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Analysis of hot D_2O emission using spectroscopically determined potentials

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Fourier transform emission spectra of D_2O vapor were recorded at a temperature of 1500 °C in the wavenumber range 380–1880 cm^{-1}. 15 346 lines were measured, of which the majority were identified as belonging to D_2O. The spectrum was analyzed using variational nuclear motion calculations based on spectroscopically determined potential-energy surfaces. Initial assignments were made using a potential surface obtained by fitting a high accuracy *ab initio* potential. The new assignments were used to refine the potential surface, resulting in additional assignments. A total of 6400 D_2O transitions were assigned and 2144 new D_2O energy levels were obtained. Transitions involving the $4\nu_2$ and $5\nu_2$ bending states, with band origins of 4589.30 ($\pm$0.02) and 5679.6 ($\pm$0.1) cm^{-1}, respectively, were assigned for the first time. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1630032]

I. INTRODUCTION

The spectrum of water is perhaps the single most important spectrum of any molecule.[1] It is also one of the most difficult to interpret. This is particularly true of the spectrum of hot water, which is both dense and irregular.

The challenge of assigning water spectra has led to the use of methods based on the variational solution of the nuclear motion problem,[2–4] which have replaced traditional methods based on perturbation theory. Methods based on perturbation theory parameterize the effective Hamiltonian in order to interpret and fit spectra. These Hamiltonians are generally not transferable, even between isotopomers of the same molecule. Conversely variational methods rely on solving the nuclear motion problem using high accuracy potential energy surfaces for the system. Within the Born–Oppenheimer approximation the potential energy surface of a molecule is unchanged by isotopic substitution and variational methods have been used to fit the spectra of several isotopomers simultaneously.[5,6]

A number of studies[7–10] have demonstrated the importance of both adiabatic and nonadiabatic corrections to the Born–Oppenheimer approximation for water. This means that a full understanding of the water problem requires a detailed treatment of these non-Born–Oppenheimer effects. Since the HDO system contains extra, symmetry-breaking terms not present in H_2O,[8] D_2O is the best system to compare with H_2O to obtain insight into the failure of the Born–Oppenheimer approximation.

In this work we report on a new hot emission spectrum of D_2O in a region that covers both the high wavenumber part of the pure rotational spectrum and the bending fundamental. To analyze this spectrum, we have constructed a new, spectroscopically determined effective potential energy surface for D_2O. This surface was refined using data from our initial assignments, allowing further assignments to be made.

II. EXPERIMENT

The hot D_2O emission spectra were recorded at the University of Waterloo with a Bruker IFS 120 HR Fourier transform spectrometer. The spectrometer was operated with a KBr beamsplitter and either a Si:B or a HgCdTe detector. The spectra reported here in the 350–2200 cm^{-1} region were recorded in three pieces. The 350–750 cm^{-1} section used a liquid He-cooled Si:B detector and a cold longwave pass filter at 750 cm^{-1}. Lines of adequate signal-to-noise ratio were measured from 380 to 748 cm^{-1} with this filter. A separate cold bandpass filter was used to cover the 750–1300 cm^{-1} region (773–1200 cm^{-1} for measured lines). The 1200–2200 cm^{-1} region (1200–1878 cm^{-1} for measured lines) was recorded with a HgCdTe detector and an uncooled 2200 cm^{-1} longwave pass filter. Note that there is a gap in the spectrum between 748 and 773 cm^{-1} because of a small gap between the bandpasses of the two filters used with the Si:B detector. The resolution was set to 0.01 cm^{-1} for all regions.

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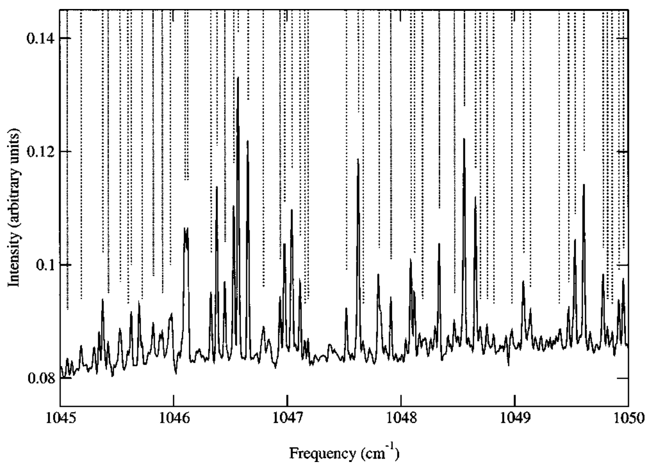

FIG. 1. D_2O emission spectrum between 1045 and 1050 cm^{-1}. Dashed lines indicated assigned transitions. A full list of the 52 line assignments is given in EPAPS archive (Ref. 17).

A KRS-5 window was used on the emission port of the spectrometer. The water vapor was heated in the center of a 1 m long, 5 cm diameter alumina tube sealed with cooled KRS-5 windows. The tube was placed inside a furnace and heated to 1500 °C. A slow flow of D_2O vapor was maintained through the cell at a pressure of about 2.5 Torr. The thermal emission from the cell was focused into the emission port of the spectrometer with an off-axis parabolic mirror. The signal-to-noise ratio was in excess of 250. The lines were measured with the PC-Decomp program of Brault and have an estimated absolute accuracy of ± 0.001 cm^{-1} for strong unblended lines. The spectrum, however, was very dense with D_2O as well as HDO and H_2O lines present. The HDO and H_2O lines were present because of desorption of trace amounts of water trapped on the inner surface of the alumina tube. The HDO and H_2O impurity lines proved useful in the calibration of the D_2O spectra.

The three spectra analyzed for this paper were calibrated using our previous measurements on hot H_2O[11,12] and HDO[13,14] in this region. This means that above 750 cm^{-1} our lines have a wavenumber scale that is in excellent agreement with that of Toth[15,16] but the 380–746 cm^{-1} region is on a slightly different scale from Toth. Fortunately, this difference is less than 0.001 cm^{-1}, our estimated absolute accuracy.

The complete list of measured transitions are given in EPAPS[17] archive. This list includes the assignments discussed below. Figure 1 gives a portion of the spectrum.

III. LINE ANALYSIS

Transitions due to hot H_2O[11] and HDO[13,14] were identified in the full linelist of 15 346 measured transitions. By comparison with our previous studies on these species,[11,13,14] 2094 lines were identified as belonging to HDO and 812 lines as H_2O. The remaining 11 440 lines are analyzed below.

The spectra of hot water and its isotopomers are difficult to analyze because of, in particular, excitation of the large amplitude bending mode, and the coupling between this mode and molecular rotation. This coupling makes states with high K_a or with significant bending excitation particularly difficult to assign and to fit. Transitions between these states are very prominent in the spectra of high temperature water vapor.

Polyansky *et al.*[2] showed that variational nuclear motion calculations based on the use of a high accuracy potential energy surface could be used to analyze spectra which could not be assigned using traditional methods based on perturbation theory. We adopt the variational approach for our D_2O work presented here.

In the course of the work, a number of variational calculations were performed using the DVR3D program suite[18] in Radau coordinates. These calculations used a DVR grid of 29 grid points in each radial coordinate and 40 angular points, where these grids are based on Morse oscillator-like functions[19] and (associated) Legendre polynomials, respectively. A final Hamiltonian matrix of dimension 1500 was used for the vibrational calculations and $300\times(J+1-p)$ for the rotational calculations, where the parity $p=0$ or 1. The masses were set at $M_D=2.013\,553$ u and $M_O=15.990\,526$ u.

In order to make initial assignments, we performed a fit to the empirically determined energy levels of D_2O.[20–29] Fits started from the recent high accuracy potential of Polyansky *et al.*[10] This *ab initio* potential reproduces all the known levels of D_2O with a standard deviation of only 0.71 cm^{-1}. Here we neglect the nonadiabatic corrections to the Born–Oppenheimer approximation which are, in any case, smaller for D_2O than H_2O. The initial fit used all observed energy levels with $J=0$, 2, and 5 lying below 8000 cm^{-1}: A total of 314 levels. Morphing the original potential energy surface[30] using 23 constants reproduced the levels used in the fit with a standard deviation of 0.019 cm^{-1}. This fit was used to generate a linelist of all D_2O transitions up to $J=30$ using a preliminary version of the dipole surface of Lynas-Gray *et al.*[31]

In computing this linelist, the computational procedure outlined above was employed except that a reduced radial grid of 21 points was employed to save computer time; this was found to give only negligible differences for the energy range considered here. This linelist was used to make the initial assignments of the D_2O transitions by a semi-automated procedure[32] which predicts transitions to unobserved states and matches them to unassigned lines in the experimental dataset. Any tentative assignments are checked by generating further transitions using combination differences.

As the energy levels and associated wavefunctions arising from these calculations are only assigned rigorous quantum numbers, J, p (parity), *ortho/para*, full assignments were made using the algorithm of Zobov *et al.*[33] that first assigns the $J=0$ vibrational states and then the associated rotational levels. This algorithm assumes that rotational levels in the (000), (100), (010), and (001) states are already known, and makes predictions for levels in higher vibrational states. For D_2O many of the high J levels for these states were unknown, so we first assigned quantum numbers to these levels, aided by the predicted intensities in the linelist.

2936 lines in the D_2O spectrum could be assigned trivi-

TABLE I. Fitted coefficients, $c_{i,j,k}$, of the morphing function, see Eq. (2) of Ref. 30. Dimensions are $a_0^{-(i+k)}$.

i j k	Fit 1	Fit 2
0 0 0	1.000 102 850 556 568	0.999 713 432 113 248
1 1 0	0.016 528 126 092 793	0.005 906 277 275 421
1 0 1	−0.038 604 499 979 067	0.005 270 895 774 731
2 0 0	0.000 103 239 880 118	0.010 440 044 337 925
3 0 0	0.017 980 919 486 867	−0.003 934 833 046 072
0 0 2	0.029 103 947 514 144	0.023 151 795 132 007
0 0 3	−0.152 787 734 562 501	−0.068 609 190 230 470
4 0 0	0.000 957 453 022 999	−0.034 315 836 582 797
0 2 0	−0.002 697 976 892 825	−0.000 067 446 145 927
0 3 0	−0.010 972 966 075 669	−0.003 341 240 709 580
0 4 0	0.014 481 278 198 816	0.005 130 781 073 013
0 1 1	0.018 057 920 648 302	0.007 997 699 941 216
2 1 0	−0.080 781 563 896 829	0.035 442 192 125 220
2 0 1	0.024 796 823 990 757	−0.072 117 405 091 268
1 2 0	−0.001 117 123 884 363	−0.021 038 305 902 325
0 2 1	−0.008 851 439 681 244	0.001 185 738 405 653
1 0 2	0.274 764 121 588 008	0.005 643 301 566 759
0 1 2	−0.048 670 652 428 175	−0.194 091 262 797 463
1 1 1	−0.134 545 361 634 936	0.082 625 181 895 958
3 1 0	0.202 425 869 866 907	−0.205 715 465 546 753
3 0 1	−0.254 961 040 714 635	0.160 218 439 996 363
1 3 0	0.093 821 461 765 364	0.007 673 608 381 676
0 3 1	0.012 911 581 693 171	0.011 247 369 348 090
1 0 3		−0.017 285 541 626 029
0 1 3		0.481 637 298 654 958

ally on the basis of previously measured energy levels.[20–29] A similar number of lines were assigned using our linelist, including some lines involving the (040) and (050) vibrational states, which had not been observed previously. This led to the determination of nearly 2000 new energy levels for D_2O. However, during the course of this analysis it became clear that our energy levels, and hence presumably our fitted potential energy surface, were significantly less reliable for states with high K_a and/or high bending excitation. It was, therefore, decided to repeat our spectroscopic fitting procedure and to include our newly determined energy levels.

The second fit included all the levels used in the first fit. In addition, our newly assigned levels and all available levels with $J=10$ were added. Furthermore the energy cutoff on levels was removed. In practice, the highest levels included belonged to the (401) vibrational state, which lies about 13 000 cm^{-1} above the ground state. This gave us a set of 720 energy levels to fit. Our first surface reproduced this larger dataset with a standard deviation of 0.27 cm^{-1}, which is an order of magnitude worse than its behavior for the initial, smaller set. The second fit again started from the *ab initio* potential; two extra constants were varied in the morphing procedure, giving a total of 25 constants (Table I). With this fit it was possible to reproduce the expanded data set with a standard deviation of 0.033 cm^{-1}.

The new fit was found to perform much better for the high K_a and high ν_2 states. In particular, using the energy levels generated in this fit allowed us to increase by about 50% the number of energy levels assigned to the (040) vibrational state and double those associated with the (050) state. The constants used to determine the two fitted potentials are given in Table I.

TABLE II. Summary of energy levels determined by the present study.

Band	Origin (cm^{-1})	Energy levels	
		Old	New
000	0.0	280	672
010	1178.379	274	587
020	2336.839	164	370
030	3474.319	174	223
040	4589.30	0	246
050	5679.6	0	46
	Totals	718	2144

IV. RESULTS

Table II summarizes the results of our assignments. It can be seen that a total 2144 new energy levels have been determined. The majority of these levels, 1224, have been confirmed by combination differences and can therefore be regarded as being secure. However, a significant number, 920, were only determined by a single transition. This situation arises largely from sequences of pure rotational transitions within a particular state and was already found in our previous study of hot H_2O.[11] In this case these one-transition assignments have proved reliable and we would expect this to be the case here.

Table II gives the band origins for the sequence of $(0n0)$ bending states. The higher states, $n=4$ and $n=5$, have not been observed previously. As we did not identify any transitions involving the 0_{00} rotational states for these two vibrational states, we do not have a direct experimental determination of the associated band origins. It is possible, however, to use our calculated energy levels and the systematic behavior of the error in our calculated levels associated with a particular vibrational state to give fairly precise estimates of these band origins. Use of this procedure has been shown to give good results previously.[34] Our estimates give 4589.30 (± 0.02) and 5679.6 (± 0.1) cm^{-1} for the band origins of the (040) and (050) states, respectively.

Figure 1 gives an illustrative portion of the spectrum. Assigned lines are marked and the 52 associated line assignments are given as a file in the EPAPS archive,[17] where a file giving all lines plus assignments can also be found.

Rotation–vibration term values were derived for the newly observed levels of D_2O by starting from values given in previous studies.[20,28] Table III present a sample of our newly determined term values: those for the (050) vibrational state. There are insufficient transitions to this state to give reliable statistical errors for each level. However experimental considerations suggest errors of ± 0.006 for levels in (050). These errors are consistant with the distribution of energies in those cases for which more than one transition determines the term value.

Table III also gives the differences, observed−calculated, for the two fits. It should be noted that most of these energy levels were not used in the fits and therefore these differences reflect the reliability of our predictions. It can be seen that Fit 2 gives a significant improvement over Fit 1 for essentially all levels, leading to both a significant reduction in the magnitude of the residuals and to a smoother

TABLE III. Energy levels, in cm^{-1}, for the (050) vibrational state of D_2O.

J	K_A	K_C	Energy	Obs−Calc Fit 1	Fit 2
4	1	3	5834.1812	−0.905	−0.222
5	1	5	5856.9679	−0.873	−0.207
5	1	4	5900.2086	−0.910	−0.211
5	2	4	5938.5413	−0.751	−0.168
6	0	6	5914.7093	−0.908	−0.211
6	1	6	5918.6908	−0.870	−0.199
6	1	5	5978.0939	−0.921	−0.210
6	2	5	6009.7010	−0.757	−0.160
6	2	4	6028.0580	−0.767	−0.121
7	0	7	5987.5537	−0.888	−0.192
7	1	7	5990.0013	−0.868	−0.191
7	2	6	6091.8586	−0.760	−0.150
7	3	5	6194.9988	−0.591	−0.102
8	0	8	6069.2830	−0.878	−0.184
8	1	7	6166.1788	−0.912	−0.192
9	0	9	6159.9786	−0.863	−0.168
9	1	9	6160.8537	−0.852	−0.165
9	1	8	6274.7531	−0.872	−0.157
9	2	8	6287.8688	−0.770	−0.138
9	2	7	6347.2161	−0.896	−0.158
10	0	10	6259.7011	−0.849	−0.152
10	1	10	6260.2192	−0.841	−0.149
10	1	9	6392.2119	−0.845	−0.139
10	2	9	6401.1459	−0.759	−0.119
11	0	11	6368.5005	−0.832	−0.132
11	1	11	6368.8057	−0.828	−0.132
11	2	10	6524.2127	−0.800	−0.153
12	0	12	6486.4035	−0.817	−0.114
12	1	11	6653.2301	−0.787	−0.101
12	2	10	6772.0662	−0.897	−0.128
12	3	9	6853.5238	−0.742	0.022
13	0	13	6613.5053	−0.727	−0.020
13	1	13	6613.5833	−0.757	−0.051
14	0	14	6749.5880	−0.789	−0.078
14	1	14	6749.6496	−0.793	−0.083
14	1	13	6949.5441	−0.717	−0.045
14	2	13	6951.0741	−0.703	−0.047
15	1	15	6894.8697	−0.834	−0.118
15	2	14	7112.1904	−0.676	−0.020
15	3	13	7291.0054	−0.610	−0.021
15	4	12	7448.5583	−0.528	−0.002
16	0	16	7049.3390	−0.754	−0.034
16	1	16	7049.3794	−0.741	−0.021
16	2	14	7465.6224	−0.336	0.064
17	1	17	7212.9643	−0.730	−0.005
17	2	16	7462.4260	−0.642	0.014

pattern of residuals. A tabulation of all the 2144 newly determined rotation–vibration term values for D_2O is given in the EPAPS archive.[17]

V. CONCLUSIONS

New Fourier transform emission spectra of hot D_2O have been analyzed using variational nuclear motion calculations based on spectroscopically determined potential energy surfaces. The large number of new D_2O levels determined in the course of this work allowed the spectroscopically determined surface to be further refined, leading to a significant number of additional assignments.

The spectroscopically determined potential energy surface also implicitly contains the non-Born–Oppenheimer, adiabatic correction surface. By determining accurate surfaces for both H_2O and D_2O, it should be possible to extract a spectroscopic estimate of the symmetric adiabatic correction surface, and indeed such a procedure has been used successfully for the H_3^+ system.[35] The value of the adiabatic correction surface for water remains uncertain since a number of calculations[7,9,10] have shown that it depends strongly on the level of theory used to determine it. The present spectra of D_2O and the resulting potential energy surfaces provide an important step in this direction.

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