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SCF–CI Studies on the Electronic Ground State of Water: Potential Energy Hypersurface and Spectroscopic Constants

Paul Hennig, Wolfgang P. Kraemer and Geerd H. F. Diercksen

Max-Planck-Institut für Physik und Astrophysik,
Föhringer Ring 6, D-8000 München, Federal Republic of Germany

Gernot Strey

Sektion Physik der Universität München, D-8000 München, Federal Republic of Germany

Large-scale Hartree–Fock self-consistent field calculations, employing extended Gaussian basis sets, and configuration interaction studies are performed to calculate the energy hypersurface of the electronic ground state of the water molecule and to investigate the accuracy requirements in view of the determination of molecular spectroscopic constants. From the calculated points on the hypersurface the theoretical equilibrium geometry, the force field through fourth order, the spectroscopic constants ω_i, x_{ij}, α_i as well as the Darling–Dennison and Fermi resonance constants are evaluated. The CI surface yields an equilibrium structure for H_2O with $r_e = 0.9501$ Å and $\alpha_e = 105.33°$ ($r_{\text{exp}} = 0.9572$ Å and $\alpha_{\text{exp}} = 104.52°$). The vibrational levels are obtained with a systematic error of about 2 percent and the rotational constants to about 1 percent compared to spectroscopic data. The relative energy maximum corresponding to the linear structure with $\alpha = \pi$ is calculated to be $11890\,\text{cm}^{-1}$, within the error limits of the values deduced from experimental measurements.

Key words: Water molecule, electronic ground state of ~

1. Introduction

Due to its outstanding importance in chemistry and biology the water molecule in its electronic ground state has been subject to a large number of experimental and theoretical investigations during the last decade [1]. From the point of view of theoretical studies the water molecule is of particular interest because it is a simple example of a general polyatomic molecule and it is small enough to be treated by accurate quantumchemical methods. In molecular spectroscopy the water molecule is considered as a prototype of an asymmetric top and it shows some interesting resonance effects. Therefore H_2O was chosen in the present study in order to check

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the accuracy requirements on the *ab initio* calculated energy hypersurface and the theoretical force field in connection with the evaluation of vibrational and rotational energy levels within reasonable error limits. A similar analysis was recently performed for a series of linear triatomic molecules of astrophysical interest [2, 3].

A short summary of some of the most relevant *ab initio* calculations, which have been performed on the electronic ground state of water during the past few years, has been given by Diercksen *et al.* [4] and can also be found in recent papers by Rosenberg *et al.* [5, 6]. The best energy value obtained within the single determinant SCF approximation was published by Popkie *et al.* [7], $E(\mathrm{SCF}) = -76.06598$ hartree, which is above the expected Hartree–Fock limit by about 0.002 hartree. Going beyond this Hartree–Fock limit the lowest variational energy was determined by Meyer [8] using the PNO-CI method [9]: $E(\mathrm{PNO\text{-}CI}) = -76.36834$ hartree. This value accounts for approximately 82 percent of the estimated total correlation energy of water. Using a conventional CI approach Rosenberg and Shavitt [5] calculated recently an energy of $E(\mathrm{CI}) = -76.33980$ hartree, which includes about 75 percent of the total correlation energy.

Almlöf *et al.* [10] determined from an *ab initio* SCF energy hypersurface only parts of the force field through fourth order. Their harmonic vibrational frequencies ω_i differ from the experimental values by 3–7 percent. In systematic studies Ermler and Kern [11] as well as Krohn *et al.* [12] investigated the influence of vibrational motions on several one-electron properties. The force constants through fourth order and the vibrational constants needed for this purpose were evaluated from an *ab initio* energy hypersurface generated within the single determinant Hartree–Fock SCF approximation using a double-zeta quality Gaussian basis set augmented by polarization functions to approximate the molecular orbitals. Recently these studies were improved by Rosenberg *et al.* [5, 6] employing an extended Slater type basis set (39 STO's) and including correlation energy effects by conventional CI calculations. However, in these studies the energy hypersurface was only determined in a range very close to the potential minimum. This introduces an uncertainty into the analytical potential expression for the outer parts of the electronic potential, which might influence the accuracy of the higher vibrational levels. This uncertainty was removed in the present study by including nuclear configurations with relatively large deviations from the equilibrium geometry.

In Sect. 2 the computational details of this study are presented, describing the calculation of the energy hypersurface as well as the evaluation of the force constants and the spectroscopic constants. In Sect. 3 the results are discussed and compared to data deduced from experimental measurements and to the recent study of Rosenberg, Ermler, and Shavitt [6], abbreviated in the following as RES.

2. Computational Details

2.1. Calculation of the Energy Hypersurface

The potential energy hypersurface was computed for 55 different nuclear configurations of the water molecule using a combination of the MUNICH [13] and the MOLECULE [14] program systems. The evaluation of the basic integrals over Gaussian functions, the Hartree–Fock self-consistent field (SCF) iterations, and the four-index transformation of the basic integrals to the molecular orbital basis were carried out by the MUNICH programs. For the calculation of the correlation energy contributions a version of the MOLECULE CI program (CIMI method [15]) interfaced to the MUNICH system was used.

The molecular orbitals were approximated as linear combinations over Gaussian type basis functions (GTO's) located at the atomic centres. The total basis set used consisted of (13*s* 8*p* 2*d*) functions at the oxygen center and of (8*s* 2*p*) functions at the hydrogens [16]. These functions were contracted to [7*s* 5*p* 2*d*] and [4*s* 2*p*] functions for oxygen and the hydrogens, respectively, in order to reduce the number of linear parameters in the SCF procedure and also the number of possible configurations in the CI expansion. The exponents of the polarization functions were optimized in SCF calculations. The basis set employed yields a SCF energy for water of $E(\mathrm{SCF}) = -76.064140$ hartree at the SCF equilibrium structure with $r_e = 0.9387$ Å and $\alpha_e = 106.48°$. The energy value is about 0.003 hartree above the Hartree–Fock limit. At the experimental equilibrium geometry a number of electric and magnetic first and second order properties have previously been calculated with the present basis set utilizing the coupled Hartree–Fock approach [17]. The results indicate that the basis set used in the present study is flexible enough to describe the electronic charge distribution properly.

All single and double excitations which can be generated within the molecular orbital basis from the single determinant Hartree–Fock reference state were included in the CI wavefunction. This amounts to a total of 30380 configurations of correct spin symmetry for an asymmetric structure of the water molecule. Within this approximation a CI energy of $E(\mathrm{CI\text{-}SD}) = -76.333723$ hartree was obtained at the CI equilibrium structure with $r_e = 0.9501$ Å and $\alpha_e = 105.33°$. This energy value contains a correlation contribution of 0.270 hartree which accounts for 73 percent of the estimated total correlation energy. Subtracting the correlation contributions originating from the oxygen 1*s* orbital, about 77 percent of the total valence correlation energy are covered by this CI-SD calculation.

As has been shown by Rosenberg and Shavitt [5] a considerable improvement of the equilibrium geometry and of the spectroscopic constants for water can be achieved by using Davidson's approximate formula [18] for estimating the contribution of certain quadruple excitations to the CI energy in a closed shell molecule. This leads to an energy value of $E(\mathrm{CI\text{-}SDQ}) = -76.348304$ hartree and to an improved equilibrium geometry with $r_e = 0.9545$ Å and $\alpha_e = 104.98°$. These values differ from the experimental geometry ($r_{\mathrm{exp}} = 0.9572$ Å and $\alpha_{\mathrm{exp}} = 104.52°$) only by -0.3 percent in the OH-distance and by $+0.4$ percent in the bond angle.

The zero-point vibrational energy level is about 4635 cm^{-1} (0.0211 hartree) above the minimum of the potential energy hypersurface and the highest experimentally known vibrational level corresponding to $v_1 = 2$, $v_2 = 0$, and $v_3 = 3$ has an energy of 22130 cm^{-1} (0.1008 hartree) relative to the minimum. Since this study was aimed to calculate the anharmonic force constants as accurate as possible within the present approximation, the different nuclear configurations were chosen such that some of the calculated points on the energy hypersurface get close to this highest measured vibrational level. Thus the maximum deviations from the equilibrium geometry were taken up to ± 0.4 bohr (22 percent) in the bond distance and $\pm 25°$ (24 percent) in the bond angle. This leads to a maximum energy difference of about 0.154 hartree for CI-SD relative to the potential minimum. In the previous *ab initio* calculations on water [6] the maximum deviations from the equilibrium structure were limited to be about ± 0.06 bohr (3 percent) and $\pm 6°$ (6 percent). The corresponding maximum energy difference was therefore 0.0029 hartree, which is only about 14 percent of the zero-point vibrational energy.

A few additional points were calculated in the present study for the linear geometry of water ($\alpha = 180°$) and various r_1 and r_2 distances in order to determine the relative energy maximum (energy hump).

2.2. *Evaluation of Force Constants and Spectroscopic Constants*

For the water molecule with its three internal degrees of freedom the *ab initio* calculated energy points corresponding to 55 different nuclear configurations describe parts of a three-dimensional energy hypersurface. Around the potential minimum this surface can be approximated by a Taylor series expansion in terms of the three internal coordinates $\Delta r_i = r_i - r_i^{(e)}$ $(i = 1, 2, 3)$, where $r_i^{(e)}$ are the equilibrium geometry parameters and where the Δr_i $(i = 1, 2)$ refer to the two OH-stretchings and Δr_3 to the HOH-bending coordinate α. Truncation of the expansion after the fourth order terms leads to the following expression:

$$\begin{aligned} V = V_e &+ f_1(\Delta r_1 + \Delta r_2) + f_3 \Delta r_3 \\ &+ \tfrac{1}{2} f_{11}(\Delta r_1^2 + \Delta r_2^2) + f_{12} \Delta r_1 \Delta r_2 + f_{13}(\Delta r_1 + \Delta r_2)\Delta r_3 \\ &+ \tfrac{1}{2} f_{33} \Delta r_3^2 + \tfrac{1}{6} f_{111}(\Delta r_1^3 + \Delta r_2^3) + \tfrac{1}{2} f_{112}(\Delta r_1 + \Delta r_2)\Delta r_1 \Delta r_2 \\ &+ \tfrac{1}{2} f_{113}(\Delta r_1^2 + \Delta r_2^2)\Delta r_3 + f_{123} \Delta r_1 \Delta r_2 \Delta r_3 \\ &+ \tfrac{1}{2} f_{133}(\Delta r_1 + \Delta r_2)\Delta r_3^2 + \tfrac{1}{6} f_{333} \Delta r_3^3 + \tfrac{1}{24} f_{1111}(\Delta r_1^4 + \Delta r_2^4) \\ &+ \tfrac{1}{6} f_{1112}(\Delta r_1^2 + \Delta r_2^2)\Delta r_1 \Delta r_2 + \tfrac{1}{6} f_{1113}(\Delta r_1^3 + \Delta r_2^3)\Delta r_3 \\ &+ \tfrac{1}{4} f_{1122} \Delta r_1^2 \Delta r_2^2 + \tfrac{1}{2} f_{1123}(\Delta r_1 + \Delta r_2)\Delta r_1 \Delta r_2 \Delta r_3 \\ &+ \tfrac{1}{4} f_{1133}(\Delta r_1^2 + \Delta r_2^2)\Delta r_3^2 + \tfrac{1}{2} f_{1233} \Delta r_1 \Delta r_2 \Delta r_3^2 \\ &+ \tfrac{1}{6} f_{1333}(\Delta r_1 + \Delta r_2)\Delta r_3^3 + \tfrac{1}{24} f_{3333} \Delta r_3^4 \end{aligned} \tag{1}$$

The expansion coefficients $f_i, f_{ij}, f_{ijk}, f_{ijkl}$ are defined to be the linear, quadratic, cubic and quartic force constants, respectively. They form the force field through fourth order. The linear force constants f_1 and f_3 in the above expansion are zero due to the fact that the potential has a minimum at $\Delta r_1 = \Delta r_2 = \Delta r_3 = 0$.

The fitting of the expansion (1) to the *ab initio* calculated energy points proceeds in two steps: Starting from a plausible initial guess for the expected equilibrium parameters $r_i^{(e)}$ and using the calculated points, the set of expansion coefficients $\{f\}$ is determined in a linear least squares fit. Since the initial guess usually does not match accurately the true minimum of the potential curve, the linear force constants f_i will not be zero. Therefore in a second step improved equilibrium geometry parameters are obtained by the Newton–Raphson method. With these new $r_i^{(e)}$-values the fitting procedure is entered again and the process is repeated until the linear force constants f_i fall below a certain convergency threshold. The potential expression thus obtained represents the *ab initio* calculated energy surface within the accuracy limits of the above expansion (1). The final standard deviations of the different force constants provide an estimate of the overall quality of the fit. They do not give, however, error limits for the individual force constants.

The rotational constants of a given vibrational state v are approximately written as:

$$X_v = X_e - \sum_i \alpha_i^X \left(v_i + \frac{d_i}{2}\right) \quad (X = A, B, C) \tag{2}$$

where α_i^X are the rotational interaction constants, v_i the vibrational quantum numbers, d_i the degeneracies of the i'th vibration, and where the equilibrium rotational constants X_e are defined as:

$$X_e = \frac{\hbar}{4\pi c I_e^X} \tag{3}$$

with I_e^X being the moment of inertia for the axis X. The vibrational levels (undisturbed by resonances) are obtained by the expansion:

$$G(v) = \sum_i \omega_i \left(v_i + \frac{d_i}{2}\right) + \sum_{i \leqslant j} x_{ij} \left(v_i + \frac{d_i}{2}\right)\left(v_j + \frac{d_j}{2}\right) \tag{4}$$

where ω_i are the harmonic wavenumbers and x_{ij} the anharmonicity constants.

The water molecule $H_2{}^{16}O$, however, shows some resonance effects. The Darling–Dennison resonance between the levels ($v_1 \geqslant 2$, v_2, v_3) and ($v_1 - 2$, v_2, $v_3 + 2$) as well as the Fermi resonance between the levels ($v_1 \geqslant 1$, v_2, v_3) and ($v_1 - 1$, $v_2 + 2$, v_3) have a strong effect on the vibrational levels and have thus to be taken into account.

The spectroscopic constants and the resonance constants γ can be expressed as functions of the equilibrium geometry parameters and the force constants:

$$\begin{aligned} X_e &= f(r_e) \\ \omega_i &= f(r_e, f_{ij}) \\ \alpha_i^X, \gamma_F &= f(r_e, f_{ij}, f_{ijk}) \\ x_{ij}, \gamma_D &= f(r_e, f_{ij}, f_{ijk}, f_{ijkl}). \end{aligned} \tag{5}$$

For the actual calculations a program by Hoy *et al.* [19] is used in the present study. The vibration-rotation Hamiltonian expressed in normal coordinates has been developed by Wilson and Howard [20] and simplified by Watson [21]. In a perturbation treatment through second order [22, 23] the eigenvalues of this Hamiltonian are determined in terms of the force constants $\{\varphi\}$, which are defined in a normal coordinate representation. Therefore the above program [19] first performs a transformation of the force field $\{f\}$ given in internal coordinates into the set of $\{\varphi\}$, which are then used to evaluate the spectroscopic constants ω_i, x_{ij}, α_i^X as well as the resonance constants γ_F and γ_D.

3. Results and Discussion

The *ab initio* calculated points on the energy hypersurface are listed in Table 1. The first entry corresponds to the experimental geometry. The entries 40, 41, 42 represent the *ab initio* results for the theoretical equilibrium structures of H_2O on the different levels of accuracy SCF, CI-SD, and CI-SDQ, respectively, using the first 39 points of Table 1 in the fitting procedure. In order to give the minimum region of the potential a somewhat higher weight in the fit, 13 additional points were chosen close to the experimental equilibrium structure (entries 43–55 in Table 1). They are actually identical to points 1–13 of Table 1 in Ref. [6]. Inclusion of these further points, however, does not lead to any substantial change in the theoretical equilibrium values. This indicates that different selections among the *ab initio* calculated points have practically no influence on the final theoretical results.

Table 1. *Ab intio* calculated points of the energy hypersurface of H_2O

No.	r_1(OH) (bohr)	r_2(OH) (bohr)	$\measuredangle$(HOH) (deg.)	*E*(SCF) (hartree)	*E*(CI-SD) (hartree)	*E*(CI-SDQ) (hartree)
1	1.8089	1.8089	104.52	−76.063446	−76.333646	−76.348305
2	1.4000	1.4000	104.52	−75.918229	−76.179737	−76.191342
3	1.5000	1.6000	104.52	−76.017546	−76.281895	−76.294485
4	1.5000	2.0000	104.52	−76.017510	−76.286678	−76.301029
5	1.6000	1.6000	104.52	−76.039545	−76.304911	−76.317854
6	1.6000	1.7500	104.52	−76.051522	−76.318562	−76.332096
7	1.7000	1.9000	104.52	−76.057885	−76.327928	−76.342542
8	1.7500	1.8089	104.52	−76.063497	−76.332968	−76.347365
9	1.7500	1.8500	104.52	−76.062280	−76.332273	−76.346860
10	1.7500	2.0000	104.52	−76.051761	−76.323782	−76.339130
11	1.8089	1.5000	104.52	−76.029377	−76.296079	−76.309508
12	1.8089	1.7000	104.52	−76.061677	−76.330552	−76.344737
13	1.8089	1.9000	104.52	−76.059675	−76.331062	−76.346157
14	1.8500	1.8089	104.52	−76.062233	−76.332959	−76.347810
15	2.0000	2.0000	104.52	−76.040108	−76.315538	−76.332141
16	2.1000	1.6000	104.52	−76.028908	−76.300583	−76.315866
17	2.1000	1.8089	104.52	−76.041067	−76.315315	−76.331508
18	2.1000	2.0000	104.52	−76.029488	−76.306439	−76.323634
19	2.2000	2.2000	104.52	−75.994162	−76.275953	−76.295078
20	1.5000	1.5000	80.00	−75.963635	−76.228677	−76.241142
21	2.1000	2.1000	80.00	−76.007653	−76.288401	−76.306691
22	1.8089	1.8089	90.00	−76.056276	−76.327405	−76.342250
23	1.5500	1.9000	95.00	−76.034308	−76.303126	−76.317252
24	1.7500	1.7500	100.00	−76.062368	−76.331314	−76.345492
25	1.8500	1.8500	100.00	−76.060334	−76.331831	−76.346928
26	1.9500	1.7000	100.00	−76.053541	−76.324482	−76.339399
27	1.7500	1.7500	110.00	−76.063480	−76.332064	−76.346163

Table 1—*continued*

No.	r_1(OH) (bohr)	r_2(OH) (bohr)	∡(HOH) (deg.)	*E*(SCF) (hartree)	*E*(CI-SD) (hartree)	*E*(CI-SDQ) (hartree)
28	1.8500	1.8500	110.00	−76.060406	−76.331445	−76.346438
29	1.6500	1.8089	110.00	−76.057814	−76.325962	−76.339909
30	2.0500	1.8089	115.00	−76.043478	−76.316567	−76.332358
31	1.8089	1.8089	120.00	−76.058608	−76.328451	−76.343016
32	1.5000	1.5000	130.00	−75.990315	−76.253904	−76.266177
33	2.1000	2.1000	130.00	−76.001026	−76.278652	−76.296176
34	1.8089	1.8089	175.00	−76.009066	−76.279895	−76.294526
35	1.6000	1.6000	180.00	−75.995248	−76.262086	−76.275259
36	1.7500	1.7500	180.00	−76.011365	−76.281049	−76.295253
37	1.8089	1.8089	180.00	−76.008406	−76.279232	−76.293862
38	1.8500	1.8500	180.00	−76.004093	−76.275722	−76.290656
39	2.0000	2.0000	180.00	−75.976985	−76.251565	−76.267655
40	1.7739	1.7739	106.48	−76.064140	−76.333390	−76.347719
41	1.7955	1.7955	105.33	−76.063892	−76.333723	−76.348246
42	1.8038	1.8038	104.98	−76.063649	−76.333702	−76.348304
43	1.8111	1.8111	104.45	−76.063356	−76.333615	−76.348296
44	1.8111	1.8111	107.45	−76.063332	−76.333473	−76.348126
45	1.8111	1.8111	101.45	−76.062890	−76.333291	−76.348002
46	1.8411	1.8411	104.45	−76.061692	−76.332720	−76.347680
47	1.7811	1.7811	104.45	−76.064025	−76.333534	−76.347944
48	1.8411	1.8411	107.45	−76.061580	−76.332481	−76.347412
49	1.8411	1.8411	101.45	−76.061321	−76.332500	−76.347493
50	1.7811	1.7811	107.45	−76.064093	−76.333492	−76.347876
51	1.7811	1.7811	101.45	−76.063461	−76.333104	−76.347542
52	1.8111	1.8111	110.45	−76.062842	−76.332888	−76.347518
53	1.8111	1.8111	98.45	−76.061912	−76.332481	−76.347227
54	1.8711	1.8711	104.45	−76.059138	−76.330954	−76.346203
55	1.7511	1.7511	104.45	−76.063586	−76.332364	−76.346511

Table 2. Experimental and *ab initio* calculated equilibrium geometry parameters and minimum energies for H_2O

	r_e (Å)		α_e (deg.)		*E* (hartree)	
Experimental	0.9572		104.52		−76.4807	
SCF [7]	0.9572	[a]	104.52	[a]	−76.06598	(0.5)
SCF [12]	0.9413	(−1.7)	106.11	(1.5)	−76.0510	(0.6)
PNO-CI [9]	0.9572	[a]	104.52	[a]	−76.368340	(0.1)
CI-SD [6]	0.9527	(−0.5)	104.93	(0.4)	−76.339802	(0.2)
CI-SDQ [6]	0.9573	(−0.01)	104.58	(0.06)	−76.354795	(0.2)
Present study:						
SCF	0.9387	(−1.9)	106.48	(1.9)	−76.0641	(0.5)
CI-SD	0.9501	(−0.7)	105.33	(0.8)	−76.333723	(0.2)
CI-SDQ	0.9545	(−0.3)	104.98	(0.4)	−76.348304	(0.2)

[a] Geometry parameters not varied.

The final equilibrium parameters and the corresponding energy values are compared to experimental data and some recent highly accurate theoretical results in Table 2. The percent deviations of the theoretical results from experiment are given in parentheses.

Table 3 shows the calculated force constants $\{f\}$ through fourth order defined in internal coordinates. They are compared to different sets of $\{f\}$ obtained from experimental data and from the theoretical study of RES [6]. Numbers in parentheses give standard deviations of the least squares fit in the last decimal places. The first set of experimental force constants is taken from Mills [23]; they are determined by a fit to the spectroscopic constants ω_i, x_{ij}, γ_D, and α_i^X for $H_2{}^{16}O$ and $D_2{}^{16}O$ published by Benedict *et al.* [24]. The second experimental set is due to a fit to slightly different spectroscopic constants resulting from an analysis of the most recent experimental vibrational frequencies [25]. In this fit the experimental value for the Fermi resonance constant γ_F for $H_2{}^{16}O$ [26] was included. Comparison between these two sets indicates the present uncertainty in the force constants deduced from spectroscopic measurements, particularly as far as the fourth order terms are concerned. Among these f_{ijkl} several constants are constrained to be zero because of the lack of available experimental data.

The harmonic force constants f_{ij} obtained within the SCF approximation are found to be too large compared to the experimental values, indicating that particularly the SCF surface is too steep around the energy minimum. This deficiency is largely reduced on the higher levels of accuracy. The average error in the values for f_{11}, f_{12}, and f_{33} decreases from 20 percent (SCF) to 10 percent (CI-SD) and to 3 percent (CI-SDQ). Most of the other theoretical force constants show a similar trend. Since the actual numerical values of the experimental force constants of higher order become rather uncertain, it is not possible to deduce precise error estimates for the theoretical results. It can be expected, however, that the average deviations of the present *ab initio* force constants (CI-SDQ) from their experimental values increase from 3 percent for the second order to 10–30 percent for the third order terms. The most important fourth order force constant f_{1111} is obtained with an error of about 15 percent. The constants f_{1113} and f_{1123} (experimental values undetermined) have probably the right order of magnitude, whereas for other theoretical f_{ijkl} values already the sign is uncertain. Inclusion of the additional points 43–55 of Table 1 in the fitting procedure does not produce any significant change in the present results. The force constants through fourth order calculated by RES [6] are essentially very similar to the results obtained in the present study.

The standard deviations given in parentheses in Table 3 provide an estimate of the quality of the potential fit. Since rather large distortions from the equilibrium geometry were partly taken into account, one can expect the standard deviations of the present fit to become large. In the recent papers by Krohn *et al.* [12] and RES [6] only geometries very close to the potential minimum were considered and a very smooth potential fit with small standard deviations was therefore obtained.

In order to get more reliable results for the third and fourth order force constants

Table 3. Force field of water in unscaled mdyn/Å units. Numbers in parentheses are standard deviations in the last figures of the least squares fit. Constrained force constants are marked with an asterisk

	Exp. (Ref. [23])	Exp. (Ref. [25])	SCF (Ref. [11])	CI-SD (Ref. [6])	CI-SDQ (Ref. [6])	SCF	CI-SD	CI-SDQ
f_{11} (mdyn Å^{-1})	8.454 (1)	8.449 (1)	9.865	8.876	8.539	9.941 (49)	8.987 (53)	8.687 (54)
f_{12} (mdyn Å^{-1})	−0.101 (1)	−0.100 (1)	−0.069	−0.083	−0.085	−0.067 (44)	−0.088 (10)	−0.098 (50)
f_{13} (mdyn)	0.219 (2)	0.199 (7)	0.242	0.258	0.262	0.240 (10)	0.253 (49)	0.256 (10)
f_{33} (mydn Å)	0.697 (1)	0.697 (1)	0.781	0.738	0.734	0.751 (3)	0.719 (3)	0.714 (3)
f_{111} (mdyn Å^{-2})	−58.2 (2.3)	−60.17 (1.83)	−66.97	−61.11	−59.54	−73.10 (1.00)	−68.16 (52)	−66.39 (42)
f_{112} (mdyn Å^{-2})	−0.8 (3)	−0.64 (11)	0.00	−0.04	−0.01	−0.35 (31)	−0.49 (15)	−0.53 (12)
f_{113} (mdyn Å^{-1})	0.4 (2)	0.46 (17)	−0.07	−0.08	−0.03	0.38 (72)	0.18 (38)	0.13 (28)
f_{123} (mdyn Å^{-1})	−0.6 (2)	−0.69 (10)	−0.52	−0.51	−0.55	−0.91 (71)	−0.67 (37)	−0.62 (27)
f_{133} (mdyn)	−0.2 (1)	−0.68 (1)	−0.28	−0.30	−0.30	−0.25 (1)	−0.23 (1)	−0.23 (1)
f_{333} (mdyn Å)	−0.9 (1)	−1.01 (1)	−0.77	−0.71	−0.69	−0.82 (3)	−0.74 (3)	−0.72 (3)
f_{1111} (mdyn Å^{-3})	367 (50)	417.3 (42.7)	414	369	401	407 (28)	410 (28)	410 (28)
f_{1112} (mdyn Å^{-3})	7 (3)	4.9 (2.4)	0	0	−8	0 (5)	0 (5)	2 (8)
f_{1113} (mdyn Å^{-2})	0 (*)	0 (*)	−1	−2	−14	−14 (23)	−11 (23)	−10 (23)
f_{1122} (mdyn Å^{-3})	6 (2)	4.9 (2.1)	0	0.5	−6	2 (8)	2 (8)	0 (5)
f_{1123} (mdyn Å^{-2})	0 (*)	0 (*)	0.5	0	5	6 (7)	5 (8)	5 (8)
f_{1133} (mdyn Å^{-1})	−2 (1)	2.4 (4)	0	0	0	5 (10)	5 (10)	5 (10)
f_{1233} (mdyn Å^{-1})	0.9 (3)	1.4 (2)	1	1	0.4	−5 (10)	−5 (10)	−5 (10)
f_{1333} (mdyn)	0 (*)	0 (*)	0.8	0.62	0.55	0.22 (3)	0.19 (3)	0.20 (13)
f_{3333} (mdyn Å)	−0.1 (2)	0.1 (1)	−1.0	0.72	−1.14	−0.86 (7)	−0.86 (7)	−0.86 (8)

it is possible to employ a potential expansion through higher order in the internal coordinates. This increases, on the other hand, the number of points enormously, which are needed for the potential fit. Such an extension of the computational effort was avoided at the present stage, because it would make the force constants calculations relatively expensive for a small molecule like H_2O.

Since the SCF surface was shown to be too steep around the energy minimum, only the CI data will be used for the further purpose of this study. The final determination of the spectroscopic constants requires a transformation of the force constants $\{f\}$ into the set of constants $\{\varphi\}$ in a normal coordinate representation. In Table 4 the φ_{ijk} and φ_{ijkl} values for $H_2{}^{16}O$ are listed as they are obtained from the data in Table 3. The difference between the two experimental sets is mainly due to the fact that in the second one the experimental value for the Fermi resonance constant γ_F is used to determine the force constants $\{f\}$. This influences particularly the values of φ_{122}, the γ_F itself, and of φ_{1122} and of φ_{2222} in Column 2. The average error of the *ab initio* calculated cubic and quartic force constants φ is about 20 percent. The theoretical result seems to confirm the value for φ_{2222} in Column 2, whereas the theoretical results for φ_{122} and φ_{1122} are much closer to the ones in Column 1. From the *ab initio* calculations it is thus not possible to decide between the two experimental sets.

The *ab initio* $\{\varphi\}$ values are needed [19] to determine the theoretical spectroscopic constants. Table 5 contains various sets of equilibrium rotational constants X_e ($X=A$, B, C) and rotational interaction constants α_i^X for $H_2{}^{16}O$. The constants in the first column are directly deduced from rotational spectra of $H_2{}^{16}O$. In the second column, the experimental equilibrium structure data derived from the rotational constants of $H_2{}^{16}O$, $HD^{16}O$, and $D_2{}^{16}O$ [24] were used to re-evaluate the X_e, while the α_i^X were obtained from the experimental force constants of Table 3. These values are compared to the results of the present *ab initio* calculations and to those of RES.

Table 4. Cubic and quartic force constants φ for $H_2{}^{16}O$ defined in normal coordinates (numbers in cm^{-1})

	Exp. (Ref. [23])	Exp. (Ref. [25])	CI-SD (Ref. [6])	CI-SDQ	CI-SD (Present work)	CI-SDQ
φ_{111}	−1876.9	−1924.9	−1824.4	−1826.4	−2053.9	−2071.5
φ_{112}	91.2	76.1	70.6	80.6	96.3	109.2
φ_{122}	346.0	192.2	323.4	303.0	358.2	337.6
φ_{133}	−1786.8	−1855.0	−1832.7	−1838.2	−2012.4	−2019.5
φ_{222}	−396.0	−425.6	−267.9	−255.1	−300.9	−289.1
φ_{233}	291.4	294.4	261.0	279.8	314.0	316.1
φ_{1111}	863.6	945.3	740.8	723.3	819.7	856.0
φ_{1122}	−361.8	−218.4	−308.2	−301.9	−362.0	−357.4
φ_{1133}	758.3	867.6	746.7	842.6	808.3	842.5
φ_{2222}	56.7	−72.2	−45.7	−102.5	−24.9	−37.4
φ_{2233}	−412.0	−337.1	−375.5	−328.8	−151.2	−140.6
φ_{3333}	746.8	864.2	748.5	861.1	794.0	828.5

Table 5. Experimental and theoretical equilibrium rotational constants $X_e (X = A, B, C)$ and rotational interaction constants α_i^X for $H_2{}^{16}O$ (in cm^{-1})

	Exp. (Ref. [23])	Exp. (Ref. [25])	CI-SD (Ref. [6])	CI-SDQ	CI-SD (Present work)	CI-SDQ
A_e	27.379	27.4346	27.953	27.466	28.367	27.875
B_e	14.5844	14.5962	14.653	14.581	14.655	14.588
C_e	9.5256	9.5273	9.614	9.525	9.663	9.576
α_1^A	0.750	0.7495	0.667	0.699	0.856	0.905
α_2^A	−2.941	−2.8966	−2.632	−2.539	−2.837	−2.742
α_3^A	1.253	1.2656	1.136	1.180	1.389	1.395
α_1^B	0.238	0.2456	0.214	0.217	0.254	0.261
α_2^B	−0.160	−0.0282	−0.165	−0.168	−0.150	−0.153
α_3^B	0.078	0.0774	0.099	0.097	0.105	0.117
α_1^C	0.2018	0.1953	0.171	0.177	0.210	0.219
α_2^C	0.1392	0.1720	0.146	0.149	0.141	0.143
α_3^C	0.1445	0.1461	0.137	0.142	0.169	0.175

The rotational constants X_e for the three main axes of inertia have a different dependence on the equilibrium geometry parameters: the constant A_e is mainly determined by $\frac{1}{2}(r_e \cos \alpha_e/2)^{-2}$, whereas B_e by $\frac{1}{2}(r_e \sin \alpha_e/2)^{-2}$, and C_e by $\frac{1}{2}(r_e)^{-2}$. Since from the *ab initio* calculations the equilibrium OH distance is obtained slightly too small and the HOH bond angle too large, these errors compensate each other somewhat in the case of the theoretical B_e value, but multiply each other to some extent in A_e. Within the CI-SDQ approximation the accuracy of the X_e values becomes thus about 2 percent for A_e, between 0.1 and 0.5 percent for B_e (depending on the experimental reference data), and about 0.5 percent for C_e. The C_e value which is essentially only a function of the OH bond is almost within the experimental uncertainty. Since the theoretical equilibrium geometry parameters of RES are slightly more accurate, their X_e results are closer to the experimental values.

The α_i^X values which are directly determined from spectroscopic measurements are reproduced by those derived from the experimental force constants with a discrepancy of about 2 percent, which is within the experimental error limits. The accuracy of the present *ab initio* calculated α_i^X values is about 10 percent, and there is no obvious improvement from CI-SD to CI-SDQ. However, since the total anharmonicity correction in (2) is small compared to the X_e values, the accuracy of the rotational constants X_v depends still essentially on the quality of the equilibrium geometry parameters. The present theoretical X_v results have an average error between 0.3 and 0.9 percent compared to the experimental values. Particularly A_v is in the average closer to experiment than the corresponding RES results.

The vibrational constants ω_i and x_{ij} as well as the resonance constants γ_D and γ_F for $H_2{}^{16}O$ are listed in Table 6. The two experimental sets in the table were derived from vibrational frequency data in different ways [24, 25], and the theoretical

Table 6. Experimental and theoretical vibrational constants for $H_2{}^{16}O$ (in cm^{-1})

	Exp.	Exp.	CI-SD	CI-SDQ	CI-SD	CI-SDQ
	(Ref. [23])	(Ref. [25])	(Ref. [6])		(Present work)	
ω_1	3832.17	3831.16	3930.6	3855.1	3953.6	3868.9
ω_2	1684.47	1651.49	1701.9	1687.1	1685.0	1670.1
ω_3	3942.53	3941.17	4035.1	3958.5	4062.4	3980.2
x_{11}	−42.58	−42.04	−42.3	−45.4	−60.6	−62.9
x_{12}	−15.93	−17.67	−13.9	−14.5	−14.7	−14.9
x_{13}	−165.82	−162.38	−165.1	−150.3	−227.1	−232.6
x_{22}	−16.81	−19.49	−17.2	−19.8	−18.6	−18.5
x_{23}	−20.22	−18.15	−21.3	−11.7	45.9	46.2
x_{33}	−47.57	−47.42	−48.3	−44.4	−65.7	−66.9
γ_D	−77.52	−77.18	−84.8	−77.4	−111.4	−113.0
γ_F	(−18.86)	−192.49	−323.4	−303.0	−358.2	−337.6

values were obtained from the corresponding force constants in Table 3. In analogy to the *ab initio* harmonic force constants the present theoretical ω_i values are slightly too large compared to experiment: the average deviation is 2 to 3 percent for CI-SD and about 1 percent for CI-SDQ. RES obtained the same error for CI-SD, their improvement for CI-SDQ, however, is somewhat better except for the bending frequency. This may be due to the fact that larger distortions from the equilibrium bond angle were taken into account in the present study providing a more accurate description of the rather flat bending potential of H_2O. Because of the inaccuracy of the higher order force constants the present results for x_{ij}, γ_D, and γ_F are very uncertain (average error about 50 percent) and there is no obvious improvement from CI-SD to CI-SDQ.

From the data in Table 6 the vibrational levels for $H_2{}^{16}O$ can be calculated. In Table 7 the present theoretical transition frequencies from the vibrational levels (v_1, v_2, v_3) to the zero-point vibrational level ($v_1=0$, $v_2=0$, $v_3=0$) are listed and compared to experimental measurements. Using only the *ab initio* CI-SD harmonic frequencies ω_i the general structure of the water spectrum is already obtained quite reasonably. The actual frequency values, however, are systematically too large by about 10 percent. Taking into account the anharmonicity correction and the Darling–Dennison resonance this average error is reduced to about 3 percent for CI-SD and to about 2 percent for the CI-SDQ data. The same percentage errors are obtained for the RES results except for their CI-SDQ approximation which gives transition frequencies slightly closer to experimental measurements (average error about 1.6 percent).

In addition to the structure of the vibrational spectrum, the shape of the bending potential is also of some interest. With $V_e=0$ and $r_1=r_2=r_e$, the potential expression (1) can be simplified to

$$V(\alpha)=\tfrac{1}{2}f_{33}\Delta\alpha^2+\tfrac{1}{6}f_{333}\Delta\alpha^3+\tfrac{1}{24}f_{3333}\Delta\alpha^4 \tag{6}$$

Table 7. Vibrational levels in cm^{-1}. Experimental and present *ab initio* results

v_1	v_2	v_3	Exp. (Ref. [25])	CI-SD(ω)	CI-SD	CI-SDQ
0	0	0	0	0	0	0
0	1	0	1595	1685	1663	1649
0	2	0	3152	3370	3290	3261
1	0	0	3657	3954	3712	3619
0	0	1	3756	4062	3840	3753
0	3	0	4667	5055	4879	4835
1	1	0	5235	5639	5360	5253
0	1	1	5331	5747	5550	5448
0	4	0	6136	6740	6430	6373
1	2	0	6775	7324	6972	6850
0	2	1	6872	7432	7222	7106
2	0	0	7201	7907	7259	7071
1	0	1	7250	8016	7325	7140
0	0	2	7445	8125	7592	7415
1	3	0	8274	9009	8546	8410
0	3	1	8374	9117	8857	8727
2	1	0	8762	9592	8905	8701
1	1	1	8807	9701	9019	8820
0	1	2	9000	9810	9336	9145
0	4	1	9834	10802	10454	10311
1	2	1	10329	11386	10677	10463
0	2	2	10523	11495	11047	10842
3	0	0	10600	11861	10595	10307
2	0	1	10613	11970	10615	10329
1	0	2	10869	12078	10983	10701
0	0	3	11032	12187	11200	10931
0	5	1	11248	12487	12015	11858
1	3	1	11813	13071	12297	12069
0	3	2	12012	13180	12723	12505

where $\Delta\alpha=\alpha-\alpha_e$. For the linear geometry of the water molecule ($\alpha=180°$) this potential has a relative maximum (energy hump) which, however, cannot be considered as an energy barrier for the vibrational motion. This maximum can influence the energy levels for excited bending vibrations and since it is not very large the water molecule has actually to be regarded as quasilinear for some higher excited states. Hougen *et al.* [27, 28] were able to describe the observed pure bending vibrations utilizing a Lorentz type potential function

$$V(\alpha)=\tfrac{1}{2}k\rho^2+\frac{K_B}{(c^2+\rho^2)}, \qquad (7)$$

where $\rho=\pi-\alpha$. The parameters k, c, and K_B were fitted to experimental data. With this empirical potential they obtained for the relative maximum a value of $h=10900\,\mathrm{cm}^{-1}$ [27] and $h=11050\,\mathrm{cm}^{-1}$ [28]. Using the present *ab initio* force constants in (6) the height of the relative maximum is here determined to be $h=11790\,\mathrm{cm}^{-1}$ for CI-SD and $h=11890\,\mathrm{cm}^{-1}$ for CI-SDQ, while the direct energy difference at the experimental equilibrium bond distance (entries 1 and 37 of Table 1) gives about $h = 11940\,\mathrm{cm}^{-1}$ in both approximations. With the experimental force constants from Table 3 the energy maximum is $h = 12190\,\mathrm{cm}^{-1}$ and $h = 11640\,\mathrm{cm}^{-1}$, respectively. This means that the present theoretical results are within the experimental error limits. Since linear configurations for H_2O were not included in the RES study, the corresponding energy maximum can only be estimated to be $14040\,\mathrm{cm}^{-1}$ for CI-SD and $11630\,\mathrm{cm}^{-1}$ for CI-SDQ.

Sorbie and Murrell [29] defined an analytical potential expression for H_2O using the force constants of Hoy *et al.* [18]. With this empirical potential they calculated the height of the relative maximum to be $h = 9485\,\mathrm{cm}^{-1}$, which is certainly too low. This indicates that it is very difficult to find an analytic potential empirically that is able to reproduce the potential hypersurface equally well over the whole region.

Sorbie and Murrell pointed out that for the linear configuration of the water molecule the OH bond distance decreases by about 0.006 Å compared to the value for the bent equilibrium structure, and that for this OH distance the hump should be reduced by about $10\,\mathrm{cm}^{-1}$. According to the present CI results the OH distance decreases by about $\Delta r = 0.035$ Å and h by about $\Delta h = 300\,\mathrm{cm}^{-1}$, while the experimental force constants of Table 3 give $\Delta r \approx 0.05$ Å and $\Delta h \approx 400\,\mathrm{cm}^{-1}$.

4. Final Remarks

Large scale self-consistent field and single reference state configuration interaction calculations were performed in order to determine parts of the energy hypersurface and the molecular force field of water. From the theoretical force constants through fourth order the rotational and vibrational spectroscopic constants were evaluated by a perturbational approach. The accuracy of the present results was checked by an extensive comparison to experimental data and to other accurate *ab initio* calculations published recently by Rosenberg *et al.* [6].

It appears that the quality of the Gaussian basis set (54 GTO's) employed here is equivalent to the Slater type basis used by RES [6]. The difference in the standard deviations particularly of the *ab initio* fourth order force constants of the present study and of RES is partly due to the different selections of points on the energy hypersurface. More reliable fourth order force constants can be obtained by employing a potential expansion through higher order. However, as was already pointed out, this would increase considerably the number of points necessary for the potential fit.

Compared to RES relatively large distortions from the equilibrium structure of H_2O were taken into account in the present study. In order to achieve a higher accuracy of the *ab initio* points on the energy hypersurface it will therefore be necessary to generate the molecular orbitals within the MCSCF approximation including at least those configurations allowing for the correct dissociations of H_2O instead of using only the single determinant SCF approach. The CI-SD treatment should then also incorporate a corresponding multi-reference state. The results of such a study will be published in a forthcoming paper.

Because of the large uncertainties of the force constants of higher order derived from experimental data and because of the rather involved dependency of the rotational and vibrational frequencies on the individual force constants, it is necessary to evaluate the observable frequencies from the theoretical force field in order to judge the accuracy of the *ab initio* calculated energy hypersurface. This can be done in different ways: by using a perturbational approach, as was done in the present study, or by using variational methods [30–32], and finally by solving the rotational-vibrational Schrödinger equation directly by numerical integrations at the *ab initio* calculated points on the potential surface [33]. The variational methods have the advantage that all the resonances of the water molecule are included, while within the present perturbation scheme off-diagonal terms are neglected except for Coriolis and Darling–Dennison resonances. However, the perturbational treatment is computationally much faster than the variational methods and it appears further to be a useful approach, since the experimental frequencies used to calculate a set of force constants are reproduced within the experimental error limits. The inaccuracies of the *ab initio* calculated surface are anyway larger than the approximations inherent in the perturbational method.

The direct method was recently used by Whitehead and Handy [33]. They calculated 72 points on the potential surface of water within the CI-SD approximation using a Slater-type orbital basis of improved double-zeta quality plus polarization function (a total of 32 STO's) and solved the rotational-vibrational Schrödinger equation numerically for the vibrational eigensolutions. The accuracy of these solutions is determined essentially by the number of grid points available for the numerical integration. Using the 72 *ab initio* calculated points Whitehead and Handy were able to obtain only the fundamental frequencies. The errors of these v_i values are similar to those of the present study ranging from 1.4 to 2.0 percent. The advantage of the direct method is clearly that no explicit potential expression is needed; it is, on the other hand, computationally very expensive. Using the perturbational approach a minimum of only 22 points on the energy hypersurface is needed for the polynomial fit. With the force constants available the calculation of the spectroscopic constants for all possible isotopic species of water can then be performed with a negligible amount of computer time.

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