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► **To cite this version:**

Alain Campargue, Samir Kassi, Andrey Yachmenev, Aleksandra A Kyuberis, Jochen Küpper, et al..
Observation of electric-quadrupole infrared transitions in water vapor. *Physical Review Research*,
2020, 2 (2), 10.1103/PhysRevResearch.2.023091 . hal-03337249

HAL Id: hal-03337249

<https://hal.science/hal-03337249>

Submitted on 22 Nov 2021

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1 Observation of electric-quadrupole infrared transitions in water vapour
2

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31 **Key words:** electric-quadrupole transitions, absorption spectroscopy, water, cavity ring down
32 spectroscopy

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35 Number of Pages: 15

36 Number of Figures: 4

37 Number of Tables: 2

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44 *Molecular absorption of infrared radiation is generally due to ro-vibrational electric-dipole*
45 *transitions. Electric-quadrupole transitions may still occur, but they are typically a million times*
46 *weaker than electric-dipole transitions, rendering their observation extremely challenging. In*
47 *polyatomic or polar diatomic molecules, ro-vibrational quadrupole transitions have never been*
48 *observed. Here, we report the first direct detection of quadrupole transitions in water vapor. The*
49 *detected quadrupole lines have intensity largely above the standard dipole intensity cut-off of*
50 *spectroscopic databases and thus are important for accurate atmospheric and astronomical remote*
51 *sensing.*

52 Spectroscopic techniques in the IR domain have advanced significantly in recent years
53 providing exciting opportunities for new generation of accurate and sensitive measurements.
54 Quadrupole electronic and ro-vibrational transitions have been detected in a number of atoms [1,2] and
55 homonuclear diatomic molecules [3,4,5], respectively, for states that cannot undergo electric dipole
56 transitions. Electric-quadrupole transitions are used for remote sensing of important diatomic
57 molecules, such as hydrogen, oxygen, and nitrogen, in spectra of Earth's atmosphere and other
58 environments [4,6,7]. When compared with dipole transitions, quadrupole transition rates are typically
59 smaller by a factor ranging from 10^8 in the IR to 10^5 in the optical spectral domain. Such extremely
60 long mean lifetimes against spontaneous emission of quadrupole excitations make them ideal
61 candidates for next-generation atomic clocks [8], high-precision tests of molecular physics [9,10,11],
62 and quantum information processing [8,12].

63 In most heteronuclear diatomic and polyatomic molecules the ro-vibrational states can be
64 excited both *via* dipole and quadrupole transitions. The dipole and quadrupole moment operators have
65 distinct selection rules. The dipole moment connects states with different parity, while for the
66 quadrupole transitions, the parity is conserved. Furthermore, states with rotational quantum numbers J
67 differing by ± 2 can only be connected by a quadrupole transition. This difference in selection rules
68 permits, in principle, the observation of well-isolated quadrupole lines. Nevertheless, in practice the
69 detection of quadrupole lines is made difficult by the fact that, even if transition frequencies differ, the
70 quadrupole lines are drowned in the line profile of the much stronger dipole lines.

71 To the best of our knowledge, quadrupole transitions have never been detected in polyatomic
72 molecules until now, although the quadrupole moment of some polyatomic molecules (CO_2 , NO_2 ,
73 OCS) have been measured using electric-field-gradient-induced birefringence method [13]. Nowadays,
74 spectroscopic line lists of the major greenhouse gas absorbers such as water vapour and carbon
75 dioxide, are limited to dipole transitions [14]. A highly-accurate and complete characterization of ro-
76 vibrational spectra of these molecules is needed for the modeling and understanding of Earth's
77 atmosphere, climate, and many remote sensing experiments [15]. At present, adequate models of the
78 water vapour absorption in the Earth's atmosphere incorporate many weak dipole lines including hot
79 band transitions, minor water isotopologues contribution, and weak absorption continua [16].
80 Obviously, failure to include weak quadrupole transitions to the total opacities of atmospherically

81 important species may contribute to systematic errors in remote sensing retrievals with a
82 corresponding impact on atmospheric simulations.

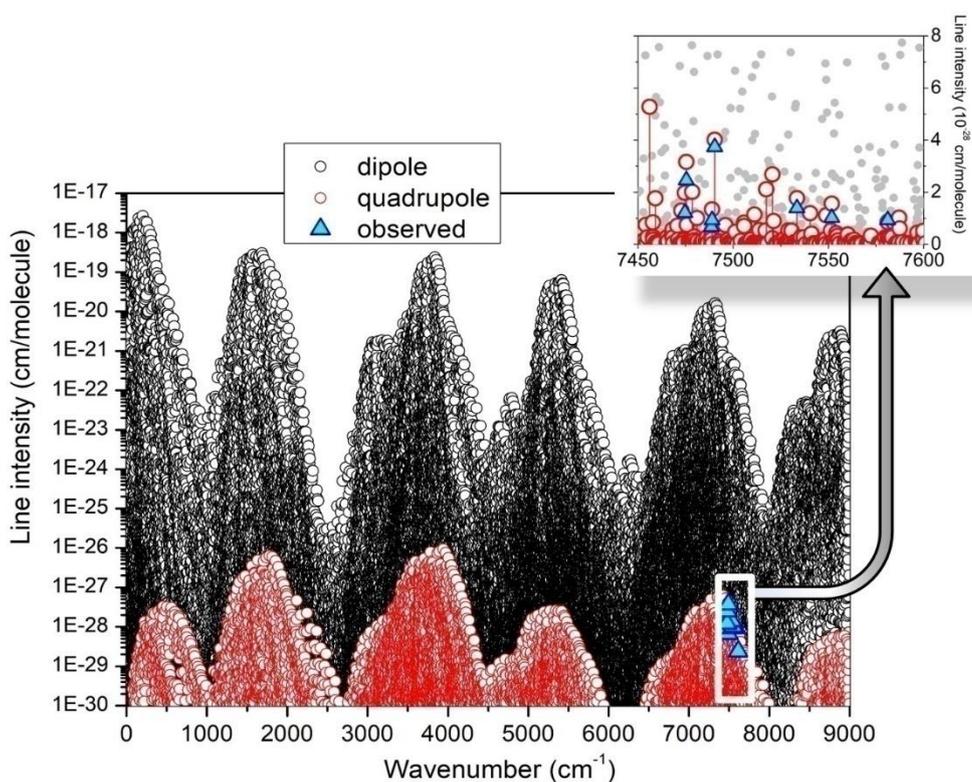
83 Here, we report the first observation of electric-quadrupole transitions in water vapour. This is
84 actually the first time that quadrupole lines of a polyatomic molecule have been detected in an IR
85 spectrum. This observation was made possible using a continuous wave diode laser cavity ring down
86 spectroscopic (CRDS) technique to measure the water absorption spectrum near 1.3 μm . The detection
87 and assignment of the measured spectral lines relied on high-accuracy predictions for both positions
88 and intensities of the quadrupole H_2^{16}O transitions. It is important to stress that the detected
89 quadrupole lines have intensity largely above the recommended dipole intensity cut-off of the standard
90 spectroscopic databases and should thus be incorporated.

91 CRDS is a high-sensitivity absorption technique which performs like a classical absorption
92 spectroscopy that would have a multi-kilometric absorption path-length. The method consists in
93 measuring the power decay rate (ring down) of a laser light trapped into a passive optical cavity, made
94 of high-reflectivity semi-transparent mirrors [17]. The presence of an absorbing gas in the cavity
95 shortens the ring down time. From the variation of the decay rate with the laser frequency, one gets the
96 absorption spectrum. Because of the extreme reflectivity of the mirrors (typically $R \sim 99.997\%$)
97 sensitivities equivalent to several hundred kilometers in a classical absorption approach are routinely
98 achieved and extremely weak absorptions are detected. A record absorption sensitivity, $\alpha_{\text{min}} \approx 5 \times 10^{-13}$
99 cm^{-1} , corresponding to a 2% light attenuation for the Earth-Moon distance, was achieved by CRDS
100 [18], allowing for the detection of extremely weak quadrupole lines of D_2 and N_2 [19]. In the last two
101 decades, the CRDS technique was extensively used to characterize weak dipole transitions of water
102 vapour in the near-IR spectral domain [20]. Tens of thousands of new dipole transition lines were
103 detected and assigned to various water isotopologues present in natural isotopic abundance. In the 1.6
104 and 1.25 μm transparency windows, lines of HD^{17}O with a natural relative abundance of 1.158×10^{-7}
105 were detected [21] and dipole lines with intensities as weak as 1×10^{-29} $\text{cm}/\text{molecule}$ were measured
106 [22].

107 At room temperature and typical sample cell pressures in the Torr range, most of quadrupole
108 transitions of water molecule are masked by much stronger dipole transitions. In order to detect them
109 in the CRDS spectrum, a highly accurate theoretical prediction of the quadrupole ro-vibrational
110 spectrum is essential.

111 The calculations, detailed in **Appendix A**, employed a state-of-the-art variational approach
112 based on high-level *ab initio* electric dipole and quadrupole moment surfaces of H_2O . The robust
113 variational approach TROVE [23,24] was used to solve the ro-vibrational Schrödinger equation for the
114 motion of nuclei, based on exact kinetic energy operator [25,26] and recently reported accurate
115 potential energy surface of H_2O [25]. The electric-quadrupole moment surface was computed *ab initio*
116 at the CCSD(T)/aug-cc-pVQZ level of theory in the frozen-core approximation using the CFOUR

117 program package [26]. The quadrupole intensities and Einstein A coefficients were calculated using
 118 the generalized approach RichMol for molecular dynamics in the presence of external electric fields
 119 [27]. The basis-set convergence of the ro-vibrational line positions was carefully examined. The
 120 remaining errors on the order of $0.01 - 0.6 \text{ cm}^{-1}$ were still too significant to unambiguously identify
 121 quadrupole lines in the CRDS spectrum. To improve the accuracy, the computed ro-vibrational line
 122 positions were adjusted according to empirical values of the lower and upper state energy levels of
 123 H_2^{16}O . These energies were carefully derived from the analysis of high-resolution spectroscopic data
 124 from more than a hundred experimental sources [28]. The average uncertainties on the order 10^{-3} cm^{-1}
 125 in the resulting line centers allowed to unambiguously identify quadrupole lines. Indeed, in the region
 126 of interest, with the sensitivity of the CRDS spectra under analysis, the spectral congestion is very
 127 high, due to dipole lines of H_2^{16}O , water minor isotopologues, as well as impurities such as CO_2 , NH_3
 128 or CH_4 present at ppm relative concentrations.



129

130 **FIG. 1** Overview of the absorption line list of H_2^{16}O at 296 K. The calculated electric-
 131 quadrupole spectrum [29] (red circles) is superimposed to the calculated electric-dipole spectrum
 132 (black circles). The CRDS measured quadrupole transitions are shown with blue triangles. The insert
 133 with intensities in linear scale shows a zoom of the $7450\text{-}7600 \text{ cm}^{-1}$ region.

134 The overview of the calculated quadrupole line list of H_2^{16}O [29] is displayed shown in **Fig. 1**
 135 superimposed to the dipole line list computed using an *ab initio* dipole moment surface [30]. Both lists
 136 include all ro-vibrational transitions of H_2^{16}O with $J \leq 30$ and upper state energies below 10000 cm^{-1}
 137 with respect to the zero-point level. The general appearance of the quadrupole and dipole line lists is
 138 similar; the spectra consist of a succession of vibrational bands whose intensity decreases with the

139 frequency. The maximum intensity values of quadrupole lines are typically seven orders of magnitude
 140 smaller than the dipole lines. Note that the strongest quadrupole lines near 4000 cm^{-1} have an intensity
 141 on the order of $10^{-26}\text{ cm/molecule}$ while the intensity cut off the water dipole transitions included in
 142 the HITRAN database [14] is three orders of magnitude smaller ($10^{-29}\text{ cm/molecule}$). Interestingly, the
 143 largest quadrupole-to-dipole intensity ratios of about 10^{-4} are predicted for the water transparency
 144 window at 2500 cm^{-1} , dominated by transitions of the bending ν_2 vibrational band. The complete
 145 quadrupole line list with transition frequencies up to 10000 cm^{-1} and $10^{-40}\text{ cm/molecule}$ intensity cut-
 146 off is provided as Supplemental Material [29].

147 The CRDS recordings of natural water vapour were performed in the frequency range between
 148 7408 and 7619 cm^{-1} at a pressure limited to 1.0 Torr and temperature maintained at 296 K . Details
 149 about the experimental setup and line parameters retrieval can be found in **Appendix B**. The noise
 150 equivalent absorption of the recordings, estimated as a root-mean-square deviation of the spectrum
 151 base line, is $\alpha_{min} \approx 5 \times 10^{-11}\text{ cm}^{-1}$. In terms of line intensity, this converts to a detectivity threshold on the
 152 order of few $10^{-29}\text{ cm/molecule}$, well below the calculated intensities of the strongest quadrupole lines
 153 in the region (up to $6 \times 10^{-28}\text{ cm/molecule}$).

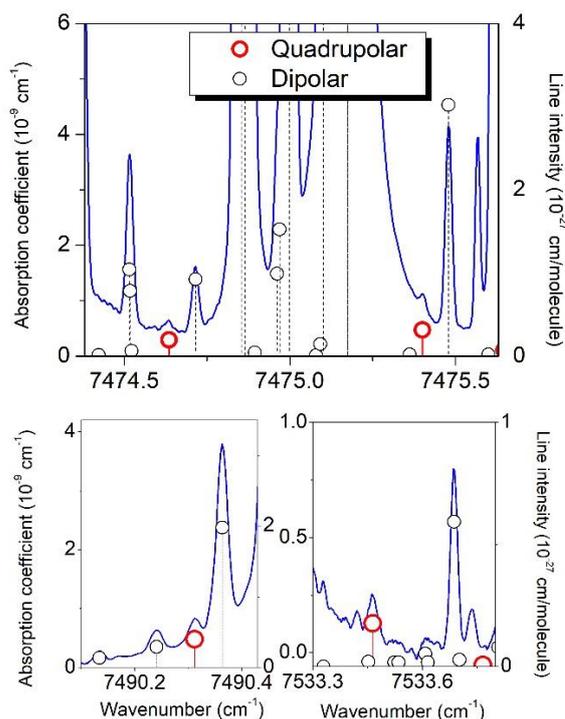


FIG. 2. Detection of electric-quadrupole lines of H_2^{16}O in the spectrum of water vapour recorded by CRDS at 1.0 Torr . The quadrupole spectrum of H_2^{16}O (red stars) calculated in this work is superimposed to the dipole stick spectrum of water in natural isotopic abundance [14] (blue circles). The four detected quadrupole lines correspond to $\Delta J=2$ transitions of the $\nu_1+\nu_3$ band.

154 As illustrated on **Fig. 2**, the remarkable position and intensity coincidences of the calculated
 155 quadrupole lines to the recorded spectra leaves no doubt that H_2^{16}O quadrupole lines are detected.
 156 Among the fifty quadrupole lines predicted with sufficient intensity in the considered region, nine
 157 could be detected (blue triangles in **Fig. 1**), the others being hidden by stronger dipole lines. As a
 158 result, **Table 1** lists the detected quadrupole lines with their measured positions and intensities
 159

160 obtained from the line profile fit described in **Appendix B**. The rovibrational assignments included in
 161 the table indicate that the detected lines belong to the $\nu_1+\nu_3$ band and correspond to $\Delta J= 2$ transitions
 162 except one line corresponding to $\Delta J= 1$. Experimental intensity values show a reasonable agreement
 163 with the calculated values (see insert in **Fig. 1**). Excluding the two weakest lines with large
 164 experimental uncertainties, the average measured/computed intensity ratio is 0.80(17).

Position (cm ⁻¹)		Int. (cm/molecule)		$J K_a K_c$					
Meas.	Calc.	Meas.	Calc.	Upper level			Lower level		
7474.6325	7474.6354	1.21E-28	1.98 E-28	6	1	5	4	2	3
7475.4020	7475.4005	2.46E-28	3.16 E-28	5	2	4	3	1	2
7488.5747	7488.5785	6.72E-29	3.23 E-29	6	6	1	5	5	0
7488.9183	7488.9215	9.34E-29	1.34 E-28	7	0	7	5	1	5
7490.3117	7490.3120	3.74E-28	4.02 E-28	7	1	7	5	0	5
7533.4649	7533.4642	1.39E-28	1.72 E-28	7	2	6	5	1	4
7551.7653	7551.7639	1.02E-28	1.56 E-28	9	1	9	7	0	7
7581.1247	7581.1172	9.32E-29	8.53 E-29	10	0	10	8	1	8
7613.8512	7613.8478	2.37E-29	1.10 E-29	10	2	9	8	1	7

165 **Table 1**

166 Assignment, transition frequencies, and intensities of the electric-quadrupole lines of the $\nu_1+\nu_3$ band of
 167 H_2^{16}O measured near 1.3 μm .
 168

169 This first detection of quadrupole transitions in the water vapour spectrum opens new
 170 perspectives for theoretical and experimental absorption spectroscopy of polyatomic molecules with
 171 expected impact in atmospheric and astronomical sciences. Despite being very weak, quadrupole
 172 absorption lines of water vapour are clearly above the background formed by the dipole spectrum and
 173 the water continuum and therefore must be included into modern atmospheric databases such as
 174 HITRAN [14] or ExoMol [31]. Water vapour, being one of the major interfering species for the trace
 175 gas analysis in air, missing quadrupole transitions may skew the optical measurement of the targeted
 176 species. In geosciences, small, but measurable natural variation of abundance ratios of water minor
 177 isotopologues are used to trace various chemical and physical processes. In this context, absorption
 178 spectroscopy is an emerging method with specific advantages compared to conventional mass
 179 spectrometers [32-35]. Due to the small relative abundance of the minor isotopologues (2×10^{-3} for
 180 H_2^{18}O and less than 4×10^{-4} for HDO and H_2^{17}O), their absorption lines are weak and any accidental
 181 coincidence between the target absorption line of the water minor isotopologue and an E2 line of the
 182 main isotopologue (H_2^{16}O) will bias the retrieved abundances.

183 Similar biases may be encountered for metrological spectroscopic measurements of line
 184 intensities or line shapes e.g. in the determination of the Boltzmann constant by Doppler-broadening
 185 thermometry of a water line [36].

186 In the case of water vapour the envelopes of the strong quadrupole and dipole vibrational bands
 187 mostly coincide as a result of molecular symmetry and corresponding selection rules. This will not be
 188 the case in other important atmospheric species such as CO_2 where, due to the linear structure of the
 189 molecule, different selection rules apply to quadrupole and dipole bands. Relatively strong quadrupole

190 bands may be located in spectral regions where dipole absorption is weak, the so-called transparency
 191 windows. In these cases, the importance of quadrupole transitions will even be more apparent.

192 This study paves the way to systematic computation of quadrupole spectra for all standard
 193 atmospheric molecules, *e.g.*, CO₂, N₂O, CH₄, HCN, CO, HF. Owing to the weak character of the
 194 quadrupole spectra, systematic calculations across wide spectral range are thus required to evaluate the
 195 significance of quadrupole transitions for atmospheric, astrophysical, and industrial applications. After
 196 validation tests by high-sensitivity measurements, quadrupole transitions should be systematically
 197 incorporated into the most currently used spectroscopic databases.

198 APPENDIX A: ELECTRONIC STRUCTURE CALCULATION

199 For water molecule in C_{2v}(M) molecular symmetry group, the rank-2 quadrupole-moment
 200 tensor Q transforms as 3A₁ + A₂ + B₁ + B₂, where A₂ and B₁ components are zero and only two
 201 out of three A₁-symmetry components are necessary, because the quadrupole tensor is traceless, *i.e.*,
 202 $Q_{A_1}^{(1)} + Q_{A_1}^{(2)} + Q_{A_1}^{(3)} = 0$. In total, three symmetry-adapted components are sufficient to describe the
 203 traceless quadrupole tensor of water, these can be constructed as

$$\begin{aligned}
 Q_{A_1}^{(i)} &= \sum_{\alpha,\beta=x,y,z} S_{i,\alpha} S_{i,\beta} Q_{\alpha,\beta} \quad \text{for } i = 1, 2, \\
 Q_{B_1} &= \sum_{\alpha,\beta=x,y,z} S_{1,\alpha} S_{2,\beta} Q_{\alpha,\beta},
 \end{aligned}
 \tag{1}$$

205 where

$$\mathbf{s}_i = \frac{r_{H_i} - r_O}{r_{OH_i}},
 \tag{2}$$

207 $Q_{\alpha,\beta}$ denotes Cartesian components of the quadrupole moment tensor, and r_{OH_i} is the O–H_i bond
 208 distance. The quadrupole moment tensor for water was computed *ab initio* at the CCSD(T)/aug-cc-
 209 pVQZ [37,38] level of theory in the frozen-core approximation. Calculations were performed on a grid
 210 of about 2000 different molecular geometries covered the wavenumber energy range up to 30 000 cm⁻¹
 211 above the equilibrium energy. Analytic CCSD(T) gradient method was used [39], as implemented in
 212 the CFOUR program package [26]. The symmetrized components in Eq. (3), were parametrized using
 213 fourth order symmetry-adapted power series expansions through least-squares fittings.

214 Ro-vibrational energies and wavefunctions

215 The variational TROVE program [23] has been used to solve the ro-vibrational Schrödinger
 216 equation for H₂O in its ground electronic state. A new implementation of the exact kinetic energy
 217 (EKE) operator developed for this study was used. The EKE is based on the bisector embedding for
 218 triatomic molecules [40,41]. Accurate potential energy surface [42], electric dipole moment surface
 219 [30] and electric-quadrupole moment surface (this work) were employed.

220 TROVE uses a multi-layer contraction scheme (see, for example, [43]). At step 1, stretching and
 221 bending primitive basis functions are constructed numerically by solving the corresponding 1D

222 Schrödinger equations. The two equivalent stretching equations are solved on a grid of 2000 points
 223 using the Numerov-Cooley approach [44,45]. For the bending solution, the associated Laguerre
 224 polynomials are used, which are optimized for the corresponding 1D Schrödinger equation on a grid of
 225 3000 points. The bending 1D Hamiltonian includes the k^2 -dependent centrifugal distortion term. The
 226 details of the model will be published elsewhere [46]. The model 1D Hamiltonian for a given mode
 227 (stretch or bend) is constructed by setting the other mode to its equilibrium value. At step 2 the 1D
 228 basis functions are then used to solve two reduced problems for the 2D stretching and 1D bending
 229 reduced Hamiltonians variationally constructed by averaging the 3D vibrational ($J=0$) Hamiltonian
 230 over the ground state basis functions as follows:

$$231 \quad \hat{H}^{(2D)} = \langle 0_3 | \hat{H} | 0_3 \rangle, \quad (3)$$

$$232 \quad \hat{H}^{(1D)} = \langle 0_1 0_2 | \hat{H} | 0_1 0_3 \rangle, \quad (4)$$

233 Where $|v_i\rangle$ band are the stretching ($i=1,2$) and bending ($i=3$) vibrational basis functions with $v=0$.

234 The eigenfunctions of these problems are symmetrized using an automatic symmetry adaptation
 235 technique [24] and form a 3D vibrational basis set for the $J=0$ Hamiltonian for step 3. The $C_{2v}(M)$
 236 molecular group symmetry is used to classify the irreducible representations. The eigenfunctions of
 237 the ($J=0$) 3D Hamiltonian are then used to form a ro-vibrational basis set for all $J>0$ calculations,
 238 where the rotational part is constructed from symmetrized rigid rotor functions [24]. Our primitive
 239 basis set comprised 18 and 48 functions for the stretching and bending modes, respectively. The
 240 atomic masses were used. An $E/hc = 40000 \text{ cm}^{-1}$ energy cut-off was used to contract the $J=0$
 241 eigenfunctions. All energies and eigenfunctions up to $J=30$ were generated and used to produce
 242 dipole and quadrupole line lists for water. The final TROVE eigenfunctions are given in a sum-of-
 243 product form:

$$244 \quad |J, m_J, l\rangle = \sum_{v,k} c_{v,k}^{(J,l)} |v\rangle |J, m_J, k\rangle, \quad (5)$$

245 Where m_J is a projection of the angular momentum on the laboratory Z-axis, k is a projection on the
 246 molecular z-axis, l is a counting state number, v is a generic vibrational ($J=0$) quantum number and
 247 $c_{v,k}^{(J,l)}$ is an expansion eigen-coefficient. In order to improve the calculated line positions, empirical
 248 energies of H_2^{16}O [28] of H_2^{16}O were used to replace the TROVE energies where available. In this
 249 replacement we took advantage of the two-file structure of the ExoMol line list consisting of a states
 250 file and a transition file [31,47].

251 As an illustration of the quality of the present calculations, **Table 2** shows a comparison of the
 252 calculated energy term values (before substitution) with the experimental IUPAC values [28]. The
 253 differences can be attributed to the artefacts of the conversion of the empirical PES of H_2O [42] to the
 254 analytical representation used in TROVE.

255 **Table 2.** Comparison of empirical (Obs.) [28] and calculated (Calc.) energy term values of H₂¹⁶O (in
256 cm⁻¹) up to 9000 cm⁻¹.

ν_1	ν_2	ν_3	Obs. (cm ⁻¹)	Calc. (cm ⁻¹)	Obs.-Calc. (cm ⁻¹)	ν_1	ν_2	ν_3	Obs. (cm ⁻¹)	Calc. (cm ⁻¹)	Obs.-Calc. (cm ⁻¹)
0	0	0	0.000	0.000	0.000	2	0	0	7249.817	7250.459	-0.642
0	0	1	1594.746	1594.748	-0.002	1	1	0	7445.366	7445.366	0.000
0	0	2	3151.630	3151.640	-0.010	0	0	5	7542.372	7542.423	-0.050
1	0	0	3657.053	3657.159	-0.106	1	0	3	8273.976	8274.070	-0.094
0	1	0	3755.929	3756.058	-0.129	0	1	3	8373.851	8373.952	-0.101
0	0	3	4666.790	4666.789	0.001	0	2	1	8761.582	8762.077	-0.495
1	0	1	5234.976	5235.077	-0.101	2	0	1	8806.999	8807.549	-0.550
0	1	1	5331.267	5331.374	-0.107	0	0	6	8869.950	8870.160	-0.210
0	0	4	6134.015	6134.017	-0.002	1	1	1	9000.410	9000.410	0.000
1	0	2	6775.094	6775.186	-0.093	1	0	4	9724.313	9724.313	0.000
0	1	2	6871.520	6871.622	-0.102	0	1	4	9833.583	9833.686	-0.103
0	2	0	7201.540	7202.099	-0.559						

257

258 **Quadrupole spectrum simulations**

259 The quadrupole spectrum has been simulated using the variational approach RichMol [27,48],
260 designed for calculations of molecular ro-vibrational dynamics in the presence of external
261 electromagnetic fields. The transition probability due to the electric-quadrupole interaction from a set
262 of $(2J + 1)$ -degenerate initial ro-vibrational states $|J, m, l\rangle$ into a set of $(2J' + 1)$ -degenerate final ro-
263 vibrational states $|J', m', l'\rangle$ is given by

$$264 \quad P_Q(J', l' \leftarrow J, l) = \sum_{m'=-J'}^{J'} \sum_{m=-J}^J \sum_{A,B=X,Y,Z} | \langle J', m', l' | Q_{A,B} | J, m, l \rangle |^2. \quad (6)$$

265 The ro-vibrational matrix elements of traceless quadrupole tensor operator $Q_{A,B}$ in the laboratory
266 frame (A, B = X, Y, Z) can generally be represented in a contracted tensor form

$$267 \quad \langle J', m', l' | Q_{A,B} | J, m, l \rangle = M_{A,B}^{(J', m', J, m)} K^{(J', l', J, l)},$$

268 with

$$269 \quad M_{A,B}^{(J', m', J, m)} = (-1)^{m'} \sqrt{(2J+1)(2J'+1)} \sum_{\sigma=-2}^2 [U]_{A,B,\sigma}^{-1} \begin{pmatrix} J & 2 & J' \\ m & \sigma & -m' \end{pmatrix} \quad (7)$$

270 and

$$271 \quad K^{(J', l', J, l)} = \sum_{k', v'} \sum_{k, v} [c_{v', k'}^{(J', l')}]^* [c_{v, k}^{(J, l)}] (-1)^{k'} \sum_{\sigma=-2}^2 \sum_{\alpha, \beta=x, y, z} \begin{pmatrix} J & 2 & J' \\ k & \sigma & -k' \end{pmatrix} U_{\sigma, \alpha\beta} \langle v' | Q_{\alpha, \beta} | v \rangle. \quad (8)$$

272

273 Here, matrix U defines the transformation of the traceless symmetric rank-2 tensor from Cartesian to
274 spherical tensor form (see, e.g., Table I in [27] for explicit expression). The ro-vibrational
275 wavefunction coefficients $c_{v, k}^{(J, l)}$ and vibrational matrix elements of quadrupole tensor operator
276 $\langle v' | Q_{\alpha, \beta} | v \rangle$ in the molecular frame were calculated using TROVE approach, as described in the

277 previous section. Using Eqs. 8-10, the expression for the ro-vibrational transition probability (in Eq. 8)
 278 can be derived as

$$\begin{aligned}
 279 \quad P_Q(J', l' \leftarrow J, l) &= [K^{(J', l', J, l)}]^2 \sum_{m'=-J'}^{J'} \sum_{m=-J}^J \sum_{A,B=X,Y,Z} |M_{A,B}^{(J', m', J, m)}|^2 = & (9) \\
 282 \quad &= 3.8(2J + 1)(2J' + 1) [K^{(J', l', J, l)}]^2.
 \end{aligned}$$

280 The expression for the integrated absorption coefficient of the quadrupole transition in units
 281 cm/molecule reads as

$$283 \quad I_Q(J', l' \leftarrow J, l) = \frac{4\pi^5 \nu^5 e^{-\frac{E_{J,l}}{kT}} \left(1 - e^{-\frac{h\nu}{kT}}\right)}{(4\pi\epsilon_0)5hcZ(T)} P_Q(J', l' \leftarrow J, l), \quad (10)$$

284 Where $\nu = (E_{J',l'} - E_{J,l})/hc$ is the transition frequency with $E_{J',l'}$ and $E_{J,l}$ being upper and lower
 285 state energies, respectively, and $Z(T)$ is the partition function. Here we used the value of $Z(T = 296$
 286 K) = 174.5813.

287

288 APPENDIX B: CRDS SETUP AND LNE PARAMETER RETRIEVAL

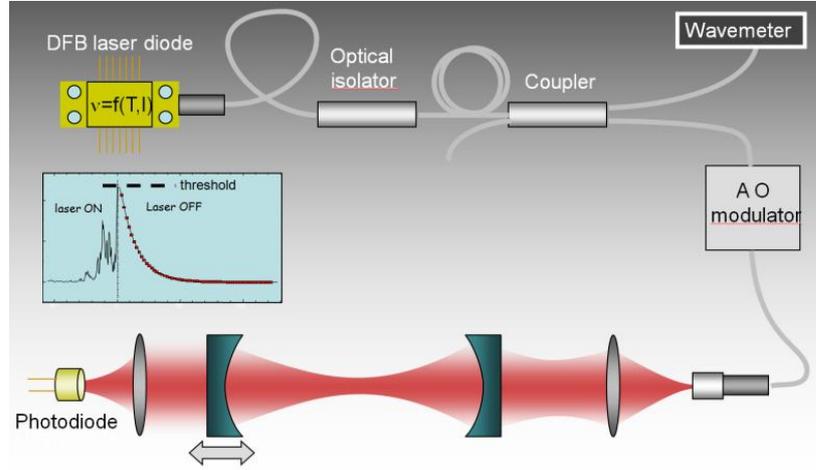
289 The CRDS spectrum of water at room temperature was recorded from 7408 to 7619 cm^{-1} with a
 290 fibred CRDS spectrometer using distributed feed-back (DFB) diode lasers as light sources. A sketch of
 291 the experimental arrangement is presented in **Fig. 1**. The stainless steel high finesse cell (HFC) ($l =$
 292 1.42 m, $\Phi_m = 11.7$ mm) is fitted by a pair of supermirrors (~99.998% reflectivity) giving rise to ring
 293 down times on the order of 200 μs . The whole spectral region was continuously covered by means of
 294 six fibred DFB lasers. The latter were supplied with a constant current of 140 mA, tuned over about
 295 35 cm^{-1} by a temperature sweep of -10 to 60°C. About 40 ring down events were averaged for each
 296 spectral data point, distant by approximately $2 \times 10^{-3} \text{ cm}^{-1}$. A complete DFB temperature scan was
 297 achieved within 65 minutes. Each time a longitudinal mode of the HFC was excited by the laser
 298 frequency, an exponential ring down (RD) event was induced by switching off the laser beam using an
 299 acousto-optic modulator (AOM). In order to excite the HFC mode whatever the laser frequency, the
 300 HFC length was modulated over one free spectral range by a piezo tube supporting the output mirror
 301 [17]. RD times, τ , were measured by fitting with a purely decreasing exponential function the
 302 transmission signal measured with an InGaAs photodiode. The obtained loss rate, $1/c\tau$, is the sum of
 303 the loss rate of the evacuated cell, $1/c\tau_0$, and of the absorption coefficient, $\alpha(\nu)$, of the gas:

$$304 \quad \frac{1}{c\tau(\nu)} = \frac{1}{c\tau_0(\nu)} + \alpha(\nu) \quad (11)$$

305 where c is the speed of light.

306 The spectra were recorded at 1.0 Torr. The pressure was continuously monitored by a
 307 capacitance gauge (Baratron) and the temperature was stabilized at about 296 K. Each 35 cm^{-1} wide

308 spectrum, corresponding to one DFB recording, was calibrated independently on the basis of the
 309 wavenumber values provided by a Fizeau type wavemeter (WSU-30 Highfinesse, 5 MHz resolution
 310 and 20 MHz accuracy). The calibration was checked and refined using reference line positions of H₂O
 311 from the HITRAN database [14].



312

313 **FIG 3.** Scheme of the CRD spectrometer. The different components include a distributed feed-
 314 back diode laser (DFB), an optical isolator, a fiber coupler, an acousto-optic (AO) modulator and a
 315 photodiode. The insert shows the time dependence of the light intensity measured by the photodiode:
 316 after a build-up period, the light intensity reaches a threshold value which triggers the switch off of the
 317 AO modulator. The ring down time is then measured from the exponential decay of the light intensity.

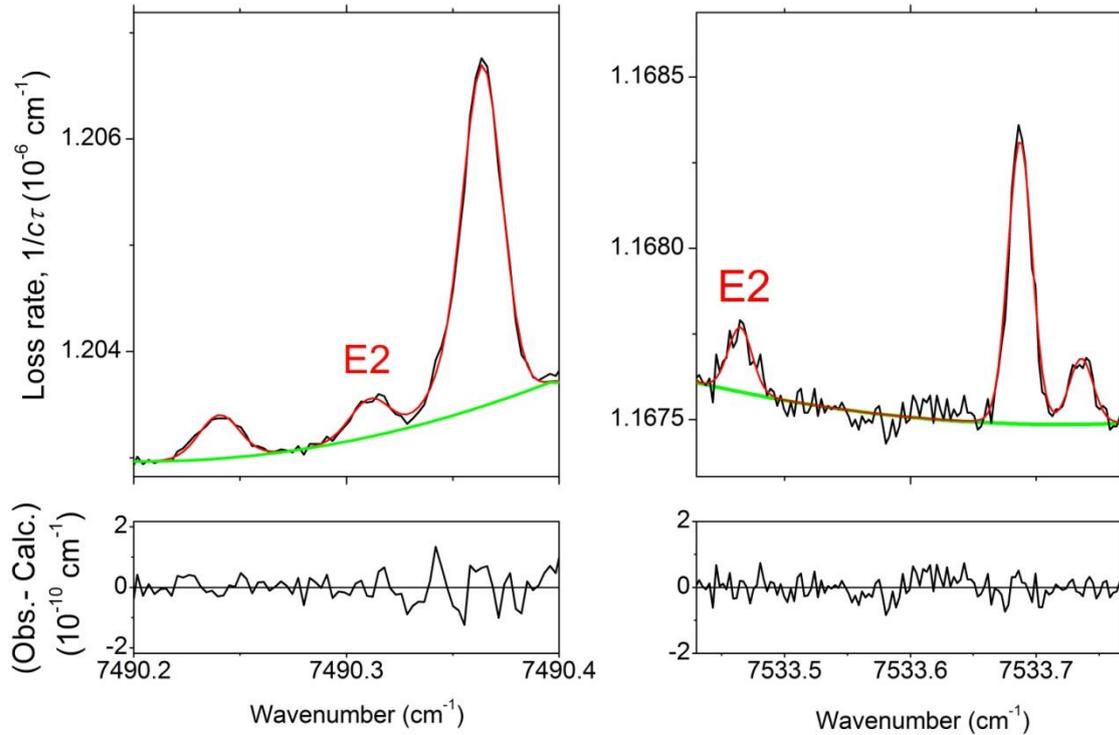
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319 The line centers and line intensities were obtained by using a homemade interactive least
 320 squares multi-lines fitting program written in LabVIEW. As the DFB line width (due to the frequency
 321 jitter) is much smaller than the Doppler broadening (1-5 MHz compared to 1 GHz), the contribution of
 322 the apparatus function to the observed profiles was neglected. The line parameter derivation consisted
 323 in choosing narrow spectral intervals with (overlapping) lines which could be fitted independently. For
 324 each interval, line centers, integrated absorption coefficients, the Lorentzian contribution of each line
 325 and a baseline (assumed to be a quadratic function of the wavenumber) were provided by the fitting
 326 procedure. The Doppler broadening was fixed according the mass and temperature of the gas and the
 327 pressure broadening was fixed according to the HITRAN default value of the self-pressure broadening
 328 coefficient (0.40 cm⁻¹/atm). **Fig. 4** illustrates the achieved spectrum reproduction close to the noise
 329 level for two E2 lines.

330 The line intensity, S_{ν_0} of a ro-vibrational transition centered at ν_0 , was obtained from the
 331 integrated absorption coefficient, A_{ν_0} (cm⁻²/molecule):

332
$$A_{\nu_0} = \int_{line} \alpha_{\nu} d\nu = S_{\nu_0}(T)N \quad (12)$$

333 Where ν is the wavenumber in cm^{-1} , α_ν is the absorption coefficient in cm^{-1} obtained from the cavity
 334 ring down time (Eq. 2) and N is the molecular concentration in $\text{molecule}/\text{cm}^3$ obtained from the
 335 measured pressure and temperature values: $P = NkT$.



336
 337 **FIG 4.** Examples of line profile fitting for the quadrupolar (E2) lines of H_2^{16}O at 7490.311 and
 338 77533.4649 cm^{-1} . The lower panels show the difference between the CRDS (black) and fitted (red)
 339 spectra in 10^{-10} cm^{-1} units. The green curve corresponds to the fitted baseline assumed to be a quadratic
 340 polynomial of the wavenumber.
 341

342 The retrieved centers and intensities of the nine quadrupolar lines are given in Table 1. As a
 343 result of the weakness of the considered lines and strong line overlapping, the error bars on the fitted
 344 line centers are estimated to be $2\text{-}3 \times 10^{-3} \text{ cm}^{-1}$ while the uncertainty on the experimental intensities
 345 ranges between 20 and 60 %.

346
 347 **ACKNOWLEDGMENTS**
 348 SY acknowledges support from the UK Science and Technology Research Council (STFC) No.
 349 ST/R000476/1. A substantial part of the calculations was performed using high performance computing facilities
 350 provided by DiRAC for particle physics, astrophysics and cosmology and supported by BIS National E-
 351 infrastructure capital grant ST/J005673/1 and STFC grants ST/H008586/1, ST/K00333X/1. The work of AAK
 352 was supported by the Foundation for the Advancement of Theoretical Physics and Mathematics BASIS. The
 353 work of A.Y. and J.K. has been supported by the Deutsche Forschungsgemeinschaft (DFG) through the clusters
 354 of excellence ‘‘Center for Ultrafast Imaging’’ (CUI, EXC 1074, ID 194651731) and ‘‘Advanced Imaging of
 355 Matter’’ (AIM, EXC 2056, ID 390715994).

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