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Vibrational energy levels of water

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Abstract

Several quartic force fields and a full sextic anharmonic force field for H₂O have been determined from high-quality ab initio calculations, the highest at the aug-cc-pVQZ CCSD(T) level of theory. These force fields have been used to determine vibrational excited state band origins up to 15 000 cm⁻¹ above the zero-point level, using both a perturbation-resonance approach and a variational approach. An optimised quartic force field has been obtained by least squares refinement of our best ab initio results to fit the observed overtone levels of 5 symmetrically substituted isotopomers of water (H₂¹⁶O, H₂¹⁷O, H₂¹⁸O, D₂O, and T₂O) with an rms error of less than 10 cm⁻¹, using the perturbation-resonance model for the vibrational calculation. Predicate least squares refinement was used to provide a loose constraint of the refined force field to the ab initio results. The results obtained prove the viability of the perturbation-resonance model for use in larger molecular systems and also highlight some of its weaknesses. © 1997 Elsevier Science B.V.

Keywords: Anharmonic force field; Perturbation-resonance model; Vibrational energy

1. Preview

Theoretical, first-principles determination of the vibrational spectra of a polyatomic molecule requires a knowledge of the form of the potential energy surface (PES). The most viable approach to the description of the PES of a polyatomic molecule involves the determination of the anharmonic (usually quartic) force field, defined as the coefficients in a Taylor-series expansion of the PES around a reference geometry, usually taken

as an equilibrium position. Such force fields are exceptionally well suited for perturbational treatments allowing determination of the required properties of the molecular system under study, and can also be employed in variational treatments.

Prediction of harmonic and anharmonic force fields by the methods of molecular electronic structure theory has received much attention in recent years, mainly due to the systematic development of analytic methods for the evaluation of derivatives of the molecular electronic energy with respect to nuclear coordinates, which was initiated in 1969 by the formulation and implementation of

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Table 1

Species for which full anharmonic (at least quartic) force fields have been determined by methods of ab initio quantum chemistry^a

3-atomic	4-atomic	5-atomic	5+-atomic
BCN, BNC, B ₂ C, Be ₃ , BeH ₂ , BrNO, CF ₂ , CH ₂ , CO₂ , CS ₂ , C ₃ , Ca ₃ , ClCN, ClNC, ClNO, FCN, FNC, FHC1 ⁻ , FNO, FSN, F ₂ O, HCN, HCO, HCP, HCO ⁺ , HNC, HNO, HO ₂ , HOC ⁺ , HOBr, HOCl, HOF, H ₂ O, H ₂ S, H ₂ Te, IHI ⁻ , KrF ₂ , NF ₂ ⁺ , NH ₂ , NOBr, NO ₂ ⁺ , NO ₂ ⁻ , N₂O , OCS, O ₃ , P ₂ O, XeF ₂	BH ₃ , Be ₄ , C ₃ H ₂ , C ₂ HF, C ₂ F ₂ , C ₄ , Ca ₄ , HNCO, H ₂ CN, H ₂ CO, H ₂ CS, H ₂ N ₂ , H ₂ O ₂ , Mg ₄ , NH ₃ , NF ₃ , PH ₂ F, PH ₂ Cl, PH ₂ Br, PH ₂ I, P ₄ , SiH ₃ ⁻	CH ₄ , CF ₂ NH, CHClF ₂ , CHF ₃ , CH ₂ ClF, CH ₂ F ₂ , C ₃ H ₂ , ClCO ₂ H, H ₂ CCO, NH ₄ ⁺ , SiH ₃ Br, XeF ₄	C ₃ H ₄ , C ₂ H ₄ O, C ₃ H ₃ ⁺ , C ₆ H ₆ , HCONH ₂

^a Species for which full sextic force fields have been reported are indicated with bold letters.

analytic forces for self-consistent-field Hartree–Fock (SCF) wave functions [1]. Following some pioneering works [2–11], the first systematic studies of vibrational anharmonicity and vibration–rotation interaction by SCF higher-derivative and electron correlation methods for asymmetric top [12] and linear [13] molecules still awaited the end of the 1980s. These studies complement the extensive literature on the experimental (sometimes called empirical) determination of anharmonic force fields, for which excellent reviews have been available for decades [14–17].

Determination of harmonic and anharmonic molecular force fields by methods of molecular electronic structure theory has now become one of the most successful applications of computational quantum chemistry. In Table 1 those species are indicated (without references to the original publications) for which full ab initio force fields have been determined, at least at the SCF level of theory and at least up to quartic force constants. The two molecules, CO₂ and N₂O, for which full sextic force field predictions have been reported [18,19] are indicated in this table with bold letters.

All previous ab initio investigations of anharmonic force fields of small and medium-sized polyatomic molecules [2–13,18–27] lead to the following conclusions about the overall precision

of theoretically determined anharmonic force fields:

(a) The contribution of electron correlation to the PES can usually be fit with low-order polynomials. Therefore, it is difficult to obtain high quality results for the calculated equilibrium geometry, and also (but to a lesser extent) for the calculated quadratic force field. On the other hand, most calculated cubic and quartic force constants show only small variation with respect to basis set extension and treatment of electron correlation, and even results obtained at the SCF level seem to be quite reliable for these force constants. If the reference geometry chosen is correct, particularly accurate cubic and quartic force constants are obtained if methods incorporating a large portion of the electron correlation energy with extended basis sets are employed.

(b) If the calculated force constants are obtained at the corresponding optimized geometry, then a substantial part of the discrepancy between calculated and experimental force constants comes from the differences in the underlying reference structures. For semi-rigid molecules, shifting the theoretical reference geometry close to the true equilibrium geometry results in force constants which are usually in dramatically better agreement with their experimental counterparts.

(c) Some of the higher-order force constants determined experimentally (especially the quintic and sextic constants) are phenomenological in nature, i.e. they do not directly correspond to the associated derivatives of the PES but are rather to be seen as fitting constants that allow for a number of small model errors.

Based on the analysis of diatomic and triatomic paradigms [20–22], the following points need to be further emphasised about the choice of the reference geometry for the ab initio prediction of harmonic and anharmonic force fields:

(a) The molecular potential energy is comprised of two sizeable terms which happen to be of similar magnitude and opposite in sign, viz. electronic (E_e) and nuclear–nuclear repulsion (V_N) contributions. The theoretical prediction of force constants becomes a rather unbalanced procedure vis-à-vis cancellation of errors, because the V_N contribution and its derivatives can be calculated exactly while the E_e contributions can only be determined approximately.

(b) The E_e and V_N contributions to the forces (linear force constants) and the quadratic force constants nearly cancel each other, but for the higher-order force constants the contributions of the derivatives of V_N become increasingly dominant. In particular, higher-order bond stretching derivatives depend strongly on nuclear–nuclear repulsions and hence on the reference geometry at which they are evaluated. The fact that the approximate E_e derivatives make smaller and smaller contribution to force constants of higher and higher order means that the anharmonic force constants can be calculated to greater precision than the geometries or the quadratic force fields.

(c) For small reference bond length variations (δr), it can be shown [23] that the percentage change (p_ω) in the predicted harmonic frequency at a given level of theory is approximately $50\rho \delta r$, where ρ is the ratio of the cubic to quadratic force constant near equilibrium. For most simple molecules $\rho \in [-7, -8] \text{ \AA}^{-1}$, and thus even a small $\delta r \approx 0.002 \text{ \AA}$ error gives rise to $p_\omega \approx -0.7\%$. Choice of the reference geometry may thus have pronounced effect (ca. 10 s of cm^{-1}) on the calculated harmonic and anharmonic wavenumbers.

In the determination of the anharmonic force field of the water molecule, the results of which are presented below, we have tried to incorporate some of the lessons to be learned from this discussion.

2. Introduction

The water molecule is an asymmetric top triatomic molecule for which many attempts, of varying sophistication, have been made to determine the anharmonic force field corresponding to its electronic ground state.

The earliest experimental attempts were based on a study from 1956 by Benedict, Gailar, and Plyler [28], who analysed a large number of vibrational transitions for H_2O , HDO , and D_2O , reporting harmonic wavenumbers ω_r , anharmonicity constants $x_{r,s}$, and vibration–rotation interaction constants α_r , D_J , etc, using the customary Dunham expansion [29] in powers of the vibrational quantum numbers v_r and rotational operators J_x , J_y , J_z . The ω_r , $x_{r,s}$ and α_r constants are the so-called ‘spectroscopic constants’, and early anharmonic force field calculations were performed by first fitting experimental data to obtain the spectroscopic constants for each isotopomer, and second finding a force field to reproduce the spectroscopic constants, by least squares refinement or by some other method. This is the method known as second-order perturbation theory (VPT2).

Kuchitsu and Morino [30] derived a quartic force field for water based on this method, but failed to treat resonances properly. Later Pariseau [31], as well as Smith and Overend [32], made further attempts to determine a quartic force field, and included both cubic (Fermi-type) and quartic (Darling–Dennison-type) resonances for the first time. Also using this approach, Hoy, Mills, and Strey [33], in an influential paper, derived an (incomplete) quartic force field for water by fitting the spectroscopic constants determined by BGP. This force field was the starting point for many later studies using more sophisticated models to calculate the vibrational spectrum. Hoy and Bunker [34] used a non-rigid bender model to

calculate the energy levels, and this was later developed and extended by Bunker and co-workers [35], culminating in the work by Jensen [36a] using his Morse oscillator rigid bender internal dynamics (MORBID) [36b] model. A number of sophisticated variational studies have been performed for water [37–45]. Carter and Handy [41] derived a full quartic force field using the HMS field as a starting point. Halonen and Carrington [42b] utilized Morse oscillators to describe the stretching motion of water, and this work was later extended by Kauppi and Halonen [42c]. Choi and Light [44] performed accurate (nearly) variational calculations employing a discrete variable representation (DVR) and determined a very large number of highly excited vibrational states of water. Polyanski et al. [45] determined an especially high-quality PES representation for the electronic ground state of H_2^{16}O by fitting it to a large number of vibration and vibration-rotation term values. Most of these variational models employed a Hamiltonian expressed directly in curvilinear internal coordinates, and derived anharmonic force fields expressed in curvilinear internal coordinates, with varying degrees of completeness regarding the number of force constants included.

As far as theoretical studies [2,7,10,12,46,47] are concerned, Shavitt et al. [46a,b] were probably the first to make an attempt to determine the force constants of water from ab initio energy calculations. In 1979, Botschwina [2] determined 19 out of the 47 sextic force constants of water, mostly at the RHF level. Bartlett et al. [10] obtained a full quartic force field at the CCSDT-1 level using a 39-STO basis set. Schaefer et al. [11,12] also included water in their studies of vibrational anharmonic effects; they considered the feasibility of using computational quantum chemistry to predict the wide variety of spectroscopic constants which characterise the vibration-rotation spectra of semi-rigid molecules. Recently Martin et al. [47] used the QCISD(T) electron correlation treatment with a number of basis sets to calculate the full quartic force field of water by a least-squares fit to a grid of calculated energy points. Thus, the anharmonic (quartic) force field of water seems to be well established both by theoretical and by experimental treatments.

There have been several motivations for our research. One was to check whether a simple perturbation-resonance approach, which can potentially be employed for considerably larger molecular systems, would be successful in calculating high-lying vibrational overtones of water up to $18\,000\text{ cm}^{-1}$ above the zero-point energy. The various isotopic relationships between the spectroscopic constants are not necessarily fulfilled if they are obtained by a fitting procedure employed independently for each isotopomer. We have therefore attempted to fit a quartic force field, expressed in curvilinear internal coordinates, directly to the observed vibrational band origins of several symmetrically substituted isotopomers of water (H_2^{16}O , H_2^{17}O , H_2^{18}O , D_2O , and T_2O) using the perturbation-resonance model. We have obtained a force field representation of the PES which gives an accuracy of a few cm^{-1} up to about $15\,000\text{ cm}^{-1}$ above the ground state. We have also made full use of high quality ab initio calculations, both to provide a starting point for the least squares refinement to the observed data, and to 'predicate' the refinement, and provide a yardstick with which to compare our results. We plan to include rotational constants in this calculation in the near future. Since a system containing protons is necessarily a difficult example for perturbational calculations due to the relatively large amplitude vibrations, the vibrational wavenumber errors for water obtained from this treatment should serve as an upper bound for the errors obtained for heavier systems. We also wanted to investigate what effect the quintic and sextic terms in the anharmonic force field of water have on the calculated vibrational levels. Since this question cannot be answered with perturbation formulas presently available, a set of variational calculations, based on the exclusive use of rectilinear dimensionless normal coordinates, have been performed using the so-called vibrational configuration interaction (CI) formalism [8]. These calculations allowed several useful observations about the numerical transformation of anharmonic force fields expressed in curvilinear internal coordinates into rectilinear normal coordinate space and about the precision of the variational calculations based on these transformed force fields.

3. Ab initio determination of anharmonic force fields

From group theoretical arguments we find that, in its C_{2v} ground electronic state, the water molecule has two geometric variables, and four quadratic, six cubic, nine quartic, 12 quintic, and 16 sextic force constants. Since analytical derivatives are available only for the lower order force constants, there is a technical difficulty to obtain the high-order derivatives (force constants) from low-order analytic data.

3.1. Differentiation techniques

The two basic methods for determining derivatives of the PES numerically are least-squares fitting and the use of finite difference expressions based on collocation polynomials. An early review of these numerical techniques for the calculation of theoretical force fields up to third order is provided in an article by Fogarasi and Pulay [48]. Pitfalls associated with least-squares procedures are emphasised there. Although the finite-difference formulas seem to be less economical, the cost associated with deriving these formulas and obtaining the necessary quantum chemical information to evaluate them is well justified by the superior numerical accuracy obtainable. Indeed, Table 1 of Allen and co-workers [13] shows how accurate finite difference formulas are by comparing the complete quartic force field of HCN calculated from analytic third derivatives, with the same result calculated from analytic first derivatives and carefully selected finite difference formulas. All the deviations observed are just a fraction of 1%, and in most cases they are even comparable with the truncation errors associated with obtaining the quartic constants by finite differences of analytic third derivatives. Sophisticated computer algebra packages, like *Mathematica* [49], used in this work, are exceptionally well suited to obtain the complicated finite-difference formulas. Furthermore, they may not only be used to determine the necessary formulas, but they may also be used to solve the resulting sets of simultaneous equations, giving directly the required force constants and thus decreasing sub-

stantially the possibilities of human error in their evaluation. For this reason and to conserve space the finite-difference formulas employed to calculate the quartic and sextic force fields of H_2O presented in Tables 2 and 3 are not detailed here. It is only noted that single, double, and triple displacements of sizes $n \times 0.02$ (Å, rad) ($n = 0, 1, 2, 3$) along the {stretch, stretch, bend} internal coordinates chosen were needed for the numerical determination of the force field. All energies and gradients computed have been converged to almost machine precision.

3.2. Computational details

The basis sets selected for this study are the augmented (aug) correlation-consistent (cc) aug-cc-pVTZ and aug-cc-pVQZ basis sets of Dunning and coworkers [50,51]. These basis sets were chosen as it was felt that the inclusion of diffuse functions on the O atom should result in higher

Table 2
Force constants for the electronic ground state of water obtained with the aug-cc-pVQZ basis set^a

Term	SCF	MP2	CCSD	CCSD(T)
f^r	0.1622	0.0085	0.0307	0.0075
f^α	-0.0162	0.0011	-0.0017	0.0000
f^{rr}	8.606	8.506	8.455	8.437
$f^{r'r}$	-0.039	-0.135	-0.087	-0.098
$f^{r\alpha}$	0.236	0.260	0.253	0.256
$f^{\alpha\alpha}$	0.765	0.690	0.713	0.706
f^{rrr}	-59.11	-58.27	-58.51	-58.51
$f^{r'r'r}$	-0.009	-0.074	-0.046	-0.055
$f^{r\alpha\alpha}$	-0.084	-0.140	-0.100	-0.106
$f^{r'r'\alpha}$	-0.533	-0.458	-0.519	-0.516
$f^{r\alpha\alpha}$	-0.316	-0.342	-0.314	-0.321
$f^{\alpha\alpha\alpha}$	-0.694	-0.706	-0.718	-0.715
f^{rrrr}	369.8	362.7	362.9	362.6
$f^{r'r'r'r}$	-0.75	-0.44	-0.65	-0.61
$f^{r'r'r'r'}$	0.44	0.19	0.36	0.31
$f^{r'r'r\alpha}$	-1.23	-1.52	-1.40	-1.44
$f^{r'r'\alpha}$	0.81	0.97	0.81	0.80
$f^{r\alpha\alpha\alpha}$	-0.24	-0.25	-0.25	-0.25
$f^{r'r'\alpha\alpha}$	0.51	0.61	0.63	0.63
$f^{r\alpha\alpha\alpha}$	0.72	0.78	0.77	0.78
$f^{\alpha\alpha\alpha\alpha}$	-1.011	-0.571	-0.645	-0.622

^a The reference geometry employed for all calculations corresponds to the best present estimate of the equilibrium geometry of water, namely $r_{OH} = 0.95843$ Å and $\angle_{HOH} = 104.44^\circ$.

Table 3
Force constants for the electronic ground state of water^a

Term	Set I	Set II	Set III	MFG ^b	IMM ^c	CH ^d	CH ^d	J ^f
f^r	-0.0031	0.0075						
f^z	0.00096	0.0000						
f^{rr}	8.493	8.437	8.456	8.448	8.454	8.454	8.446	8.439
$f^{rr'}$	-0.089	-0.098	-0.115	-0.103	-0.101	-0.101	-0.102	-0.105
f^{rz}	0.260	0.256	0.277	0.261	0.219	0.219	0.243	0.306
f^{zz}	0.697	0.706	0.708	0.709	0.697	0.696	0.700	0.707
f^{rrr}	-58.9	-58.51	-58.49	-59.0	-59.4	-58.2	-58.9	-55.4
$f^{rrr'}$	-0.092	-0.055	-0.051	-0.055	0.253	-0.8	-0.003	-0.32
f^{rrrx}	-0.100	-0.106	-0.101	-0.096	0.40	0.4	-0.01	-0.25
$f^{rr'x}$	-0.502	-0.516	-1.017	-0.492	-0.40	-0.6	-0.52	-0.45
f^{rzz}	-0.296	-0.321	-0.497	-0.300	-0.23	-0.2	-0.29	-0.34
f^{zzz}	-0.682	-0.715	-0.831	-0.692	-0.88	-0.670	-0.672	-0.73
f^{rrrz}	365.3	362.6	366.0	375.1	384	367	377	306
$f^{rrr'}$	-0.069	-0.61	-0.59	-0.635	-5	7		2.6
$f^{rrr'r}$	0.180	0.31	0.32	0.023	0.6	0.6		1.9
f^{rrrz}	-1.406	-1.44	-1.45	-1.60	—	-9.7		-6.1
$f^{rrr'z}$	0.384	0.80	-1.45	0.193	—	2.3		-3.2
f^{rrzz}	-0.163	-0.25	-0.24	-0.379	-1.4	-1.5		-0.95
$f^{rr'zz}$	0.660	0.63	-0.36	0.577	0.6	0.8		0.12
f^{rzzz}	0.805	0.78	0.73	0.736	—	1.8		0.9
f^{zzzz}	-0.334	-0.622	-0.211	-0.660	-0.1	-0.38	-1	-0.24
f^{rrrr}	-2429.1						-2268	
$f^{rrrr'}$	3.89							
$f^{rrrr'r}$	2.66							
f^{rrrrz}	0.82							
$f^{rrrr'z}$	0.86							
$f^{rrr'rz}$	-2.86							
f^{rrrzz}	0.36							
$f^{rrr'zz}$	-1.00							
f^{rrzzz}	0.28							
$f^{rr'zzz}$	-1.66							
f^{rzzzz}	-1.36							
f^{zzzzz}	-3.41							
f^{rrrrr}	16855.6							
$f^{rrrrr'}$	-56.1							
$f^{rrrr'r}$	-20.7							
$f^{rrrr'r'}$	-44.3							
f^{rrrrrz}	-18.0							
$f^{rrrr'z}$	-11.8							
$f^{rrrr'rz}$	-2.0							
f^{rrrrzz}	-20.5							
$f^{rrrr'zz}$	-7.6							
$f^{rrr'zzz}$	-4.0							
f^{rrrzzz}	-6.6							
$f^{rrr'zzz}$	16.8							
f^{rrzzzz}	-1.7							
$f^{rr'zzzz}$	-1.1							
f^{rzzzzz}	-4.1							
f^{zzzzzz}	-18.3							

[9]

^a Units of the force constants are consistent with energy measured in aJ, distances in Å, and angles in radian. The Set I and Set II force fields were obtained from aug-cc-pVTZ CCSD(T) and aug-cc-pVQZ CCSD(T) calculations, respectively. Set III contains a refined set of force constants (for details see text). ^b [47]. ^c [33]. ^d [41]. ^e Potential energy function (PEF) B of [2]. Values in brackets are taken from PEF A. ^f [36a].

precision for the calculated constants, especially those involving the bending mode. Only the pure spherical components of the basis functions have been employed. Electronic wave functions have been determined in this study at several different levels: self-consistent-field restricted Hartree–Fock (SCF), [52–54] second-order Møller–Plesset [53–55], coupled-cluster singles and doubles (CCSD) [56,57], and the coupled-cluster singles and doubles level including a perturbative estimation of connected triples [58] [usually abbreviated as CCSD(T)]. Analytic geometric first derivatives have been determined at the CCSD(T) level employing the aug-cc-pVTZ basis set. The program system ACES II [59] has been used for the ab initio calculations. No orbitals have been kept frozen during these calculations. All anharmonic force field transformations, least-square refinements, and the determination of spectroscopic constants have been performed with a newly developed set of codes [60].

3.3. Anharmonic force fields

Anharmonic force fields for H₂O, determined at various levels of ab initio theory as part of the present study, are reported in Tables 2 and 3 along with some of the available theoretical and experimental anharmonic fields determined previously.

In Table 2 quartic force fields obtained in this study at the aug-cc-pVQZ SCF, MP2, CCSD, and CCSD(T) levels are presented. The reference geometry chosen for these calculations, with $r_e(\text{OH}) = 0.95843 \text{ \AA}$ and $\alpha_e(\text{HOH}) = 104.44^\circ$, is believed to be very close to the true equilibrium geometry of free water. Furthermore, by performing all calculations at the same reference geometry, the direct and indirect effects [23] (in other words, changes related to improved description of the electronic structure and changes due principally to the shift of the true reference geometry at the particular level of theory, respectively) of inclusion of electron correlation into the calculations of force constants can be separated, and attention can be focused on the genuine direct effects. The aug-cc-pVQZ basis set is considered to be close to the basis set limit; it principally lacks

only basis functions which would be adequate to describe core-core and core-valence correlation effects [23]. Therefore, the SCF results presented should be very close to the Hartree–Fock limit. Treatment of electron correlation offered by the CCSD(T) method, especially with an aug-cc-pVQZ basis set, is of very high quality; near full-configuration-interaction (FCI) results are expected. Thus, the aug-cc-pVQZ CCSD(T) quartic force field should give a very good representation of the true electronic ground state PES of free water around the equilibrium structure. Breakdown of the Born–Oppenheimer approximation, on which the concepts of geometry and the PES are based, and neglect of relativistic effects from the calculations, is expected to produce only marginal changes in the force constants, unimportant even at the level of precision we seek. Therefore, almost all remaining errors in this force field should be assigned to core-core and core-valence correlation effects, not considered explicitly in this study. These have indeed been shown to be important for the accurate prediction of geometries and quadratic force constants [23], although at higher orders their effects seem to be small. (Also, in the case of water, the two hydrogens have no core electrons, so the bending motion is expected to be influenced much less than the stretching modes). This imprecision of the quartic force field can easily be corrected by slight adjustment of the calculated force constants to reproduce the experimental vibrational band origins in a least-squares calculation (see below). In summary, the high quality of the SCF constants and the rapid convergence of most higher-order force constants toward the almost exact CCSD(T) values is clearly evident from Table 2. These results prove once again the considerable utility of SCF quadratic and especially higher-derivative force constants.

It is evident from Table 3 that all the experimental quadratic and cubic force constants agree quite well with each other and with the calculated values. Variances among correlated level force fields seem to be acceptable. Most ab initio higher-order stretch–stretch coupling constants are small, usually orders of magnitude smaller than the diagonal stretching force constants. Thus, they could safely be neglected in an empiri-

cal fit, unless they become important due to their role in resonance interactions. The bending mode of H₂O appears to be quite harmonic, at least up to 4 quanta. The diagonal bending constants in higher orders are rather small, as are the stretch-bend interaction constants.

Among the quadratic constants only the magnitude of f^{rz} warrants discussion. All high-level theoretical calculations of both this and previous studies agree that its value is close to 0.26 aJ Å⁻¹ rad⁻¹, while results from empirical force field refinements range from 0.219 [33] to 0.306 aJ Å⁻¹ rad⁻¹, clearly bracketing the theoretical value.

All cubic force constants are predicted to be negative by all ab initio calculations, and also in most empirical refinements, including the first reliable published quartic force field of water [32]. Therefore, the fact that f''' and $f'''x$ have been predicted to be positive in some experimental force field refinements (e.g. Hoy, Mills, and Strey [33] obtained values of 0.253 (15) aJ Å⁻³ and 0.404 (200) aJ Å⁻² for these two constants) should be regarded as weaknesses in their calculation rather than indications that there were problems in the ab initio calculations. It is also noteworthy that the cubic stretch-stretch interaction constant f''' is determined to be much smaller in absolute magnitude in the ab initio calculations (around -0.09 aJ Å⁻³) than in empirical refinements; for example, Carter and Handy [41] found a value of -0.8 (3) aJ Å⁻³ for this constant. Note, however, that our own least-squares refinements (vide infra) also changed the value of f''' considerably.

In the quartic part of the force field pronounced deviations exist for some of the constants. First of all, it is noteworthy how different the calculated f^{xxxx} constants are. This is probably due not only to basis set effects but also to higher-order contamination (round-off) and truncation effects during their determination.

No meaningful comparison is possible for the quintic and sextic force constants as the only previous values have been determined by Botschwina [2] at a rather low level of theory, and then only for a few of the constants. Nevertheless, both sextic constants f^{rrrrr} and $f^{\alpha\alpha\alpha\alpha\alpha}$

determined by Botschwina appear to be unreliable.

Finally, it is interesting to note that the signs of the stretch-stretch coupling constants in higher order do not seem to follow any simple rule, while the signs of the quadratic and cubic constants can be rationalized using simple arguments [13–15,61].

4. A perturbation-resonance approach

As shown here, a perturbation-resonance approach, i.e. an approach which employs the VPT2 formalism but takes into consideration all cubic and quartic resonances identified, is able to result in highly accurate vibrational levels for water even up to 15 000 cm⁻¹ above the zero-point level.

4.1. Second-order vibrational perturbation theory (VPT2)

Second-order vibrational perturbation theory (VPT2) [12–17,62] results in relatively simple formulas for the calculation of vibrational anharmonicity corrections and vibrational energy levels. In this approach only the quartic part of the anharmonic force field enters the formulas. However, one has to consider different types of resonances between the normal modes.

VPT2 results in an approximate effective Hamiltonian \tilde{H} which is diagonal in the vibrational quantum numbers. The diagonal elements of the effective vibrational Hamiltonian for an asymmetric top molecule are given by:

$$H_{\lambda\lambda}/hc = \sum_r \omega_r(v_r + 1/2) + \sum_{r \leq s} x_{rs}(v_r + 1/2)(v_s + 1/2) \quad (1)$$

where ω_r are the harmonic vibration wavenumbers, x_{rs} are the vibrational anharmonicities, v_r and v_s are the vibrational quantum numbers for the state λ , and higher-order terms do not enter the expansion at this level of approximation. The standard expressions for x_{rs} for an asymmetric top molecule are

$$x_{rr} = \frac{1}{16} \phi_{rrrr} - \frac{5}{48} \frac{\phi_{rrr}^2}{\omega_r} - \frac{1}{16} \sum_{s(\neq r)} \phi_{rrs}^2 \left[\frac{2}{\omega_r} - \frac{1}{2(2\omega_r - \omega_s)} + \frac{1}{2(2\omega_r + \omega_s)} \right] \quad (2a)$$

and for $r \neq s$

$$x_{rs} = \frac{1}{4} \left(\phi_{rrss} - \sum_k \frac{\phi_{rrk} \phi_{kss}}{\omega_k} \right) - \frac{1}{2} \sum_k \frac{\phi_{rsk}^2 \omega_k (\omega_k^2 - \omega_r^2 - \omega_s^2)}{\Delta_{rsk}} + \sum_\gamma B_\gamma^z (\zeta_{rs}^\gamma)^2 \left(\frac{\omega_r}{\omega_s} + \frac{\omega_s}{\omega_r} \right) \quad (2b)$$

Here

$$\Delta_{rsk} = (\omega_r + \omega_s + \omega_k)(\omega_r - \omega_s - \omega_k) \times (-\omega_r + \omega_s - \omega_k)(-\omega_r - \omega_s + \omega_k) \quad (3)$$

and the B_γ^z and ζ_{rs}^γ quantities are rotational constants and Coriolis coupling constants, respectively, for the principal axes $\gamma = a, b$, and c . Thus, the x_{rs} contain second-order contributions from the cubic force constants and first-order contributions from the quartic force constants.

If no resonances are present, the effective vibrational Hamiltonian \tilde{H} has no off-diagonal matrix elements. The true Hamiltonian H does have off-diagonal matrix elements; for example the matrix elements of cubic and quartic anharmonic terms in the potential energy always have off-diagonal matrix elements. However, the second-order perturbation treatment transforms the true Hamiltonian H into an effective Hamiltonian \tilde{H} , which has diagonal elements modified by the perturbation treatment but no off-diagonal elements. This VPT2 treatment will obviously fail if cross terms in H connect nearly degenerate vibrational states. In this case one talks about resonances. Cubic anharmonic resonances are generally known as Fermi resonances, and various quartic resonances are possible of which the most familiar examples are Darling–Dennison resonances. If either cubic or quartic vibrational resonances are present, it becomes necessary to abandon the perturbation

treatment of those particular off-diagonal elements, reintroduce the necessary off-diagonal matrix elements explicitly into \tilde{H} (see below), and diagonalize the resulting blocks of the effective Hamiltonian. In the case of a cubic vibrational resonance the formulas given for x_{rs} break down, and terms containing a resonance denominator (e.g. $2\omega_r - \omega_s$ in x_{rr}) must be removed. The modified anharmonicity constants are then usually denoted with an asterisk, x_{rs}^* .

4.2. Resonance terms

It is necessary to consider two types of vibrational resonance for water, which introduce off-diagonal elements into the effective vibrational Hamiltonian. The first one is a cubic (Fermi-type) resonance of the type

$$\langle v_1, v_2, v_3 | \hat{H}/hc | v_1 - 1, v_2 + 2, v_3 \rangle = \frac{1}{2} \phi_{122} [v_1(v_2 + 1)(v_2 + 2)]^{1/2} \quad (4)$$

(e.g. $v_1, v_2 = 1, 0$). The second one is a quartic (Darling–Dennison-type) resonance, for which the matrix elements can be written as

$$\langle v_1, v_2, v_3 | \hat{H}/hc | v_1 - 2, v_2, v_3 + 2 \rangle = \frac{1}{4} K_{11,33} [(v_1 + 1)(v_1 + 2)(v_3 + 1)(v_3 + 2)]^{1/2} \quad (5)$$

These expressions are based on the so-called harmonically coupled anharmonic oscillator (HCAO) approximation [63]. ϕ_{122} is a cubic force constant in dimensionless normal coordinates, and the quartic resonance constant $K_{11,33}$ is given by [64]

$$K_{11,33} = \frac{1}{4} \phi_{1133} - 4C(\zeta_{13}^c)^2 + \frac{1}{12} \frac{\phi_{111} \phi_{133}}{\omega_{13}} + \frac{1}{4} \frac{\phi_{112} \phi_{223} \omega_2}{4\omega_{13}^2 - \omega_2^2} - \frac{\phi_{133}^2}{2\omega_3} \quad (6)$$

where $\omega_{13} = (\omega_1 + \omega_3)/2$. In all these expressions the numbering of the fundamental vibrations of water follows the standard convention [62], i.e. v_1 and v_3 are quantum numbers for the symmetric A_1 and asymmetric B_2 stretching vibrations, respectively, and v_2 is the quantum number for the A_1 symmetry bending motion.

There are also Coriolis resonances which affect the rotational but not the vibrational energies, which are not been further considered here.

Several numerical values have been published for ϕ_{122} of H_2^{16}O . Pariseau [31] found $|\phi_{122}| = 302.1 \text{ cm}^{-1}$, indicating, correctly, the great significance of the related cubic resonance interaction. Smith and Overend [32] obtained a much smaller value, 71.7 cm^{-1} . Kuchitsu and Morino [30] and Hoy et al. [33] obtained 255.4 cm^{-1} and 167.5 cm^{-1} , respectively. The MFG, Set I, and Set II force fields result in the following values for $|\phi_{122}|$: 313.5 , 324.6 , and 307.5 cm^{-1} , respectively. These high-quality ab initio values are to be compared with 258.6 cm^{-1} , the value obtained after a least-squares refinement of the Set II quartic force field (for details see section 4.4). From the MFG, Set I, Set II and Set III force fields the following values can be determined for K_{1133} : -196.1 , -196.9 , -197.6 , and -193.1 cm^{-1} , respectively. The appropriate theoretical values of the resonance constants of water thus seem to be well established. The changes observed in the ϕ_{122} and $K_{11,33}$ constants upon force field refinements obviously allow for the compensation of small model errors.

4.3. Spectroscopic constants

While comparison of anharmonic force constants is possibly the most meaningful way to compare different force field representations of the PES of a molecule, it is more usual to compare the anharmonic force fields by their ability to predict/reproduce standard rovibrational spectroscopic constants. Therefore, the harmonic frequencies ω_r and anharmonicity constants x_{rs} , and the vibration–rotation interaction constants α_r , are presented in Table 4 for five symmetrically substituted isotopomers of water. One has to realise that the spectroscopic constants depend strongly on the quadratic part of the force field which is perhaps least accurately determined by methods of molecular electronic structure theory. Therefore, both the aug-cc-pVQZ CCSD(T) (Set II) and the refined (Set III, see below) set of force constants have been used to determine the spectroscopic constants. Agreement between theoretic-

cal and experimental spectroscopic constants is as good as one should expect [7,9–13,65]. The excellent agreement between the present ab initio and the experimentally determined x_{rs} constants is due to the good reproduction of the observed vibrational level structure of all water isotopomers based on these surfaces (see sections 4.5 and 5.2 below). Note, however, the considerable change in the value of x_{12} upon refinement of the quartic force field. The theoretical α values, obtained from the MFG, Set II, and Set III force fields agree with each other very well. On the other hand, agreement between the theoretical and experimental (empirical) α constants is not as impressive as seen for the x_{rs} constants. The detailed ab initio results of Allen et al. [12,13] showed much larger variations among the α values obtained at different levels of theory than for the x values. This observation has been confirmed in the present study though not detailed in here. It is also concluded that ab initio values for the α constants converge to their limiting values much more slowly.

For molecules containing two equivalent bonds of the general formula XH_2 , the so-called x – K relations [64,66] relate some of the vibrational anharmonicity constants x_{ij} and the quartic resonance constant $K_{11,33}$ as follows:

$$x_{11} = x_{33} = \frac{1}{4} x_{13} = \frac{1}{4} K_{11,33} = \frac{1}{2} x_m \quad (7)$$

where x_m is the anharmonicity constant of the equivalent diatomic XH molecule. These relations are based on an approximate model, but they provide a useful check on the calculations because it has been observed experimentally that they hold well for all the diatomic hydrides of the type XH_2 . As the appropriate entries of Table 4 testify, the interrelations presented in Eq. (7) hold very well for the directly determined ab initio spectroscopic constants.

4.4. Least-squares refinements

In attempts to refine theoretical anharmonic force fields, the most useful set of experimental data include measured fundamentals, overtones, and combination bands, or alternatively the vibra-

Table 4
Effective spectroscopic parameters (cm^{-1}) for five symmetrically substituted isotopomers of water^a

	H_2^{16}O			H_2^{17}O			H_2^{18}O			D_2^{16}O			T_2^{16}O				
	Set I	Set II	Set III	Expt. ^c	Set I	Set II	Set III	Set I	Set II	Set III	Set I	Set II	Set III	Expt. ^c	Set I	Set II	Set III
ω_1	3830.1	3828.9	3829.5	3832.2	3824.6	3825.3	3820.8	3821.5	2760.1	2759.6	2763.8	2298.0	2296.9	2763.8	2298.0	2296.9	2296.9
ω_2	1650.2	1652.3	1651.9	1648.5	1648.7	1648.2	1645.4	1645.0	1209.3	1209.4	1206.4	1017.3	1017.7	1206.4	1017.3	1017.7	1017.7
ω_3	3941.3	3937.7	3945.9	3942.5	3929.2	3937.4	3921.6	3929.9	2885.1	2891.2	2888.8	2436.1	2441.2	2888.8	2436.1	2441.2	2441.2
χ_{11}	-43.22	-43.14	-42.5	-42.6	-43.06	-42.4	-42.99	-42.4	-22.36	-21.7	-22.6	-15.58	-14.9	-22.6	-15.58	-14.9	-14.9
χ_{12}	-15.83	-16.50	-28.3	-15.9	-16.47	-28.1	-16.45	-28.0	-8.36	-15.3	-7.6	-5.63	-10.9	-7.6	-5.63	-10.9	-10.9
χ_{13}	-165.80	-166.60	-162.1	-165.8	-166.18	-161.7	-165.80	-161.4	-86.63	-84.2	-87.1	-6.69	-6.3	-87.1	-6.69	-6.3	-6.3
χ_{22}	-17.00	-17.39	-16.7	-16.8	-17.31	-16.6	-17.23	-16.6	-9.40	-8.9	-9.2	-6.69	-6.3	-9.2	-6.69	-6.3	-6.3
χ_{23}	-20.48	-20.08	-16.6	-20.3	-20.06	-16.7	-20.05	-16.7	-10.34	-8.2	-10.6	-7.28	-5.6	-10.6	-7.28	-5.6	-5.6
χ_{33}	-48.70	-48.64	-50.9	-48.29	-48.29	-50.6	-47.97	-50.3	-27.43	-28.9	(-26.1)	-20.45	-21.6	(-26.1)	-20.45	-21.6	-21.6
α_1^A	0.709	0.685	0.60	0.750	0.687	0.60	0.689	0.60	0.221	0.19	0.246	0.102	0.09	0.246	0.102	0.09	0.09
α_1^B	0.218	0.221	0.24	0.238	0.218	0.24	0.216	0.24	0.094	0.10	0.096	0.059	0.06	0.096	0.059	0.06	0.06
α_1^C	0.179	0.177	0.18	0.202	0.177	0.18	0.177	0.18	0.068	0.07	0.077	0.042	0.04	0.077	0.042	0.04	0.04
α_2^A	-2.578	-2.617	-2.70	-2.941	-2.597	-2.68	-2.580	-2.66	-1.041	-1.08	-1.161	-0.629	-0.65	-1.161	-0.629	-0.65	-0.65
α_2^B	-0.164	-0.156	-0.12	-0.160	-0.155	-0.11	-0.154	-0.11	-0.063	-0.05	-0.082	-0.039	-0.03	-0.082	-0.039	-0.03	-0.03
α_2^C	0.144	0.147	0.15	0.139	0.147	0.15	0.146	0.15	0.056	0.06	0.050	0.031	0.03	0.050	0.031	0.03	0.03
α_3^A	1.169	1.159	1.32	1.253	1.143	1.30	1.129	1.29	0.512	0.58	0.593	0.340	0.38	0.593	0.340	0.38	0.38
α_3^B	0.100	0.099	0.06	0.078	0.100	0.06	0.100	0.06	0.030	0.02	0.042	0.014	0.01	0.042	0.014	0.01	0.01
α_3^C	0.145	0.143	0.14	0.145	0.142	0.14	0.141	0.14	0.051	0.05	0.054	0.027	0.03	0.054	0.027	0.03	0.03

^a Harmonic wave numbers, ω_i , anharmonicity constants, χ_{ij} , and vibration-rotation interaction constants, α_i , are all in cm^{-1} . See Table 3 for the Set II and Set III force fields.

^b See last column of Table 3 of Ref. [47] for the quartic force field obtained at the [5s4p2d1f.3s2p] QCISD(T) level.

tional term values of all known vibrational states referred to the ground state, and also rotational constants of the individual vibrational levels. In this study only vibrational band origins have been employed, although we plan to extend our program to include rotational constants in due course.

To refine the anharmonic force field, a large non-linear least-squares calculation has to be performed to give the best agreement between the observed and calculated data. The derivatives of each of the data (in our case, measured vibrational wavenumber term values λ_i) are formed with respect to each of the force constants f^j regarded as a one-dimensional vector array, to form the Jacobian

$$J_{ij} = (\partial \lambda_i / \partial f^j) \quad (8)$$

The J_{ij} values form an n deep by p wide matrix \mathbf{J} , where n is the total number of data and p is the total number of force constants refined. In our program we calculate the Jacobian elements numerically by finite differences, using single-sided displacements of an appropriate magnitude.

If all force constants are being refined simultaneously, the differences between the observed and calculated data, $e_i = \lambda_i(\text{obs}) - \lambda_i(\text{calc})$, and the derivatives J_{ij} , are calculated for each datum λ_i , and the corresponding contributions are added to the scalar sum of weighted squares of differences $e^T \mathbf{W} e$, to the $p \times 1$ vector $\mathbf{J}^T \mathbf{W} e$, and to the $p \times p$ matrix $\mathbf{J}^T \mathbf{W} \mathbf{J}$, where in this work we have taken the weight matrix \mathbf{W} to be diagonal. The normal equations are then formed as

$$\mathbf{J}^T \mathbf{W} \mathbf{J} \Delta f = \mathbf{J}^T \mathbf{W} e \quad (9)$$

and the $p \times 1$ vector of corrections to the force constants is obtained by inverting the matrix $\mathbf{J}^T \mathbf{W} \mathbf{J}$ followed by a matrix–vector multiplication:

$$\Delta f = (\mathbf{J}^T \mathbf{W} \mathbf{J})^{-1} (\mathbf{J}^T \mathbf{W} e) \quad (10)$$

Even when data on a number of isotopomers are included in the fit it may well be that a simultaneous refinement of all force constants gives an ill-conditioned problem, which results in numerical difficulties in the inversion of the matrix $\mathbf{J}^T \mathbf{W} \mathbf{J}$. To make full use of the results of our

ab initio calculations in which we have a lot of confidence and to overcome possible convergence problems, we have made use of the method of ‘predicate observations’, originally described by Bartell [67]. We do this by treating the ab initio values of the force constants as additional data, which are added to the experimental data, and are given uncertainties σ_i and hence weights $W_i = 1/\sigma_i^2$ that reflect our confidence in the quantum chemical calculation. This allows us to use the complete set of anharmonic force constants as refining parameters without risk of ill-conditioning, because we can always constrain individual force constants by predicating them with a small uncertainty if this should prove necessary to make the least squares refinement stable.

The Set III force field of Table 3 was obtained by the use of the just described predicate least-squares approach. Success of a predicate least-squares refinement of a high-quality ab initio quartic force field, as is the case in this study, rests basically upon the choice of the relative uncertainties (weights) of the force constants and the observables. Many different choices have been explored during the course of this work. With reasonable weights only relatively small variations in the values of the refined force constants were observed. Furthermore, the final values of most (including all important) force constants did not prove to be too sensitive to the choice of the original force field (MFG, Set I, or Set II) and, just as importantly, force constants of all order could be refined simultaneously. The following force field elements deviated the most from their original, calculated values if the refinement conditions allowed: $f^{rr'}$, $f^{rr'x}$, f^{rxx} , $f^{rr'x'}$, $f^{rr'xx}$, and f^{xxxx} . At the end, the following choices were made for the refinement whose results are reported in the different tables: (a) all the elements of the Set II force field are used as predicate values to complement the observed band origins; (b) the diagonal stretching and bending force constants were given an uncertainty of 0.25% of their original value; and (c) all other force constants were given an uncertainty of 1% of their original value. Such weights attached to the anharmonic force field elements proved to be broadly consistent with the following uncertainties employed for the experi-

mental vibrational band origins: 0.1 cm^{-1} for the $P = 1$ and $P = 2$ levels, 0.25 cm^{-1} for $P = 3, 4$, 1.0 cm^{-1} for $P = 5, 6$, and 2.5 cm^{-1} for $P = 7$ and 8 (for the definition of the polyad quantum number P see Eq. (11) below). With this and most other choices of the weights the refinement could be considered converged after the second step, all further steps made only marginal adjustments of the force constants. It is clear from comparison of the Set II and Set III force fields of Table 3 that the Set II field is rather similar to the refined Set III field although the latter reproduces the experimental vibrational band origins with an average error considerably smaller than the former field.

4.5. Vibrational levels

Because of the resonances present in water between certain normal modes, the most meaningful way to describe the vibrational spectrum of water in a perturbation-resonance approach is through the eigenvalues of a series of resonance polyad matrices characterised by the polyad quantum number P defined as

$$P = 2\nu_1 + \nu_2 + 2\nu_3 \quad (11)$$

Both the Fermi resonance and the Darling–Dennison resonance described earlier fall within the resonance blocks defined by the quantum number P , thus giving rise to a mixing of the basis functions described by the same value of P . The Hamiltonian is thus represented as a block-diagonal matrix, with blocks of increasing dimension as we go up in energy.

The vibrational levels calculated from some of the quartic force fields determined as part of this study are collected in Table 5. It is immediately clear that the MFG and the Set II force fields produce similar vibrational levels, deviation between the two sets of vibrational levels is seldomly larger than 15 cm^{-1} , it is typically below 5 cm^{-1} . The overall agreement between the calculated vibrational levels and the experimental band origins is excellent. Without any adjustment of the quartic force field elements, the mean error of the fundamentals is only about 6 cm^{-1} . As usual, most of the discrepancy comes from the harmonic and not the anharmonic part of the force fields.

Inclusion of core-valence correlation during the theoretical calculation of the force field [23,68] would decrease the remaining errors. The sometimes relatively large, $20\text{--}40 \text{ cm}^{-1}$ error of the calculated vibrational overtone levels mostly decreases to a few wavenumbers upon refinement of the force field for levels below some $12\,000 \text{ cm}^{-1}$. Comparison of theoretical vibrational levels determined from the refined, Set III, force field and experiment shows the considerable apparent precision of the underlying quartic force field.

The barrier for linearization for H–O–H configurations is rather low, around $11\,200 \text{ cm}^{-1}$. This means that (a) energy spacings between consecutive ‘pure’ bending states decrease from around 1550 to 1100 cm^{-1} as ν_2 increases from 2 to 6 , complicating the resonance patterns throughout the energy levels; and (b) since the simple quartic expansion of the potential does not take into account the true symmetry of the bending motion of water, it cannot be expected that energy level calculations, based on perturbation theory and on this potential, will yield reasonable highly excited bending states. Indeed, the uncorrected Set II quartic force field reproduces the first four experimentally measured pure bending levels with an average error of only 2.6 cm^{-1} (the average error is 4.0 cm^{-1} for the MFG force field), but for the $(0\ 5\ 0)$ level the calculated value is larger than the experimental one by 22 cm^{-1} , indicating a fast breakdown of the simple perturbation approach above $\nu_2 = 4$, i.e. above about half of the barrier height. Furthermore, spacings of the bending progression $(0\ \nu_2\ 0)$ decreases constantly in the present calculations, while in the more detailed variational calculations of Choi and Light [44], where the potential is corrected to have the proper bending behavior, it is shown to go through a minimum around $\nu_2 = 9$, after which it increases again.

5. A variational approach

While historically perturbation theory was used first, in recent decades much effort has been devoted toward the variational determination of vibrational energy levels of polyatomic molecules.

Table 5 (continued)

P/S	$H_2^{16}O$	$H_2^{17}O$			$H_2^{18}O$			$D_2^{16}O$			$T_2^{16}O$		
		MFG [47]	Set II	Set III	Obs.	Set III	Obs.	Set III	Obs.	Set III	Obs.	Set III	Obs.
8	11 637.5	11 632.5	11 682.7	11 661.1	11 641.8	8835.6	7536.5						
	12 566.3	12 558.5	12 511.0	—	12 490.2	9358.8	7938.1						
	13 232.3	13 224.6	13 170.9	—	13 150.4	9795.4	8278.3						
	13 430.6	13 426.2	13 434.0	—	13 408.6	10 038.7	8532.7						
	13 642.9	13 630.1	13 611.7	—	13 591.6	10 125.5	8546.1						
	13 844.9	13 828.7	13 796.3	13 828.3 ^b	13 776.6	10 296.2	8698.9						
	14 009.1	13 999.6	13 948.0	13 910.8 ^b	13 925.9	10 368.6	8789.7						
	14 273.6	14 262.2	14 236.4	14 221.1 ^b	14 217.5	10 565.0	8941.0						
	14 552.5	14 540.5	14 539.1	14 536.9 ^b	14 514.6	10 867.3	9250.1						
	12 564.2	12 563.1	12 620.3	—	12 595.7	9477.3	8066.4						
	13 251.6	13 244.7	13 232.9	—	13 209.9	9883.6	8384.8						
	13 649.3	13 636.6	13 631.9	13 652.7 ^b	13 610.8	10 177.5	8622.8						
13 848.2	13 832.2	13 809.1	13 830.9 ^b	13 788.4	10 326.1	8751.5							
14 064.3	14 057.7	14 071.4	14 066.2 ^b	14 045.2	14 021.9	8932.3							
14 373.0	14 360.8	14 363.8	14 318.8 ^c	14 341.2	14 321.2	10 722.5							

^a P denotes the polyad quantum number (for details see text), while S the symmetry (only the lowest band within a P subgroup belonging to B_2 is indicated by the symbol B_2).

^b [36a]

^c [42b].

^d L.S. Rothman, R.R. Gamache, R.H. Tipping, C.P. Rinsland, M.A.H. Smith, D.C. Benner, V. Malathy Devi, J.-M. Flaud, C. Camy-Peyret, A. Perrin, A. Goldman, S.T. Massie, L.R. Brown, and R.A. Toth, *J. Quantum Spectrosc. Radiat. Transfer*, 48 (1992) 469.

^e J.-P. Chevillard, J.-Y. Mandin, J.-M. Flaud, and C. Camy-Peyret, *Can. J. Phys.* 65 (1987) 777f [45b].

New variants of the traditional variational technique [37]b[39] have successfully been employed for several tri- and tetra-atomic species [41,43,44,69–72]. Suggestions for the improved determination of the appropriate kinetic and potential energy operators in curvilinear internal coordinates, as well as new techniques for choosing compact basis sets made the procedure more appealing [73–77]. Still, it is not seen how these techniques could be employed for the determination of highly excited vibrational states of molecules containing more than 5 atoms even in the distant future.

A conceptually and technically simpler variational technique, based on the exclusive use of dimensionless normal coordinates, has been suggested [8,78,79]. In the present study implementation of this technique in ANHAR, the vibrational CI program of Pulay [8,80], has been employed. The purely vibrational Hamiltonian of this approach is written as

$$H = \frac{1}{2} \sum_i \omega_i (p_i^2 + q_i^2) + V_{anh}(\mathbf{q}) \quad (12)$$

where the ω s are the harmonic frequencies, the q s are the dimensionless normal coordinates, the p s are the conjugate momenta, and the potential function is given as a power series expansion not restricted to quartic terms. An advantage of using normal coordinates is that the kinetic energy takes a diagonal form. Some of the disagreements between the perturbation-resonance and the variational approaches, *vide infra*, may be due to the fact that the kinetic energy operator of Eq. (12), used in the variational calculations, is not the same as the one employed in the perturbation resonance approach. Because all symmetry-allowed off-diagonal anharmonic force constants appear in V_{anh} , the Hamiltonian is represented as a single giant matrix, block-diagonalised only as required by symmetry. It is worthwhile reiterating two key features [8] of the approach of Pulay: (1) to avoid the exponential increase of basis set size with increasing number of modes, an extensive configuration selection procedure is employed, analogous to that used in electronic structure theory. (2) Explicit formulation of the Hamiltonian matrix is avoided, by a method similar to that used in the direct CI method of electronic

structure theory. The desired eigenvalues and eigenstates are determined iteratively using Davidson's matrix diagonalization method [81].

5.1. Force field transformations

The nonlinear transformation of an anharmonic force field expressed in curvilinear internal coordinate space into rectilinear normal coordinate space can be accomplished either analytically or numerically. Analytic transformation formulas, based on the so-called \mathbf{L} -tensor formalism [33,82], transform an n th-order field in internal space into an n th-order field in normal coordinate space. Specific transformation formulas have been published [33] for the basic types of internal coordinates up to $n = 4$, but can be generalized to higher orders (A.G. Császár and I.M. Mills, unpublished results). A numerical transformation technique, based on orthogonal polynomials and least-square minimization, has been developed by Dunn [8]. In this approach a surface in normal coordinates is fitted to data generated from the curvilinear force constants. An advantage of the numerical transformation procedure over the analytic one is that the resulting normal coordinate surface may contain terms of arbitrary order (in fact, up to 8th order in the present program, VIBFIT [8]). This is important since higher than quartic terms in the potential are needed for accurate determination of higher vibrational levels when rectilinear coordinates are used in the variational procedure. In effect, the higher-order terms in the rectilinear normal coordinate representation of the potential compensate for the fact that molecular motion is curvilinear.

Several force fields of H_2^{16}O in dimensionless normal coordinates are reported in Table 6. They all have been obtained from the same theoretical anharmonic internal coordinate force field determined at the aug-cc-pVTZ CCSD(T) level (Set I of Table 3). The Set A and Set B fields of Table 6 have been obtained from the complete internal coordinate quartic force field (Set I) by numerically transforming it into normal coordinate space including all quartic and sextic terms, respectively. The Set C and Set D fields have been obtained from the complete internal coordinate sextic field

Table 6

Elements of the anharmonic force field of H₂¹⁶O in dimensionless normal coordinates obtained from aug-cc-pVTZ CCSD(T) calculations^a

Term	Exact	Set A	Set B	Set C	Set D
ω_1	3843.74	3844.50	3843.79	3843.77	3843.79
ω_2	1641.18	1640.11	1641.19	1641.22	1641.19
ω_3	3948.48	3949.19	3948.52	3948.50	3948.52
Φ_{111}	1821.86	1800.96	1822.09	1823.12	1821.90
Φ_{112}	78.05	70.30	78.02	78.20	78.05
Φ_{122}	-324.26	-355.18	-324.54	-323.85	-324.26
Φ_{222}	-263.76	-262.42	-263.76	-263.62	-263.75
Φ_{133}	1822.10	1799.28	1822.31	1823.31	1822.14
Φ_{233}	269.18	264.29	269.19	269.40	269.19
Φ_{1111}	758.08	752.50	758.18	758.50	758.11
Φ_{1112}	62.12	59.40	62.10	62.09	62.12
Φ_{1122}	-308.94	-309.85	-309.04	-309.12	-308.95
Φ_{1222}	-162.67	-157.84	-162.64	-162.57	-162.67
Φ_{2222}	-10.65	9.00	-10.41	-10.97	-10.65
Φ_{1133}	761.96	755.76	762.05	762.35	761.99
Φ_{1233}	119.54	117.43	119.54	119.61	119.54
Φ_{2233}	-371.19	-370.28	-372.26	-371.34	-371.20
Φ_{3333}	765.43	758.90	765.52	765.82	765.47
Φ_{11111}			-1.75	321.94	329.28
Φ_{11112}			-2.54	26.91	30.48
Φ_{11122}			-185.99	-185.99	-179.07
Φ_{11222}			-83.54	-88.98	-91.14
Φ_{12222}			110.49	131.94	126.85
Φ_{22222}			188.32	113.91	116.73
Φ_{11133}			-2.43	334.56	342.29
Φ_{13333}			-4.55	334.17	342.01
Φ_{22233}			-92.79	-87.24	-85.40
Φ_{23333}			32.23	62.75	63.63
Φ_{11233}			16.52	53.36	54.54
Φ_{12333}			-200.34	-204.85	-199.30
Φ_{111111}			-0.70	145.12	148.14
Φ_{111112}			-1.12	16.84	18.93
Φ_{111122}			-49.50	-106.70	-106.00
Φ_{111222}			-27.35	-60.48	-63.81
Φ_{112222}			96.41	93.19	89.52
Φ_{122222}			103.07	95.94	101.38
Φ_{222222}			-40.41	-194.39	-194.15
Φ_{111133}			-0.94	156.15	159.38
Φ_{113333}			-1.56	156.71	160.01
Φ_{222233}			118.68	123.08	120.72
Φ_{223333}			-55.67	-111.64	-111.66
Φ_{112233}			-54.14	-112.63	-112.67
Φ_{122233}			-32.45	-43.12	-43.39
Φ_{123333}			9.38	33.98	34.62
Φ_{333333}			-2.33	161.05	163.04

^a Exact = complete quartic internal coordinate force field transformed using the analytic *L*-tensor formalism. Set A = complete internal coordinate quartic force field transformed into normal coordinate space up to quartic terms; Set B = complete internal coordinate quartic force field transformed into normal coordinate space up to sextic terms; Set C = complete internal coordinate sextic force field transformed into normal coordinate space up to sextic terms; Set D = complete internal coordinate sextic force field transformed into normal coordinate space up to octic terms, only terms up to sextic are reported. For the anharmonic force field in internal coordinates see the Set I results of Table 3.

Table 7
Vibrational term values, in cm^{-1} , of non-rotating H_2^{16}O determined from variational calculations^a

(v_1, v_2, v_3)	Exact	Set A	Set B	Set C	Set D	Obs.
(0 0 0)	4660.9	4665.4	4666.5	4653.8	4654.1	
(0 1 0)	1572.6	1575.9	1583.5	1577.1	1577.1	1594.7
(0 2 0)	3113.7	3119.3	3137.5	3115.9	3116.4	3151.6
(1 0 0)	3705.8	3716.3	3726.7	3671.2	3676.7	3657.1
(0 0 1)	3788.8	3798.3	3806.6	3750.4	3747.7	3755.9
(0 3 0)	4606.6	4612.7	4662.0	4607.6	4608.7	4666.8
(1 1 0)	5233.3	5254.9	5301.6	5228.9	5232.5	5235.0
(0 1 1)	5288.0	5305.5	5351.3	5281.7	5277.4	5331.2
(0 4 0)	6031.5	6036.4	6159.4	6044.8	6046.5	6134.0
(1 2 0)	6743.4	6777.0	6848.6	6748.5	6751.7	6775.1

^a For details see footnote to Table 6 and text.

by numerically transforming it into normal coordinate space including all sextic and octic terms, respectively. The quartic normal coordinate constants labelled 'exact' in Table 6 have been obtained by the analytic transformation of the Set I quartic force field.

Precision of the numerical transformation of the Set I quartic force field in internal coordinates into a quartic field in dimensionless normal coordinates (Set A results of Table 6) does not seem to be satisfactory as deviations of some 20 cm^{-1} from the 'exact' constants are observed for certain constants. Once terms up to sextic are included in the numerical transformation procedure, the quartic part of the transformed force field reproduces the analytically obtained field to better than 0.1 cm^{-1} on the average, as seen from comparison of the 'exact' and 'Set B' results. Although some quintic and sextic normal coordinate force constants are significantly different from zero in the Set B field, they become well determined only if a full sextic force field in internal coordinates is transformed into the normal coordinate space. It is expected that the quintic and sextic terms are converged only in the Set D field, i.e. when terms up to octic are included in the numerical transformation procedure. The almost perfect agreement between the analytically transformed ('exact') and the Set D quartic force fields is also noteworthy.

5.2. Vibrational levels

While in Table 5 no particular labeling, except the one offered by the use of the polyad quantum number P , is given, in Table 7 the low-lying vibrational states of H_2^{16}O are labelled according to the normal mode picture. Normal vs. local mode labeling and transitions between the two descriptions have been dealt with extensively for a number of molecules [42,62], among which water has become a paradigm. Therefore, no further discussion of the subject is offered in this paper.

As observed repeatedly in previous studies of a similar nature [41,83], the same quartic force field as used in the VPT2 treatment (column 'exact' of Table 6) produces quite different vibrational levels variationally. Some deviations between the two treatments are as large as 60 cm^{-1} for the low-lying vibrational states of water. As a result, the excellent agreement between experiment and the energy levels determined by the perturbation-resonance approach becomes rather poor. Therefore, at least for vibrations involving the hydrogen atom, quartic force fields expressed in dimensionless normal coordinates seem to be better suited for perturbation-resonance treatments than for variational ones.

Some more important observations about the variational vibrational level calculations of this study: (a) The deviations up to 10 cm^{-1} observed between the 'exact' and 'Set A' force field results move the Set A band origins even further away

from the experimental values. (b) The Set B–Set D fields yield considerably more precise theoretical vibrational levels than the ‘pure’ quartic force fields (exact or Set A), i.e. inclusion of higher than quartic terms in the normal coordinate expansion of the potential seems to be clearly beneficial. (c) Vibrational levels calculated from the Set C and Set D force fields are, as expected, very similar. (d) Description of the pure bending vibrational levels is especially poor with all force fields except Set B, although the quartic internal coordinate force field, using the perturbation-resonance approach, proved to be rather accurate in this respect. The good agreement obtained after expansion of the quartic aug-cc-pVTZ CCSD(T) force field in internal coordinates into a sextic field in normal coordinate space (the Set B results) is only fortuitous, as all other force field representations give considerably less precise but, when compared with each other, more consistent vibrational levels. (e) Comparison of the pure bending vibrational levels determined from the ‘exact’ and Set D force fields shows that proper inclusion of higher than quartic bending terms in the anharmonic normal coordinate force field does not improve the description of the bending modes of water. (f) Inclusion of the quintic and sextic stretching force constants produces significant changes in the related vibrational levels; for example, comparison of the ‘exact’ and ‘Set D’ vibrational levels shows that ν_1 and ν_3 change by -29 and -41 cm^{-1} , respectively. In both cases the fundamentals calculated from the sextic field (Set D) are in much better agreement with experiment than the fundamentals calculated from the quartic (‘exact’) field.

6. Conclusions

Several quartic force fields and a full sextic anharmonic force field for water have been determined from high-quality ab initio calculations, the highest at the aug-cc-pVQZ CCSD(T) level of theory. All calculations have been performed at a fixed reference geometry ($r_e(\text{OH}) = 0.95843$ Å and $\alpha_e(\text{HOH}) = 104.44^\circ$) taken from the literature and believed to be very close to the true equilibrium

geometry of free water. With this choice evaluation of the quality of the force fields determined at different theoretical levels (SCF, MP2, CCSD, and CCSD(T) with basis sets of spdf and spdfg quality) is made easier as attention can be focused on the genuine direct correlation effects, i.e. on changes in the force field related to an improved description of the electronic structure. Previous experience suggests that almost all remaining errors in the aug-cc-pVQZ CCSD(T) force field should be assigned to core-core and core-valence correlation effects, not considered explicitly in this study. It is believed that elements of the aug-cc-pVQZ CCSD(T) force field of this study should be very close to the appropriate derivatives of the ‘true’ PES of water.

Two approaches have been utilized to calculate vibrational energy levels directly from the anharmonic molecular force fields. In the first, so-called perturbation-resonance approach the diagonal elements of the vibrational Hamiltonian have been calculated from the standard formulas of VPT2 theory, while the only off-diagonal elements were obtained from the consideration of two resonances: a cubic (Fermi-type) resonance and a quartic (Darling–Dennison-type) resonance. All spectroscopic constants and most lower-lying vibrational energy levels calculated with this approach are in good agreement with the available experimental (empirical) results, proving the high quality of the underlying anharmonic (quartic) force field and the viability of the perturbation-resonance approach at the same time. For example, the unadjusted aug-cc-pVQZ CCSD(T) force field predicts the vibrational fundamentals of 5 symmetrically substituted isotopomers of water (H_{16}^2O , H_{17}^2O , H_{18}^2O , D_2O , and T_2O) with an average error of less than 5 cm^{-1} , and the first 4(2) pure bending levels of H_2^{16}O (D_2O) with an average error of only 2 cm^{-1} . Agreement between the calculated and measured vibrational levels of water could even further be improved after a predicate least-squares refinement of the quartic force field based on the same perturbation-resonance approach. All available vibrational band origins up to 15000 cm^{-1} above the zero-point level of the same five isotopomers mentioned above have been included in the fitting procedure as experi-

mental data. Keeping the geometry fixed, all quartic force field elements were refined simultaneously while predicated toward their values obtained from the aug-cc-pVTZ CCSD(T) calculations performed at the same geometry. The resulting force field reproduces the vibrational excited states considered with an rms error of less than 10 cm^{-1} . It is believed that the refined force field predicts vibrational levels even somewhat further up the energy ladder with a similar precision for all states but those in which the bending mode is highly excited. Since a system containing protons is necessarily a difficult example for perturbational calculations due to the relatively large amplitude vibrations, the vibrational wavenumber errors for water obtained from this treatment should serve as an upper bound for the errors expected for heavier systems.

It has been observed that a numerical transformation procedure, based on orthogonal polynomials and a least-squares minimization and employed to transform a quartic force field expressed in curvilinear internal coordinates into fields expressed in rectilinear dimensionless normal coordinates, is able to reproduce the field obtained by an exact nonlinear transformation to better than 0.1 cm^{-1} . Therefore, this numerical transformation scheme has been employed to transform the complete sextic internal coordinate force field of water, determined for the first time, to the space of dimensionless normal coordinates. These normal coordinate force fields have then been used in a variational CI procedure to calculate certain low-lying vibrational levels of H_2^{16}O . The results obtained indicate that (a) quartic force fields expressed in dimensionless normal coordinates seem to be better suited for perturbation-resonance treatments than for variational ones; (b) the stretching fundamentals calculated variationally from the full sextic force field in normal coordinates are in considerably better agreement with experiment than the fundamentals calculated from the quartic part of the force field; and (c) difficulties arising from the use of rectilinear coordinates are especially pronounced for the bending levels.

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