Monodromy in the water molecule

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Abstract

The change in the energy level structure of a bent molecule as it starts to sample linear geometries has been discussed in terms of monodromy found in simple two dimensional model problems. Infrared spectra of hot ($T \sim 3000$ K) water are analysed for transitions involving states with high bending excitation which can sample linear HOH geometries. 134 new experimental energy levels are determined for bending states with $5 \leq v_2 \leq 9$ including band origins for $7\nu_2$, $8\nu_2$ and $9\nu_2$. Plots of those levels with $J = K_a$ show the characteristic rearrangement of energy levels predicted for a system displaying quantum monodromy. Quantum monodromy for water occurs about the $\nu_2 = 7, J = 0$ level. The barrier to linearity in $H_2{}^{16}O$ is estimated to lie at 11114 ± 5 cm^{-1}.

1 INTRODUCTION

Monodromy, which means once round, is a concept arising from classical mechanics [1–3]. Monodromy in quantum mechanical systems implies the absence

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of a single, smoothly-varying set of quantum numbers with which to characterise the system. A proto-typical example of a problem displaying monodromy is the energy levels of a Mexican-hat shaped potential (also sometimes likened to the shape at the bottom of a champagne bottle). In these potentials one set of quantum numbers, characterised by free angular motion around the rim of the hat and the perpendicular vibration, exists at low energy. Once the energy levels reach the peak of the hat, the monodromy point, the energy levels restructure and require a new set of quantum numbers.

As noted by Child *et al.* [4] the rotation-vibration energy levels of bent molecules display monodromy when they sample linear geometries. Child *et al.* illustrate this behaviour with calculated energy levels for water. Similar conclusions have been drawn from a theoretical analyses of the HCP molecule [5] and the isomerising LiNC/LiCN system [6]. Despite many experimental studies on bent molecules with low barriers to linearity (see for example, B. Winnewisser's review [7]), it would appear that thus far published spectroscopic studies of these quasi-linear systems have either been for problems for which the barrier to linearity is so low that the energy level structure characteristic of a bent system does not really exist, or where the barrier to linearity is so high that insufficient excitation has been achieved to probe levels that cross it. Very recently, Winnewisser *et al.* [8] have returned to the study of the pure rotational spectrum of the NCNCS molecule, which also clearly displays monodromy. Conversely a study of levels about the barrier to isomeration in the HCN/HNC system showed the absence of monodromy meaning that all bending modes in this system could be assigned on the basis of a single, global bending quantum number [9].

The precise height of the barrier to linear HOH geometries in water has been the subject of a series of theoretical studies [10–13] and is thought to be close to 11100 cm^{-1} [12, 13]. The eighth bending overtone, $9\nu_2$, and possibly the seventh bending overtone, $8\nu_2$, are predicted to be the lowest bending states with sufficient energy to sample linear geometries [4, 14]. In this paper we report analysis of infrared spectra of hot water which yield transitions involving levels of $v_2 = 9$ for the first time. Plots of these energy levels and appropriate ones for lower bending overtones show the clear signature one would expect for a system displaying monodromy.

2 METHOD

The results reported in this letter are based on the analysis of two complementary spectra of hot water. The first spectrum is the recently reported laboratory emission spectrum of water vapour at about 3000 K recorded using an oxy-acetylene torch by Coheur *et al.* [15]. This spectrum spans most of the in-

frared, although only the regions with pure rotational transitions and bending transitions will concern us here. The second spectrum analysed is an absorption spectrum recorded in a sunspot spanning the 722 – 1011 cm^{-1} region [16]. This spectrum is dominated by absorptions by water which is thought to have a temperature of 3200 K. The sunspot spectrum, in particular, has been available and partially assigned for some time [17, 18].

These spectra contain information on the pure rotational transitions, which lie mostly below 1000 cm^{-1}, and bending transitions, which lie mostly in the 1000 – 2000 cm^{-1} region. In both cases it is not possible to analyse transitions involving states of high bending excitation without also considering similar transitions involving states of lower bending excitation. Previous studies on hot water have characterised the levels for $5\nu_2$ [19] and $6\nu_2$ [20, 21]. Our recent analysis of the torch and sunspot spectra [15] extended the results for $6\nu_2$ and identified levels for both $7\nu_2$ and $8\nu_2$; in particular the 10 levels (tentatively) ascribed to $8\nu_2$ were the first assigned to this state.

New assignments were made by comparison with predictions made from variational nuclear motion calculations. These calculations were based on a spectroscopic potential energy surface which was specifically tuned to treat the bending motions. Starting from the best available *ab initio* potential [22], the surface was morphed [23] to fit the experimentally observed bending states for $n\nu_2$ with $n = 0-7$ with total rotational quantum number J equal to 0, 2, 5 and 10. This new potential reproduced these bending level with a standard deviation of 0.05 cm^{-1}, although it performed much worse for states with stretching excitation. This is a significant improvement for bending levels on our previous best spectroscopically-determined potential [23], which gave residuals of up to 1 cm^{-1} for certain levels in the $7\nu_2$ and $8\nu_2$ vibrational states. This fit finds of the lowest HOH linear geometry for $R_{\mathrm{OH}} = 0.93329$ Å at a point 11114 cm^{-1} above the minimum of the potential energy surface, for which $R_{\mathrm{OH}} = 0.95785$ Å. A conservative estimate for the error in the barrier height is 5 cm^{-1}.

3   RESULTS

The new line assignments made as part of this work lead to 134 additional experimental energy levels being characterised: 25 for $5\nu_2$, 45 for $6\nu_2$, 25 for $7\nu_2$, 25 for $8\nu_2$ and, for the first time, 14 for $9\nu_2$, see Table 1. The errors in these energy levels are about 0.05 cm^{-1}, which is comparatively large for a spectroscopic study. However both spectra were obtained at very high temperatures so show significant Doppler broadening, furthermore the torch spectrum was recorded at atmospheric pressure and the lines are all significantly pressure broadened, see [15], and the sunspot spectrum was recorded at a resolution of only 0.02 cm^{-1}. Finally several of the transitions assigned in this study are

blended.

Our analysis gives the first experimental values for the band origins of $7\nu_2$, $8\nu_2$ and $9\nu_2$ at 10086.0 $\pm$0.1, 11254.0 $\pm$0.2 and 12533.7 $\pm$0.3 cm^{-1}, respectively. The last two states thus lie at energies above the linear HOH geometry.

For the higher states there was usually only one strong transition associated with each level in the experimental spectra. This means that many levels, and in particular all those with $J = K_a$ for $7\nu_2$, $8\nu_2$ and $9\nu_2$, have not been confirmed by combination differences.

The most straightforward way of detecting monodromy in the bending spectrum of water is to analyse the patterns given by rotation-vibration levels which differ in the bending quantum number, v_2, and have rotational quantum numbers characterised by $J = K_a$. K_a is the bent molecule, ie asymmetric top, quantum number which approximately characterises motion along the A axis for which the moment of inertia tends to zero as the molecule become linear. States with $J = K_a$ are the quantum mechanically allowed states which come closest to undergoing free rotation about the monodromy point. Conversely the bending series corresponds to the perpendicular motion. As shown previously, plots of these levels show the characteristic pattern expected for a system for which the level structure is rearranging about a monodromy point, see Figure 1 of ref. [4].

A plot of all the experimentally-determined energy levels taken from this work and previous studies [19–21, 25] with $v_2 \geq 5$ and $J = K_a \leq 9$ is given in fig. 1. To make the monodromy structure transparent in this figure, all levels with $J = K_a \neq 0$ have been plotted twice, once for positive K_a and once for negative K_a.

Figure 1 shows the characteristic change in energy level structure one associates with monodromy. Thus, for example, the levels for $5\nu_2$ and $6\nu_2$ form a smooth parabola through the $J = 0$ level, whereas those for $8\nu_2$ and $9\nu_2$ have a clear discontinuity in the slope about the $K_a = 0$ level but are well represented by a straight line either side of this point. The levels of $7\nu_2$ seem to be intermediate between these two behaviours which can be characterised as those of a bent and a (quasi-)linear molecule, respectively.

Table 1: Energies of the newly assigned levels of $H_2{}^{16}O$ obtained by analysing the laboratory torch spectrum of Coheur *et al.* [15] or the sunspot spectrum of Wallace *et al.* [16].

J	K_a	K_c	$v_1 v_2 v_3$	Energy

2	1	1	050	7682.89
4	0	4	050	7770.40
4	2	2	050	8002.56^a
5	4	2	050	8608.10
6	1	6	050	8024.94^a
6	5	1	050	9054.36
7	1	7	050	8162.64^a
8	0	8	050	8307.65
8	1	7	050	8529.70^a
9	1	8	050	8747.25^a
9	5	4	050	9645.93^a
9	9	1	050	10944.10
9	9	0	050	10944.10
10	4	7	050	9570.46^a
10	5	5	050	9869.81^a
11	2	9	050	9430.25^a
11	8	3	050	11139.14
12	0	12	050	9120.19^a
12	8	5	050	11426.92
13	7	6	050	11404.91
13	8	5	050	11736.39
14	0	14	050	9632.85^a
14	7	8	050	11737.65^a
15	4	11	050	11141.74^a
15	5	10	050	11409.57
1	0	1	060	8893.52^a
2	1	2	060	9038.76^a
2	1	1	060	9058.37^a

3	0	3	060	9008.72^a
3	1	3	060	9099.65
3	1	2	060	9138.72^a
3	2	2	060	9343.04
4	0	4	060	9098.94^a
4	1	4	060	9180.36^a
4	1	3	060	9245.18
4	3	1	060	9725.86
5	0	5	060	9209.63^a
5	1	5	060	9280.75^a
5	1	4	060	9377.06^a
5	3	3	060	9846.72^a
5	3	2	060	9847.10
6	0	6	060	9339.23
6	3	3	060	9992.54
6	4	2	060	10316.98^a
6	5	2	060	10666.55
6	5	1	060	10666.55
7	0	7	060	9487.55^a
7	1	7	060	9539.20^a
7	1	6	060	9714.47^a
7	2	6	060	9861.56^a
7	2	5	060	9888.80^a
7	3	5	060	10158.51
8	0	8	060	9653.84^a
8	1	8	060	9696.93^a
8	1	7	060	9918.13^a
8	2	6	060	10088.40^a
8	8	1	060	12109.38

8	8	0	060	12109.38
9	0	9	060	9837.79[a]
9	1	9	060	9873.56[a]
9	1	8	060	10143.61[a]
9	2	8	060	10254.77[a]
9	2	7	060	10312.11[a]
9	5	4	060	11250.40
10	0	10	060	10039.60[a]
10	1	9	060	10390.02
10	2	8	060	10558.58
10	5	6	060	11491.06
11	1	10	060	10656.35[a]
12	0	12	060	10497.84
0	0	0	070	10086.04
1	0	1	070	10109.15
4	4	1	070	11619.13
5	0	5	070	10427.99[a]
5	3	2	070	11354.67
5	4	1	070	11741.89
5	5	0	070	12138.84[a]
6	0	6	070	10562.57[a]
6	4	3	070	11888.16
6	5	2	070	12286.11
6	6	1	070	12686.74
7	0	7	070	10718.86
7	2	5	070	11296.03
7	4	3	070	12061.42
7	5	2	070	12456.44[a]

7	7	1	070	13245.19
7	7	0	070	13245.19
8	0	8	070	10896.61
8	2	6	070	11481.59
9	0	9	070	11097.10[a]
11	1	11	070	11652.06
11	4	7	070	12935.73
12	1	12	070	11902.75[a]
13	1	13	070	12180.31
13	1	12	070	12673.08[a]
0	0	0	080	11253.99[b]
1	0	1	080	11277.12
1	1	1	080	11668.90[b]
1	1	0	080	11676.06
2	0	2	080	11322.97[a]
2	1	2	080	11709.23[a]
3	2	1	080	12219.47
3	3	0	080	12660.74
4	2	3	080	12318.24[b]
4	3	2	080	12760.72
4	4	1	080	13203.76
5	0	5	080	11601.29
5	1	4	080	12061.30
5	2	3	080	12427.19
5	3	2	080	12877.59[b]
5	5	0	080	13771.83
6	1	6	080	12079.37
6	4	3	080	13471.77

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6	6	1	080	14348.09
6	6	0	080	14348.09
7	0	7	080	11889.98
8	1	8	080	12367.67[a]
9	0	9	080	12284.81
11	0	11	080	12789.28
11	1	10	080	13444.72
0	0	0	090	12533.72[b]
1	1	0	090	13060.42[b]
2	2	1	090	13628.63
3	3	0	090	14211.96
4	1	4	090	13234.76[b]
4	4	1	090	14805.74
5	0	5	090	12880.60
5	5	1	090	15412.32
5	5	0	090	15412.32
6	1	6	090	13461.76
8	1	8	090	13781.23
9	0	9	090	13611.87
10	1	10	090	14203.64
11	0	11	090	14162.66

[a] Level determined with combination differences.
[b] Level determined from sunspot spectrum.

4   CONCLUSIONS

The technique of using variational nuclear motion calculations to fit iteratively
experimentally determined energy levels to aid in the assignment of transitions

of higher lying energy levels has been used previously to analyse spectra of hot water [15, 24]. Here we adapt this technique to the specific problem of identifying transitions between states with high levels of bending excitation because the bending potential near the region where water approaches linear geometries is poorly characterised by previous experimental studies [12]. Our fitted potential gives the best currently available empirical estimate of the barrier to linearity in water of 11114 ± 5 cm^{-1}, which is in very good agreement with the current best *ab initio* value of 11119 ± 15 cm^{-1} [13] and improves on the previous best empirical value of 11105 ± 5 cm^{-1} [12] because of the extra data now available for the higher bending states.

This potential has allowed us to assign 134 new energy levels for states with 5 or more quanta of bending excitation. In particular we have obtained energy levels for the $9\nu_2$ bending excited state of water for the first time and the first empirical values for the $7\nu_2$, $8\nu_2$ and $9\nu_2$ band origins. Particular emphasis was placed on assigning states with $J = K_a$, since they are the key states for identifying changing behaviour; these states are generally harder to identify that states with low K_a which lie at lower energies and therefore are associated with higher intensity transitions. Appropriate plots of energy levels from these vibrational states show the clear change in behaviour predicted by Child *et al.* [4] on theoretical grounds. Our analysis strongly suggests that the bending levels of water behave as if there is a monodromy point close to the $7\nu_2$ band origin at 10086 cm^{-1}.

Acknowledgements

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Figure caption

Figure 1. Experimental energy levels of $H_2{}^{16}O$ for bending states with $J = K_a$. States are plotted for both positive and negative J to emphasise the change in behaviour about the level with $J = 0$ as the degree of bending excitation is increased.