were simulated by a sequence of two pulses with energies of 3.490 and 4.716 eV, respectively. The resulting mechanism is as follows.

To augment the yield of the product $CpMn(CO)_3^+$ as much as possible, the first subpulse must avoid excitation of the predissociative b^1A'' state, because the population in this state would transfer nonadiabatically to the repulsive a^1A'' state. This transfer would cause a competing formation of the parent ion and the undesired daughter ion when the second (ionizing) subpulse is applied. Instead, the first subpulse should excite preferably the bound c^1A' state, which lies slightly above the b^1A'' one (Fig. 3). The choice of the wavelength of the reference pulse, which is slightly shorter (800 nm) than the one used in the pump-probe experiment ($402.5 \times 2 = 805$ nm), facilitates the transition to the c^1A' state. In addition, the algorithm's learning loop generates a first subpulse, which contains the high-frequency components of the input field (798.7 nm).

Next, the second subpulse can transfer the population of the neutral c^1A' state to the parent ion exclusively, provided that it contains frequency components for a transition to the ionic PES. The wave packet propagates in the potential well of the c^1A', and after 85 fs it arrives at the outer turning point located at 2.3 Å (Fig. 3B). This position serves as a transient Franck-Condon window for the transition to the ionic state b^2A'. Hence, the learning loop produces a second subpulse of 800.09 nm, and, in doing so, it optimizes the ionization step as well. This subpulse could promote additional population in the c^1A' state, which would be ionized after another 85-fs delay by the third subpulse (801.12 nm).

Similar discoveries of the mechanisms of optimal control should be possible for other systems with three important properties similar to those found in the present system. First, the target should be produced by few, preferably just two, main sequential processes (for example, excitation or photodissociation followed by ionization). Each process should use a small number of photons to avoid substantial Stark-shifts in the pump-probe experiment; in intense control pulses, such Stark-shifts may open the door to interfering competing channels. Finally, it should be possible to select the target ion while suppressing the competing ones, by means of well-placed subpulses with slightly different frequencies within the band/width of the reference pulse. The last requirement points to systems with a sufficiently large density of electronic excited and ion states leading to the target in addition to competing channels.

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High-Accuracy ab Initio Rotation-Vibration Transitions for Water

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The spectrum of water vapor is of fundamental importance for a variety of processes, including the absorption and retention of sunlight in Earth's atmosphere. Therefore, there has long been an urgent need for a robust and accurate predictive model for this spectrum. In our work on the high-resolution spectrum of water, we report first-principles calculations that approach experimental accuracy. To achieve this, we performed exceptionally large electronic structure calculations and considered a variety of effects, including quantum electrodynamics, which have routinely been neglected in studies of small many-electron molecules. The high accuracy of the resulting ab initio procedure is demonstrated for the main isotopomers of water.

The absorption and emission of light by water vapor is responsible for ~70% of the known absorption of sunlight and the majority of the greenhouse effect (*1*). Hot steam is also a major product of most combustion processes and a dominant atmospheric constituent of cool stars. Therefore, water spectra have been the subject of immense scientific effort, but some proper-

ties, such as the details of atmospherically important, weak line absorptions or the spectrum of superheated water, are extremely difficult to determine experimentally. Similarly, despite substantial progress in this area (2), there exists no complete and accurate theoretical model with which one can predict the high-resolution spectrum of water.

Here, we report first-principles calculations that determine the vibration-rotation energy level structure of water to better than 1 cm^{-1} on average. To achieve this accuracy, we not only performed very elaborate nonrelativistic electronic structure calculations, but also considered a variety of small physical effects arising from a fully relativistic treatment, breakdown of the Born–Oppenheimer (BO) approximation, and quantum electrodynamics. All of these corrections are routinely neglected, even in high-accuracy treatments of small molecules. As we demonstrate here, only the combination of extrapolated large basis set electronic structure calculations and exotic corrections enables one to approach experimental accuracy during prediction of the spectrum of water.

First-principles quantum mechanical treatments of molecular spectra are usually based on the BO approximation. According to this approximation, the motions of electrons can be separated from those of atomic nuclei because the former are much lighter than the latter. Thus, approximate solutions to the electronic motion problem can be obtained for a series of calculations at fixed nuclear geometries. The points are then fitted or otherwise interpolated to give an electronic potential energy surface (PES), which is independent of the masses of the nuclei. Nuclear motion calculations performed on such surfaces yield vibration-rotation energy levels and, hence, high-resolution spectra.

Only for few-particle systems, such as H_3^+ (two electrons, three nuclei), have first-principles calculations approached the accuracy of high-resolution spectroscopy experiments (3, 4). For systems with more than two electrons, the goal of achieving predictions of near-spectroscopic accuracy (better than 1 cm^{-1}) has so far proved elusive. Water (10 electrons, three nuclei) has long been a benchmark system. Partridge and Schwenke (PS) (5) performed the first ab initio calculations for water to be accu-

rate enough to be useful for detailed spectroscopic analysis. Yet at higher energies, their calculated vibrational band origins (VBOs) are still up to 20 cm^{-1} away from experimental values. It is also difficult to accurately determine how much energy it takes to distort water from its usual bent structure to a linear geometry (6, 7). One reason why water is so challenging is that upon bending, the oxygen valence electrons rehybridize from sp^3 to sp, causing substantial changes, even to the oxygen 1s orbital.

To obtain high accuracy for first-principles rotation-vibration spectra, one must treat both the electronic and the nuclear motion problems accurately. For triatomic molecules moving on a given PES, the coupled rotation-vibration problem can be considered solved. Methods based on the Variational Principle give very accurate nuclear motion energy levels [see, e.g., (4)]. Similarly, the independent particle model for the motion of the electrons, whereby each electron moves in the average field of all others, has been solved for water, yielding the so-called "Hartree–Fock limit" (8). The main focus of the present work is the solution of the electronic structure problem and the coupling between electronic and nuclear motion.

To improve upon the independent particle model, one must account for the correlated motion of the electrons. An exact solution is offered by the full configuration interaction (FCI) technique involving every possible electron configuration. FCI calculations are only feasible for small basis sets. Very accurate approximations to FCI have been developed, and the one we use is called multireference configuration interaction (MRCI) (9). The required computations were performed with the parallel version of the electronic structure package MOLPRO (10). Correlation energy only converges slowly with increasing basis set size (11). Dunning (12) has developed a series of correlation consistent (cc) Gaussian basis sets, which can be used for systematic studies. Here we report a series of calculations using Dunning's aug-cc-pVnZ basis sets with n = 3, 4, 5, and 6 (13) (denoted nZ below). In this notation, n stands for the number of basis functions used per physical atomic orbital, and aug specifies that this basis is augmented with diffuse, low-exponent Gaussian functions. As n increases, the basis set approaches completeness, both by increasing the flexibility for a given symmetry and by including higher angular momentum components. The largest basis we considered has n = 6 and consists of s, p, d, f, g, h and i functions. We found full augmentation of the basis to be of particular importance. The oxygen 1s core electrons were kept frozen during these calculations.

At the 6Z MRCI level, a calculation required 2 hours and 64 processors of an Origin 3000 machine for a single nuclear geometry. A total of 346 points were computed with each basis set; the initial grid of ~200 points spanned

geometries up to 30,000 cm^{-1} above the water minimum. Further geometries were chosen according to their importance in determining the fitted PES.

Use of the valence-only 6Z surface plus corrections given below still gives residual errors of up to 19 cm^{-1} in the VBOs and a standard deviation for all VBOs, σ, of 5.5 cm^{-1} (Table 1). The slow convergence with respect to n is due to the form of the electronic wave function employed in all electronic structure packages. Nevertheless, the smooth behavior of the energies as n is systematically increased has been exploited by extrapolating the surface to the complete basis set (CBS); that is, $n = \infty$, limit (8, 14, 15, 16).

Even at the CBS limit, our MRCI model does not include the entire valence electron correlation energy. This can only be achieved by performing a FCI computation, which cannot presently be performed for water with basis sets larger than about 2Z. Comparison of FCI and MRCI calculations at this level (17) showed a smooth variation in the difference, which rose to only 1 cm^{-1} at 25,000 cm^{-1} above the PES minimum. Because this effect is small and probably cannot be modeled accurately at the 2Z level, it has not been allowed for in the results presented below.

The largest error in our extrapolated CBS MRCI surface is due to the contribution to electron correlation effects neglected by freezing the oxygen core electrons. Partridge and Schwenke computed a correction surface (5), which they denoted "CV" for core-valence, although in practice it also allows for core-core correlation effects. Recalculation of several points on this surface with a variety of procedures and basis sets (18) showed that the surface calculated by Partridge and Schwenke gives a reliable estimate of core correlation effects, and it is used here unchanged. Augmentation of the CBS MRCI PES with this correction surface reduces the errors of the predicted VBOs by almost a factor of 3 (Table 1).

The next most important correction to the electronic energies comes from the finite speed of light, not taken into account in nonrelativistic treatments of the electron motions. The inclusion of special relativity, which can formally be done with the Dirac Hamiltonian, gives rise to several effects (19–21). The dominant effect is a one- electron contribution arising from the high velocity of the electrons. We computed the resulting energy correction using first-order perturbation theory through the mass velocity and Darwin terms (19) by extending the available surface (22) to higher energies. This one-electron mass-velocity and Darwin (MVD1) correction surface gives most of the relativistic energy correction for closed-shell molecules composed of light elements. Comparisons with full Dirac Hamiltonian calculations of Quiney and others (23), who used small basis sets and less accurate wave functions, showed differences in the mag-

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Table 1. Predicted VBOs for various theoretical models. Results are presented as differences from the observed values (Obs) in cm^{-1} (*34*). The standard deviation, σ, is for all experimentally known VBOs. 5Z, aug-cc-pV5Z MRCI calculation; 6Z, aug-cc-pV6Z MRCI calculation; CBS, MRCI calculation extrapolated to the complete basis set limit; PS, partially augmented cc-pV5Z MRCI calculation plus core correlation owing to Partridge and Schwenke (*5*); CBS + CV, CBS with core correlation correction; Rel, CBS + CV with relativistic effects included; QED, Rel with one electron Lamb shift included; BODC, QED with Born–Oppenheimer diagonal correction included; Nonad, BODC with vibrational nonadiabatic effects included. Dashes indicate no data available.

State	Obs	5Z	6Z	CBS	PS	CBS + CV	Rel	QED	BODC	Nonad
(010)	1,594.74	–2.99	–2.29	–0.32	–2.79	0.48	–0.81	–0.75	–0.32	–0.27
(020)	3,151.63	–4.22	–2.38	–0.78	–5.38	1.16	–1.57	–1.44	–0.56	–0.44
(030)	4,666.78	–6.30	–3.24	–1.52	–7.91	2.05	–2.37	–2.16	–0.78	–0.60
(040)	6,134.01	–9.81	–5.53	–2.74	–10.38	3.20	–3.30	–3.00	–1.06	–0.83
(050)	7,542.43	–14.70	–9.18	–4.71	–12.90	4.82	–4.45	–4.02	–1.41	–1.14
(101)	7,249.81	12.51	10.76	9.32	–4.78	–5.35	1.70	1.43	0.60	2.00
(201)	10,613.35	18.72	16.46	13.97	–6.96	–7.47	2.98	2.57	1.23	–
(301)	13,830.93	25.72	22.81	18.74	–8.41	–8.95	4.59	4.06	2.05	–
(401)	16,898.84	32.56	28.92	23.06	–9.47	–10.17	6.11	5.49	2.74	–
(501)	19,781.10	40.72	35.96	28.68	–9.31	–10.72	9.04	8.28	4.65	–
(601)	22,529.44	51.14	43.41	34.17	–7.61	–11.88	11.69	10.81	5.94	–
(701)	25,120.27	63.29	51.75	38.66	–5.49	–13.13	13.70	12.75	6.46	–
All	σ	22.84	19.74	16.56	10.44	7.85	4.23	3.83	1.90	–

nitude of this correction but excellent agreement in its variation with geometry, which is the key property for spectroscopy. The minuscule, two-electron contribution to the Darwin term (D2), which serves to correct point-like charge distributions, was also included (*24*). The Coulomb interaction, because of its instantaneous character, is not consistent with special relativity and needs to be supplemented by the Breit interaction (*20*). The Breit term was calculated (*24*) with the Dirac Hamiltonian and the program BERTHA (*25*).

One further effect was included in our PES: the one-electron Lamb shift. This lowest order quantum electrodynamic effect was modeled with the prescription of Pyykkö and others (*26*). We know of no case where the use of quantum electrodynamics (QED) has had any impact on molecular physics. However, our calculations are of such accuracy that incorporating this effect yields a clear, systematic improvement in the results.

Thus far, our treatment remained within the framework of the BO approximation, which decouples electronic and nuclear motions. If high accuracy is required for the prediction of molecular spectra, coupling between these motions must be considered. Corrections to the BO approximation can be computed efficiently by means of the second-order contact transformation method of Bunker and Moss (*27*). This introduces two terms: (i) the simple, first-order Born– Oppenheimer diagonal correction (BODC), which allows for the action of the nuclear motion kinetic energy operator on the ground-state electronic wave function and gives rise to a mass-dependent correction surface, and (ii) the more difficult, second-order (or nonadiabatic) correction, which introduces coupling between electronic states and primarily results in corrections to the kinetic energy operator.

For this work, an isotopomer-dependent BODC surface was computed with an MRCI wave function (*28*). Two methods of including

Table 2. Standard deviation, σ, with which our final (CBS + CV + Rel + QED + BODC) potential reproduces the vibrational-rotation term values for various water isotopomers with rotational excitation $\leq J_{max}$. N levels are considered in each case [N(levels)]. Also given is the maximum deviation for each isotopomer, in cm^{-1}, and the associated value of J. The H$_2$O isotopomer calculations include rotational nonadiabatic effects. Dashes indicate not applicable.

Isotopomer	σ (cm^{-1})	J_{max}	N(levels)	Maximum deviation	
				Obs – calc	J
H$_2{}^{16}$O	1.17	20	9,426	6.5	7
H$_2{}^{17}$O	0.56	12	1,083	1.4	12
H$_2{}^{18}$O	0.65	12	2,460	2.3	6
D$_2{}^{16}$O	0.71	12	2,807	3.0	7
HD^{16}O	0.47	12	2,019	–1.2	11
All	0.95	20	17,795	–	–

nonadiabatic corrections to the vibrational motion were explored. The method of Schwenke (*29*) (involving explicit coupling of the ground electronic state to electronically excited states) was compared to a much simpler, two-term adjustment of the vibrational kinetic energy operator with parameters taken from Schwenke's study (*30*). The results of the two methods agree to better than 0.1 cm^{-1}. These nonadiabatic treatments are only valid for energies up to 10,000 cm^{-1}, and their effect is small (Table 1). Vibrational nonadiabatic effects have therefore not been included in our final calculations. Rotational nonadiabatic corrections are, however, important for high values of the rotational quantum number, J. These are included in the results presented for H$_2$O isotopomers in Table 2. Again, the full (*29*) and reduced (*30*) methods of including this correction gave very similar results; the latter was used for our final calculations.

Except for the nonadiabatic corrections, energies for each of the above effects were generated on a grid of points. These energies were then fitted to a suitable functional form for use in the nuclear motion calculations. Very accurate fits were obtained for all contributions to the PES, except the ones due to the valence MRCI

calculations. The 346 CBS MRCI data points were fitted using 113 parameters, with an accuracy of 0.69 cm^{-1} (*31*).

The resulting compound surface gives the equilibrium structure of H$_2{}^{16}$O, with an OH bond length of 0.95785 Å and a bond angle of 104.501°, both with an uncertainty of ~5 units in the final digit. This accuracy is significantly better than that of any previous (ab initio or empirical) attempt (*32*) and is a reflection of the precision of our procedure for energies up to 15,000 cm^{-1}. The barrier to linear HOH geometries is 11,123 ± 5 cm^{-1} for an OH bond length of 0.93323 Å.

The results of our rotation-vibration energy level calculations are summarized in Tables 1 and 2. Nuclear motion calculations were performed with two independent codes (*29*, *33*), which gave results agreeing to within 0.01 cm^{-1} for the same model.

For H$_2{}^{16}$O, there are 104 experimentally known VBOs that arise from vibration-rotation spectra, which uniquely extend into the ultraviolet (*34*). Similarly, analysis of hot (temperature, 3000 K) water spectra (*2*) has yielded rotational energies also reaching 25,000 cm^{-1} (*34*). Table 1 shows how the errors in the VBOs change as the model is systematically improved.

In our final models, the errors are dominated by states with high excitation in the v_1 (symmetric stretching) modes.

Table 1 demonstrates the necessity of using both large basis sets, extrapolation to the CBS limit, and the four additional corrections to achieve sub–wave number accuracy. This accuracy is more than an order of magnitude better than that achieved by the previous most accurate ab initio study, (PS, Table 1).

Table 2 summarizes the results of extensive calculations on the five major isotopomers of water with rotational energy levels up to $J = 20$ for $H_2^{16}O$ and $J = 12$ for other isotopomers for which there are little data for $J > 12$. As shown in Table 2, the overall standard deviation for more than 17,000 levels is only 0.95 cm^{-1}, and hence our procedure, which results in a mass-dependent PES, is equally valid for all isotopomers.

We studied the change in our VBOs as the MRCI calculation is increased from 5Z to 6Z and then extrapolated to the CBS limit. These comparisons show that the source of error for high v_1 is caused by the limitations of the 6Z basis set. Increasing the basis set to the 7Z level (35), at an increased computational cost of about an order of magnitude, and extrapolating to a new CBS limit will affect the lower energy levels little but, according to our estimates, reduces the discrepancy of high v_1 states to <1 cm^{-1}. Further improvement can be achieved with a denser grid of MRCI points. Nuclear motion calculations using PESs fitted to 250, 300, and 346 MRCI points show a systematic improvement in our predictions. The use of a grid of at least 1000 MRCI points should reduce the fitting error and improve σ by 0.2 cm^{-1}. The final factor that should yield further improvement in the accuracy is the use of an accurate FCI correction. Our estimates show that including this correction could shift the highest VBOs by up to 1 cm^{-1}, giving an improvement of up to 0.2 cm^{-1} in σ.

The ultimate goal of theoretical rotation-vibration spectroscopy of water must be to model all water spectra, on the sun, in the stars, in the atmosphere, in flames, and in the laboratory within a linewidth (or within the upper limit of the experimental accuracy) of 0.02 cm^{-1} or better. Our study improves the accuracy of the ab initio surface and energy levels of water by an order of magnitude in comparison with previous high-accuracy work. Our calculations predict individual line positions, for which there is often substantial cancellation of systematic errors, with a typical accuracy of 0.2 cm^{-1}. For example, analysis of the 571 transitions observed in sunspots and assigned to water with $J \leq 21$ (2) shows that the frequencies of these lines are reproduced by our calculations with a standard deviation of 0.204 cm^{-1}.

As well as accurate line positions and wave functions, very accurate dipole moment surfaces are required for reliable models of water spectra,

including those used in atmospheric models to account for anomalous absorption and the greenhouse effect. The accurate experimental values of the Stark dipoles obtained recently (36) provide a stringent test of ab initio dipole moment surfaces. The electronic wave functions computed as part of our work have been used to generate accurate dipole moment surfaces, which are being tested. The benchmark results and procedures we describe here can be used to predict the spectrum of other small polyatomic molecules to similar accuracy.

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Vibrationally Resolved Fluorescence Excited with Submolecular Precision

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Tunneling electrons from a scanning tunneling microscope (STM) were used to excite photon emission from individual porphyrin molecules adsorbed on an ultrathin alumina film grown on a NiAl(110) surface. Vibrational features were observed in the light-emission spectra that depended sensitively on the different molecular conformations and corresponding electronic states obtained by scanning tunneling spectroscopy. The high spatial resolution of the STM enabled the demonstration of variations in light-emission spectra from different parts of the molecule. These experiments realize the feasibility of fluorescence spectroscopy with the STM and enable the integration of optical spectroscopy with a nanoprobe for the investigation of single molecules.

Single-molecule spectroscopy has potential applications in ultrasensitive chemical identification (1, 2) and as a probe of the local molecular

environment and single-biomolecule dynamics in vivo (3, 4). The influence of the conformational structure on the properties of a molecule