

# A spectroscopically determined potential energy surface for the ground state of H<sub>2</sub>16O: A new level of accuracy

Oleg L. Polyansky and Per JensenJonathan Tennyson

Citation: **101**, (1994); doi: 10.1063/1.468258

View online: <http://dx.doi.org/10.1063/1.468258>

View Table of Contents: <http://aip.scitation.org/toc/jcp/101/9>

Published by the [American Institute of Physics](#)

---

---

# A spectroscopically determined potential energy surface for the ground state of H<sub>2</sub><sup>16</sup>O: A new level of accuracy

Oleg L. Polyansky<sup>a)</sup> and Per Jensen<sup>b)</sup>

Physical Chemistry Institute, Justus Liebig University Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany

Jonathan Tennyson

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom

(Received 14 June 1994; accepted 19 July 1994)

The potential energy function for the electronic ground state of the water molecule has been obtained by fitting rotation-vibration term values involving  $J \leq 14$  for 24 vibrational states of H<sub>2</sub><sup>16</sup>O together with 25 additional vibrational term values belonging to higher excited states. The fitting was carried out by means of an exact kinetic energy Hamiltonian. It was found that the differences between the exact kinetic energy calculations and calculations with the MORBID program (i.e., calculations with an approximate kinetic energy operator) depend only very slightly on the parameters of the potential. This fact allowed us to make an inexpensive fitting using the MORBID approach and still get the accuracy obtainable with the exact kinetic energy Hamiltonian. The standard deviation for 1600 term values was 0.36 cm<sup>-1</sup>. For 220 ground state energy levels the standard deviation was 0.03 cm<sup>-1</sup>. With the fitted potential, calculations of term values with  $J \leq 35$  were carried out. This showed the excellent predictive power of the new potential. For the  $J=20$  term values in the vibrational ground state, the deviations from experiment are typically below 0.2 cm<sup>-1</sup>. The discrepancy for the observed level with the highest  $K_a$  value,  $J_{K_a K_c} = 20_{200}$ , is only 0.008 cm<sup>-1</sup>. The calculated term value for the observed level with the highest  $J$ ,  $35_{035}$ , deviates 0.1 cm<sup>-1</sup> from experiment. Because of the level of accuracy achieved in these calculations, we can for the first time demonstrate the breakdown of the Born–Oppenheimer approximation for the water molecule. The high  $K_a$  level calculations allow us to show that the rotational energy level structure in water is at least of a very different nature than the fourfold cluster structures observed for H<sub>2</sub>Se and calculated for H<sub>2</sub>S, H<sub>2</sub>Se, and H<sub>2</sub>Te.

## I. INTRODUCTION

Variational calculations from *ab initio* potential energy surfaces have been very useful for assigning rovibrational spectra of many triatomic molecules, molecular ions, and radicals. The deviations from experimental values obtained for vibrational energy spacings in such work are typically a few cm<sup>-1</sup>, even for high-level calculations. This accuracy is often sufficient for assigning at least the lowest vibrational states. However, for very detailed studies involving, for example, highly excited states, the accuracy of *ab initio* surfaces is not satisfactory. When experimental spectroscopic data are available, we can in principle increase the accuracy of the rotation-vibration calculations significantly by optimizing the potential energy surface to reproduce the known experimental data. Potential functions for many triatomic molecules have been obtained in this way. In particular, in recent years several optimized potential energy surfaces for the water molecule have been reported.<sup>1–6</sup> Clearly there are several reasons for the considerable interest in the water potential surface. First, water is a classic subject of molecular spectroscopy, whose spectrum has been extensively studied

so that a large amount of experimental data on very highly excited rotational and vibrational levels is available in the literature. Second, there are numerous applications in which a precise knowledge of the water spectrum is essential, e.g., the physics of the Earth atmosphere, of the atmospheres of other planets and of stars, the physics of the interstellar medium, technical applications, etc. On the basis of potential energy surfaces derived from experimental data, rotation-vibration energies for water could be calculated with an accuracy much higher than that obtained with *ab initio* surfaces. With the fitted potentials, it is possible to calculate the lowest rotation-vibration energy levels to within a fraction of a cm<sup>-1</sup> of the experimental value, but the discrepancies increase to become around 10 cm<sup>-1</sup> for the highest excited states observed. The purpose of this paper is to decrease these discrepancies by one or two orders of magnitude. This level of accuracy immediately opens new opportunities for water spectrum analysis. Here, we shall consider two examples; the breakdown of the Born–Oppenheimer approximation and the fourfold clustering effect. Other possible applications of the new potential energy function, such as the assignment of transitions involving highly excited states, are obvious.

## II. FITTING PROCEDURE

In the MORBID approach<sup>7</sup> to the calculation of the rotation-vibration energies of a triatomic molecule, the ki-

<sup>a)</sup>Permanent address: Applied Physics Institute, Russian Academy of Science, Uljanov Street 46, 603 600 GSP-120 Nizhni Novgorod, Russia.

<sup>b)</sup>Permanent address: FB 9-Theoretische Chemie, Bergische Universität-Gesamthochschule Wuppertal, D-42097 Wuppertal, Germany.

netic energy operator is approximated by a truncated Taylor series expansion in the stretching coordinates. Owing to this approximation (and other less significant approximations) highly excited rotational energies can be calculated in a rather inexpensive way. For example, one iteration in the fitting of the H<sub>2</sub><sup>16</sup>O data used in the present work (see below), which involved  $J \leq 14$ , used approximately two hours of cpu time on an IBM RISC/6000 340 workstation. It is in principle also feasible to perform the fitting of the potential surface from high  $J$  data in the framework of an exact kinetic energy (EKE) Hamiltonian,<sup>5,8</sup> but the corresponding iteration would take more than 10 h of cpu time on a Cray YMP.

This difference in performance is due to the fact that in order to obtain a given level of convergence, the EKE calculations of the present work require the diagonalization of much larger effective matrices than those diagonalized in the MORBID approach. In the present case explicit diagonalization of the largest matrices is avoided by a series of intermediate diagonalizations but this can lead to significant time being spent on transformations.<sup>9</sup> For example, in these EKE calculations, the largest matrix explicitly diagonalized (for  $J=14$ ) was of dimension 2250 but was obtained as a result of transforming the results from 138 600 raw basis functions. The corresponding MORBID matrix had the dimension 1026. The enhanced efficiency of the MORBID program is due to its choice of basis functions for the bending motion. These functions are obtained by an inexpensive numerical integration technique as the eigenfunctions of a simplified Hamiltonian describing the angle bend (with the bending potential for the molecule in question) and rotation around the molecule-fixed axis with the smallest moment of inertia. Consequently, they form a very good basis set.

Clearly it would be preferable to use the cheaper MORBID procedure for carrying out the least squares fitting, provided that we can attain the accuracy of the EKE calculations. The approximations inherent in the MORBID approach cause its results to differ from the EKE results. Our calculations showed that for  $J=20$  in vibrational ground state, the differences become as large as 10 cm<sup>-1</sup> and increase with increasing vibrational excitation. The differences between calculated band origins are as large as 10 cm<sup>-1</sup> for highly excited vibrational states. For low  $J$  and  $v$  values, however, the typical difference is around 0.1 cm<sup>-1</sup>.

By carrying out MORBID and EKE calculations with a number of different potentials, all of which yielded standard deviations (relative to the observed values) for the band origins on the order of 5 cm<sup>-1</sup>, we discovered that the differences between the two sets of results were largely independent of the values of the potential parameters. Consequently, when the parameters of the potential surface change during the least squares fitting, the differences between the EKE calculations and the MORBID results remain relatively stable. This fact allows us to use these differences, obtained with the starting values of the potential parameters, as corrections to the MORBID energies during all iterations of the least squares fit. In other words, during the entire fitting the inexpensive MORBID calculations of the energy levels with the corrections added give us energy values equal to those obtained in EKE calculations. When the starting potential is relatively far

from the final potential, this procedure requires that the least squares fitting be interrupted once or twice so that the corrections can be recalculated at intermediate parameter values. When the MORBID fitting has converged, one final EKE calculation is needed in order to verify that we have achieved the true minimum of the standard deviation within the EKE framework.

### III. COMPUTATIONAL DETAILS

The MORBID calculations reported here were carried out with the basis sets and parameter values used also in Ref. 6.

The EKE calculations were performed with a new suite of computer programs developed specifically for treating highly excited states of water and other H<sub>2</sub>X molecules. For the vibrational problem Radau coordinates and a discrete variable representation (DVR) in all three internal coordinates were used. The program DVR3D (Ref. 10) was upgraded to allow fully symmetrized Radau coordinates.<sup>11</sup> This approach has some similarities with those of Choi and Light<sup>12</sup> and of Bramley and Carrington.<sup>13</sup> However while Choi and Light chose to transform their Radau coordinates into a symmetric and an antisymmetric linear combination, we instead symmetrized the DVR grid points given by the Radau coordinates. Further details of this program can be found elsewhere.<sup>11</sup>

In order to preserve the symmetry of the rotation-vibration problem, we have chosen the body-fixed axis system so that the  $x$ -axis is along the bisector of the Radau angle (i.e., midway between the two H atoms). This so-called bisector embedding<sup>14</sup> (i.e., this choice of the molecule-fixed axis system) introduces technical problems as it results in integrals which are singular for linear geometries.<sup>14</sup> However, as it can be assumed that the wave function has negligible amplitude for OHH linear geometries, judicious use of the DVR in the angular coordinate means that these singularities can be avoided.<sup>15</sup> Previous implementations of this method proved to be computationally very expensive<sup>9</sup> and were effectively abandoned. However analysis of the rotational problem using a 3D DVR representation for the vibrations<sup>16</sup> suggested that the saving generated by treating the radial problem in a DVR meant that the bisector embedding could be implemented efficiently. We have therefore developed a new rotational program, ROTLEV3B, which is driven by the upgraded DVR3D module. These programs have also been augmented by a new DVR based dipole transition moments program, DIPOLE3. This program suite will be published elsewhere.<sup>17</sup>

In this work the radial basis was represented by 21 DVR grid points based on previously optimized<sup>18</sup> Morse oscillatorlike functions, and 40 angular DVR points based on (associated) Legendre polynomials. Band origins were calculated using a final Hamiltonian of dimension 2000. Calculations for the rotationally excited levels were performed using our usual two-step procedure for rotational excitation<sup>19</sup> with a first step Hamiltonian of dimension 1000. The second rotational step retained the lowest  $150 \times (J+1)$  functions from the first step in each calculation. These bases were sufficient to converge nearly all the energy levels we were concerned with to better than 0.01 cm<sup>-1</sup>, although the

convergence of some higher levels was worse than this. In particular these calculations had insufficient radial DVR points to give a satisfactory representation of the higher extreme local mode stretching states. However, for reasons discussed below, these states were omitted from our fit.

#### IV. INPUT DATA

It was shown in Ref. 8 that for H<sub>3</sub><sup>+</sup> and its isotopomers the Born–Oppenheimer approximation breaks down so that it becomes necessary to use different potential functions for different isotopomers. Further, it was shown in Ref. 20 that the effective potentials for H<sub>3</sub><sup>+</sup> and D<sub>3</sub><sup>+</sup> can be written as sums of a dominant mass-independent term and a mass-scaled correction potential  $V_{\text{ad}}$ . This led us to suspect that similar effects could be observed for the water molecule. Consequently, we have used only H<sub>2</sub><sup>16</sup>O data as input for the fitting reported here. As input data we used the energy levels of water reported in numerous papers,<sup>21–34</sup> mostly by Flaud, Camy-Peyret, and co-workers. The input data involved the same rotation-vibration states as did the H<sub>2</sub><sup>16</sup>O data used by Jensen *et al.*,<sup>6</sup> except that for the vibrational ground state and the (010) state, we added term values for the observed rotational states up to  $J=14$ . However, in the present work we fit directly rotation-vibration term values which are all measured from the  $J_{K_a K_c} = 0_{00}$  level of the vibrational ground state of H<sub>2</sub><sup>16</sup>O. We did not separate the data into vibrational and rotational spacings as was done in Ref. 6. Rotationally excited energy levels were included in the fitting for 24 vibrational states. Other states were represented by their band origins only.

The rotation-vibration term values used as input for the fitting were assigned relative weights inversely proportional to the squares of their experimental uncertainties. This weighting has no statistical meaning since the residuals obtained in the fit are considerably larger than the experimental uncertainties, and it is most appropriate to think of it as an instrument for manipulating the fitting. The weighting scheme employed favors the low- $J$  levels of the vibrational ground state and the fundamental states and produces increasingly lower weights for higher rotational and vibrational states. In particular, it produces very low weights for the band origins above 10 000 cm<sup>-1</sup>. Clearly it is not practicable to give here the individual weight factors for each input data point; this information is available from the authors on request.

#### V. THE ANALYTICAL FORM OF THE POTENTIAL ENERGY

The analytical representation of the potential energy function used in the present work is given as (see Refs. 7 and 35),

$$V(\Delta r_1, \Delta r_3, \bar{\rho}) = V_0(\bar{\rho}) + \sum_j F_j(\bar{\rho}) y_j + \sum_{j \leq k} F_{jk}(\bar{\rho}) y_j y_k + \sum_{j \leq k \leq m} F_{jkm}(\bar{\rho}) y_j y_k y_m + \sum_{j \leq k \leq m \leq n} F_{jkmn}(\bar{\rho}) y_j y_k y_m y_n, \quad (1)$$

where all of the indices  $j, k, m,$  and  $n$  assume the values 1 or 3. The quantity  $y_j$  in Eq. (1) is given by

$$y_j = 1 - \exp(-a_j \Delta r_j), \quad (2)$$

where the  $a_j$  are molecular constants and  $\Delta r_j = r_j - r_j^e$ ,  $j=1$  or 3, is defined as a displacement from the equilibrium value  $r_j^e$  of the distance  $r_j$  between the “outer” nucleus  $j=1$  or 3 and the “center” nucleus 2. The quantity  $\bar{\rho}$  is the instantaneous value of the bond angle supplement (see Fig. 1 of Ref. 7). The  $F_{jkm\dots}$  expansion coefficients of Eq. (1) are functions of  $\bar{\rho}$  and defined as

$$F_j(\bar{\rho}) = \sum_{i=1}^4 f_j^{(i)} (\cos \rho_e - \cos \bar{\rho})^i, \quad (3)$$

and

$$F_{jkm\dots}(\bar{\rho}) = f_{jkm\dots}^{(0)} + \sum_{i=1}^N f_{jkm\dots}^{(i)} (\cos \rho_e - \cos \bar{\rho})^i, \quad (4)$$

where  $\rho_e$  is the equilibrium value of  $\bar{\rho}$  and the  $f_{jkm\dots}^{(i)}$  are expansion coefficients. The function  $F_{jk}(\bar{\rho})$  has  $N=3$ ,  $F_{jkl}(\bar{\rho})$  has  $N=2$ , and  $F_{jklm}(\bar{\rho})$  has  $N=1$ . The function  $V_0(\bar{\rho})$  is the potential energy for the molecule bending with bond lengths fixed at their equilibrium values, and here we parameterize it as

$$V_0(\bar{\rho}) = \sum_{i=2}^8 f_0^{(i)} (\cos \rho_e - \cos \bar{\rho})^i, \quad (5)$$

where the  $f_0^{(i)}$  are expansion coefficients.

As the starting point for the fitting, we took the potential energy function (potential II), obtained in Ref. 6 using the MORBID approach. Calculations with the DVR3D program showed that, as outlined in Ref. 6, spurious minima (“holes”) are present in this potential. Analysis of the role of various terms in the expression for the potential surface, with regard to these holes, led us to constrain to zero the expansion coefficient  $f_{1133}^{(1)}$ , which was found in Ref. 6 to be  $-15\,008\text{ cm}^{-1}$ . By carrying out fittings with different parameter sets, we found that with the input of the present work, constraining  $f_{1133}^{(1)}$  to zero did not lead to any significant degradation of the standard deviation in the final fit, but it gave a function whose holes could be removed by addition of the corrective term suggested by Choi and Light.<sup>12</sup>

In the course of the fitting procedure it became obvious that the band origins of states which might be designated as local modes states (doublets at 13 830 cm<sup>-1</sup>, 16 898 cm<sup>-1</sup>, and 19 781 cm<sup>-1</sup> and some higher excited states) have the biggest residuals (obs.–calc.). These local mode band origin

TABLE I. Fitted potential energy parameters for H<sub>2</sub>O.

$\rho_e/\text{deg}$	75.489 92(350) <sup>a</sup>	$f_{11}^{(1)}/\text{cm}^{-1}$	-3 042.6(440)
$r_1^2/\text{\AA}$	0.957 625 7(110)	$f_{11}^{(2)}/\text{cm}^{-1}$	-3 669.(110)
$a_1/\text{\AA}^{-1}$	2.226 <sup>b</sup>	$f_{13}^{(0)}/\text{cm}^{-1}$	-1 046.63(170)
$f_0^{(2)}/\text{cm}^{-1}$	18 902.4(60)	$f_{13}^{(1)}/\text{cm}^{-1}$	6 109.8(310)
$f_0^{(3)}/\text{cm}^{-1}$	1 961.5(110)	$f_{11}^{(0)}/\text{cm}^{-1}$	-1 309.3(220)
$f_0^{(4)}/\text{cm}^{-1}$	4 134.9(180)	$f_{11}^{(1)}/\text{cm}^{-1}$	1 731.(450)
$f_0^{(5)}/\text{cm}^{-1}$	-1 959.6 <sup>c</sup>	$f_{11}^{(2)}/\text{cm}^{-1}$	-1 423.(130)
$f_0^{(6)}/\text{cm}^{-1}$	4 484.1 <sup>c</sup>	$f_{13}^{(0)}/\text{cm}^{-1}$	-1 255.9(95)
$f_0^{(7)}/\text{cm}^{-1}$	3 961.8(710)	$f_{13}^{(1)}/\text{cm}^{-1}$	9 863.(120)
$f_0^{(8)}/\text{cm}^{-1}$	-4 751.6(300)	$f_{13}^{(2)}/\text{cm}^{-1}$	3 712.(210)
$f_1^{(1)}/\text{cm}^{-1}$	-6 132.4(400)	$f_{111}^{(0)}/\text{cm}^{-1}$	4 159.0(240)
$f_1^{(2)}/\text{cm}^{-1}$	-3 022.9(290)	$f_{111}^{(1)}/\text{cm}^{-1}$	560.(500)
$f_1^{(3)}/\text{cm}^{-1}$	-5 951.(100)	$f_{111}^{(2)}/\text{cm}^{-1}$	-221.1(110)
$f_1^{(4)}/\text{cm}^{-1}$	1 030.6(900)	$f_{113}^{(0)}/\text{cm}^{-1}$	-7 238.1 <sup>c</sup>
$f_{11}^{(0)}/\text{cm}^{-1}$	42 927.83(200)	$f_{113}^{(1)}/\text{cm}^{-1}$	0.0

<sup>a</sup>Quantities in parentheses are standard errors in units of the last digit given.

<sup>b</sup>Constrained to the value determined in Ref. 36 from the *ab initio* data of Ref. 37.

<sup>c</sup>Constrained to value determined in a preliminary least squares fit.

values are influenced mostly by the potential terms involving  $f_{11}^{(0)}$ ,  $f_{111}^{(0)}$ , and  $f_{1111}^{(0)}$ . By introducing a term of the form  $f_{11111}^{(0)}(y_1^2 + y_3^2)$  in the potential for the EKE calculations, and choosing the ad hoc value of 1000 cm<sup>-1</sup> for  $f_{11111}^{(0)}$ , we could show that such a term has a large influence on exactly these energy levels so that in many cases, the discrepancies of the local mode band origins could be reduced by an order of magnitude. The influence on all other levels was much smaller. Hence it would seem that in order to improve significantly the agreement with experiment for the local mode levels, at least the fifth order term given above must be fitted. In view of this, we have excluded the local mode states from the fitting. We plan to extend the potential energy function used in the MORBID program by fifth and sixth order terms in the  $y_i$ , but this requires major software changes and we will report it in a separate publication.

## VI. RESULTS

The optimized parameters of the potential function of Eqs. (1) for H<sub>2</sub><sup>16</sup>O are presented in Table I. The standard deviation for 1600 rovibrational term values obtained with these values of the potential parameters was 0.36 cm<sup>-1</sup>. The root-mean-square (rms) deviation for 40 fitted band origins was 0.6 cm<sup>-1</sup>. These standard deviations, together with all

TABLE II. Root-mean-square deviations for the separate vibrational states of H<sub>2</sub><sup>16</sup>O, calculated by with the potential energy parameters from Table I.

$\nu_1\nu_2\nu_3$	$J_{\text{max}}^a$	$N^b$	$\sigma^c/\text{cm}^{-1}$
000	14	221	0.035
010	14	209	0.095
020	9	95	0.118
100	10	109	0.134
030	6	45	0.303
001	10	110	0.207
all	14	1600	0.359

<sup>a</sup>Maximum  $J$  value considered for the  $\nu_1\nu_2\nu_3$  state.

<sup>b</sup>Number of input data for the  $\nu_1\nu_2\nu_3$  state.

<sup>c</sup>Root-mean-square deviation of the input data for the  $\nu_1\nu_2\nu_3$  state.

TABLE III. Observed and calculated values of the energy levels of water for  $J=20$  of the ground vibrational state (in cm<sup>-1</sup>). Observed values are from Ref. 21.

$J$	$K_a$	$K_c$	obs.	calc.	obs.-calc.
20	0	20	4048.252	4048.285	-0.033
20	1	20	4048.252	4048.285	-0.033
20	1	19	4412.317	4412.335	-0.018
20	2	19	4412.317	4412.335	-0.018
20	2	18	4738.624	4738.623	0.001
20	3	18	4738.636	4738.634	0.002
20	3	17		5031.77	
20	4	17	5031.977	5031.968	0.009
20	4	16	5292.096	5292.056	0.040
20	5	16	5294.035	5293.995	0.040
20	5	15	5513.266	5513.146	0.120
20	6	15	5527.046	5526.980	0.066
20	6	14		5680.64	
20	7	14	5739.23	5739.15	0.08
20	7	13		5811.92	
20	8	13	5947.33	5947.25	0.08
20	8	12		5966.72	
20	9	12	6167.91	6167.68	0.23
20	9	11	6170.96	6170.80	0.16
20	10	11		6407.09	
20	10	10		6407.45	
20	11	10	6664.14	6664.20	-0.06
20	11	9	6664.17	6664.23	-0.06
20	12	9	6935.42	6935.53	-0.11
20	12	8	6935.43	6935.54	-0.11
20	13	8	7217.56	7217.71	-0.15
20	13	7	7217.56	7217.71	-0.15
20	14	7	7507.57	7507.77	-0.20
20	14	6	7507.57	7507.77	-0.20
20	15	6	7802.7	7802.9	-0.2
20	15	5	7802.7	7802.9	-0.2
20	16	5	8100.3	8100.5	-0.2
20	16	4	8100.3	8100.5	-0.2
20	17	4	8397.6	8397.9	-0.3
20	17	3	8397.6	8397.9	-0.3
20	18	3	8691.9	8692.1	-0.2
20	18	2	8691.9	8692.1	-0.2
20	19	2	8979.8	8980.0	-0.2
20	19	1	8979.8	8980.0	-0.2
20	20	1	9257.408	9257.416	-0.008
20	20	0	9257.408	9257.416	-0.008

calculated results presented in the tables mentioned below, are obtained with the EKE program used with the potential energy parameters of Table I. Since significantly different weighting factors were given to the levels in various vibrational states, the separate rms deviations for some low lying vibrational states are also informative. We present them in Table II. The highest weights were given to the levels of the ground vibrational state.

Let us consider the level of accuracy achieved for the ground state in more detail. As could be seen from Table II the overall rms deviation for 220 levels up to  $J=14$  is 0.035 cm<sup>-1</sup>. For the 86 fitted levels up to  $J=8$  the rms deviation was 0.005 cm<sup>-1</sup>. It is also worth mentioning that for 20 of these levels, the deviation from experiment was less than 3 MHz. This is the experimental accuracy of the best Fourier transform spectrometers. Obviously, the lower limit for the standard deviation is the experimental accuracy, and the re-

TABLE IV. Observed and calculated values of the energy levels of water for  $J=24$  of the ground vibrational state (in cm<sup>-1</sup>). Observed values are from Ref. 21.

$J$	$K_a$	$K_c$	obs.	calc.	obs.-calc.
24	0	24	5 713.25	5 713.30	-0.05
24	1	24	5 713.25	5 713.30	-0.05
24	1	23	6 147.79	6 147.81	-0.02
24	2	23	6 147.79	6 147.81	-0.02
24	2	22	6 536.44	6 536.44	0.00
24	3	22	6 536.44	6 536.44	0.00
24	3	21		6 889.69	
24	4	21	6 889.73	6 889.71	0.02
24	4	20		7 210.27	
24	5	20	7 210.55	7 210.50	0.05
24	5	19		7 498.38	
24	6	19		7 500.36	
24	6	18		7 747.93	
24	7	18		7 760.88	
24	7	17		7 943.99	
24	8	17		7 998.88	
24	8	16		8 095.24	
24	9	16		8 229.27	
24	9	15		8 259.77	
24	10	15		8 468.42	
24	10	14		8 474.35	
24	11	14		8 724.82	
24	11	13		8 725.68	
24	12	13		8 998.15	
24	12	12		8 998.15	
24	13	12		9 286.05	
24	13	11		9 286.05	
24	14	11	9 584.41	9 584.46	-0.05
24	14	10	9 584.42	9 584.47	-0.05
24	15	10	9 890.48	9 890.72	-0.24
24	15	9	9 890.48	9 890.72	-0.24
24	16	9	10 202.10	10 202.27	-0.17
24	16	8	10 202.10	10 202.27	-0.17

sults of the present work suggest that this goal is within reach. The extrapolation power of our potential is illustrated by Tables III–IV, where the results of the calculation of the ground state levels with  $J=20$  and  $24$  are presented. The significant digits quoted for the observed levels indicate the experimental precision. The residuals (obs.–calc.) in these tables show that the accuracy of extrapolation to these high  $J$  values is within the standard deviation of the fitted data. Only a few levels for  $J=28$ ,  $J=32$ , and  $J=35$  are known experimentally. In Table V we compare observed and calculated energies for these levels. Again, extremely good agreement is obtained for most energy levels. Only the two levels with  $J_{K_a K_c} = 32_{230}$  and  $32_{330}$  have significant residuals of  $1.72 \text{ cm}^{-1}$ . The most likely explanation for this discrepancy would seem to be a misassignment of the observed lines believed to involve these levels. This assumption is confirmed by recent work of Coudert<sup>38</sup> who carried out a fit to the ground state rotational energy levels of water using an effective Hamiltonian. In this fitting, he obtained residuals comparable to ours for the two states mentioned above, and he excluded them from the fit.

Finally, the potential energy function obtained in the present work gives striking agreement with experiment also for states with high  $K_a$  values. In all previous work on the

TABLE V. Observed and calculated values of the energy levels of water for  $J=28$ ,  $J=32$ , and  $J=35$  of the ground vibrational state (in cm<sup>-1</sup>). Observed values are from Ref. 21.

$J$	$K_a$	$K_c$	obs.	calc.	obs.-calc.
28	0	28	7 648.16	7 648.21	-0.05
28	1	28	7 648.16	7 648.21	-0.05
28	1	27	8 150.78	8 150.81	-0.03
28	2	27	8 150.78	8 150.81	-0.03
28	2	26	8 594.55	8 594.55	0.00
28	3	26	8 594.55	8 594.55	0.00
28	3	25		9 001.70	
28	4	25	9 001.73	9 001.70	0.03
32	0	32	9 843.99	9 844.04	-0.05
32	1	32	9 843.99	9 844.04	-0.05
32	1	31	10 412.07	10 412.09	-0.02
32	2	31	10 412.07	10 412.09	-0.02
32	2	30	10 901.35 <sup>a</sup>	10 899.63	1.72
32	3	30	10 901.35 <sup>a</sup>	10 899.63	1.72
35	0	35	11 656.18	11 656.07	0.11
35	1	35	11 656.18	11 656.07	0.11

<sup>a</sup>These states are likely to be misassigned (see text).

water potential, these states have shown the largest discrepancies. The best previous potentials have given discrepancies around  $1 \text{ cm}^{-1}$  for the  $10_{100}$  level and  $15 \text{ cm}^{-1}$  for the  $20_{200}$  level. The  $20_{200}$  state (Table III) has the highest  $K_a$  value for which the rotation-vibration energy has been derived experimentally. The energy value<sup>21</sup> is  $9257.41 \text{ cm}^{-1}$ . For this level, the potential energy function of the present work gives a deviation from experiment of  $0.008 \text{ cm}^{-1}$ . However, this low value is clearly somewhat fortuitous since levels with lower  $K_a$  from Table III have deviations around  $0.2 \text{ cm}^{-1}$ .

## VII. FOURFOLD CLUSTERING EFFECT IN WATER

Reference 39 provided experimental evidence for the formation of fourfold rovibrational energy clusters in the H<sub>2</sub>Se molecule. Further experimental studies<sup>40–42</sup> and variational calculations were performed showing this effect in H<sub>2</sub>S,<sup>43</sup> H<sub>2</sub>Se,<sup>44,45</sup> and H<sub>2</sub>Te.<sup>46</sup> On the basis of these investigations it would appear likely that the high  $K_a$  levels in water would also exhibit this phenomenon.

When clusters are formed, the energy difference between the two quasidegenerate doublets with  $J_{K_a K_c} = J_{J_0}, J_{J_1}$  and  $J_{(J-1)_1}, J_{(J-1)_2}$  will decrease with increasing  $J$ , starting at a characteristic  $J$  value,  $J_{\text{critical}}$ . This is in contradiction to the rigid rotor model. The formation of the fourfold clusters from two doublets in H<sub>2</sub>S, H<sub>2</sub>Se, and H<sub>2</sub>Te can be considered as an established fact. For  $J > J_{\text{critical}}$  fourfold degenerate clusters form rapidly for these molecules. This is accompanied with a rapid increase of the intercluster distance (the distance between different clusters).

Calculations for the vibrational ground state were therefore performed for  $J$  up to 35 using the EKE programs and the same basis sets described above which gave very good convergence for the levels of the vibrational ground state considered here. The calculated high- $K_a$  energy levels of water show that at  $J=18$ , the energy distance between the two highest doublets in each  $J$  multiplet starts decreasing with increasing  $J$ . However, the energy spacing which might be

TABLE VI. High- $K_a$  energies<sup>a</sup> in the vibrational ground state of H<sub>2</sub><sup>16</sup>O (in cm<sup>-1</sup>).

$J$	$E(J_{J0})^b$	$\Delta^c$	$E[J_{(J-1)1}]^b$	$\Delta^c$	$E[J_{(J-2)2}]^b$	$\Delta^c$	$E[J_{(J-3)3}]^b$
16	6 290.17	277.84	6 012.33	279.18	5 733.15	277.27	5 455.88
18	7 723.80	280.27	7 443.53	286.18	7 157.35	288.53	6 868.82
20	9 257.41	277.41	8 980.00	287.87	8 692.13	294.25	8 397.88
24	12 587.50	258.94	12 328.56	278.86	12 049.70	292.71	11 756.99
28	16 217.56	227.57	15 989.99	258.30	15 731.69	279.02	15 452.67
32	20 104.19	195.22	19 908.97	231.58	19 677.39	259.10	19 418.29
35	23 282.	159.	23 123.	339.	22 784.	112.	22 672.

<sup>a</sup>The energies for  $J=16$  and  $18$  are derived from experiment (Ref. 21); the other ones are from the calculations of the present work.

<sup>b</sup> $E(J_{K_a K_c})$  is the doubly degenerate energy for the states  $J_{K_a K_c}$  and  $J_{K_a K_c+1}$  measured relative to the  $0_{00}$  level of the vibrational ground state.

<sup>c</sup>Difference between adjacent columns.

called the intercluster distance for the other H<sub>2</sub>X molecules is decreasing with increasing  $J$  as well. In addition, the distances between the energy levels change much more slowly with increasing  $J$  than in the other H<sub>2</sub>X molecules. So we can speak about a slow supercluster formation, where all levels in one  $J$  multiplet converge to form one supercluster; this type of clustering is known to happen near dissociation. These phenomena are illustrated by Table VI, which gives the energies of the levels with highest  $K_a$  for  $J=18, 20, 24, 28, 32,$  and  $35$ . The table gives the energies of the four highest degenerate doubles for each  $J$  multiplet. We denote these as  $E(J_{J0}), E[J_{(J-1)1}], E[J_{(J-2)2}],$  and  $E[J_{(J-3)3}]$ , where  $E(J_{K_a K_c})$  is the doubly degenerate energy for the states  $J_{K_a K_c}$  and  $J_{K_a K_c+1}$  measured relative to the  $0_{00}$  level of the vibrational ground state. From  $J=20$  through  $32$ , all energy differences between neighboring doublets decrease with increasing  $J$ . Between  $J=32$  and  $J=35$ , however, a dramatic change takes place in that the differences  $E(J_{J0}) - E[J_{(J-1)1}]$  and  $E[J_{(J-2)2}] - E[J_{(J-3)3}]$  decrease significantly, while the intercluster distance  $E[J_{(J-1)1}] - E[J_{(J-2)2}]$  increases. This could indicate the beginning of fourfold cluster formation. However, even if these clusters do form, the rotational energy level structure in H<sub>2</sub>O is clearly significantly different from those of H<sub>2</sub>S, H<sub>2</sub>Se, and H<sub>2</sub>Te.

## VIII. BREAKDOWN OF THE BORN-OPPENHEIMER APPROXIMATION

The results of a calculation of the fundamental band origins (carried out with the potential energy function of Table I) for the symmetric D<sub>2</sub><sup>16</sup>O and T<sub>2</sub><sup>16</sup>O and asymmetric HD<sup>16</sup>O and HT<sup>16</sup>O isotopomers of the water molecule are presented in Table VII. These results are compared with ex-

TABLE VII. The differences between observed<sup>a</sup> and calculated values of the fundamental band origins for isotopomers of water (in cm<sup>-1</sup>).

$\nu_1 \nu_2 \nu_3$	H <sub>2</sub> <sup>16</sup> O	D <sub>2</sub> <sup>16</sup> O	T <sub>2</sub> <sup>16</sup> O	HD <sup>16</sup> O	HT <sup>16</sup> O
010	0.04	0.09	0.1	0.09	
100	-0.09	0.05	0.17	0.58	0.64
001	0.06	0.3	0.4	-0.25	-1.24

<sup>a</sup>For the experimental values, see Refs. 47–57.

perimental data from Refs. 47–57. For these molecules, the agreement with experiment is much poorer than for H<sub>2</sub><sup>16</sup>O. This fact provides strong evidence for a breakdown of the Born–Oppenheimer approximation. The order of magnitude of the residuals obtained for the isotopically substituted molecules is consistent with that found for H<sub>2</sub>D<sup>+</sup>, D<sub>2</sub>H<sup>+</sup>, and D<sub>3</sub><sup>+</sup>, when calculated with a potential energy function fitted for H<sub>3</sub><sup>+</sup>.<sup>8,20</sup> Our results for water indicate that it is necessary to consider explicitly the breakdown of the Born–Oppenheimer approximation in order that all isotopomers can be fitted simultaneously with a standard deviation comparable to that attained for H<sub>2</sub><sup>16</sup>O in the present work. As mentioned above, this requires that the potential energy function for a particular isotopomer be written as the sum of a mass-independent potential (the Born–Oppenheimer potential) and mass-dependent correction terms. Further, Bunker and Moss<sup>58,59</sup> have shown that corrections to the kinetic energy operator are also introduced, and they derived expressions for these corrections in the framework of the Hougen–Bunker–Johns Hamiltonian.<sup>60</sup> Work to introduce terms describing the breakdown of the Born–Oppenheimer approximation for water in the EKE formalism is in progress.

## IX. CONCLUSION

The H<sub>2</sub><sup>16</sup>O potential energy function has been obtained by fitting to experimental data. The fitting was carried out by means of a combination of exact kinetic energy (EKE) and approximate kinetic energy (MORBID) programs. Rotation–vibration energies calculated with the new potential function are in considerably better agreement with experiment than those calculated using previous potentials. We have demonstrated the excellent extrapolation power of the new potential for calculating energies of states with higher  $J$  and  $K_a$  values. Our results provide strong evidence for a breakdown of Born–Oppenheimer approximation in water. Finally, we have investigated the rotational energy level structure in the vibrational ground state of water and have found it to be very different from those of the related molecules H<sub>2</sub>S, H<sub>2</sub>Se, and H<sub>2</sub>Te.

In the present work, we have presented an inexpensive, very accurate method for obtaining the potential energy surface of a triatomic molecule from experimental spectroscopic data. Our results indicate that the ultimate goal of achieving

an agreement with experiment comparable to the experimental uncertainty in this type of fit is within reach. Since our calculations employ an exact kinetic energy operator and are well converged, the only source of error would seem to be connected with the particular analytical form chosen for the potential function and with the breakdown of the Born–Oppenheimer approximation. Further work, which is in progress, is concerned with the addition of more terms to the potential function given by Eq. (1) and with the explicit consideration of the Born–Oppenheimer breakdown.

## ACKNOWLEDGMENTS

We thank N. G. Fulton for help running his updated version of DVR3D, and P. R. Bunker and B. P. Winnewisser for critically reading the manuscript and suggesting improvements. This work was supported by the Deutsche Forschungsgemeinschaft through Forschergruppe Grant No. Bu 152/12-3 and by the U.K. Science and Engineering Research Council. P.J. acknowledges further support from the Fonds der Chemischen Industrie. O.L.P. gratefully acknowledges a Humboldt Fellowship for 1993–94, and he is grateful to the Institute of Physical Chemistry at the Justus Liebig University Giessen, and particularly to B. P. Winnewisser and M. Winnewisser, for hospitality. The work of O.L.P. was supported in part by the Russian Fund for Fundamental Studies (Grant No. 94-02-05424-a) and the International Science Foundation (Reg. No. Ph3-1137).

- <sup>1</sup>S. Carter and N. C. Handy, *J. Chem. Phys.* **87**, 4294 (1987).
- <sup>2</sup>L. Halonen and T. Carrington, Jr., *J. Chem. Phys.* **88**, 4171 (1988).
- <sup>3</sup>P. Jensen, *J. Mol. Spectrosc.* **133**, 438 (1989).
- <sup>4</sup>E. Kauppi and L. Halonen, *J. Phys. Chem.* **94**, 5779 (1990).
- <sup>5</sup>C. D. Pause and J. Tennyson, *J. Mol. Spectrosc.* (in press).
- <sup>6</sup>P. Jensen, S. A. Tashkun, and V. G. Tyuterev, *J. Mol. Spectrosc.* (in press).
- <sup>7</sup>P. Jensen, *J. Mol. Spectrosc.* **128**, 478 (1988).
- <sup>8</sup>B. M. Dinelli, S. Miller, and J. Tennyson, *J. Mol. Spectrosc.* **163**, 71 (1994).
- <sup>9</sup>J. R. Henderson, J. Tennyson, and B. T. Sutcliffe, *Philos. Mag. B* **69**, 1027 (1994).
- <sup>10</sup>J. R. Henderson, C. R. Le Sueur, and J. Tennyson, *Comput. Phys. Commun.* **75**, 379 (1993).
- <sup>11</sup>N. G. Fulton, Ph.D. thesis, University of London, 1994.
- <sup>12</sup>S. E. Choi and J. C. Light, *J. Chem. Phys.* **97**, 7031 (1992).
- <sup>13</sup>M. J. Bramley and T. Carrington, Jr., *J. Chem. Phys.* (in press).
- <sup>14</sup>B. T. Sutcliffe and J. Tennyson, *Int. J. Quantum Chem.* **29**, 183 (1991).
- <sup>15</sup>J. Tennyson and B. T. Sutcliffe, *Int. J. Quantum Chem.* **42**, 941 (1992).
- <sup>16</sup>J. Tennyson, *J. Chem. Phys.* **98**, 7191 (1993).
- <sup>17</sup>J. Tennyson, J. R. Henderson, and N. G. Fulton (to be published).
- <sup>18</sup>J. A. Fernley, S. Miller, and J. Tennyson, *J. Mol. Spectrosc.* **150**, 597 (1991).
- <sup>19</sup>J. Tennyson, S. Miller, and J. R. Henderson, in *Methods in Computational Chemistry*, edited by S. Wilson (Plenum, New York, 1992), Vol. 4.
- <sup>20</sup>J. Tennyson and O. L. Polyansky, *Phys. Rev. A* **50**, 314 (1994).
- <sup>21</sup>J.-M. Flaud, C. Camy-Peyret, and J.-P. Maillard, *Mol. Phys.* **32**, 499 (1976).
- <sup>22</sup>J. W. C. Johns, *J. Opt. Soc. B* **2**, 1340 (1985).
- <sup>23</sup>R. A. Toth, *J. Opt. Soc. B* **8**, 2236 (1991).
- <sup>24</sup>R. A. Toth, *J. Opt. Soc. B* **10**, 1526 (1993).
- <sup>25</sup>R. A. Toth, *J. Opt. Soc. B* **10**, 2006 (1993).
- <sup>26</sup>J.-M. Flaud, C. Camy-Peyret, J.-P. Maillard, and G. Guelachvili, *J. Mol. Spectrosc.* **65**, 219 (1977).
- <sup>27</sup>C. Camy-Peyret and J.-M. Flaud, Thèse de doctorat es sciences, Université Pierre et Marie Curie, Paris, 1975.
- <sup>28</sup>J.-M. Flaud and C. Camy-Peyret, *Mol. Phys.* **32**, 499 (1976).
- <sup>29</sup>C. Camy-Peyret, J.-M. Flaud, and J.-P. Maillard, *J. Phys. Lett.* **41**, L23 (1980).
- <sup>30</sup>C. Camy-Peyret, J.-M. Flaud, J. P. Maillard, and G. Guelachvili, *Mol. Phys.* **33**, 1641 (1977).
- <sup>31</sup>J.-Y. Mandin, J.-P. Chevillard, J.-M. Flaud, and C. Camy-Peyret, *Can. J. Phys.* **66**, 997 (1988).
- <sup>32</sup>J.-P. Chevillard, J.-Y. Mandin, J.-M. Flaud, and C. Camy-Peyret, *Can. J. Phys.* **67**, 1065 (1989).
- <sup>33</sup>K. Nakamo, A. Saito, and N. Ohashi, *J. Mol. Spectrosc.* **131**, 405 (1988).
- <sup>34</sup>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. Quant. Spectrosc. Radiat. Transfer* **48**, 469 (1992).
- <sup>35</sup>P. Jensen, in *Methods in Computational Molecular Physics*, edited by S. Wilson and G. H. F. Diercksen (Plenum, New York, 1992).
- <sup>36</sup>P. Jensen, *J. Mol. Struct.* **190**, 149 (1988).
- <sup>37</sup>R. J. Bartlett, S. J. Cole, G. D. Purvis, W. C. Ermler, H. C. Hsieh, and I. Shavitt, *J. Chem. Phys.* **87**, 6579 (1987).
- <sup>38</sup>L. H. Coudert, *J. Mol. Spectrosc.* **165**, 406 (1994).
- <sup>39</sup>I. N. Kozin, S. P. Belov, O. L. Polyansky, and M. Yu. Tretyakov, *J. Mol. Spectrosc.* **152**, 13 (1992).
- <sup>40</sup>M. Yu. Tretyakov, I. N. Kozin, S. P. Belov, and O. L. Polyansky, *J. Mol. Spectrosc.* **154**, 163 (1992).
- <sup>41</sup>I. N. Kozin, O. L. Polyansky, S. I. Pripolsin, and V. Vaks, *J. Mol. Spectrosc.* **156**, 504 (1992).
- <sup>42</sup>I. N. Kozin, S. Klee, P. Jensen, O. L. Polyansky, and I. M. Pavlichenkov, *J. Mol. Spectrosc.* **158**, 409 (1993).
- <sup>43</sup>I. N. Kozin and P. Jensen, *J. Mol. Spectrosc.* **163**, 483 (1994).
- <sup>44</sup>P. Jensen and I. N. Kozin, *J. Mol. Spectrosc.* **160**, 39 (1993).
- <sup>45</sup>I. N. Kozin and P. Jensen, *J. Mol. Spectrosc.* **161**, 186 (1993).
- <sup>46</sup>P. Jensen, Y. Li, G. Hirsch, R. J. Buenker, T. J. Lee, and I. N. Kozin, *Chem. Phys.* (in press).
- <sup>47</sup>R. A. Toth, *J. Mol. Spectrosc.* **162**, 41 (1993).
- <sup>48</sup>N. Papineau, J.-M. Flaud, and C. Camy-Peyret, *J. Mol. Spectrosc.* **92**, 451 (1982).
- <sup>49</sup>G. Wilemski, *J. Quant. Spectrosc. Radiat. Transfer* **20**, 291 (1978).
- <sup>50</sup>H. A. Fry, L. H. Jones, and J. E. Barefield, *J. Mol. Spectrosc.* **103**, 41 (1984).
- <sup>51</sup>S. D. Cope, D. K. Russel, H. A. Fry, L. H. Jones, and J. E. Barefield, *J. Mol. Spectrosc.* **120**, 311 (1984).
- <sup>52</sup>R. A. Toth, *J. Mol. Spectrosc.* **162**, 20 (1993).
- <sup>53</sup>N. Papineau, C. Camy-Peyret, J.-M. Flaud, and G. Guelachvili, *J. Mol. Spectrosc.* **92**, 451 (1982).
- <sup>54</sup>R. A. Toth and J. Brault, *Appl. Opt.* **22**, 908 (1983).
- <sup>55</sup>O. N. Ulenikov, V. N. Cherepanov, and A. B. Malikova, *J. Mol. Spectrosc.* **146**, 97 (1991).
- <sup>56</sup>P. Helminger, F. C. De Lucia, W. Gordy, P. A. Staats, and H. W. Morgan, *Phys. Rev. A* **10**, 1072 (1974).
- <sup>57</sup>S. D. Cope, D. K. Russel, H. A. Fry, L. H. Jones, and J. E. Barefield, *J. Mol. Spectrosc.* **127**, 464 (1988).
- <sup>58</sup>P. R. Bunker and R. E. Moss, *J. Mol. Spectrosc.* **80**, 217 (1980).
- <sup>59</sup>P. R. Bunker and R. E. Moss, *Mol. Phys.* **33**, 417 (1977).
- <sup>60</sup>J. T. Hougen, P. R. Bunker, and J. W. C. Johns, *J. Mol. Spectrosc.* **34**, 136 (1970).