A new electronic state of water revealed by gas phase multiphoton ionization spectroscopy

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A new electronic state of water revealed by gas phase multiphoton ionization spectroscopy[a)]

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The potential of multiphoton ionization (MPI) spectroscopy for unraveling details of the vacuum ultraviolet (VUV) absorption spectra of small polyatomic species (e.g., NH_3,[1,2] NO_2,[3] H_2O,[4] H_2S,[5] and CH_3[6]) is rapidly gaining recognition. Here we report the discovery, by this technique, of a new excited state of the water molecule. This state was populated by the simultaneous absorption of three monochromatic photons; subsequent absorption of a fourth photon during the lifetime of the excited state results in ion formation and detection.

Many excited electronic states of H_2O have been identified previously.[7] Two regions of continuous absorption, centered around 165 and 130 nm and assigned to the $3sa_1 \leftarrow 1b_1$ ($\tilde{A}\,^1B_1 \leftarrow \tilde{X}\,^1A_1$) and $3sa_1 \leftarrow 3a_1$ ($\tilde{B}\,^1A_1 \leftarrow \tilde{X}\,^1A_1$) excitations, respectively, are followed to shorter wavelengths by the structured $3pa_1 \leftarrow 1b_1$ ($\tilde{C}\,^1B_1 \leftarrow \tilde{X}\,^1A_1$)[4,8] and more diffuse $3pb_1 \leftarrow 1b_1$ ($\tilde{D}\,^1A_1 \leftarrow \tilde{X}\,^1A_1$) Rydberg features whose electronic origin bands in H_2O occur at ~124.1 and ~121.9 nm, respectively. The degeneracy of these two $3p \leftarrow 1b_1$ excitations is split by the asymmetry of the molecular core; the third ($^1A_2$) component of this $L = 1$ complex (which arises from the electric dipole forbidden $3pb_2 \leftarrow 1b_1$ electronic promotion) remains unobserved to date but is predicted[8] to lie at longer wavelengths (~128.5 nm). At still shorter wavelengths ($113 \geqslant \lambda \geqslant 110$ nm) transitions to at least two,[7,9] and possibly as many as four,[10,11] of the five possible $3d \leftarrow 1b_1$ Rydberg transitions in H_2O and D_2O have been reported.

In the present experiments static 10 Torr samples of previously vacuum distilled H_2O or D_2O vapor were contained in separate MPI cells equipped with parallel plate nickel electrodes and biased with ~120 V dc.

3 + 1 MPI spectra were obtained by focusing (20 cm f.l. lens) the linearly polarized output of an excimer pumped, intensity stabilized,[12] pulsed dye laser into these samples and recording the resulting positive ion current as a function of laser wavelength. Absolute wavelength calibration was provided by the optogalvanic signals from a neon hollow cathode lamp.

The vibronic bands of H_2O and D_2O which we associate with the new $\tilde{D}'$ electronic state all exhibit rotational structure and are prominent in 3 + 1 MPI. Spectral analysis is greatly simplified by the experimental observation that the bands virtually disappear under circularly polarized photoexcitation, indicating a dominant role for the first rank tensor component of the initial three photon transition probability[13] and thus the applicability of simple one photon selection rules and Honl–London rotational line strength factors. Figure 1(a) displays one vibronic band associated with this $\tilde{D}' \leftarrow \tilde{X}$ transition in H_2O. Rotational analysis identified this as a type C band, indicating an upper state of B_1 symmetry. The refined set of upper state rotational constants presented in the caption to the computer simulation of this particular band [Fig. 1(b)] was obtained by least squares fitting 39 resolved features in the experimental spectrum ($\sigma = 0.91$ cm^{-1}) and adopting literature values for the ground state rotational constants.[14] The analysis is borne out by the excellent accord between the experimental spectrum [Fig. 1(a)] and that calculated for just the b_1 first rank tensor component of the transition probability [Fig. 1(b)].[13]

No comparable features to the red of this band could be identified in the 3 + 1 MPI spectrum of H_2O or D_2O. This observation, and the fact that the equivalent, longest wavelength feature in the spectrum of D_2O shows a
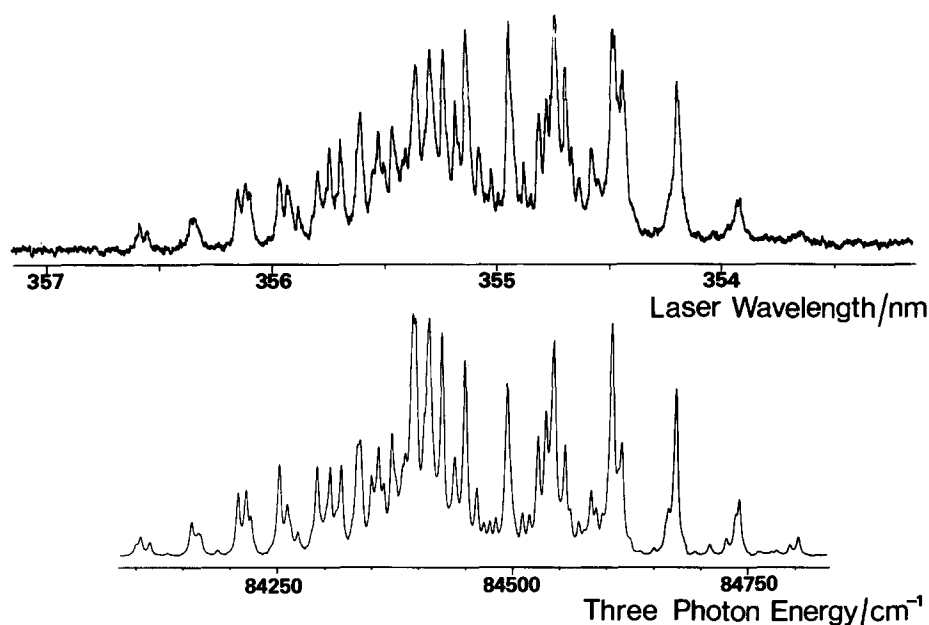
FIG. 1. (a) 3+1 MPI spectrum of H_2O ($\tilde{D}'-\tilde{X}$) origin transition together with (b) a simulation of this band using excited state rotational constants $A' = 31.30$, $B' = 11.31$, $C' = 8.09$, and $\Delta'_K = 0.062$ cm^{-1}; other quartic distortion constants were constrained to their ground state values.

similar isotope shift ($\nu_{H_2O} - \nu_{D_2O} = -212$ cm^{-1}) to that observed for the origin bands of the $\tilde{C}\,^1B_1-\tilde{X}\,^1A_1$ transitions in H_2O and D_2O,[8] encourages assignment of these two features to the respective $\tilde{D}'\,^1B_1-\tilde{X}\,^1A_1$ origin band transitions. Short progressions attributable to excitation of the upper state symmetric stretch ν'_1 and bending ν'_2 vibrations were discerned in both molecules: band origins and proposed vibronic assignments are listed in Table I. The limited extent of these excited state progressions, and the values of the rotational constants associated with the H_2O ($\tilde{D}'\,^1B_1$) zero-point level (consistent with HÔH ~ 114°), both reflect a comparatively small molecular geometry change upon electronic excitation.

Thus we conclude that the $\tilde{D}'$ state arises as a result of electron promotion from the highest occupied, nonbonding $1b_1$ molecular orbital rather than the strongly H—H bonding $3a_1$ orbital. The detailed identity of the acceptor orbital is less clear. Having decided, on the basis of geometry considerations, that the transition involves excitation of a $1b_1$ electron we are forced to assign the $\tilde{D}'$ state to a member of a Rydberg series converging on the first ionization potential ($101\,746 \pm 8$ and $101\,890 \pm 8$ cm^{-1} for H_2O and D_2O, respectively.[15] As-

suming, on energetic grounds, that its principal quantum number $n = 3$, the term values associated with the $\tilde{D}'$ origin bands in H_2O and D_2O are consistent with a quantum defect $\delta \sim 0.48$. Whilst such a value for a quantum defect is ordinarily considered typical for excitation of a nonbonding electron to a p-type Rydberg orbital,[16] such an assignment appears unlikely in this particular case as the only possible singlet state of B_1 symmetry arising from a $3p$ Rydberg orbital is already characterized—the well documented $\tilde{C}\,^1B_1$ state ($\delta \sim 0.72$).[4,8] Tentatively, therefore, we propose that this new $\tilde{D}'\,^1B_1$ excited state arises via a $3da_1 \leftarrow 1b_1$ electronic promotion. A more complete spectroscopic analysis of the vibronic bands associated with this hitherto undocumented electronic transition in water, together with discussion of the predissociation mechanisms operating within the excited $\tilde{D}'$ state, will be the subject of a future, longer publication.

TABLE I. Frequencies (in cm^{-1}) and assignments of vibronic levels observed in the $\tilde{D}'\,^1B_1-\tilde{X}\,^1A_1$ transitions in H_2O and D_2O.

| Excited state | Origin frequency | |
vibronic level	H_2O	D_2O
(000)	$84\,434 \pm 2$	$84\,646 \pm 2$
(010)	$85\,574 \pm 6$	$85\,502 \pm 2$
(020)	$86\,852 \pm 6$	•••
(100)	$87\,434 \pm 15$	$86\,812 \pm 2$
(110)	•••	$87\,718 \pm 6$

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Rotational spectroscopic constants and structure of the mercury–hydrogen chloride van der Waals complex

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We have made high resolution measurements of the rotational transitions of nine isotopic forms of a weakly bound 1:1 gas phase complex formed between mercury and hydrogen chloride. The experimental technique used here is pulsed Fourier transform microwave spectroscopy carried out in a Fabry–Perot cavity.[1,2] For this experiment we used a Fabry–Perot spectrometer that had been previously used to make rotational Stark measurements.[3] In addition to removing the Stark plates, modifications to the spectrometer included the placement of a cold trap in the vacuum line between the diffusion pump and the rough pump, and the use of a solenoid gas valve with a mercury reservoir that can be heated to 250°C. This valve incorporates a modified General Valve model 8-14-900 solenoid to produce the gas pulse, and will be described in a later report.

The data set consists of 21 measured R branches, each consisting of two doubly degenerate $\Delta F = +1$ transitions resulting from the chlorine nuclear quadrupole interaction. For ^{198}Hg (10%), ^{199}Hg (17%), ^{200}Hg (23%), ^{202}Hg (30%), and ^{204}Hg (7%) complexed to H^{35}Cl the $J = 5 \to 6$, $6 \to 7$, and $7 \to 8$ transitions were measured. For ^{200}Hg and ^{202}Hg complexed to H^{37}Cl the $J = 6 \to 7$ and $J = 7 \to 8$ transitions were measured, and the $J = 6 \to 7$ transitions were measured for ^{198}HgH^{37}Cl and ^{199}HgH^{37}Cl. In Fig. 1 we show a power spectrum of the $J = 6 \to 7$, $\Delta F = +1$ components of ^{202}HgH^{37}Cl.

The observed data were fit to the $K = 0$ symmetric top Hamiltonian given by[4]

$$H = \bar{B}_0 J(J+1) - D_J J^2(J+1)^2 + \mathbf{V} : \mathbf{Q} , \qquad (1)$$

where $\bar{B}_0$ is the rotational constant, D_J is the centrifugal distortion constant, and $\mathbf{V}$ and $\mathbf{Q}$ are the electric field gradient and nuclear quadrupole moment tensors for the chlorine nucleus. Fitting the observed transitions to Eq. (1) gives the vibrational ground state constants for ^{202}HgH^{35}Cl: $\bar{B}_0 = 998.0064(2)$, $D_J = 0.003697(1)$, and χ_{aa} (^{35}Cl) $= -40.350(94)$, and for ^{202}HgH^{37}Cl: $\bar{B}_0 = 953.0469(8)$, $D_J = 0.003375(6)$, and χ_{aa} (^{37}Cl)

$= -31.894(400)$, in units of MHz, where χ_{aa} is the chlorine nuclear quadrupole coupling constant. These spectroscopic constants are consistent with a mercury-to-chlorine distance of 4.097 Å, with an average angle between the HCl figure axis and the Hg–HCl center of mass axis of 31°, obtained as $\arccos(\langle\cos^2\theta\rangle)^{1/2}$, as in the rare gas–hydrogen halide systems.[2] The chlorine substitution data are consistent only with the proton being located between the two heavy atoms.

The heavy atom separation of 4.097 Å in HgHCl exceeds the corresponding value of 4.006 Å in ArHCl[5] by about 0.09 Å, giving an effective van der Waals radius for mercury in mercury–hydrogen chloride of 1.99 Å. This result falls within the range of 1.7–2.0 Å proposed
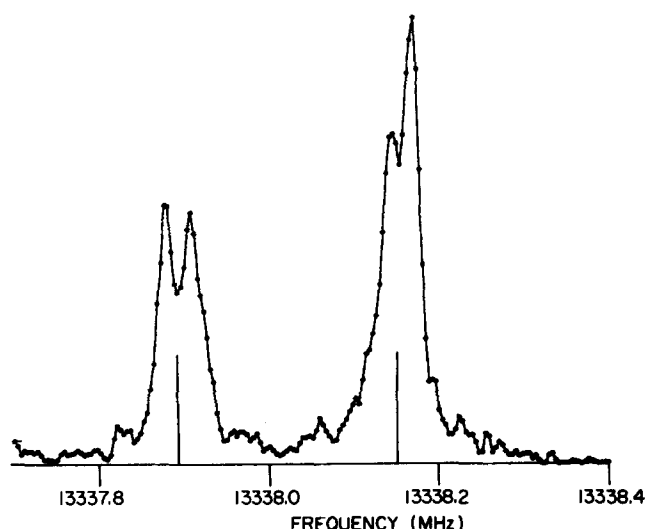

FIG. 1. Power spectrum of the ^{202}HgH^{37}Cl $J = 6 \to 7$, $F = 7/2$, $9/2 \to F' = 9/2$, $11/2$, and $F = 11/2$, $13/2 \to F' = 13/2$, $15/2$ transitions at 13.3 GHz. Doppler splitting is resolved. Vertical bars mark the frequencies to be reported. Data was taken in 1 min.