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A new analysis of the ν_2 fundamental band of H_2O^+*

Zheng Rui(郑 锐), Li Song(李 松), Hou Shun-Yong(侯顺永),
Huang Guang-Ming(黄光明), and Duan Chuan-Xi (段传喜)†

College of Physical Science and Technology, HuaZhong Normal University, Wuhan 430079, *China*

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This paper reports that the absorption spectra of H_2O^+ have been measured by tunable mid-infrared diode laser spectroscopy in the spectral range of 1100–1380 cm^{-1}. The H_2O^+ ions are generated in an AC glow discharge of the gaseous mixtures of H_2O/He and detected with the velocity modulation technique. Forty new lines are assigned to the ν_2 fundamental band of H_2O^+ ($\tilde{X}^2B_1$). The observed lines together with other data published previously are fitted to the standard effective Hamiltonian of an asymmetric top, yielding a set of improved rotational constants, spin-rotation constants and their quartic and sextic centrifugal distortion constants for the ν_2=1 vibrational state of H_2O^+.

Keywords: infrared spectra, water cations, rotational analysis
PACC: 3320E, 3520P, 3310E

1. Introduction

The water cation (H_2O^+) has been extensively studied for many decades since it was postulated to be present in comet tails by Whipple in 1950.[1] The first high resolution electronic emission spectrum of the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ band system of H_2O^+ was reported by Lew and Heiber in 1973.[2] Later, Lew performed a detailed analysis of the emission spectrum in 1976.[3] The high resolution absorption spectrum of H_2O^+ has been reported in visible,[4,5] near-infrared,[6,7] mid-infrared,[8−10] and far-infrared region.[11,12] Das and Farley[4] and Wu *et al*[5] measured the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ transition in the visible range with a dye laser. Huet *et al*[6] and Gan *et al*[7] measured the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ transition in the near-infrared range with a Ti : Sapphire laser. Dinelli *et al* observed the ν_3 band in the region 3100–3400 cm^{-1} with a tunable difference frequency spectrometer.[8] Brown *et al* recorded the ν_2 and $2\nu_2 - \nu_2$ bands in the region 1270–1750 cm^{-1} with a diode laser spectrometer.[9] Huet *et al* measured the ν_1 and $\nu_2 + \nu_3 - \nu_2$ bands in the region 3180–3390 cm^{-1} with a colour centre laser spectrometer.[10] The far-infrared laser magnetic resonance spectroscopy has also been used to measure the pure rotational transitions of H_2O^+ in the ground state.[11,12]

From a theoretic point of view, H_2O^+ is also a prototype for studying the Renner–Teller effect. The ground and the first excited electronic states of H_2O^+ are degenerated into a $^2\Pi_u$ state in the linear configuration. Several *ab initio* calculations have been carried out on this system.[13−17] Among them, the calculations by Weiss *et al*[16] and Brommer *et al*[17] were widely used to guide and compare with the experimental measurement. Recently, Wu *et al* performed an *ab initio* calculations of the electronic dipole moment components for the $\tilde{A}^2A_1$ and $\tilde{X}^2B_1$ electronic states and the electronic transition moment for the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ transition of H_2O^+.[18]

During our previous work on H_3O^+, we observed some lines of molecular ions which could not be assigned to the $\nu_2(1^- \leftarrow 0^+)$ band of H_3O^+.[19] They were most probably from the ν_2 fundamental or hot bands of H_2O^+ in a glow discharge of the mixtures of H_2O/He. Though Brown *et al* have derived a set of molecular constants for the $\nu_2 = 0$, 1 and 2 vibrational states by recording 85 lines of the ν_2 fundamental band and 20 lines of the $2\nu_2 - \nu_2$ hot–band of H_2O^+ in the region 1270–1750 cm^{-1},[9] the discrepancies between our observed line positions and the predicted frequencies based on their molecular parameters were quite large. Therefore we performed a spectral scan from 1100 to 1380 cm^{-1} with our available laser diodes in order to make an extension to their measurement and refine the molecular parameters.

In this paper, we present a new measurement and

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†Corresponding author. E-mail: cxduan@phy.ccnu.edu.cn

analysis of the ν_2 fundamental band of H_2O^+. Our observed lines together with those reported in Ref.[9] are fitted to the standard effective Hamiltonian of an asymmetric top. It derives a set of improved rotational constants, spin-rotation constants and their quartic and sextic centrifugal distortion constants for the $\nu_2 = 1$ vibrational state of H_2O^+.

2. Experiment

The tunable mid-infrared diode laser spectrometer used to investigate the absorption spectra of H_2O^+ is identical to that used in our previous work on H_3O^+[19] and D_2O^+[20]. The velocity modulation technique is used to eliminate signals from neutral species.[21] Briefly, the mid-infrared radiations are emitted from a tunable lead-salt diode laser which is mounted in a liquid-nitrogen cooled Dewar (Model L5736, Laser Components). After a single pass through a 10 mm bore, 1 m long water-cooled discharge cell, the main part of the laser beam is detected by a liquid-nitrogen cooled HgCdTe detector. A small portion of laser beam is reflected by the front CaF_2 window of the discharge cell. Then it is modulated by a mechanical chopper at a frequency of about 600 Hz. This chopped beam is split into two parts further before they transmit through a referential gas cell and a Ge etalon separately. The absorption of the reference gas and the interference fringes are also detected by two liquid-nitrogen cooled HgCdTe detectors. Three lock-in amplifiers are used to demodulate signals from three HgCdTe detectors separately. The scan of the current of the diode laser and the data acquisition from three lock-in amplifiers are controlled by a home-developed LabView program simultaneously.

In this paper, the H_2O^+ ions were generated by an AC glowed discharge with a flowing gas mixture of distilled water vapour and high-purity helium ($> 99.999\%$). The typical discharge frequency and peak-to-peak current were 42 kHz and 300 mA respectively. The optimal gas mixture was at a total pressure of $\sim$1.5 Torr (1 Torr = 133 Pa), which was measured by a Pirani vacuum gauge at the downstream of the discharge cell. The H_2O^+ ions have been also observed in a $He/H_2/O_2$ discharge.[8−10] The main differences of the plasma chemistry between these two discharge systems have been qualitatively illustrated by Huet *et al.*[10] Four laser diodes were used to cover about 20% of the 1100–1380 cm^{-1} region. The absorption spectra of H_2O^+ were calibrated by using the accurate line positions of N_2O and SO_2 from the HITRAN database[22] and the Ge etalon fringes (FSR $\sim$ 0.049 cm^{-1}). The absolute accuracy of the calibration was estimated to be better than 0.005 cm^{-1}.

3. Results and analysis

Under the experimental conditions described above, more than one hundred lines of molecular ions were recorded in the range 1100–1380 cm^{-1}, in which 40 new lines were assigned to the ν_2 fundamental band of H_2O^+ with the aid of molecular parameters reported in Ref.[9]. Fourteen lines were re-measured at better accuracy. The measured frequencies and their assignment are listed in Table 1. Due to our improved signal-to-noise ratio, some blended lines reported in Ref.[9] were well resolved in this work, as shown in Fig.1.

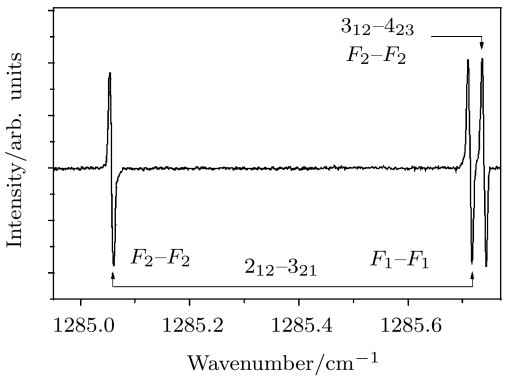


Fig.1. A typical spectrum of the ν_2 fundamental band of H_2O^+. The assigned transitions are $2_{12}F_2 \leftarrow 3_{21}F_2$ (1285.059 cm^{-1}), $2_{12}F_1 \leftarrow 3_{21}F_1$ (1285.713 cm^{-1}) and $3_{12}F_2 \leftarrow 4_{23}F_2$ (1285.739 cm^{-1}). The latter two transitions are well resolved in this work, but were blended with each other in Ref.[9] and observed at 1285.713 cm^{-1}.

Table 1. Transitions of the ν_2 fundamental band of H_2O^+.

N'	K'_a	K'_c	J'	N''	K''_a	K''_c	J''	Obs./cm^{-1}	Obs. - Calc./$10^{-3}cm^{-1}$
5	3	3	5.5	6	4	2	6.5	1193.067[a]	–10
5	3	3	4.5	6	4	2	5.5	1193.081[a]	6
6	2	4	5.5	7	3	5	6.5	1205.111[a]	6
6	2	4	6.5	7	3	5	7.5	1205.395[a]	11

Table 1 *Continued*

N'	K'_a	K'_c	J'	N''	K''_a	K''_c	J''	Obs./cm^{-1}	Obs. - Calc./10^{-3}cm^{-1}
4	2	3	4.5	5	3	2	5.5	1224.693[a]	16
8	1	7	8.5	9	2	8	9.5	1231.022[a]	0
8	1	7	7.5	9	2	8	8.5	1231.081[a]	3
3	3	1	3.5	4	4	0	4.5	1236.775[a]	–1
3	3	0	3.5	4	4	1	4.5	1236.830[a]	0
3	3	1	2.5	4	4	0	3.5	1237.088[a]	0
3	3	0	2.5	4	4	1	3.5	1237.141[a]	0
8	0	8	8.5	9	1	9	9.5	1245.328[a]	–1
8	0	8	7.5	9	1	9	8.5	1245.432[a]	3
3	2	2	2.5	4	3	1	3.5	1248.748[a]	–3
3	2	2	3.5	4	3	1	4.5	1249.019[a]	0
3	2	1	3.5	4	3	2	4.5	1252.144[a]	–1
3	1	3	2.5	4	2	2	3.5	1252.541[a]	0
3	1	3	3.5	4	2	2	4.5	1253.167[a]	0
8	2	7	7.5	9	1	8	8.5	1253.243[a]	–5
2	2	1	1.5	3	3	0	2.5	1271.516[a]	0
2	2	1	2.5	3	3	0	3.5	1271.618[a]	–3
2	2	0	1.5	3	3	1	2.5	1272.136[a]	1
2	2	0	2.5	3	3	1	3.5	1272.237[a]	–3
4	1	3	3.5	5	2	4	4.5	1272.901[a]	–1
8	1	8	8.5	8	2	7	8.5	1279.167[a]	–11
6	0	6	6.5	7	1	7	7.5	1279.188[a,c]	–11
6	0	6	5.5	7	1	7	6.5	1279.277[a,c]	2
2	1	2	1.5	3	2	1	2.5	1285.059[a]	–2
2	1	2	2.5	3	2	1	3.5	1285.713[a,c]	–4
3	1	2	2.5	4	2	3	3.5	1285.739[a,c]	0
3	1	2	3.5	4	2	3	4.5	1286.142[b]	2
8	0	8	7.5	8	1	7	7.5	1287.300[b,d]	–49
8	0	8	8.5	8	1	7	8.5	1287.768[a]	6
5	0	5	4.5	6	1	6	5.5	1294.918[b]	–10
5	0	5	5.5	6	1	6	6.5	1294.999[b]	–7
7	1	7	6.5	7	2	6	6.5	1295.035[b]	–2
7	1	7	7.5	7	2	6	7.5	1295.583[b]	–1
2	1	1	1.5	3	2	2	2.5	1300.551[b]	–1
2	1	1	2.5	3	2	2	3.5	1301.071[b]	–3
5	1	5	5.5	6	0	6	6.5	1302.414[a,c]	–4
5	1	5	4.5	6	0	6	5.5	1302.571[a,c]	–2
7	0	7	7.5	7	1	6	7.5	1308.744[a]	14
4	0	4	3.5	5	1	5	4.5	1309.859[a,c]	5
4	0	4	4.5	5	1	5	5.5	1309.937[a,c]	6
6	1	6	5.5	6	2	5	5.5	1310.064[a]	–3
6	1	6	6.5	6	2	5	6.5	1310.642[b]	3
1	1	1	0.5	2	2	0	1.5	1312.728[b]	1
1	1	1	1.5	2	2	0	2.5	1313.334[b]	–3
6	4	2	5.5	6	5	1	5.5	1315.175[a]	–1
6	4	2	6.5	6	5	1	6.5	1315.301[a]	1
7	2	6	7.5	7	3	5	7.5	1316.877[b]	–5
1	1	0	0.5	2	2	1	1.5	1317.563[b]	10

Table 1 *Continued*

N'	K'_a	K'_c	J'	N''	K''_a	K''_c	J''	Obs./cm^{-1}	Obs. - Calc./10^{-3}cm^{-1}
1	1	0	1.5	2	2	1	2.5	1318.064[b]	1
5	3	3	5.5	5	4	2	5.5	1320.807[b]	0
4	3	1	3.5	4	4	0	3.5	1321.642[b,d]	323
4	3	1	4.5	4	4	0	4.5	1321.759[b]	0
5	3	2	5.5	5	4	1	5.5	1322.029[b]	4
4	1	4	4.5	5	0	5	5.5	1322.175[b]	0
4	1	4	3.5	5	0	5	4.5	1322.391[b]	2
6	3	3	6.5	6	4	2	6.5	1323.162[a]	–3
5	1	5	4.5	5	2	4	4.5	1323.388[b]	3
5	2	4	5.5	6	1	5	6.5	1323.808[a]	9
5	1	5	5.5	5	2	4	5.5	1324.001[a,c]	0
3	0	3	2.5	4	1	4	3.5	1324.097[b]	5
3	0	3	3.5	4	1	4	4.5	1324.248[b]	7
7	3	4	6.5	7	4	3	6.5	1325.266 [b,d]	81
5	2	4	4.5	5	3	3	4.5	1328.375[b]	1
5	2	4	5.5	5	3	3	5.5	1328.830[b]	1
6	0	6	5.5	6	1	5	5.5	1328.872[b]	2
6	0	6	6.5	6	1	5	6.5	1329.211[b]	9
3	2	2	3.5	3	3	1	3.5	1334.356[a,c]	2
4	1	4	3.5	4	2	3	3.5	1334.688[a,c]	–4
4	1	4	4.5	4	2	3	4.5	1335.372[a,c]	–9
2	0	2	1.5	3	1	3	2.5	1338.392[b]	–2
4	2	2	4.5	4	3	1	4.5	1339.503[b]	2
8	1	7	8.5	8	2	6	8.5	1340.772[a]	–11
5	2	3	4.5	5	3	2	4.5	1343.064[a]	–10
3	1	3	2.5	4	0	4	3.5	1343.355[a]	–14
3	1	3	3.5	3	2	2	3.5	1344.606[b]	1
2	1	2	2.5	2	2	1	2.5	1351.526[b]	–1
7	2	5	6.5	7	3	4	6.5	1351.984[b]	–5
7	2	5	7.5	7	3	4	7.5	1352.281[b]	–6
1	0	1	1.5	2	1	2	2.5	1354.064[a,c]	4
8	2	6	8.5	8	3	5	8.5	1354.077[a]	8
6	1	5	5.5	6	2	4	5.5	1361.607[b]	8
6	1	5	6.5	6	2	4	6.5	1361.833[b]	–3
2	1	1	1.5	2	2	0	1.5	1362.314[b]	1
4	0	4	4.5	4	1	3	4.5	1363.567[b]	4
5	1	4	4.5	5	2	3	4.5	1366.171[a]	1
3	1	2	3.5	3	2	1	3.5	1366.192[a]	0
5	1	4	5.5	5	2	3	5.5	1366.474[a]	–8
4	1	3	3.5	4	2	2	3.5	1367.248[b]	–1
4	1	3	4.5	4	2	2	4.5	1367.673[b]	–5
0	0	0	0.5	1	1	1	1.5	1371.206[a,c]	1
3	0	3	2.5	3	1	2	2.5	1374.935[b]	4
2	0	2	1.5	2	1	1	1.5	1382.782[b]	2
2	0	2	2.5	2	1	1	2.5	1383.286[b]	4
5	2	4	5.5	4	3	1	4.5	1434.414[b]	7
1	1	1	0.5	0	0	0	0.5	1450.851 [b]	2

Table 1 *Continued*

N'	K'_a	K'_c	J'	N''	K''_a	K''_c	J''	Obs./cm^{-1}	Obs. - Calc./10^{-3}cm^{-1}
3	0	3	2.5	2	1	2	1.5	1454.826[b]	–1
3	0	3	3.5	2	1	2	2.5	1455.126[b]	4
2	1	2	2.5	1	0	1	1.5	1466.346[b]	–13
4	2	2	4.5	4	1	3	4.5	1468.959[b]	–4
5	2	3	5.5	5	1	4	5.5	1469.888[b]	–10
4	2	2	3.5	4	1	3	3.5	1469.992[b]	4
2	2	0	2.5	2	1	1	2.5	1474.109[b]	–2
6	2	4	6.5	6	1	5	6.5	1474.844[b]	2
4	0	4	4.5	3	1	3	3.5	1476.678[b]	9
2	2	0	1.5	2	1	1	1.5	1476.823 [b,d]	60
3	1	3	2.5	2	0	2	1.5	1481.556[b]	–4
3	1	3	2.5	2	0	2	2.5	1481.733[b,d]	37
7	2	5	6.5	7	1	6	6.5	1485.070[b]	–4
2	2	1	2.5	2	1	2	2.5	1485.302[b]	1
3	2	2	3.5	3	1	3	3.5	1491.607[b]	19
3	2	2	2.5	3	1	3	2.5	1493.171[b]	–3
4	2	3	3.5	3	1	2	2.5	1552.053[b]	–0
3	2	1	2.5	2	1	2	1.5	1552.154[b]	2
8	2	7	7.5	8	1	8	7.5	1552.365[b]	10
5	2	4	5.5	4	1	3	4.5	1563.864[b]	–5
4	2	2	3.5	3	1	3	2.5	1583.320[b]	1
3	3	1	3.5	2	2	0	2.5	1596.114[b]	–6
3	3	0	3.5	2	2	1	2.5	1596.795[b]	6
4	3	1	3.5	3	2	2	2.5	1620.706[b]	–5
4	4	0	3.5	3	3	1	2.5	1677.566[b]	1

[a]: From this work.
[b]: From Ref.[9].
[c]: Lines are also reported in Ref.[9] but our measured frequencies are adopted in the final fit.
[d]: Lines are not in accord with the others and omitted in the final fit.

H_2O^+ has three vibrational modes in the $\tilde{X}^2B_1$ state: symmetric stretching (ν_1), bending (ν_2) and asymmetric stretching (ν_3). The ν_2 fundamental mode obeys the b-type selection rules for an asymmetric top: $\Delta N = 0, \pm 1$; $\Delta K_a = \pm 1(\pm 3, \pm 5, \ldots)$; $\Delta K_c = \pm 1(\pm 3, \pm 5, \ldots)$. The interaction of the single unpaired electron and the rotation motion splits each rotational level into two spin components (F_1: $J = N+1/2$; F_2: $J = N - 1/2$). The $\Delta J = \Delta N$ doublets have the dominant intensity while the $\Delta J \neq \Delta N$ doublets only have reasonable intensity at low N. The nuclear spin of the hydrogen atom ($I = 1/2$) gives a nuclear spin statistical weight of 3 for rotational levels with (K_a, K_c) = (e, e), (o, o), and 1 for levels with (K_a, K_c) = (e, o), (o, e), when the vibrational eigenfunction of the lower level is totally symmetric.

The rotational structure of the ground and $\nu_2 = 1$ vibrational states of H_2O^+ ($\tilde{X}^2B_1$) can be described by the A-reduced asymmetric top Hamiltonian H_R of Watson[23] with additional A-reduced spin-rotation Hamiltonian H_{SR} of Brown and Sears:[24]

$$\begin{aligned} H_R = {} & AN_a^2 + BN_b^2 + CN_c^2 - \Delta_N N^4 \\ & - \Delta_{NK} N^2 N_a^2 - \Delta_K N_a^4 \\ & - \frac{1}{2}[\delta_N N^2 + \delta_K N_a^2, (N_+^2 + N_-^2)]_+ \\ & + H_N N^6 + H_{NK} N^4 N_a^2 \\ & + H_{KN} N^2 N_a^4 + H_K N_a^6 + \ldots, \qquad (1) \\ H_{SR} = {} & \varepsilon_{aa} N_a S_a + \varepsilon_{bb} N_b S_b + \varepsilon_{cc} N_c S_c \\ & + \Delta_N^S N^2 (N \cdot S) + \frac{1}{2}\Delta_{NK}^S [N^2, N_a S_a]_+ \\ & + \Delta_{KN}^S N_a^2 (N \cdot S) + \Delta_K^S N_a^3 S_a + \ldots, \qquad (2) \end{aligned}$$

where A, B, C are rotational constants, Δ_N, Δ_{NK}, Δ_K, δ_N, δ_K are quartic rotational centrifugal distortion constants, and H_N, H_{NK}, H_{KN}, H_K are sextic rotational centrifugal distortion constants; ε_{aa}, ε_{bb}, ε_{cc} are spin-rotation interaction constants, and Δ_N^S,

Δ^S_{NK}, Δ^S_{KN}, Δ^S_K are quartic spin-rotational centrifugal distortion constants.

Our measured lines together with those reported in Ref.[9] were used to determine molecular parameters for the ground and $\nu_2 = 1$ vibrational states of H_2O^+ simultaneously by using Pickett's program SPFIT.[25] In the final fit, 120 lines were fitted to 35 parameters. Five lines measured by Brown *et al* were excluded from the fit since they were not in accord with the others.[9] Our measured frequencies were adopted for those re–measured 14 lines. The standard deviation of the fit was $0.0057\,cm^{-1}$, close to the accuracy of measurement. The resulting parameters are listed in Tables 2 and 3. The differences between all the observed line positions and their calculated values are listed in Table 1.

Table 2. The molecular constants (in cm^{-1}) for the ground vibrational state of H_2O^+. (Figures in parentheses represent one standard deviation in units of the last digit.)

Parameter	This work	Ref.[9]	Ref.[10]	Ref.[3]	Ref.[12]
A	29.03970(57)	29.0366(37)	29.0359(21)	29.0256(9)	29.039508(19)
B	12.41917(22)	12.4170(15)	12.42298(58)	12.4224(5)	12.420949(14)
C	8.46877(24)	8.4684(13)	8.46921(58)	8.4693(5)	8.468088(14)
$10^3\Delta_N$	0.9515(58)	0.937(50)	1.015(13)	1.000(7)	0.97396(30)
$10^3\Delta_{NK}$	–5.037(33)	–5.63(19)	–5.007(71)	–4.73(3)	–5.0788(32)
$10^3\Delta_K$	45.466(80)	45.72(73)	44.20(63)	41.87(6)	45.7162(81)
$10^3\delta_N$	0.34916(89)	0.312(10)	0.3817(24)	0.3700(3)	0.37477(28)
$10^3\delta_K$	1.689(13)	1.60(12)	1.795(50)	1.97(6)	1.9308(52)
10^6H_N	0.334(42)	1.89(60)	0.33(14)	–	–
10^6H_{NK}	–7.15(44)	–9.7(29)	–5.1(11)	–	–
10^6H_{KN}	–4.03(90)	52(21)	–	–	–24.21(26)
10^5H_K	20.52(30)	20.3(27)	15.1(44)	–	25.935(95)
ε_{aa}	–1.0763 (19)	–1.1049(72)	–1.0882(43)	–1.092(6)	–1.088215(63)
ε_{bb}	–0.1153(11)	–0.1237(37)	–0.1130(19)	–0.120(3)	–0.114439(41)
$10^3\varepsilon_{cc}$	3.06(81)	–6.1(25)	3.2(19)	4(3)	1.294(41)
$10^3\Delta^s_{KN}$	–0.307(36)	–0.98(4)	–0.72(23)	–	–0.543(12)
$10^3\Delta^S_K$	5.83(14)	12.6(8)	6.32(71)	5.0(3)	7.456(28)

Table 3. The molecular constants (in cm^{-1}) for the $\nu_2 = 1$ vibrational state of H_2O^+. (Figures in parentheses represent one standard deviation in units of the last digit.)

Parameter	This work	Ref.[9]	Ref.[3]
A	33.40521(73)	33.3930(42)	33.3601(20)
B	12.47766(24)	12.4765(12)	12.4765(12)
C	8.31554(24)	8.3138(11)	8.3188(20)
$10^3\Delta_N$	1.0247(68)	0.944(44)	1.22(10)
$10^3\Delta_{NK}$	–7.850(41)	–8.13(29)	–7.35(31)
$10^3\Delta_K$	97.37(12)	92.6(10)	82.13(32)
$10^3\delta_N$	0.39854(97)	0.372(8)	0.26(7)
$10^3\delta_K$	4.579(18)	5.00(18)	4.96(43)
10^6H_N	0.479(62)	1.34(57)	–
10^6H_{NK}	–32.27(48)	–3.7(7)	–
10^6H_{KN}	14.3(32)	–13.5(59)	–
10^5H_K	106.26(68)	94.1(36)	–
ε_{aa}	–1.6158(24)	–1.621(10)	–1.645(10)
ε_{bb}	–0.1171(11)	–0.1349(39)	–0.125(4)
$10^3\varepsilon_{cc}$	3.55(93)	–9.4(28)	13(5)
$10^3\Delta^s_{KN}$	–1.04(11)	2.92(72)	–
$10^3\Delta^S_K$	17.33(33)	7.05(205)	18(13)
ν_0	1408.4074(14)	1408.4153(65)	1408.404(10)

4. Discussion and conclusions

Molecular constants for the ground state of H_2O^+ are compared with previous studies in Table 2. Our results are more precise than those of Brown *et al*[9] from the analysis of the ν_2 fundamental band, and those of Huet *et al*[10] from the analysis of the combination differences from the ν_1 and ν_3 fundamental bands and the electronic emission spectrum. The rotational constants and quartic centrifugal distortion rotational constants from our fit are very close to those of Mürtz *et al* from a weighted nonlinear, least–squares analysis with the LMR data and the combination differences from the ν_3 band and the electronic emission spectrum.[12] We didn't fix the molecular parameters for the ground vibrational state at the values reported in Ref.[12] in our fitting, because transitions with $N = 9$ and $K_a = 5$ have been measured in this work, but their term values cannot be extrapolated accurately with the molecular parameters reported in Ref.[12]. All the sextic rotational centrifugal distortion constants have been determined significantly in this work.

Molecular constants for the $\nu_2 = 1$ vibrational state are compared with those of Brown *et al*[9] and of Lew[3] in Table 3. Our results show better precision than others. The band centre of the ν_2 fundamental band was determined to be $1408.4074(14)\,cm^{-1}$, which agrees well with the value $1408.4153(65)\,cm^{-1}$ determined by Brown *et al.*[9]

In summary, we have reported an extension of the previous measurement of the ν_2 fundamental band of H_2O^+. Forty new lines have been assigned and analysed together with the data published previously. Molecular constants for the $\nu_2 = 1$ vibrational state have been better determined, which can be used to characterize the rotational levels up to $N = 9$ and K_a =5 precisely.

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