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David von Seggern
(vsegg@seismo.unr.edu) University of Nevada
July 2012, page 10
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Written by Edgar McCarroll, 14 July 2012 19:59

A linear 1B_2 state of the water molecule

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Spectra of the lowest 1B_2 state of H_2O and D_2O have been recorded. The state is linear in its equilibrium geometry and has a bond length of 1.02 Å. The spectra exhibit vibrational bending progressions and are rotationally resolved. They were recorded from energies of 80 000 to 90 000 cm^{-1} via two-photon, laser-induced fluorescence (LIF) and 2 + 1 multiphoton ionization (MPI).

INTRODUCTION

The excited electronic states of the water molecule have long been a subject of study; as a result a good deal is known about both their structure and photophysics. Whereas the ground-state electron configuration is usually written in terms of molecular orbitals as $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$, the higher orbitals are considered to be Rydberg in nature.¹ Of the ten singlet states resulting from the excitation of one electron out of the $1b_1$ orbital to the $3s$, $3p$, $4s$, or $3d$ Rydberg orbitals, nine have been identified in various spectra.²⁻⁹ [The exception is ${}^1A_2(3pb_2 \leftarrow 1b_1)$, which is one-photon forbidden and supposed to be heavily dissociative.]⁸ The vibrational structure of the various spectra, and the rotational structure if it exists, have been analyzed. Lumped np and nd Rydberg series have also been reported.^{9,10} Fewer of the states stemming from excitation out of the $3a_1$ orbital have been positively identified. The $\tilde{B}{}^1A_1(3sa_1 \leftarrow 3a_1)$ state is responsible for the "second continuum" which peaks at about 128 nm; conflicting analyses of its vibrational structure have been published.^{3,11} A lumped nd series⁹ and rotationally resolved transitions to $5s$ ¹² have also been reported. All the states resulting from promotion of a bonding $3a_1$ electron have in common the interesting property of an apparently linear geometry.

We report in this paper the observation and rotational analysis of the 1B_2 state which results from the promotion $3pb_2 \leftarrow 3a_1$. This electronic state is of particular interest because, as it turns out, it is both the lowest stable linear state and also the lowest state of 1B_2 symmetry. Our spectra were obtained through two-photon laser-induced fluorescence (LIF) and 2 + 1 multiphoton ionization (MPI). In total we recorded spectra from 80 000 to 90 000 cm^{-1} and observed three vibrational bands of H_2O and two of D_2O .

EXPERIMENTAL

The third harmonic of a Nd:YAG laser (Quanta-Ray DCR-20), operating at 10 Hz with a pulse width of 10 ns, was used to pump a dye laser (Lambda Physik FL2002) which contained various Coumarin dyes. The output of the dye laser was frequency doubled in a BBO crystal (also obtained from Lambda Physik) to produce 1 mJ pulses of ul-

traviolet light. The beam was then collimated at a width of 1 cm and brought to a focus with a 1 m lens.

When using multiphoton ionization to detect the transitions the focal point was located between two steel plates, separated by a gap of 1 cm, and contained in a glass cell. Water vapor was allowed to flow slowly through the cell at a pressures of 10 to 15 Torr. About 500 V were applied to the plates, which produced signals of about 20 mV per pulse across a 100 Ω resistor. The signal was passed through a fast 10X amplifier and then into a gated integrator (Stanford Research Systems SR250). The bands reported in this paper were relatively weak and there was always a large, nonresonant background signal; the source of this background is unclear.

When observing laser-induced fluorescence the focal point was located inside a 20 cm length of fused quartz tubing (o.d. 25 mm) containing water vapor at 1 atm; the beam passed along the axis. The lower end of the vertical tube was sealed into a flask of boiling water by using a stopper of aluminium foil and the upper end was open to the atmosphere. In this way we avoided the use of any grease, O rings or cements, all of which gave unacceptable background fluorescence. The fluorescence, most of which is in the visible portion of the spectrum, exited through the sides of the quartz tube, was collected with a glass lens and imaged onto a 1P28 photomultiplier. We estimate that on a peak we could observe 1000 photons per pulse, enough to disperse through a monochromator.

All three bands of H_2O were observed using both LIF and MPI. There were no discernable differences between the linewidths or relative intensities recorded by the two methods. Generally, the LIF produced better signals and it was sometimes possible to partially suppress interfering bands by placing an appropriate filter in front of the photomultiplier. However, since the observation of LIF required that we boil off a liter of water per hour, this method was not used when studying D_2O .

The spectra of water were calibrated against the optogalvanic spectra of a neon discharge using Striganov's compilation of neon lines.¹³ A hollow cathode, atomic absorption lamp with neon as the fill gas was operated at 10 mA. The residual fundamental of the dye laser (after doubling) was defocused and directed into the cathode cup. This yielded signals of several millivolts across a 15 K Ω resistor. The signal was fed directly into another gated integrator with a

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TABLE I. Band origins and rotational constants of the observed vibrational levels. All constants are in units of wave numbers. The uncertainty of the band origins is 1 cm^{-1} and of the B values, 0.05 cm^{-1} .

	v_2'	ν_0	B'	$D'(\times 10^3)$
H_2O	1	84 126.6	7.99	-0.8
	3	85 714.0	8.02	2
	5	87 379.5	7.99	0
D_2O	7	87 326.6	4.02	-1
	9	88 581.7	4.09	0.1

gate width of $10 \mu\text{s}$. Most of the lines listed by Striganov were observed although their relative strengths could differ greatly from those reported.

The outputs of both the gated integrators were sent to a chart recorder. We typically scanned through 25 cm^{-1} of the spectra (calculated in the VUV) in about a minute.

RESULTS AND DISCUSSION

We recorded three vibrational bands of H_2O and two of D_2O (see Table I); all originate from $\tilde{X}^1A_1, v'' = (0, 0, 0)$ as determined by rotational combination differences. Figures 1 and 2 show, respectively, the bands of H_2O and D_2O which are the least cluttered by overlapping electronic transitions.

Two identical photons may induce a transition from the

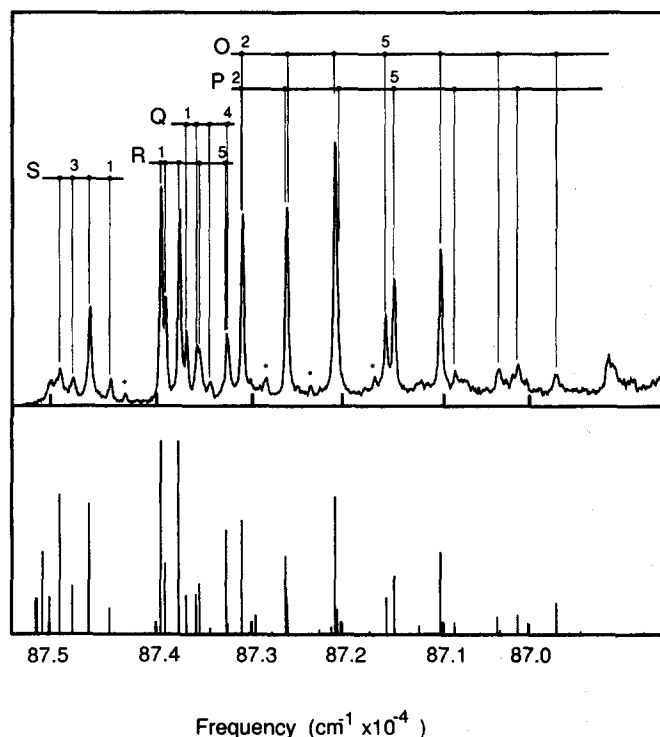


FIG. 1. Two-photon LIF spectrum of $\text{H}_2\text{O}, ^1B_2(0,5,0) - \tilde{X}^1A_1(0,0,0)$. All transitions initiate from levels with $K'' = 1$ and terminate in levels with $K' = 0$. The asterisks denote peaks belonging to the $\tilde{D}''^1A_2(0,1,0) - \tilde{X}(0,0,0)$ band. The stick spectrum depicts the calculated two-photon transition strengths and does not include effects due to predissociation.

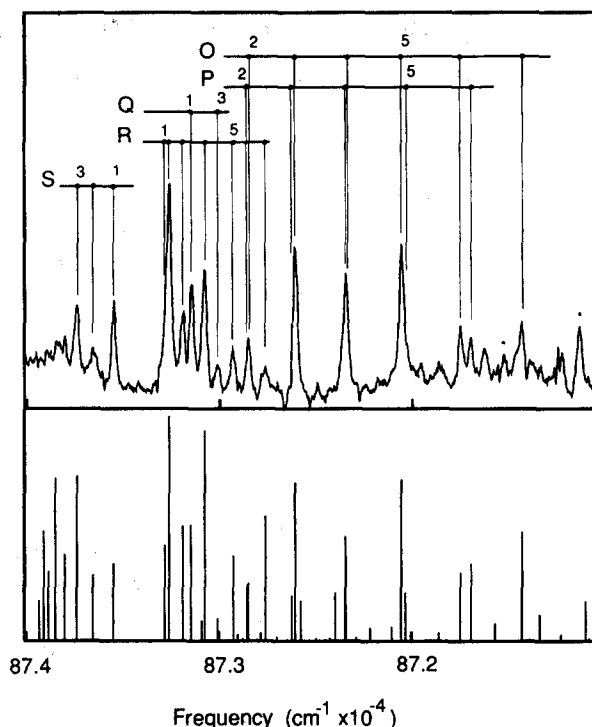


FIG. 2. $2 + 1$ MPI spectrum of $\text{D}_2\text{O}, ^1B_2(0,7,0) - \tilde{X}^1A_1(0,0,0)$. All transitions initiate from levels with $K'' = 1$ and terminate in levels with $K' = 0$. The asterisks denote peaks belonging to the $\tilde{D}''^1A_2(0,1,0) - \tilde{X}(0,0,0)$ band. The stick spectrum depicts the calculated two-photon transition strengths and does not include effects due to predissociation.

\tilde{X}^1A_1 state to a 1B_2 state, the relevant operator being represented by the ± 1 components of a second rank irreducible spherical tensor.¹⁴⁻¹⁶ We therefore expect transitions with $\Delta K = \pm 1$ to be predominant and this is what we find. Since, due to the point group symmetry, only the second rank operator has a nonzero value, the relative intensities of the various rotational transitions will be independent of the polarization of the exciting light. In contrast with any of the other electronic states we have seen ($\tilde{C}, \tilde{D}', \tilde{D}''$),¹⁷ each observed rotational transition terminates in a level with $K' = 0$ (a Σ vibronic level). No bands with $K' > 0$ have been identified. This point is discussed below.

The asymmetric top, rotational wave functions, and their energies were obtained by diagonalization in a symmetric top basis with the axis of quantization parallel with the b (or y) molecular axis.¹⁸ For the \tilde{X} state we used the rotational constants of Benedict *et al.*;¹⁹ the resulting eigen energies were used for making the initial rotational assignments, however during the final fits we used published tables of frequencies derived from infrared spectra.¹⁹⁻²² The rotational transition strengths were calculated as described in Refs. 14 and 16.

In fitting the spectra we used the reciprocal moment of inertia, B' , and a centrifugal distortion constant, D' ; the latter was always found to be less than its associated uncertainty. The fitted parameters are collected in Table I. Assuming a rigid linear rotor, we find an effective bond length of 1.02 \AA . This result agrees nicely with the work of Theodorakopoulos *et al.*²³ who, using CI methods, concluded that the

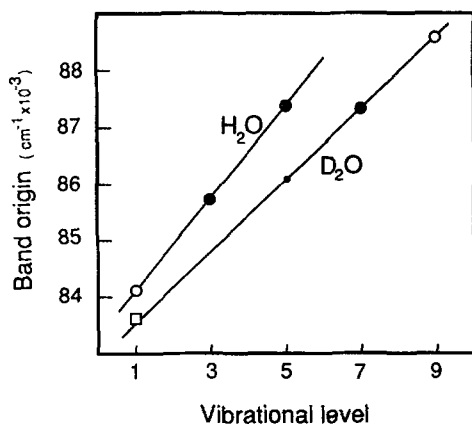


FIG. 3. Band origins for the bending progressions. The unshaded circles denote bands which we have observed while the (smaller) shaded circles denote bands reported by Bell (Ref. 4). (Bell actually listed the positions of "prominent features.") The band denoted by a square has not been observed, its position was estimated from the expected isotope shift.

minimum of the potential should occur at a linear geometry with a bond length of 1.01 Å.

The results of the calculations are shown as stick spectra in Figs. 1 and 2. The calculated positions agree well with our experimental observations. The intensities of the lines are also well reproduced for $J' < 5$; these lines exhibit widths narrower than our resolution of 2.4 cm^{-1} . The intensities of lines corresponding to $J' > 5$ are appreciably lower than expected and the widths are somewhat broadened through predissociation. Within the limits of our resolution, and the bands we have observed, the predissociation rates do not seem to increase with increasing vibration. Whereas the rate of predissociation increases only slowly with J' , no levels of $K' > 0$ are observed and it can thus be assumed that they dissociate much more rapidly than those of $K' = 0$. This is a distinctly abrupt behavior and differs from that encountered in the studies of other electronic states in which the predissociation rates increase gradually with K' .^{8,24}

The band origins ν_0 of the vibrational levels are recorded in Table I and plotted in Fig. 3. As can be seen, several of these bands had been observed by Bell in absorption spectra,⁴ although he was unable to assign them. We were not able to see $\nu'_2 = 5$ of D_2O which in our two-photon spectrum is obscured by an intense $\tilde{D}''^1A_2 \leftarrow \tilde{X}$ band; the latter is forbidden as a one-photon transition. Conversely, we were able to obtain a spectrum of the $\nu'_2 = 1$ band of H_2O by using a glass filter to (partially) suppress the emission due to the overlapping, and stronger, $\tilde{C}''^1B_1(1,0,0) \leftarrow \tilde{X}$ absorption.²⁵ Using three-photon excitation, Ashfold *et al.*⁸ have searched most of the same energy range but have not reported observing this state. The three-photon transitions are allowed but are presumably weak. This is made obvious by a comparison of their Fig. 5 with our Fig. 1, the two of which extend over the same spectral region. The two-photon spectrum is seen to be dominated by transitions to the 1B_2 state whereas in the three-photon spectrum only transitions to $\tilde{D}''(1,0,0)$ and $\tilde{D}''(0,1,0)$ appear. Several weak lines belonging to the latter band are marked by asterisks in our spectra.

In its linear geometry the 1B_2 state correlates to a Π_g state and its electronic angular momentum along the molecular axis ($\Lambda' = 1$) will couple with the vibrational angular momentum from the bending ($l' = \nu'_2, \nu'_2 - 2, \dots, 1$ or 0) to give K' . Since only levels with $K' = 0$ are observed it is necessary that $l' = 1$ and therefore each of the bands must terminate in a vibrational level with an odd number of bending quanta. The approximately 1600 cm^{-1} spacing of the Σ vibronic levels can then be assigned as due to the odd levels of a bending progression, yielding a bending frequency of about 800 cm^{-1} (600 cm^{-1} for D_2O). This is comparable to the bending frequency of the linear, 2A_1 state of singly ionized water;^{26,27} the Rydberg series of which the 1B_2 state is a member converges to the 2A_1 state. The absolute vibrational numbering is tentative; it is suggested by the absence of observed bands at longer wavelengths and by the isotope shift (see below). No other vibrational modes were evident in the spectra.

We were not able to observe $\nu'_2 = 1$ for D_2O . However, since the 1B_2 is a Rydberg state, the isotope shift should be fairly close to that of the corresponding ionic transition, in this case $H_2O^+ \ ^2A_1(\nu'_2 = 1) \leftarrow H_2O \ \tilde{X}(0,0,0)$. Photoelectron spectra of this transition have been recorded and modeled by Dixon *et al.*²⁷ Using their results (their Table 4, Calc. C) we thus expect an isotope shift of 500 cm^{-1} . This is close to the shift of 580 cm^{-1} which we find when our D_2O data are extrapolated to $\nu'_2 = 1$. Increasing the assigned vibrational numberings of both molecules by 2 would lead to a shift of about 250 cm^{-1} which is still reasonably close to the expected value. Other choices of the numberings give what seem to be unreasonably large deviations from the predicted 500 cm^{-1} .

The data contained in Fig. 3 may be compared with the results of *ab initio* calculations which predict an equilibrium energy, T_e , of $80\,000 \text{ cm}^{-1}$ (Ref. 23) and a vertical transition energy of $90\,400^{28}$ or $92\,400 \text{ cm}^{-1}$.¹ Due to the large change in equilibrium geometry, vertical transitions should terminate in levels of high ν'_2 . The photoelectron spectra of H_2O ^{26,27} show that the vibrational overlap of $\tilde{X}(0,0,0)$ with levels of the 2A_1 ionic state is at a maximum about 8300 cm^{-1} higher in energy than the transition to $\nu'_2 = 1$. Applying this figure to our own data, we find that the expected maximum is at roughly $92\,400 \text{ cm}^{-1}$, in agreement with the quoted theoretical values for the vertical transition energy. We presume that our spectra reveal only levels of low ν'_2 because higher levels also have higher rates of dissociation.

Whereas for the 2A_1 state of the ion both even and odd quanta of ν'_2 are seen, including Π , Δ , and Φ bands, we have reliably identified only Σ bands. Close by some of the bands there are additional (red shifted) lines but these are broad and we have not been able to assign them; they may well be higher vibrations of other electronic states. This absence of lines with higher values of K' is explained as follows. The 1B_2 state can be considered as the upper component of a Π_g state split by the Renner-Teller effect. The other component of the splitting is the (as yet unobserved) $^1A_2(3p_a \leftarrow 1b_1)$ state mentioned above. It is known²⁹ that in a Renner-Teller splitting levels with $K \neq 0$ are not eigenfunctions of either

one of the two electronic potentials, but rather must be considered as existing on both surfaces simultaneously. Levels with $K = 0$, however, are confined to one or the other of the two surfaces. Since in this case the other electronic surface (1A_2) deriving from the Π state is expected to cause rapid dissociation, it is not surprising that levels which are subject to its potential (those with $K' > 0$) should dissociate before they can either emit a photon or absorb another to produce the ion. They will therefore be absent from the LIF and MPI spectra, leaving to be seen only those levels confined to the upper, bound, 1B_2 state.

Having found and partially characterized these levels we can now go on to use them as a tool to probe other surfaces. As matters now stand, most of our knowledge of any electronically excited state of water derives from transitions out of the ground state and is thus accurate only in the Franck-Condon region characterized by bent geometries of about 105° and bond lengths of about 0.96 \AA . It has, however, been shown that dispersed emission from states excited through two-photon absorption is strong enough to be used as an additional probe of the lower surfaces, allowing us to examine these surfaces in the different geometries assumed by the fluorescing states.^{24,25,30} The fluorescence from the levels reported herein is mainly associated with transitions to the \tilde{B} state. This state is not only important as the source of the "second continuum" but also, through surface crossings, strongly affects the photophysics of other electronic states.^{24,31} Accurate information concerning its linear configuration is particularly welcome since in this geometry there is an intersection with the \tilde{A} surface, providing a path of radiationless transfer which is followed by an estimated 50% of the molecules excited via the $\tilde{B} \leftarrow \tilde{X}$ transition. Such information should be forthcoming from an analysis of the ${}^1B_2 \rightarrow \tilde{B}$ emission.

CONCLUSIONS

We have identified several vibrational bands of the lowest electronic state of 1B_2 symmetry. The state is linear in its equilibrium geometry with a bond length of 1.02 \AA . The spectra are rotationally resolved and levels of low J' have a relatively long lifetime of at least several picoseconds. Only levels of $K' = 0$ are observed; levels of higher K' appear to be rapidly dissociated due to a Renner-Teller induced mixing with the dissociative 1A_2 state. The bending frequency is approximately 800 cm^{-1} for H_2O and 600 cm^{-1} for D_2O . We

expect to be able to use this state as a valuable probe of the lower, \tilde{B} , surface.

ACKNOWLEDGMENT

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- ¹ W. A. Goddard and W. J. Hunt, *Chem. Phys. Lett.* **24**, 464 (1974).
- ² N. Henriksen, J. Zhang, and D. G. Imre, *J. Chem. Phys.* **89**, 5607 (1988).
- ³ H.-t. Wang, W. S. Felps, and S. P. McGlynn, *J. Chem. Phys.* **67**, 2614 (1977).
- ⁴ S. Bell, *J. Mol. Spectrosc.* **16**, 205 (1965).
- ⁵ J. W. C. Johns, *Can. J. Phys.* **41**, 209 (1963).
- ⁶ J. W. C. Johns, *Can. J. Phys.* **49**, 944 (1971).
- ⁷ M. N. R. Ashfold, J. M. Bayley, and R. N. Dixon, *Chem. Phys.* **84**, 35 (1984).
- ⁸ M. N. R. Ashfold, J. M. Bayley, and R. N. Dixon, *Can. J. Phys.* **62**, 1806 (1984).
- ⁹ E. Ishiguro, M. Sasanuma, H. Masuko, Y. Morioda, and M. Nakamura, *J. Phys. B* **11**, 993 (1978).
- ¹⁰ P. Gurtler, V. Saile, and E. E. Koch, *Chem. Phys. Lett.* **51**, 386 (1977).
- ¹¹ K. Weide and R. Schinke, *J. Chem. Phys.* **90**, 7150 (1989).
- ¹² J. P. Connerade, M. A. Baig, S. P. McGlynn, and W. R. S. Garton, *J. Phys. B* **13**, L705 (1980).
- ¹³ A. R. Striganov and N. S. Sventitskii, *Table of Spectral Lines of Neutral and Ionized Atoms* (IFI/Plenum Data, New York, 1968).
- ¹⁴ W. M. McClain and R. A. Harris, in *Liquids and Gases in Excited States*, edited by E. C. Lim (Academic, New York, 1977), vol. III.
- ¹⁵ F. Metz, W. E. Howard, L. Wunsch, H. J. Neusser, and E. W. Schlag, *Proc. R. Soc. London Ser. A* **363**, 381 (1978).
- ¹⁶ R. N. Dixon, M. M. Bayley, and M. N. R. Ashfold, *Chem. Phys.* **84**, 21 (1984).
- ¹⁷ E. H. Abramson, J. Zhang, and D. G. Imre (to be published).
- ¹⁸ H. W. Kroto, *Molecular Rotation Spectra* (Wiley, New York, 1975).
- ¹⁹ W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.* **24**, 1139 (1956).
- ²⁰ J.-M. Flaud, C. Camy-Peyret, and A. Valentin, *J. Phys. (Paris)* **33**, 741 (1972).
- ²¹ F. W. Dalby and H. H. Nielsen, *J. Chem. Phys.* **25**, 934 (1956).
- ²² F. P. Dickey and J. M. Hoffman, *J. Chem. Phys.* **23**, 1718 (1955).
- ²³ G. Theodorakopoulos, I. D. Petsalakis, R. J. Buenker, and S. D. Peyerimhoff, *Chem. Phys. Lett.* **105**, 253 (1984).
- ²⁴ M. P. Docker, A. Hodgson, and J. P. Simons, *Mol. Phys.* **57**, 129 (1986).
- ²⁵ J. Zhang, E. H. Abramson, and D. G. Imre (to be published).
- ²⁶ L. Karlsson, L. Matsson, R. Jadrny, R. G. Albridge, S. Pinchas, T. Bergmark, and K. Siegbahn, *J. Chem. Phys.* **62**, 4745 (1975).
- ²⁷ R. N. Dixon, G. Duxbury, J. W. Rabalais, and L. Asbrink, *Mol. Phys.* **31**, 423 (1976).
- ²⁸ R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys. Lett.* **29**, 253 (1974).
- ²⁹ J. A. Pople and H. C. Longuet-Higgins, *Mol. Phys.* **1**, 372 (1958).
- ³⁰ V. Engel, G. Meijer, A. Bath, P. Andresen, and R. Schinke, *J. Chem. Phys.* **87**, 4310 (1987).
- ³¹ A. Hodgson, J. P. Simons, M. N. R. Ashfold, J. M. Bayley, and R. N. Dixon, *Mol. Phys.* **54**, 351 (1985).