number of resonances, these deserve to be discussed in some detail. As mentioned above, the automatic procedure used to define possible Fermi interactions (Fermi: DFT; Fermi: CC) has been compared to the results where all Fermi interactions (Fermi: INP) postulated to be important[62] have been considered. A total of 16 (DFT) or 13 (CC) Fermi-type interactions have been pointed out by the automatic procedure, and the corresponding vibrational energy levels have been included in the variational treatment. As the *ad hoc* definition of additional interactions (leading to a total of 33 and 41 resonances for DFT and CC, respectively) does not improve the agreement with experimental results, the present results confirm the reliability of our "black-box" procedure, which takes into account both the zero-order energy difference between two resonant states and the strength of the coupling. Furthermore, we note that in the present case, due to the overall good accuracy of B3LYP/aug-N07D harmonic frequencies, similar results are obtained either by the *a posteriori* approach or by including best estimates for harmonic frequencies in the perturbative treatment. However, this conclusion is not of general validity. As a matter of fact, previous studies[37,39] unambiguously showed that in difficult cases, i.e., when the DFT harmonic frequencies present significant discrepancies with respect to best estimates, proper inclusion of accurate harmonic frequencies into the perturbative expressions leads to significant improvements. In general, the hybrid scheme (in particular Fermi: CC) has to be recommended whenever feasible, since it guarantees reliable harmonic frequencies as well as a proper definition of Fermi resonances. For the latter problem, the development and validation of alternative, more general VPT2 approaches that completely avoid resonant terms is in progress.[79]

Harmonic Vibrational Intensities. As concerns IR intensities computed within the double harmonic approximation, it has been shown by Schaefer et al.[85,86] that improvements in the electron-correlation treatment lead to converged values and that quantitative IR intensity predictions can be obtained at the CCSD(T) level in conjunction with basis sets of at least aug-cc-pVTZ quality.[86] In the present work, the extent of various contributions to IR intensities (within the harmonic approximation) has been investigated by means of the composite scheme introduced in the Methodology and Computational Details section. The results, reported in Table 4, show a slow convergence to the CBS limit, unlike what was observed for harmonic frequencies. In fact, differences up to tens of kilometers per mole are obtained by comparing the MP2/cc-pVTZ and MP2/cc-pVQZ levels (see the sixth column). Even for this property, CV corrections appear to be small, being negligible in most cases. Even if not explicitly reported in Table 4, we note that the effects of diffuse functions (pointed out by comparing MP2-cc-pVTZ and MP2-aug-cc-pVTZ) are in most cases on the order of 10%, which means for the most intense transitions intensity enhancements of even 60−90 kcal/mol. The same conclusion is drawn for higher-order correlation contributions, i.e., $\Delta I((T))$ corrections.

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Table 4. Double Harmonic IR Intensities (km/mol) of Uracil

assignment	B3LYP/aug-N07D	B3LYP/aug-cc-pVTZ	MP2/aug-cc-pVTZ	ΔCV	Δ(QZ-TZ)	Δ(T)	best^a estimate
ν(N1−H)	105.55	102.37	122.44	1.16	3.24	−14.40	112.44
ν(N3−H)	68.51	65.58	77.11	1.01	3.89	−9.48	72.53
ν(C5−H)	1.19	1.19	2.58	0.19	0.54	−1.22	2.09
ν(C6−H)	2.50	2.31	2.08	−0.10	−0.46	0.28	1.80
ν(C2=O)	626.64	599.84	753.68	−0.09	28.12	−55.76	725.95
ν(C4=O)	770.74	774.96	568.37	6.84	56.71	88.39	720.31
ν(C5=C6)	60.30	66.95	19.00	−0.42	−2.15	17.68	34.12
δ(N1−H)	88.66	81.81	121.62	2.39	−5.10	−13.07	105.84
δ(C6−H)	92.71	86.84	66.33	3.20	5.62	27.71	102.86
δ(N3−H)	9.89	7.88	38.65	−4.72	−9.11	−20.23	4.59
δ(C5−H)	35.17	56.65	9.86	−0.48	0.10	2.68	12.17
ν(ring)	2.76	10.86	15.54	1.14	2.71	0.17	19.57
ν(ring)	106.52	104.44	108.11	−2.04	2.21	2.36	110.64
ν(ring)	5.59	4.75	5.43	0.28	−0.59	1.30	6.41
ν(ring)	7.17	7.35	8.05	0.02	0.44	−0.24	8.28
ν(ring)	0.04	0.10	0.48	−0.04	−0.10	0.15	0.49
ν(ring)	3.27	3.65	3.67	−0.01	0.26	0.16	4.08
δ(ring)	36.66	41.70	40.88	0.80	1.03	−2.55	40.16
δ(ring)	6.52	7.39	6.57	−0.00	0.27	−0.27	6.57
δ(ring)	21.29	21.64	18.35	0.11	0.62	1.47	20.55
δ(C=O)	20.97	20.74	20.68	0.13	0.40	1.32	22.53
γ(C6−H)	9.35	10.93	10.91	−0.14	0.41	−0.28	10.90
γ(C5−H)	61.73	60.69	49.90	0.74	−2.22	1.60	50.01
γ(C2=O)	30.98	34.35	30.31	0.64	0.98	−0.43	31.51
γ(C4=O)	17.79	15.48	9.61	0.55	1.47	0.59	12.22
γ(N3−H)	75.93	68.57	81.97	−1.20	−1.98	3.16	81.94
γ(N1−H)	4.64	4.53	3.00	0.03	0.15	0.38	3.56
γ(ring)	24.03	20.98	23.41	−0.36	−1.67	2.58	23.97
γ(ring)	0.24	0.08	0.35	−0.06	0.05	0.43	0.67
γ(ring)	1.57	1.93	0.93	0.11	0.19	−0.33	0.90

^{a} From eq 2.

Effects of diffuse functions and core correlation are not always in the same direction. For example, they are both positive for ν(C4=O), while they nearly cancel out for ν(C2=O). On general grounds, it might be of some interest to note that the vibrational modes that show the largest corrections are once again the C−O stretchings. Furthermore, while they exhibit comparable intensities when effects of triple excitations are included, very different intensities are observed at the MP2 level. On the whole, the present results confirm that the prediction of IR intensities is more demanding than band positions.[9] Since they depend on dipole moment derivatives, reliable estimates require an accurate description of the electronic charge density and its variation along normal modes. In turn, these conditions imply that IR intensities are sensitive to electron-correlation effects and basis-set extension. In view of the large extent of some contributions and the lack of literature on this topic, it is difficult to estimate the accuracy of our best estimated values. For these reasons, a benchmark investigation on IR intensities for small- to medium-sized molecules is in progress.

By comparing the results obtained at different levels of theory, it is worth noting that the MP2 level generally tends to overestimate IR intensities with respect to CCSD(T). DFT performs quite well with respect to our best estimated values, with a MAE of about 10 and 13 km/mol for the B3LYP/aug-N07D and B3LYP/aug-cc-pVTZ levels, respectively. In Table 2, the available experimental data are reported. Even though our computed harmonic intensities are able to reproduce on average the experimental trend, a quantitative comparison is not possible at the present stage. Work along this direction is in progress, and it mainly concerns benchmark studies in view of verifying the accuracy obtainable by QM computations as well as the investigation of resonance effects on anharmonic contributions.

■ CONCLUSIONS

Vibrational frequencies and intensities have been investigated within the harmonic approximation at a high level of theory. Following our previous work,[45] a composite scheme has been exploited in order to account for basis-set effects and to include core-correlation corrections. As the accuracy in vibrational frequencies evaluation is mostly related to the harmonic force field, the computational approach introduced paves the way toward spectroscopic accuracy for molecules with a larger and larger number of atoms. In particular, the approach presented is expected to be accurate and reliable for all types of systems, also when DFT fails in a proper description of the electronic structure. The comparison to available experimental data points out that the use of hybrid CC/DFT schemes with the proper

account of Fermi interactions allows one to obtain state-of-the-art anharmonic frequencies for a system as challenging as uracil. Within pure DFT approaches, for both frequencies and intensities, the present study confirms that the aug-N07D basis set is able to provide results close to or even better than those obtained with the larger aug-cc-pVTZ set. We also note that, in the present case, the accuracy of DFT results is at least comparable to that of MP2 computations employing extended basis sets, but with a considerable savings of computational time and thus a much better scaling with the dimensions of the system.

In conclusion, even if further developments are still required and under consideration, in our opinion, the results of the present investigation show the remarkable performance of composite schemes as well as of integrated CC and DFT approaches in the field of vibrational spectroscopy.

■ AUTHOR INFORMATION

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