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We report here a new determination of the $H_2{}^{16}O$ potential energy surface from experimental data. The calculations have been carried out by means of the very accurate and highly efficient method proposed and applied to $H_2{}^{16}O$ in a previous paper [Polyansky, Jensen, and Tennyson, J. Chem. Phys. **101**, 7651 (1994)]. This previous work has been significantly improved by inclusion of additional terms in the analytical expression used to represent the potential energy surface. Previously, 1600 rotation-vibration term values for $H_2{}^{16}O$ were fitted with a standard deviation of 0.36 cm^{-1}. With the extended model of the present work, this standard deviation could be improved to 0.25 cm^{-1}. With the extended model and the new fitted potential function we have calculated a data set comprising 3200 term values, all of which can be compared with experimentally derived values. The standard deviation for this data set is 0.6 cm^{-1}. The data set contains rotationally excited energy levels for all the 63 vibrational states which have been characterized by high resolution spectroscopy. The potential energy function obtained in the present work improves drastically the agreement with experiment for the highly excited local mode stretching states above $20\,000$ cm^{-1}. For the vibrational band origins of these states, the highest of which is measured at $25\,118$ cm^{-1}, our previous fitted potential produced discrepancies of more than 100 cm^{-1}. These deviations are reduced to less than 1 cm^{-1} by the potential energy function of the present work. We show that no significant improvement of the fit can be obtained by extending the analytical expression for the potential energy by further high-order terms. An analysis of the residuals shows that at the level of accuracy achieved, the major contribution to the error originates in the neglect of nonadiabatic correction terms in the Born-Oppenheimer kinetic energy operator. We conclude that any further improvement of the potential energy surface requires that such correction terms be included in the Hamiltonian. With the present potential, reliable extrapolations towards higher rotational and vibrational energies can be carried out, and we expect that such calculations can be very helpful in the assignment of experimental spectra involving highly excited states. © *1996 American Institute of Physics.* [S0021-9606(96)02839-5]

I. INTRODUCTION

There is an ever present demand for very accurate predictions of the rotation-vibration energies of the water molecule, in particular for highly excited states. In order to calculate such predictions, it is imperative to obtain a potential energy surface of water with the highest possible accuracy. The energies determined from such a potential will find numerous applications in molecular physics, astrophysics, atmospheric physics and other fields of research. Recent experimental studies of the hot water spectrum both in the laboratory[1] and in the Sun[2] provide examples of experimental data that can be assigned with the help of water energy predictions, but they also demonstrate that these predictions must be extremely accurate to be helpful. The spectra are very dense–on the average there are 14 lines/cm^{-1} in the laboratory spectrum[1] and about 50 lines/cm^{-1} in the Sun spectrum.[2] Obviously, in order for an unambiguous assignment of the lines to be possible on the basis of a theoretical prediction of the transition wavenumbers, this prediction is required to have an accuracy much better than 0.1 cm^{-1}. In recent years, there has been considerable interest in determining the potential energy surface of water by least squares fitting to experimental data, and seven such potentials have been published.[3–9] A very high level of accuracy was achieved in Ref. 3, henceforth referred to as I, where the advantages of the Exact Kinetic Energy (EKE) approach to the variational calculation of the molecular energy levels were combined with those of the approximative kinetic energy approach in its particular Morse oscillator rigid bender internal dynamics (MORBID) (Ref. 10) form.

In I, we represented the dependence of the potential energy function on the bond lengths as an expansion in Morse-

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transformed bond length functions. We found that the accuracy obtained in the fitting of I was limited by the fact that this expansion was truncated after the fourth-order terms. Consequently, in the analytical potential expression employed in the present work we have allowed for terms with powers in the Morse-transformed functions up to and including 7, and we have modified the MORBID program to account for the additional terms. With the extended model, we can significantly improve the fitting reported in I, and the present paper describes the new refined potential energy function thus obtained.

II. THE ANALYTICAL FORM OF THE POTENTIAL ENERGY

The analytical representation of the potential energy function used in the present work is an extension of the form presented previously in Refs. 10 and 11:

$$V(\Delta r_1, \Delta r_3, \overline{\rho}) = V_0(\overline{\rho}) + \sum_j F_j(\overline{\rho}) y_j + \sum_{j \leqslant k} F_{jk}(\overline{\rho}) y_j y_k$$
$$+ \sum_{j \leqslant k \leqslant m} F_{jkm}(\overline{\rho}) y_j y_k y_m$$
$$+ \sum_{j \leqslant k \leqslant m \leqslant n} F_{jkmn}(\overline{\rho}) y_j y_k y_m y_n + V_1,$$
(1)

where all of the indices j, k, m, and n assume the values 1 or 3. The additional potential term V_1, which has been added in the present work, in principle contains all 5th-, 6th-, and 7th-order terms in y_1 and y_3 with constant expansion coefficients $f_{ijk \ldots}$, that is

$$V_1 = \sum_{j \leqslant k \leqslant m \leqslant n \leqslant o} f_{jkmno} y_j y_k y_m y_n y_o$$
$$+ \sum_{j \leqslant k \leqslant m \leqslant n \leqslant o \leqslant p} f_{jkmnop} y_j y_k y_m y_n y_o y_p$$
$$+ \sum_{j \leqslant k \leqslant m \leqslant n \leqslant o \leqslant p \leqslant q} f_{jkmnopq} y_j y_k y_m y_n y_o y_p y_q, \quad (2)$$

where all of the indices j, k, m, n, o, p, and q assume the values 1 or 3. In practice, however, we found that in the fitting we could only usefully vary the coefficients of the terms involving y_j^5, y_j^6, and y_j^7 so that we actually use a V_1 term given by

$$V_1 = f_{11111}(y_1^5 + y_3^5) + f_{111111}(y_1^6 + y_3^6) + f_{1111111}(y_1^7 + y_3^7),$$
(3)

where we have imposed the symmetry restraints appropriate for the water molecule. The quantities y_j in Eqs. (1)–(3) are given by the Morse transformation

$$y_j = 1 - \exp(-a_j \Delta r_j),$$
(4)

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 $\overline{\rho}$ is the instantaneous value of the bond angle supplement (see Fig. 1 of Ref. 10). The $F_{jkm \ldots}$ expansion coefficients of Eq. (1) are functions of $\overline{\rho}$ and defined as

$$F_j(\overline{\rho}) = \sum_{i=1}^{4} f_j^{(i)} (\cos\rho_e - \cos\overline{\rho})^i$$
(5)

and

$$F_{jk \ldots}(\overline{\rho}) = f_{jk \ldots}^{(0)} + \sum_{i=1}^{N} f_{jk \ldots}^{(i)} (\cos\rho_e - \cos\overline{\rho})^i,$$
(6)

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

$$V_0(\overline{\rho}) = \sum_{i=2}^{12} f_0^{(i)} (\cos\rho_e - \cos\overline{\rho})^i,$$
(7)

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

The MORBID computer program has been modified to accommodate the terms given in Eq. (2). This necessitated the calculation of ''primitive'' matrix elements of the type $\langle n_j | y_j^n | n_j' \rangle$ for $n=5$, 6, and 7, where $|n_j\rangle$ and $|n_j'\rangle$ are Morse oscillator eigenfunctions.[11] We calculate these matrix elements by numerical quadrature.

As the starting point for the fitting, we used the potential energy function obtained in I. We will call this potential PJT1.

III. INPUT DATA

In I we used a combined EKE/MORBID procedure to obtain a highly accurate water potential. EKE calculations for water, carried out on this potential energy surface, showed that the discrepancies between theory and experiment contain significant contributions from the breakdown of the Born-Oppenheimer approximation. Consequently, it is not feasible to fit data from different water isotopomers simultaneously, and we follow I in using only H$_2$^{16}O data as input for the fitting. However, we have significantly extended the input data set relative to I.

The previous attempts to fit the water potential energy surface, it was necessary to limit the input data set for different reasons. When the fitting was carried out entirely within the framework of the computationally heavy EKE approach,[4] limitations in computer time and memory precluded the fitting of all but the very lowest J values. When the fitting was done entirely within the MORBID approach,[6,9] the limiting factor was the inaccuracy originating in the approximate kinetic energy operator. This inaccuracy increases with increasing J. In the combined EKE/MORBID approach used here and in I, the accuracy is limited only by the flexibility of the analytical expression used to represent the potential energy function. Clearly we can improve this flexibility by adding more terms to the ana-

lytical expansion. In the present work, we use an analytical representation so flexible that for the first time, it becomes possible to include virtually all the known energy levels of $H_2^{16}O$ in the input data for the fitting.

We have set up the following data set: For the 11 vibrational states whose high-J rotational levels have been derived from experimental data, rotation-vibration term values with $J \leqslant 14$ have been included in the input data set.[12-28] (In I only the energy levels of the (000) and (010) states were included up to $J = 14$.) In the present work, we extend the data by including the $J \leqslant 6$ term values of 36 vibrational states, for the most of which only $J = 0$ energies were included in I. There still remain 18 observed vibrational states. We use some of their $J \leqslant 2$ energies for comparison with calculated values in order to demonstrate the extrapolation power of the calculated potential energy function. In total, we have compiled a data set consisting of 3200 rovibrational levels.

It is noteworthy that the total number of experimentally known rovibrational levels for $H_2^{16}O$ is only slightly higher than 4000, and most of the levels not contained in our data set have J values larger than 14. We did not include further rotation-vibration energies for a number of reasons. Firstly, the CPU time and memory required for the calculations increase significantly with J. Secondly, we have already demonstrated the excellent extrapolation power of the PJT1 potential, and we are confident that the present work will yield a potential energy function with similar properties. Thirdly, the high-J levels are significantly affected by the breakdown of the Born-Oppenheimer approximation (see below) so that we might degrade the fit if we include them without accounting for J-dependent nonadiabatic effects. The data set of the present work, which is extended significantly in comparison with that of I, represents the largest possible amount of data which these limiting factors allow us to consider.

IV. RESULTS

All calculations used atomic masses. As in I, the EKE calculations were performed using the DVR3D program suite.[29] For calculations with $J > 0$, 21 symmetrized DVR grid points in each radial coordinate and 40 angular DVR grid points were used. It proved necessary to increase the number of the radial grid points to 28 and the final Hamiltonian matrix dimension from 1000 to 2000 for the calculation of the band origins, since the previous basis set was poorly converged for the highest local mode stretching levels, for example the $(v_1 v_2 v_3) = (503)$ energy at 25 118 cm^{-1} was only converged to within a few tens of a cm^{-1}.

We have made additional convergence tests in order to rule out the possibility that some of the final discrepancies are due to residual convergence errors. These tests show that the basis chosen set gives a very good convergence. For rotational levels where non-adiabatic effects become a concern (see below), the levels were converged to $\sim 10^{-5}$ cm^{-1}. Initially, we used the extended EKE/MORBID model of the present work to fit the 1600 data points already fitted in I. The optimized parameters of the

TABLE I. Fitted potential energy parameters for $H_2^{16}O$.

ρ_e/deg	75.5003530	$f_{11}^{(1)}$/cm^{-1}	-2767.1919717
r^e/Å	0.9579205	$f_{11}^{(2)}$/cm^{-1}	-3394.2470551
a_1/Å^{-1}	2.2260000	$f_{13}^{(0)}$/cm^{-1}	-1031.9305520
$f_0^{(2)}$/cm^{-1}	18902.4419343	$f_{13}^{(1)}$/cm^{-1}	6023.8343525
$f_0^{(3)}$/cm^{-1}	1893.9978814	$f_{111}^{(1)}$/cm^{-1}	124.2352938
$f_0^{(4)}$/cm^{-1}	4096.7344377	$f_{111}^{(2)}$/cm^{-1}	-1282.5066122
$f_0^{(5)}$/cm^{-1}	-1959.6011328	$f_{113}^{(0)}$/cm^{-1}	-1146.4910952
$f_0^{(6)}$/cm^{-1}	4484.1589338	$f_{113}^{(1)}$/cm^{-1}	9884.4168514
$f_0^{(7)}$/cm^{-1}	4044.5538881	$f_{113}^{(2)}$/cm^{-1}	3040.3402183
$f_0^{(8)}$/cm^{-1}	-4771.4504354	$f_{1111}^{(0)}$/cm^{-1}	2040.9674526
$f_1^{(1)}$/cm^{-1}	-6152.4014118	$f_{1113}^{(0)}$/cm^{-1}	-422.0339419
$f_1^{(2)}$/cm^{-1}	-2902.1391226	$f_{1113}^{(1)}$/cm^{-1}	-7238.0997940
$f_1^{(3)}$/cm^{-1}	-5732.6846068	$f_{11111}^{(0)}$/cm^{-1}	-4969.2454493
$f_1^{(4)}$/cm^{-1}	953.8876083	$f_{111111}^{(0)}$/cm^{-1}	8108.4965235
$f_{11}^{(0)}$/cm^{-1}	42909.8886909	$f_{1111111}^{(0)}$/cm^{-1}	90.0000000

potential function of Eqs. (1)–(3) for $H_2^{16}O$ are presented in Table I. The standard deviation for these 1600 rovibrational term values, obtained with the EKE approach with the parameters of Table I as input, was $\sigma = 0.25$ cm^{-1}. This is significantly better than the σ value of 0.36 cm^{-1} obtained in I. The accuracy of the calculation of the highly excited vibrational levels has improved dramatically. The local mode stretching levels above 20 000 cm^{-1} were not included in the fit of I because the deviations of their experimental energies from the calculated values were unacceptably high (up to 100 cm^{-1}), and attempts to fit these energies degraded the fit of all other data significantly. With the potential energy function resulting from the present fit, we could calculate the energies of these states with deviations from experiment of less than 1 cm^{-1}. Moreover, the EKE calculation of all 3200 levels in our data set resulted in an astonishing σ value of 0.6 cm^{-1}. If we discard the 300 data points with the largest discrepancies, the remaining 2900 data points have a σ value of 0.4 cm^{-1} only.

After these promising initial results, we attempted a fit of all 3200 levels. After a few iterations of the fit, we obtained a standard deviation of about 0.45 cm^{-1} (calculated using MORBID). However, the resulting potential had spurious minima (''holes'') at large displacements of the internal coordinates. For this particular potential, we cannot obtain the standard deviation and the residuals within the EKE approach, since the EKE program does not produce meaningful results when the potential energy function has holes, even when these minima are separated from the ''real'' minimum by very large potential energy barriers. However, we expect from previous experience that if we would be able to select carefully the fitted parameters to avoid holes, we would be able to produce a ''hole-free'' potential energy function which, in the EKE approach, would give a standard deviation similar to that obtained with the MORBID program for the original potential exhibiting the holes.

Even though the fitting of the 3200 input data led to some reduction of the standard deviation relative to the value obtained with the parameters of Table I, the systematic trends exhibited by the residuals obtained with the parameters of Table I were significantly less obvious in the new

TABLE II. Number of input data points, root-mean-square deviations σ, and maximum J values for the fitted H$_2^{16}$O data.

$(v_1v_2v_3)$	N [a]	σ/cm^{-1} [b]	J_{max} [c]	$(v_1v_2v_3)$	N [a]	σ/cm^{-1} [b]	J_{max} [c]
(000)	221	0.087	14	(121)	47	0.30	6
(010)	217	0.186	14	(201)	48	0.88	6
(020)	154	0.307	14	(003)	48	0.22	6
(100)	189	0.191	14	(211)	22	0.43	4
(030)	99	0.476	14	(320)	5	0.46	6
(110)	47	0.077	6	(202)	44	1.10	6
(040)	17	0.56	6	(122)	19	0.48	6
(120)	47	0.41	6	(400)	44	0.44	6
(200)	35	0.47	5	(004)	30	1.10	6
(002)	32	0.26	5	(212)	39	0.65	6
(130)	41	0.46	6	(410)	20	0.20	5
(210)	35	0.16	6	(221)	46	0.68	6
(012)	47	0.32	6	(301)	46	1.20	6
(220)	16	0.24	5	(023)	35	1.20	6
(300)	48	0.78	6	(103)	46	0.55	6
(102)	48	0.39	6	(231)	41	1.10	6
(001)	215	0.41	14	(311)	47	1.00	6
(011)	224	0.52	14	(113)	39	0.61	6
(021)	154	0.82	14	(310)	39	0.65	6
(021)	140	0.57	14	(112)	41	0.62	6
(101)	162	0.87	14	(211)	48	0.93	6
(031)	48	0.49	6	(131)	44	0.89	6
(111)	146	0.76	14	(013)	44	0.61	6
(041)	35	0.40	5	All	3169	0.58	14

[a]Number of fitted rovibrational term values for the vibrational state in question.

[b]Root-mean-square deviation obtained for the rovibrational term values of the vibrational state.

[c]Maximum J value of the rovibrational term values fitted for the vibrational state.

fitting. These systematic trends are attributed to the neglect of nonadiabatic correction terms in the Hamiltonian (see below), and an attempt to eliminate the systematic residuals without introducing nonadiabatic corrections does not seem justified. In consequence, we consider the parameters of Table I to define the ''optimum'' potential obtainable with the present set of data and the present functional form of the potential, which we will call PJT2.

As in I, our input data sets consist of rotation-vibration term values, measured relative to the $(v_1v_2v_3)J_{K_aK_c}$ = $(000)0_{00}$ level of H$_2^{16}$O. It is not practicable to present here the 3200 energy levels with their assignments and residuals. We give in Table II a summary of the fitted data points. The table defines the vibrational states, for which rotation-vibration term values were included in the input data set, and gives for each of them the number of such term values, N, the maximum J value for the rotation-vibration states involved, J_{max}, and the root-mean-square deviation σ obtained for the N term values in the EKE approach. Table III compares observed and calculated vibrational energy values for all vibrational states of H$_2^{16}$O whose energies have been determined experimentally (not all of these data points were included in the input data for the fitting; see Table II). The calculated vibrational energies are obtained in the EKE approach for the parameter values in Table I. Table IV illustrates the extrapolation power of the potential in that it gives

a comparison between EKE and experimental values for the rotational term values with $J \leqslant 2$ belonging to the highest vibrational state characterized experimentally. As described above, the experimental data given in Table IV were not used as input for the fit of PJT2.

In the present work, we have extended the original MORBID approach by the potential energy terms in Eq. (2) and by the terms involving $f_0^{(9)}$–$f_0^{(12)}$ in Eq. (7). We have tried to vary all the new parameters introduced through these terms. In all these attempts, however, we have only achieved marginal reductions of the standard deviation, while the new parameters turned out to be poorly determined and highly correlated with other parameters already present in the fit. This presumably indicates that analytical expression for the potential energy function used in the present work contains all terms necessary to describe satisfactorily the water molecule in all vibrational states that have been experimentally characterized. That is, even though we have significantly improved the fit of Ref. 3 by introducing certain higher order term in our analytical expression for V, we cannot achieve any further improvement by adding still more terms. In the next two sections we will discuss two possible reasons for that.

V. COSINE EXPANSION OF THE POTENTIAL ENERGY FUNCTION

The y_j expansion in Eq. (1) has proved highly suitable for representing the dependence of the potential energy function V on the stretching (bond length) coordinates in all previous fits of the water potential energy.[3–9] In contrast, the use of a cosine expansion involving the bending angle coordinate [Eqs. (5)–(6)] has only been used in fittings based on the MORBID approach[3,6,9] and is thus less well established. It has the obvious advantage of providing the correct behavior (i.e., a minimum or a maximum) at both linear configurations, but it might be less flexible than, for example, the ''restricted'' power series expansion (in $\bar{\rho} - \rho_e$) used by Carter and Handy,[4] in which the expansion coefficients were constrained to ensure correct behavior at linearity. Other workers, for example Halonen and Carrington,[5] have used ''unrestricted'' power series expansions which do not have the correct behavior at linearity. In this section we shall compare the cosine expansion with the unrestricted power series expansion. The reason that we must pay special attention to the dependence of the potential energy function on the bending coordinate has to do with the fact that the highest value of the bending quantum number v_2 found in our data set is $v_2=4$. It is very desirable to obtain a potential energy function capable of a reasonable extrapolation to higher v_2 values, and such extrapolation properties obviously depend on the chosen analytical form for the potential energy.

The unrestricted power series expansion for the potential energy function is also implicitly used in calculations of water levels by conventional (perturbative) methods. For example, it has been used in attempts to derive information about the $(v_1v_2v_3)=(050)$ (Ref. 30) and (070) (Ref. 31) excited bending states of H$_2^{16}$O by considering the rovibra-

TABLE III. Comparison between observed and fitted values for the vibrational band origins of $H_2{}^{16}O$ (in cm^{-1}).[a]

A_1 vibrational states				B_2 vibrational states			
$(v_1 v_2 v_3)$	E_{obs}	E_{calc}	Obs. − Calc.	$(v_1 v_2 v_3)$	E_{obs}	E_{calc}	Obs. − Calc.
(010)	1594.7	1594.68	−0.0	(001)	3755.93	3755.83	0.1
(020)	3151.6	3151.53	0.1	(011)	5331.27	5331.42	−0.1
(100)	3657.1	3657.15	0.0	(021)	6871.52	6871.63	−0.1
(030)	4666.8	4667.89	−1.1	(101)	7249.8	7249.93	−0.1
(110)	5235.0	5234.99	0.0	(031)	8373.8	8374.03	−0.2
(040)	6134.0	6133.16	0.9	(111)	8807.0	8806.88	0.1
(120)	6775.1	6775.25	−0.1	(041)	9833.6	9832.77	0.8
(200)	7201.5	7202.23	−0.7	(121)	10328.7	10328.58	0.1
(002)	7445.1	7444.75	0.4	(201)	10613.4	10613.84	−0.4
(130)	8274.0	8273.92	0.1	(003)	11032.4	11032.67	−0.4
(210)	8761.6	8761.83	−0.2	(131)	11813.2	11812.67	−0.5
(012)	9000.1	9000.14	0.0	(211)	12151.3	12152.30	−1.0
(220)	10284.4	10284.64	−0.2	(013)	12565.0	12565.48	−0.5
(300)	10599.7	10600.87	−1.1	(221)	13652.7	13652.84	−0.1
(102)	10868.9	10868.63	−0.3	(301)	13830.9	13831.44	−0.5
(310)	12138.9	12139.73	−0.8	(023)	14066.2	14066.96	−0.8
(112)	12407.6	12406.97	0.6	(103)	14318.8	14319.55	−0.8
(320)	13642.2	13642.82	−0.6	(231)	15119.0	15118.92	0.1
(202)	13828.3	13829.29	−1.0	(311)	15347.9	15348.22	−0.3
(122)	13910.9	13910.38	0.5	(113)	15832.8	15833.33	−0.5
(400)	14221.2	14221.94	−0.7	(321)	16821.6	16822.91	−1.3
(004)	14536.9	14538.83	−1.9	(203)	16898.8	16898.30	0.5
(330)	15107.	15107.37	0.4	(123)	17312.5	17313.78	−1.3
(212)	15344.5	15345.57	−1.1	(401)	17495.5	17496.89	−1.4
(410)	15742.8	15742.85	0.0	(213)	18393.3	18394.41	−1.1
(222)	16825.2	16823.65	1.5	(411)	18989.9	18991.98	−2.1
(302)	16898.4	16898.13	0.3	(303)	19781.1	19780.72	0.4
(420)	17227.7	17227.49	0.2	(501)	20543.1	20545.56	−2.5
(104)	17458.3	17460.65	−2.3	(511)	21221.8	21223.76	−2.0
(500)	17748.1	17750.76	−2.6	(403)	22529.4	22528.89	0.5
(312)	18393.0	18393.92	−0.9	(503)	25118.4	25118.31	0.1
(610)	21221.6	21223.21	−1.6				

[a]The observed energy values are from Refs. 12–28. The root-mean-square deviation for all term values in the table is 0.94 cm^{-1}.

tional levels of these states as perturbers (''dark'' states) of the experimentally observed (130) and (220) rovibrational levels. There are no observed transitions whose upper levels can be characterized as predominantly belonging to the (050) or (070) vibrational states. In order to fit observed transitions in the (130) and (220) bands, however, Refs. 30 and 31 have postulated interactions of the upper states with (050) and (070) rovibrational levels, respectively. Hence, the rotation-vibration parameters of the (050) and (070) states influence the observed transition wavenumbers and can be optimized in least-squares fits. This should lead to an indirect determination of the (050) and (070) energies.

Table V gives a comparison of energy values for the $(v_1 v_2 v_3) = (050)$ state of $H_2{}^{16}O$ derived by the ''dark'' state technique with the results of variational calculations using cosine expansion potentials[3,6] and an unrestricted power series expansion potential.[5] Clearly, the energy resulting from the unrestricted power series potential is in best agreement with the dark-state value. In fact, we have attempted to include the dark-state values for the (050) and (070) energies in the input data for our fitting, but we were not able to reproduce these energies satisfactorily even when we varied

all bending potential parameters [Eq. (7)] up to $f_0^{(12)}$. There are two possible explanations for this failure and for the results of Table V. (a) The cosine expansion in Eq. (7) has very poor extrapolation power, or (b) the dark-state values for the (050) and (070) energies are seriously in error, and their agreement with energy values obtained from the unrestricted power series potential is simply an artifact caused by the fact that the dark-state perturbative technique implicitly assumes the potential energy function to be given by an unrestricted power series expansion. If the ''true'' experimental value for the (050) energy (i.e., an energy value obtained from experimental transitions to rovibrational levels belonging predominantly to the (050) state) were available, we would be able to resolve this problem.

Unfortunately, direct experimental measurements of the wavenumbers for transitions to the (050) and (070) bending states has so far proved impossible for $H_2{}^{16}O$ due to the low intensity of such lines. However, the corresponding band of HDO has higher intensity and could be measured. Such measurements have been reported recently,[32] where the value for the (050) band origin of HDO was given as 6690 cm^{-1}. The

TABLE IV. Comparison between observed and calculated values for the $J=1$ and 2 rotational term values in highly excited $(v_1 v_2 v_3)$ states of H$_2$^{16}O (in cm^{-1}).

$J_{K_a K_c}$	E_{obs}[a]	E_{calc}	Obs.−Calc.	E_{obs}[a]	E_{calc}	Obs.−Calc.
	(321)			(203)		
1_{01}	16844.0	16845.2	1.2	16920.9	16920.3	0.6
1_{11}	16859.3	16860.6	1.3	16932.3	16931.5	0.8
1_{10}	16865.0	16866.2	1.2	16937.3	16936.6	0.7
2_{02}	16887.4	16888.4	1.0	16964.0	16963.7	0.3
2_{12}	16898.4	16899.5	1.1	16971.4	16970.6	0.8
2_{11}	16915.4	16916.4	1.0	16986.7	16985.7	1.0
2_{21}	16959.6	16960.8	1.2	17021.8	17020.4	1.4
2_{20}	16960.7	16961.4	0.7	17023.1	17021.8	1.3
	(123)			(401)		
1_{01}	17335.3	17336.4	1.1	17517.7	17519.1	1.4
1_{11}	17349.8	17350.3	0.5	17527.6	17528.9	1.3
1_{10}	17355.8	17356.4	0.6	17532.9	17534.1	1.2
2_{02}	17379.3	17380.4	1.1	17560.6	17561.8	1.2
2_{12}	17389.6	17390.0	0.4	17566.2	17567.2	1.0
2_{11}	17407.3	17407.8	0.5	17583.5	17584.9	1.4
2_{21}	17451.8	17453.8	2.0	17612.3	17613.4	1.1
2_{20}	17453.2	17455.2	2.0	17613.9	17614.9	1.0
	(331)			(213)		
1_{01}	18288.1	18283.7	4.4	18415.5	18416.6	1.1
1_{11}	18308.2	18308.9	0.7	18429.4	18430.3	0.9
1_{10}	18314.3	18315.0	0.7	18434.9	18435.8	0.9
2_{02}	18331.7	18327.3	4.4	18458.8	18459.8	1.0
2_{12}	18346.9	18347.5	0.6	18468.7	18469.5	0.8
2_{11}	18365.1	18365.5	0.4	18485.2	18485.9	0.7
2_{21}				18525.8	18526.0	0.2
2_{20}	18422.1	18423.1	1.0	18527.1	18527.3	0.2
	(303)			(501)		
1_{01}	19802.5	19802.1	0.4	20566.2	20566.6	0.4
1_{11}	19813.6	19812.9	0.7	20574.9	20577.2	2.3
1_{10}	19818.6	19817.8	0.8			
2_{02}	19843.9	19843.1	0.8	20607.7	20610.2	2.5
2_{12}	19852.0	19850.5	1.5	20615.2	20615.4	0.2
2_{11}	19866.7	19865.5	1.2	20628.7	20630.7	2.0
2_{21}	19900.4	19898.5	1.9	20659.9	20662.2	2.3
2_{20}	19901.7	19899.7	2.0	20661.5	20663.7	2.2
	(313)			(403)		
1_{01}				22550.3	22550.1	0.2
1_{11}	21258.1	21260.1	2.0	22560.2	22559.9	0.3
1_{10}	21263.7	21265.6	1.9	22565.0	22564.4	0.6
2_{02}	21285.4	21286.9	1.4			
2_{11}	21312.5	21314.1	1.6			
2_{21}	21355.8	21357.0	1.2			
2_{20}	21356.9	21358.1	1.2			

[a]From Refs. 26–28.

results of EKE calculations of this band origin using different potentials are given in Table VI. The unrestricted power series potential of Halonen and Carrington[5] produces an energy value approximately 10 cm^{-1} higher than the experimental value, whereas the two different cosine-expansion potentials give slightly higher and lower values, respectively. Consequently, it would be no problem to reproduce the experimental value in a fitting using the cosine-expansion potential. This observation should be contrasted with the fact that we were not able to fit the dark-state value for the (050) vibrational energy of H$_2$^{16}O, and it throws some doubt on the dark-state determinations of the (050) and (070) vibrational

TABLE V. Values of the energy for the $(v_1 v_2 v_3) = (050)$ vibrational state of H$_2$^{16}O calculated with different methods.

Method of determination	E_{vib}/cm^{-1}
''Dark-state'' perturbative treatment[a]	7552
EKE calculation[b]	7551
EKE calculation[c]	7539
EKE calculation[d]	7537

[a]From Ref. 30.
[b]''Unrestricted'' power series potential from Ref. 5.
[c]Cosine expansion potential from Ref. 6.
[d]Cosine expansion potential from Ref. 3.

energies of H$_2$^{16}O. In order that the (050) and (070) vibrational energies can be accurately determined from a dark-state analysis, precise values of the rotational energy spacings in the (050) and (070) vibrational states must be available. In Refs. 30 and 31, these rotational energies were obtained by means of an empirical Hamiltonian. We suspect that inaccuracies in the resulting rotational spacings lead to non-negligible errors in the dark-state values for the (050) (Ref. 30) and (070) (Ref. 31) vibrational energies of H$_2$^{16}O.

In the present context, it should also be noted that all the bending states discussed here are well below the potential barrier to linearity in the water molecule, which is in excess of 10 000 cm^{-1}. We are interested in extrapolating to bending states close to the top of the barrier and above it. For such states the unrestricted power series expansion will fail because, as a function of the bond angle, it does not have zero slope at linearity. The restricted power series expansion used by Carter and Handy[4] could then be considered as an alternative to the cosine expansion. Fernley et al.[33] carried out EKE calculations for water on the basis of several different potential energy functions and obtained erratic results for the $(0 v_2 0)$ energies with $v_2 > 3$, when they used the unrestricted power series potential from Ref. 5 as input for their calculations, whereas restricted power series and cosine expansion potentials produced consistent results.

The arguments given above provide no reasons for abandoning the cosine expansion for expressing the dependence of the potential energy function on the bending angle. For states well below the barrier, the cosine expansion gives a better extrapolation to highly excited bending states than an unrestricted power series expansion, and it has correct be-

TABLE VI. Values of the energy for the $(v_1 v_2 v_3) = (050)$ vibrational state of HD^{16}O determined with different methods.

Method of determination	E_{vib}/cm^{-1}
Experiment[a]	6690
EKE calculation[b]	6704
EKE calculation[c]	6695
EKE calculation[d]	6687

[a]From Ref. 32.
[b]''Unrestricted'' power series potential from Ref. 5.
[c]Cosine expansion potential from Ref. 6.
[d]Cosine expansion potential from Ref. 3.

havior at linearity. We can conclude that the analytical expression for the potential energy function used in the present work is well suited to describing the energy variation with both stretching and bending coordinates. This conclusion is supported by our fit of the H_2S potential energy surface, which include the (050) energy as an input data point.[34]

VI. BREAKDOWN OF THE BORN-OPPENHEIMER APPROXIMATION: NONADIABATIC CORRECTION

As mentioned above, it was shown in I that in the fits carried out with the combined EKE/MORBID method, we achieved an accuracy sufficiently high that effects from the breakdown of the Born-Oppenheimer approximation yield significant contributions to the discrepancies between theory and experiment. In the EKE approach, which provides the energies ultimately compared with experiment, we use a kinetic energy operator exact within the Born-Oppenheimer approximation. Hence, if we assume that our analytical expression for the potential energy function is sufficiently flexible to fit the data, the breakdown of the Born-Oppenheimer approximation is indeed the only limiting factor preventing us from fitting the data to experimental accuracy. If we are to extend our theoretical approach to account for the Born-Oppenheimer breakdown, we must extend the Hamiltonian with both adiabatic and nonadiabatic corrections.

In a fit of the type reported here, the adiabatic corrections are ''effectively'' included in the resulting potential energy surface. Since we fit term values for $H_2^{16}O$ only, we obtain the effective potential energy surface for this isotopomer, which comprises the true, isotope-independent Born-Oppenheimer potential energy function and the added, isotope-dependent adiabatic correction. When we fit one isotopomer only, we have no way of separating these two contributions.

Some contributions to the non-adiabatic corrections are dependent on the rotational quantum numbers. These have been well studied for diatomic molecules.[35] The expressions for the nonadiabatic correction to the energies of triatomic molecules were derived in the framework of Hougen-Bunker-Johns-type Hamiltonian.[36] For the H_3^+ molecular ion, it was recently found[37] that the J-dependent nonadiabatic corrections contribute significantly to the energies for high J values, and that an accurate treatment of high-J states would require the inclusion of nonadiabatic correction terms in the Hamiltonian.

Analysis of our residuals shows that we obtain J-dependent deviations between theory and experiment with an order of magnitude comparable to that found for H_3^+.[37] Further, the deviations have signs consistent with the signs of the J-dependent corrections terms given by Bunker and Moss.[36] In consequence, we believe that in order to obtain a further improvement of the potential energy function obtained in the present work, it is necessary to account explicitly for the (J, K_a)-dependent correction terms resulting from the breakdown of the Born-Oppenheimer approximation. This conclusion is supported by our recent results for the H_2S molecule.[34]

VII. SUMMARY AND CONCLUSION

The $H_2^{16}O$ potential energy function has been refined by fitting to experimental data. The actual fit presented here used the same set of input data as was employed in a previous fit,[3] but we have shown that the new potential function improves significantly the representation of highly excited rotational and vibrational states. In particular, the discrepancies between theory and experiment for the highly excited stretching states observed above 20 000 cm^{-1} have been reduced by two orders of magnitude in comparison with previous fitted potential surfaces. This improvement has been achieved by an extension of the analytical function used to represent the potential energy function. We believe that it will not be possible to improve further the reproduction of experiment by adding more terms to the potential energy function. Such an improvement will require the explicit consideration of the breakdown of the Born-Oppenheimer approximation by inclusion of J-dependent nonadiabatic correction terms.

Our new potential, PJT2, is the most accurate available for $H_2^{16}O$. It is being used both to analyze the many unassigned lines in the hot water spectrum and to produce a new line list for modeling of the atmospheres of cool stars (see Ref. 38 for an example) and for related applications.

Note added in proof. Since the completion of this work, Polyansky *et al.*[39] have assigned transitions in the $5\nu_2 - 4\nu_2$ hot band observed in a 1000 °C emission spectrum of water. They obtain a value of 7542.4 cm^{-1} for the $5\nu_2$ band origin, significantly lower than the value obtained previously from dark state analysis,[30] and close to the values predicted here.

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