
An Evaluation of Gas Phase Enthalpies of Formation for Hydrogen-Oxygen (H_xO_y) Species

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We have compiled gas phase enthalpies of formation for nine hydrogen-oxygen species (H_xO_y) and selected recommended values for H, O, OH, H_2O , HO_2 , H_2O_2 , O_3 , HO_3 , and H_2O_3 . The compilation consists of values derived from experimental measurements, quantum chemical calculations, and prior evaluations. This work updates the recommended values in the NIST-JANAF (1985) and Gurvich et al. (1989) thermochemical tables for seven species. For two species, HO_3 and H_2O_3 (important in atmospheric chemistry) and not found in prior thermochemical evaluations, we also provide supplementary data consisting of molecular geometries, vibrational frequencies, and torsional potentials which can be used to compute thermochemical functions. For all species, we also provide supplementary data consisting of zero point energies, vibrational frequencies, and ion reaction energetics.

Key words: ab initio thermochemistry; atomization energies; bond dissociation energies; enthalpy of formation; hydrogen-oxygen species; thermochemical network; thermodynamic properties.

Accepted: March 11, 2016

Published: March 30, 2016

<http://dx.doi.org/10.6028/jres.121.005>

1. Introduction

We have compiled gas phase enthalpies of formation for nine hydrogen-oxygen species (H_xO_y) and selected recommended values for H, O, OH, H_2O , HO_2 , H_2O_2 , O_3 , HO_3 , and H_2O_3 . Compared to uncertainties for the recommended values in the NIST-JANAF tables (1998) [1] and the thermochemical tables of Gurvich et al. (1989) [2], the updated values are (50 to 100) times more precise for H atom, O atom, and O_3 , (5 to 10) times more precise for OH and HO_2 , and (25 to 35)% more precise for H_2O and H_2O_2 . Enthalpies of formation for the species HO_3 and H_2O_3 , which are important in atmospheric chemistry, are not found in prior thermochemical evaluations. For these species, we also provide molecular geometries, vibrational frequencies, and torsional potentials which can be used to compute thermochemical functions (C_p , S° , H° , and $\Delta_f H^\circ$).

This compilation of gas phase enthalpies of formation consists of values derived from experimental measurements, quantum chemical calculations, and prior evaluations. We list not only recent, more precise values, but older values for archival purposes. Uncertainties (where available) are given along with the enthalpies of formation. The uncertainties listed are in general 2σ (a coverage factor of 2 having a level of confidence of approximately 95 %) [3]. Many workers did not explicitly state whether the uncertainties are 1σ (standard uncertainty) or 2σ – in these cases, we provide the uncertainties as reported.

In the tables of enthalpies of formation for each species, we also provide a column identifying the (experimental or computational) method used to derive the enthalpies of formation. A glossary for the notations used in the methods column is provided in Sec. 4. We also provide the reported values for dissociation energies, heats of reaction, appearance energies, or other quantities used to derive the enthalpy

of formation. We provide these values in the original reported units. We utilized the following conversion factors: $1 \text{ kJ mol}^{-1} \equiv 83.593472(4) \text{ cm}^{-1}$, $1 \text{ eV} \equiv 96.4853365(21) \text{ kJ mol}^{-1}$, $1 \text{ eV} \equiv 8065.544005(50) \text{ cm}^{-1}$, $1 \text{ hartree} \equiv 2625.49962(13) \text{ kJ mol}^{-1}$, and Rydberg Constant (R_∞) $\equiv 109737.31568539(55) \text{ cm}^{-1}$ taken from the CODATA values for the fundamental constants by Mohr et al. [4] and $1 \text{ kcal mol}^{-1} = 4.184 \text{ kJ mol}^{-1}$ from the NIST-JANAF tables [1].

For each of the species, we provide a table of gas phase enthalpies of formation along with a short discussion in Sec. 2.1 to Sec. 2.9. This is followed by a summary table of the selected values of the enthalpies of formation in Sec. 2.10.

Many of the values selected for the H_xO_y species are based on the ATcT (Active Thermochemical Tables) thermochemical network approach of Ruscic and coworkers [5-10]. We only include those ATcT values from published work and not those available only online (which have neither documentation nor references) [11, 12].

In addition to the compilation of gas phase enthalpies of formation for these hydrogen-oxygen species, in Sec. 3, we provide supplementary data consisting of zero point energies, vibrational frequencies, and ion reaction energetics. Zero point energies (ZPEs) are necessary when deriving ground state total atomization energies (ΣD_0) used to compute enthalpies of formation $\Delta_f H^\circ(0 \text{ K})$ from electronic total atomization energies (ΣD_e) obtained from quantum chemical calculations. In Sec. 3.1, we provide a table with vibrational frequencies, both experimental fundamental frequencies and calculated (or derived) harmonic frequencies. In Sec. 3.2, molecular geometries, vibrational frequencies, and torsional potentials for two species, HO_3 and H_2O_3 , are given, along with discussion of their use in computing thermochemical functions. In Sec. 3.3, ion reaction energetics, such as ionization energies, electron affinities, and appearance energies, are provided. These quantities are utilized to compute enthalpies of formation using thermochemical cycles involving ions.

2. Hydrogen-Oxygen Species

2.1 H Atom

Literature values for the gas phase enthalpy of formation of H atom are given in Table 1. The majority of the measurements are based on the dissociation energy of H_2 . The selected enthalpy of formation $\Delta_f H^\circ(298.15 \text{ K})$ for H atom is based on the H_2 photoionization measurements of Liu et al. (2009) [20] and Zhang et al. (2004) [22] who determined the dissociation energy to 0.0004 cm^{-1} and 0.01 cm^{-1} , respectively. These values translate to an uncertainty of on the order of less than $0.0001 \text{ kJ mol}^{-1}$ in the enthalpy of formation of H atom (such a small uncertainty is not important from any practical chemical perspective). Earlier, Eyler, and Melikechi (1993) [24] measured substantially the same dissociation energy, but with a higher uncertainty of 0.04 cm^{-1} . We select the experimentally-derived value from Zhang et al. (2004), because the higher precision value from Liu et al. (2009) is partially dependent upon quantum calculations for $\text{D}_0(\text{H}_2^+)$ in an ion thermochemical cycle (although the uncertainty in the theoretical component for $\text{D}_0(\text{H}_2^+)$ is negligible). In addition, the difference between two values is less than $0.0001 \text{ kJ mol}^{-1}$ – a chemically-negligible amount. The measured value of the dissociation energy is essentially identical to that from the relativistic-corrected Born-Oppenheimer energy quantum calculations of Piszczatowski et al. (2009) [36]. Ruscic et al. (2013, 2004) [6, 9] have evaluated the enthalpy of formation for H atoms using a thermochemical network approach and recommend the same value within the uncertainty limits.

2.2 O Atom

Literature values for the gas phase enthalpy of formation of O atom are given in Table 2. The selected enthalpy of formation for O atom is largely derived from the photodissociation measurements of $\text{O}_2 \rightarrow \text{O}({}^3\text{P}) + \text{O}({}^1\text{D})$ by Gibson et al. (1991) [54] and Lewis et al. (1985) [55]. The singlet excited $\text{O}({}^1\text{D}_2)$ state produced in the reaction is $15867.862 \text{ cm}^{-1}$ ($189.82178 \text{ kJ mol}^{-1}$) above the ground state $\text{O}({}^3\text{P}_2)$ oxygen atom [51]. A weighted average of the results from the photodissociation measurements shown in the table

Table 1. Gas phase enthalpies of formation $\Delta_f H^\circ(298.15\text{ K})$ for H atom

$\Delta_f H^\circ$ (kJ mol^{-1})	Uncert (kJ mol^{-1})	Reference	Method	Notes
Evaluation				
217.9979	0.0001	This work	Selected	2004ZHA/CHE [22]
217.9979	<0.0001	2014RUS/FEL [9]	Thermo network	$\Delta_f H^\circ(0\text{ K})=216.0340\text{ kJ/mol}$
217.9979	<0.0001	2011SPR/JUN [13]	Review	$D_0=36118.06962(37)\text{ cm}^{-1}$
217.998	0.001	2011SAN/ABB [14]	Review	
217.9978	<0.0001	2004RUS/PIN [6]	Thermo network	
217.9978	0.0002	2001STO [15]	Review	$D_0=36118.06(4)\text{ cm}^{-1}$
217.999	0.006	1998CHA [1]	Review	$\Delta_f H^\circ(0\text{ K})=216.035\text{ kJ/mol}$ Data last reviewed 1982
217.998	0.012	1989COX/WAG [16]	Review	
217.998	0.006	1989GUR/VEY [2]	Review	$\Delta_f H^\circ(0\text{ K})=216.035\text{ kJ/mol}$
218.001	0.003	1970STW [17]	Review	$D_0=36118.6(5)\text{ cm}^{-1}$
217.96	0.02	1970DAR [18]	Review	$D_0=432.00(0.04)\text{ kJ/mol}$
217.995	0.012	1969JEZ/KOT [19]	Review	$D_0=36117.5(2.0)\text{ cm}^{-1}$
Experimental				
217.9979	<0.0001	2009LIU/SAL [20] 2012LIU/SPR [21]	Ioniz/Quantum	$D_0=36118.06962(37)\text{ cm}^{-1}$
217.9979	0.0001	2004ZHA/CHE [22]	Photodissoc	$D_0=36118.062(10)\text{ cm}^{-1}$
217.9979	0.0001	2004ZHA/CHE [22]	Photodissoc	$D_0=36118.073(4)\text{ cm}^{-1}$ (alternate threshold)
217.9982	0.0005	1994BAL/SMI [23]	Photodissoc	$D_0(1S+2S)=118377.06(4)\text{ cm}^{-1}$ $D_0=36118.11(8)\text{ cm}^{-1}$
217.9979	0.0002	1993EYL/MAL [24]	Photodissoc	$D_0(1S+2S)=118377.00(7)\text{ cm}^{-1}$ $D_0=36118.06(4)\text{ cm}^{-1}$ (double resonance)
217.9982	0.0005	1992BAL/SMI [25]	Photodissoc	$D_0(1S+2S)=118377.06(4)\text{ cm}^{-1}$ $D_0=36118.11(8)\text{ cm}^{-1}$ (fluorescence excitation)
217.9991	0.0012	1991MCC/EYL [26]	Photodissoc	$D_0(1S+2S)=118377.23(20)\text{ cm}^{-1}$ $D_0=36118.26(20)\text{ cm}^{-1}$
217.999	0.008	1970HER [27]	Absorp limit	$D_0=36118.3(14)\text{ cm}^{-1}$
217.968	0.002	1960HER/MON [28]	Absorp limit	$D_0=36113.0(3)\text{ cm}^{-1}$
217.99	0.04	1936BEU/JUN [29]	Absorp limit	$D_0=36116(6)\text{ cm}^{-1}$
217.4	3.9	1929RIC/DAV [30]	Absorp limit	$D_0=4.465(40)\text{ eV}$
213	10	1927DIE/HOP [31]	Absorp limit	$D_0=4.38\text{ eV}$
210	12	1915ISA [32]	Absorp limit	$D_0=416\text{ kJ/mol}$ See also 1924WOL [33]
205		1915LAN [34] 1926LAN [35]	Flame	$D_0=406\text{ kJ/mol}$
Calculation				
217.9979	<0.0001	2009PIS/LAC [36]	Quantum	$D_0=36118.0695(10)\text{ cm}^{-1}$
217.9979	<0.0001	1995WOL [37]	Quantum	$D_0=36118.069(1)\text{ cm}^{-1}$
217.9978		1993KOL/RYS [38]	Quantum	$D_0=36118.049\text{ cm}^{-1}$
217.9979	0.0001	1993WOL [39]	Quantum	$D_0=36118.06(1)\text{ cm}^{-1}$
217.9979		1987SCH/LER [40]	Quantum	$D_0=36118.074\text{ cm}^{-1}$
217.9980		1986KOL/SZA [41]	Quantum	$D_0=36118.088\text{ cm}^{-1}$
217.9976		1983WOL [42]	Quantum	$D_0=36118.01\text{ cm}^{-1}$
217.9970		1978BIS/CHE [43]	Quantum	$D_0=36117.92\text{ cm}^{-1}$
217.998		1975KOL/WOL [44]	Quantum	$D_0=36118\text{ cm}^{-1}$
217.996		1972BUN [45]	Quantum	$D_0=36117.8\text{ cm}^{-1}$
217.994		1968KOL/WOL [46]	Quantum	$D_0=36117.4\text{ cm}^{-1}$
217.995	0.004	1966HUN [47]	Quantum	$D_0=36117.59\text{ cm}^{-1}$
217.973		1964KOL/WOL [48]	Quantum	$D_0=36113.9\text{ cm}^{-1}$
217.975		1960KOL/ROO [49]	Quantum	$D_0=36114.2\text{ cm}^{-1}$
217.9	1.0	1933JAM/COO [50]	Quantum	$D_e=4.73(2)\text{ eV}$

Table 2. Gas phase enthalpies of formation $\Delta_f H^\circ(298.15\text{ K})$ for O atom

$\Delta_f H^\circ$ (kJ mol ⁻¹)	Uncert (kJ mol ⁻¹)	Reference	Method	Notes
Evaluation				
249.229	0.002	This work	Selected	2014RUS/FEL [9]
249.229	0.002	2014RUS/FEL [9]	Thermo network	$\Delta_f H^\circ(0\text{ K})=246.844\text{ kJ/mol}$
249.229	0.002	2011SAN/ABB [14]	Review	
249.229	0.002	2004RUS/PIN [6]	Thermo network	
249.17	0.10	1998CHA [1]	Review	Data last reviewed 1982
249.160	0.007	1992COS/HUE [52]	Review	$D_0(\text{B})=57125.4(1.1)\text{ cm}^{-1}$ $\text{O}_2(\text{B}^3\Sigma_u^-) \rightarrow \text{O}(^1\text{D}_2) + \text{O}(^3\text{P}_2)$
249.180	0.10	1989GUR/VEY [2]	Review	$\Delta_f H^\circ(0\text{ K})=246.795\text{ kJ/mol}$
249.18	0.1	1989COX/WAG [16]	Review	
249.18	0.2	1970DAR [18]	Review	$D_0=493.59(0.4)\text{ kJ/mol}$
Experimental				
249.215	0.004	1997MAR/HEP [53]	Ion pair dissociation	$\text{IPF}(\text{O}^+, \text{O}^-/\text{O}_2)=139319.1(0.7)\text{ cm}^{-1}$ $D_0=41266.7(0.7)\text{ cm}^{-1}$
249.226	0.005	1991GIB/LEW [54]	Photodissociation	$D_0(\text{B})=57136.4(0.9)\text{ cm}^{-1}$
249.223	0.003	1985LEW/BER [55]	Absorption limit	$D_0(\text{B})=57136.0(0.5)\text{ cm}^{-1}$
249.22	0.018	1985LEW/BER [55]	Reevaluation	Reevaluated 1954BRI/HER [61] $D_0(\text{B})=57135(3)\text{ cm}^{-1}$
249.2		1981BLY/POW [56]	Ion cycle	$\text{AE}(\text{O}^+/\text{O}_2^+)=18.734\text{ eV}$ $D_0=41263\text{ cm}^{-1}$
249.19	0.02	1979PER/DUR [57]	Photofragmentation	$D_0=41256.6(3.8)\text{ cm}^{-1}$
249.22	0.06	1978ALB/MOS [58]	Photofragmentation	$D_0=41262(10)\text{ cm}^{-1}$
249.16	0.06	1975DEH/CHU [59]	Ion pair dissociation	$\text{IPF}(\text{O}^+, \text{O}^-/\text{O}_2)=139316.6(9.7)\text{ cm}^{-1}$ $D_0=41257.7\text{ cm}^{-1}$
249.17		1972DAN/ELA [60]	Absorption limit	$D_0(\text{B})=57128\text{ cm}^{-1}$
249.17	0.03	1954BRI/HER [61]	Absorption limit	$D_0(\text{B})=57128(5)\text{ cm}^{-1}$
Calculation				
249.07	0.29	2014FEL/PET [62]	CC/cbs	$D_e=502.79(0.50)\text{ kJ/mol}$ this work using expt ZPE
249.52		2014LIU/SHI [63]	MRCI/cbs	$D_e=5.2203\text{ eV}$ this work using expt ZPE
249.07		2010BYT/MAT [64]	FCI/cbs	$D_e=42030.1\text{ cm}^{-1}$ this work using expt ZPE
248.5		2007VAR [65]	MRCI/cbs	$D_e=191.08\text{ mHartree}$
248.7		2005BYA/RUE [66]	FCI(CEEIS)/cbs	$D_e=191.2\text{ mHartree}$
247.7		1997PET/WIL [67]	CC/cbs	$D_e=499.99\text{ kJ/mol}$
247.7		1997PET/WIL [67]	MRCI/cbs	$D_e=499.99\text{ kJ/mol}$
243.8		1996CSA/ALL [68]	CC/pVQZ	$D_e=492.2\text{ kJ/mol}$
239.6		1991COL/HAS [69]	CC/6-311G	$D_e=5.15\text{ eV}$
217.2		1977GUB [70]	CISD/DZ	$D_e=4.99\text{ eV}$

yields a value $\Delta_f H^\circ(298.15\text{ K}) = 249.225 \pm 0.005\text{ kJ mol}^{-1}$, while the thermochemical network evaluation of Ruscic et al. (2013) [9] provides a value of $249.229 \pm 0.002\text{ kJ mol}^{-1}$ with a slightly lower uncertainty. Ruscic et al. corrected the bond dissociation energies reported by others to the lowest rovibrational level of O_2 , and we select the recommended (and corrected) value from Ruscic et al.

Values from the quantum chemical calculations of Feller et al. (2014) [62] and Bytautas et al. (2010) [64] are in excellent agreement with the experimental enthalpy of formation of O atom (within about 0.2 kJ mol^{-1}). Please note that in order to derive the enthalpy of formation from the calculated dissociation energies of $D_e = 42030.1\text{ cm}^{-1}$ from both Feller et al. and Bytautas et al., we used the experimentally-derived ZPE of 787.4 cm^{-1} (see Sec. 3.1) rather than the computed anharmonic ZPEs that were used in those studies.

2.3 OH (hydroxyl radical)

The selected value of the gas phase enthalpy of formation of OH is derived from the experimental work of Boyarkin et al. (2013) [76] and Maksyutenko et al. (2006) [77] who both directly measured the

dissociation energy of water by determining the onset of the dissociative continuum $D_0(\text{HO-H}) = 41145.9(0.1) \text{ cm}^{-1}$. Ruscic et al. (2014) [9] have evaluated the enthalpy of formation for OH using a thermochemical network approach using these two measurements and other input data and recommend a value that is within the uncertainties of the direct experimental determinations.

The selected value is in excellent agreement with the high level quantum calculations of Boyarkin et al. (2013) [76] (within 8 cm^{-1} or 0.1 kJ mol^{-1} – the estimated uncertainty in the calculations). The range of other quantum calculations given in Table 3 are almost as good, providing values within about 0.3 kJ mol^{-1} of the selected value.

Table 3. Gas phase enthalpies of formation $\Delta_f H^\circ(298.15 \text{ K})$ for OH

$\Delta_f H^\circ$ (kJ mol^{-1})	Uncert (kJ mol^{-1})	Reference	Method	Notes
Evaluation				
37.51	0.03	This work	Selected	2013BOY/KOS [76]
37.50	0.03	2015GAN/CSO [71]	Thermo network	$\Delta_f H_0(0 \text{ K})=37.25 \text{ kJ/mol}$
37.492	0.026	2014RUS/FEL [9]	Thermo network	$\Delta_f H_0(0 \text{ K})=37.253 \text{ kJ/mol}$
37.36	0.13	2011SAN/ABB [14]	Review	$\Delta_f H_0(0 \text{ K})=37.11 \text{ kJ/mol}$
37.50	0.03	2010RUS [72]	Thermo network	$\Delta_f H_0(0 \text{ K})=37.26 \text{ kJ/mol}$
37.36	0.13	2006RUS/PIN [73]	Thermo network	$\Delta_f H_0(0 \text{ K})=37.11 \text{ kJ/mol}$
37.3	0.3	2005RUS/BOG [8]	Review	$\Delta_f H_0(0 \text{ K})=37.25 \text{ kJ/mol}$
37.3	0.3	2002RUS/WAG [74]	Thermo network	$\Delta_f H_0(0 \text{ K})=37.0 \text{ kJ/mol}$
37.4	0.1	2001JOE [75]	Thermo network	$D_0(\text{OH})=35584(10) \text{ cm}^{-1}$
38.987	1.2	1998CHA [1]	Review	$\Delta_f H_0(0 \text{ K})=38.390 \text{ kJ/mol}$ Data last reviewed 1977
39.349	0.21	1989GUR/VEY [2]	Review	$\Delta_f H_0(0 \text{ K})=39.110 \text{ kJ/mol}$
Experimental				
37.51	0.03	2013BOY/KOS [76]	Dissoc continuum	$D_0(\text{H}_2\text{O})=41145.92(0.12) \text{ cm}^{-1}$
37.51	0.03	2006MAK/RIZ [77]	Dissoc continuum	$D_0(\text{H}_2\text{O})=41145.94(0.15) \text{ cm}^{-1}$
37.3	0.3	2002RUS/WAG [74]	Ion cycle	Various AP(OH+/H ₂ O)
37.3	0.7	2002HER/HAN [78]	Kinetics/equil	H ₂ /O ₂ shock tube modeling
37.20	0.38	2001RUS/FEL [79]	Ion cycle	AP(OH+/H ₂ O)=18.115(0.004) eV
37.58	0.07	2000HAR/HWA [80]	Photodissoc	$D_0(\text{H}_2\text{O})=41151(5) \text{ cm}^{-1}$
37.2	0.5	1992WIE/TON [81]	Ion cycle	IP(OH)=104989(2) cm^{-1} see 2002RUS/WAG [74]
37.2	0.8	1976MCC [82]	Ion cycle	AP(OH+/H ₂ O)=18.115(0.008) eV
<39.4	0.2	1969CAR/DAL [83]	Spec dissoc limit	$D_0(\text{OH})<35420(15) \text{ cm}^{-1}$
39.1	1.2	1956BAR [84]	Spec dissoc limit	$D_0(\text{OH})=35450(100) \text{ cm}^{-1}$
39.9	2.7	1944DWY/OLD [85]	Equilibrium	4OH → 2H ₂ O + O ₂ $\Delta_f H(0 \text{ K})=641.8(10.9) \text{ kJ/mol}$
33.2	3.9	1934RIE/SEN [86]	Equilibrium	H ₂ O → H + OH $\Delta_f H(298 \text{ K})=493.0(3.9) \text{ kJ/mol}$
Calculation				
37.5	0.1	2013BOY/KOS [76]	CC/cbs	$D_0(\text{H}_2\text{O})=41145(8) \text{ cm}^{-1}$
37.2	0.2	2010CSA/FUR [87]	NEAT	
37.1		2010CSA/MAT [88]	MRCl/pV6Z	$D_0(\text{H}_2\text{O})=41109 \text{ cm}^{-1}$
37.7	0.4	2009GRA/DIX [89]	CC/cbs	
37.1		2009GRE/BOY [90]	MRCl/pCV6Z	$D_0(\text{H}_2\text{O})=41108 \text{ cm}^{-1}$
37.2		2008HAR/VAZ [91]	HEAT	$D_0(\text{H}_2\text{O})=41116 \text{ cm}^{-1}$
37.7	0.4	2008FEL/PET [92]	CC/cbs	
37.4		2005MA/BIA [93]	MRCl/cbs	$D_0(\text{OH})=35569 \text{ cm}^{-1}$
37.9		2002PEE/MAR [94]	CC/cbs	$D_0(\text{H}_2\text{O})=492.6 \text{ kJ/mol}$
37.3	0.8	2002RUS/WAG [74]	CC/cbs	$D_0(\text{OH})=35591(42) \text{ cm}^{-1}$
34.0		2002JAN/ROS [95]	G3MP2B3	
37.4	0.7	2001RUS/FEL [79]	CC/cbs	$D_0(\text{H}_2\text{O})=41135(55) \text{ cm}^{-1}$
37.4		2001MAR [96]	CC/cbs	$D_0(\text{OH})=4.4124 \text{ eV}$
36.8		2001PAR/MAR [145]	W2	
37.7		1998CUR/RAG1 [97]	CBS-Q	
35.1		1998CUR/RAG2 [98]	G3	
36.8		1998MCK/WRI [99]	G2MP2	$D_0(\text{O-H})=426.3 \text{ kJ/mol}$

2.4 H₂O (water)

The gas phase enthalpy of formation of H₂O (water) is largely based on the combustion measurements of liquid water by Rossini (1939) [102-104] decades ago. The gas phase enthalpy of formation was computed using the heat of vaporization for water (see Rossini). Ruscic and coworkers [6, 9, 100] included H₂O in thermochemical network evaluations (ATcT) – and the most recent ATcT value differs by only about 0.04 kJ mol⁻¹ from the original value of Rossini (on the order of the uncertainty in the measurement). We select the slightly more precise recommended value from the thermochemical network approach of Ruscic et al. The high level quantum chemical calculations of Feller et al. [92] are in excellent agreement with the experimentally-derived value (within about 0.04 kJ mol⁻¹). All available literature values for the gas phase enthalpy of formation of H₂O are given in Table 4.

Table 4. Gas phase enthalpies of formation $\Delta_f H^\circ(298.15\text{ K})$ for H₂O

$\Delta_f H^\circ$ (kJ mol ⁻¹)	Uncert (kJ mol ⁻¹)	Reference	Method	Notes
Evaluation				
-241.831	0.026	This work	Selected	2013RUS [100]
-241.831	0.026	2013RUS [100]	Thermo network	$\Delta_f H_0(0\text{ K}) = -238.928\text{ kJ/mol}$
-241.826	0.040	2011SAN/ABB [14]	Review	$\Delta_f H_0(0\text{ K}) = -238.923\text{ kJ/mol}$
-241.818	0.033	2004RUS/PIN [6]	Thermo network	$\Delta_f H_0(0\text{ K}) = -238.916\text{ kJ/mol}$
-241.826	0.042	1998CHA [1]	Review	$\Delta_f H_0(0\text{ K}) = -238.921\text{ kJ/mol}$ Data last reviewed 1979
-241.826	0.040	1989COX/WAG [16]	Review	
-241.826	0.040	1989GUR/VEY [2]	Review	$\Delta_f H_0(0\text{ K}) = -238.923\text{ kJ/mol}$
Experimental				
-241.833	0.12	1968KIN/ARM [101]	Heat combustion	$\Delta_f H_0(l) = -285.84(0.12)\text{ kJ/mol}$
-241.788	0.040	1939ROS [102-104]	Heat combustion	$\Delta_f H_0(l) = -285.795(0.040)\text{ kJ/mol}$ $\Delta_v H = 44.007(0.013)\text{ kJ/mol}$
Calculation				
-241.79	0.38	2014FEL/PET [62]	CC/cbs	$\Delta_f H_0(0\text{ K}) = -238.86\text{ kJ/mol}$
-240.7	1.6	2014ALM [105]	FCI(SCI)/cbs	
-241.1	0.2	2010CSA/FUR [87]	NEAT	
-241.8	0.4	2009FEL/PET [106]	CC/cbs	
-241.8	0.8	2009GRA/DIX [89]	CC/cbs	
-241.8	0.8	2008FEL/PET [92]	CC/cbs	
-241.9	1.1	2006BYT/RUE [107]	FCI(CEEIS)/cbs	
-242.7		2001PAR/MAR [145]	W2	
-243.9		2001PAR/MAR [145]	W1	
-242.3		1998CUR/RAG1 [97]	CBS-Q	
-240.6		1998CUR/RAG2 [98]	G3	
-241.9	5.3	1997HEL/KLO [108]	CC-R12/cbs	

2.5 HO₂ (hydroperoxyl radical)

We have selected the gas phase enthalpy of formation for HO₂ from the Active Thermochemical Tables (ATcT) work of Ruscic et al. (2006) [73], but with a slightly higher uncertainty. Our rationale for assigning a higher uncertainty is as follows. The neutral and ion reaction energetics available to derive the enthalpy of formation for HO₂ as compiled in Table 5 all have uncertainties of about (1.5 to 2.5) kJ mol⁻¹ (much higher than the 0.25 kJ mol⁻¹ assigned by Ruscic et al.), while the quantum chemical calculations have (reported) uncertainties of about (0.3 to 0.8) kJ mol⁻¹. Thus, the ATcT value and its uncertainty are strongly influenced by theoretical values. Additionally, the enthalpies of formation from quantum calculations are dependent upon computed ZPEs (zero point energies) and there is about a 16 cm⁻¹ (0.2 kJ mol⁻¹) uncertainty in computing anharmonic ZPEs (see Sec. 3). Although enthalpies of formation from the quantum calculations are much more precise than those derived from experimental measurements, we suggest a higher uncertainty (0.35 kJ mol⁻¹) than assigned by Ruscic et al. considering the factors above. We do not recommend use of the value from the thermochemical network approach of Ganyecz et al. (2015), because of the limited data used in their thermochemical network and their value is substantially inconsistent with most experimentally-derived and calculated values.

Table 5. Gas phase enthalpies of formation $\Delta_f H^\circ(298.15\text{ K})$ for HO₂

$\Delta_f H^\circ$ (kJ mol ⁻¹)	Uncert (kJ mol ⁻¹)	Reference	Method	Notes
Evaluation				
12.30	0.35	This work	Selected	2006RUS/PIN [73]
11.92	0.22	2015GAN/CSO [71]	Thermo network	$\Delta_f H^\circ(0\text{ K})=14.85\text{ kJ/mol}$
12.30	0.25	2011SAN/ABB [14]	Review	$\Delta_f H^\circ(0\text{ K})=15.22\text{ kJ/mol}$
12.27	0.16	2010RUS [72]	Thermo network	
12.30	0.25	2006RUS/PIN [73]	Thermo network	$\Delta_f H^\circ(0\text{ K})=15.21\text{ kJ/mol}$
2.09	8.4	1998CHA [1]	Review	$\Delta_f H^\circ(0\text{ K})=5.01\text{ kJ/mol}$ Data last reviewed 1978
9.689	3.0	1989GUR/VEY [2]	Review	$\Delta_f H^\circ(0\text{ K})=12.600\text{ kJ/mol}$
14.6	4.2	1983SHU/BEN1 [109]	Review	
19.7	4.0	1970DAR [18]	Review	
Experimental				
13.4	2.1	2002RAM/BLA [110]	Ion cycle	EA(HO ₂)=1.078(0.006) eV
14.5	2.1	1998CLI/WEN [111]	Ion cycle	EA(HO ₂)=1.089(0.006) eV
13.8	3.3	1998LIT/RUS [112]	Ion cycle	AE(HO ₂ [•] /H ₂ O ₂)=15.112(0.035) eV IE(HO ₂)=11.352(0.007) eV
12.1	2.5	1998LIT/RUS [112]	Ion cycle	Revised by 2006RUS/PIN [73]
13.4	5.0	1990FIS/ARM [113]	Ioniz threshold	Revised by 2006RUS/PIN [73]
15.9	5.0	1990FIS/ARM [113]	Ioniz threshold	CH ₄ + O ₂ ⁺ → CH ₃ ⁺ + HO ₂ E _T =0.20(0.05) eV
13.4	2.6	1985OAK/HAR [114]	Ion cycle	EA(HO ₂)=1.078(0.017)
12.6	1.7	1984HIL/HOW [115]	Kinetics	OH + ClO → HO ₂ + Cl $\Delta_r H=-6.3\text{ kJ/mol}$
12.1	1.7	1984HIL/HOW [115]	Kinetics	Revised by 2006RUS/PIN [73]
>12.6		1983SHU/BEN2 [116]	Kinetics	HI + O ₂ → HO ₂ + I
13.8	2.5	1982LEE/HOW [117]	Kinetics	Cl + HO ₂ → OH + ClO $\Delta_r H=5.0\text{ kJ/mol}$
6.7	10.5	1982KHA/NIA [118]	Equilibrium	Estimated from CH ₃ + O ₂ → CH ₃ O ₂
10.5	2.5	1980HOW [119]	Equilibrium	HO ₂ + NO = OH + NO ₂ $\Delta_r H=-28.7\text{ kJ/mol}$
15.5		1980HOW [119]	Equilibrium	HO ₂ + NO → OH + NO ₂ Analyzed by 1975GLA/TRO [120]
3.8		1974KOC/MO [121]	Kinetics	HX + O ₂ → HO ₂ + X (Cl,Br,I)
20.9	8.4	1962FON/HUD [122]	Ion cycle	AP(HO ₂ [•] /H ₂ O ₂)=15.36(0.05) eV IP(HO ₂)=11.53(0.02) eV
<10.5	6.3	1959ROS/WIS [123]	Kinetics	HBr + O ₂ → HO ₂ + Br E _a =159.0 kJ/mol
21.3	8.4	1955FON/HUD [124]	Ion cycle	AP(HO ₂ [•] /H ₂ O ₂)=15.41 (0.1) eV IP(HO ₂)=11.53(0.1) eV
Calculation				
11.88	0.33	2015GAN/CSO [71]	CC/cbs	
12.5		2014SPR/IRI [125]	CC-F12	
12.18	0.32	2010CSA/FUR [87]	NEAT	
12.38	0.59	2009KAR/PAR [126]	W4	
12.44	0.82	2008FEL/PET [92]	CC/cbs	
12.10	0.74	2006BOM/VAZ [127]	HEAT	
12.38	0.42	2004FLO/SZA [128]	CC/cbs	
12.24	0.70	2004TAJ/SZA [129]	HEAT	
15.2		2002DIX/FEL [130]	CC/cbs	
13.4		2002JAN/ROS [95]	G3MP2B3	
12.1	3.0	2001BLA/RAM [115]	CBS-Q/APNO	
11.7	0.8	1999KAR/OSH [131]	QCI/6-311G	
15.8		1998MCK/WRI [99]	G2MP2	D ₀ (HOO-H)=364.3 kJ/mol
9.3		1998MCK/WRI [99]	G2MP2	D ₀ (HO-O)=270.9 kJ/mol
11.9		1996JUN/SEI [132]	CBS-Q/APNO	
11.7	2.1	1993BAU/PAR [133]	CC/cbs	

2.6 H₂O₂ (hydrogen peroxide)

As shown in Table 6, there are only two relatively direct measurements leading to a value for the gas phase enthalpy of formation of H₂O₂ – the calorimetry measurement of Giguere (1955) [140] and the D₀(O-O) dissociation energy of Luo et al. (1992) [138]. We have selected the inherently more precise spectroscopic value from Luo et al., but assigned a higher uncertainty of 0.16 kJ mol⁻¹ in consideration of the (0.33 kJ mol⁻¹) range of recommended values by Ganyecz et al. (2015) [71], Ruscic (2013) [134], Ruscic (2010) [72], and Ruscic et al. (2006) [73]. In the ATcT evaluations by Ruscic and coworkers, there are no details given on either the reactions used to compute the enthalpy of formation of H₂O₂ or why the two ATcT values differ outside their uncertainties.

The enthalpies of formation derived from quantum chemical calculations are within about 1.0 kJ mol⁻¹ of the selected value. These values depend upon the zero point energy (ZPE) of the molecule and different anharmonic corrections were computed. In Sec. 3.1 “Zero Point Energies and Vibrational Frequencies,” we show that the computed anharmonic ZPEs have an apparent uncertainty of about 0.4 kJ mol⁻¹ and this may contribute to part of the difference between the computed and experimentally-derived values.

Table 6. Gas phase enthalpies of formation $\Delta_f H^\circ(298.15\text{ K})$ for H₂O₂

$\Delta_f H^\circ$ (kJ mol ⁻¹)	Uncert (kJ mol ⁻¹)	Reference	Method	Notes
Evaluation				
-135.51	0.16	This work	Selected	1992LUO/FLE [138]
-135.51	0.06	2015GAN/CSO [71]	Thermo network	$\Delta_f H^\circ(0\text{ K})=-129.481\text{ kJ/mol}$
-135.442	0.064	2013RUS2 [134]	Thermo network	
-135.9	0.2	2011SAN/ABB [14]	Review	$\Delta_f H^\circ(0\text{ K})=-129.9\text{ kJ/mol}$
-135.44	0.07	2010RUS [72]	Thermo network	
-135.77	0.17	2006RUS/PIN [73]	Thermo network	$\Delta_f H^\circ(0\text{ K})=-129.75\text{ kJ/mol}$
-135.9	0.2	2003DOR/IOR [135]	Review	
-136.106	8.4	1998CHA [1]	Review	$\Delta_f H^\circ(0\text{ K})=-129.808\text{ kJ/mol}$ Data last reviewed 1960
-135.880	0.22	1989GUR/VEY [2]	Review	$\Delta_f H^\circ(0\text{ K})=-129.890\text{ kJ/mol}$
-138.8	2.1	1970DAR [18]	Review	D ₀ (O-O)=207.1(2.1) kJ/mol
-136.1		1955GIG/LIU [136]	Review	
-140.6		1936BIC/ROS [137]	Review	
Experimental				
-136.7	0.4	1998LIT/RUS [112]	Ion cycle	AE(OH+/H ₂ O ₂)=1464.1(0.4) kJ/mol IE(OH)=1255.95(0.04) kJ/mol
-135.51	0.05	1992LUO/FLE [138]	Dissoc continuum	D ₀ (O-O)=17051.8(3.4) cm ⁻¹
-132	12	1958FOR [139]	Kinetics	H ₂ O ₂ → OH + OH $\Delta_f H^\circ=201.3(12.1)$
-135.9	0.2	1955GIG/MOR [140]	Calorim decomp	$\Delta_f H(1)=-187.78(0.08)\text{ kJ/mol}$ $\Delta_v H=51.92(0.15)\text{ kJ/mol}$ 1920MAA/HAT [141]
-135.8	0.2	1929MAT/MAA [142]	Calorim decomp	$\Delta_f H(1)=-187.72(0.08)\text{ kJ/mol}$ $\Delta_v H=51.92(0.15)\text{ kJ/mol}$
Calculation				
-136.2		2014SPR/IRI [125]	CC-F12	
-135.0	0.6	2009KAR/PAR [126]	W4	
-135.1	0.6	2009DEN/ORN [143]	CC/cbs	$\Delta_f H^\circ(0\text{ K})=-129.00\text{ kJ/mol}$
-124.2		2009SEL/GEO [144]	CASPT2/pVTZ	D _e (O-O)=214.2 kJ/mol
-133.9	1.3	2009GRA/DIX [89]	CC/cbs	
-133.9	1.3	2008FEL/PET [92]	CC/cbs	
-136.4		2001PAR/MAR [145]	W1	
-134.3		2001PAR/MAR [145]	W2	
-132.6	2.9	2001BLA/RAM [146]	CBS-APNO	
-130.6		1999KUH/RIZ [147]	MRSDCI/pVTZ	D _e (O-O)=18439 cm ⁻¹
-136.8		1998CUR/RAG1 [97]	CBS-Q	
-131.0		1998CUR/RAG2 [98]	G3	
-141.1		1998MCK/WRI [99]	G2MP2	D ₀ (O-O)=208.8 kJ/mol

2.7 O₃ (ozone)

The selected gas phase enthalpy of formation for O₃ (ozone) is taken from Ruscic et al. (2004) [6] which is largely based on the photofragment excitation measurements of Masumi and coworkers (1997, 1999) [149, 150]. The other experimental determinations shown in Table 7 are in good agreement with this value within their stated uncertainties. Ruscic et al., in a thermochemical network evaluation, corrected the bond dissociation energies of Masumi and coworkers to the lowest rotational (J=0) level for the O₂ products – changing the computed enthalpy of formation by about 0.15 kJ mol⁻¹. The quantum chemical calculations of Dixon and coworkers (2008, 2009) [89, 92] are within about 0.1±1.6 kJ mol⁻¹ of the recommended value – excellent, and likely fortuitous, agreement given the unpaired electrons in ozone (multiconfigurational character causes problems for single reference methods).

Table 7. Gas phase enthalpies of formation $\Delta_f H^\circ(298.15\text{ K})$ for O₃

$\Delta_f H^\circ$ (kJ mol ⁻¹)	Uncert (kJ mol ⁻¹)	Reference	Method	Notes
Evaluation				
141.73	0.04	This work	Selected	2004RUS/PIN [6]
141.75	0.04	2011RUS [148]	Thermo network	
141.732	0.039	2011SAN/ABB [14]	Review	$\Delta_f H^\circ(0\text{ K})=144.386\text{ kJ/mol}$
141.732	0.039	2004RUS/PIN [6]	Thermo network	$\Delta_f H^\circ(0\text{ K})=144.386\text{ kJ/mol}$
142.674	1.7	1998CHA [1]	Review	$\Delta_f H^\circ(0\text{ K})=145.348\text{ kJ/mol}$ Data last reviewed 1961
141.800	2.0	1989GUR/VEY [2]	Review	$\Delta_f H^\circ(0\text{ K})=144.454\text{ kJ/mol}$
Experimental				
141.67	0.17	1999TAN/TAK [149]	Photofragment	O ₃ → O(¹ D) + O ₂ (a ¹ Δ _g) D ₀ =386.59(0.04) kJ/mol
142.61	0.35	1997TAK/KIS [150]	Photofragment	O ₃ → O(³ P ₂) + O ₂ (X ³ Δ _g ⁻) D ₀ =101.53(0.25) kJ/mol
141.00	0.84	1965CLY/MCK [151]	Kinetics/Equil	O ₂ + O → O ₃ $\Delta_r H = -101.25\text{ kJ/mol}$
141.8	1.3	1932GUN/WAS [152]	Equilibrium	O ₃ → 3/2 O ₂
144.3	4.2	1910KAI/JAH [153]	Heat Reaction	O ₃ → 3/2 O ₂
Calculation				
144.2		2010HOL/SZA [154]	MR-CISD	D _c =1.117 eV
141.8	1.7	2009GRA/DIX [89]	CC/cbs	
141.8	1.7	2008FEL/PET [92]	CC/cbs	
143.8	2.4	2003FLE/GRE [155]	MRCI+Q/cbs	D _c =1.121 eV
140.6		1998CUR/RAG1 [97]	CBS-Q	
146.0		1998CUR/RAG2 [98]	G3	

2.8 HO₃ (hydrotrioxyl radical)

HO₃ has been termed an “elusive” radical [160, 164, 167, 169] with regard to detection, molecular structure, vibrational frequencies, and enthalpy of formation – from both experimental and theoretical points of view. The first measurement of its gas phase enthalpy of formation was derived indirectly from correlations in electron transfer efficiencies of the positive ion HO₃⁺ with the ionization energies of a series of neutral electron donors by Speranza (1996) [165]. This value had a very high uncertainty (about 20 kJ mol⁻¹). Subsequent high level quantum chemical calculations, however, put the enthalpy of formation on the order of (20 to 40) kJ mol⁻¹ higher – and the quantum calculations showed a wide spread (see Table 8). Thus, the experimental value from Speranza was much lower (about 25 kJ mol⁻¹) than the currently accepted value and the theoretical values were much higher (about (10 to 15) kJ mol⁻¹) than the currently accepted value.

More recently, Lester and coworkers [161-164] measured the vibrational predissociation of HO₃ putting an upper limit on its bond dissociation energy D₀(HO-OO) moving the estimate for the enthalpy of formation upward by about (10 to 15) kJ mol⁻¹. In 2010, Le Picard et al. [160], using a spectroscopic kinetic/equilibrium measurement at low temperatures (87 K to 100 K), determined the bond dissociation energy (D₀) relatively precisely (reportedly within about 0.5 kJ mol⁻¹) and thus, pinned down the enthalpy

Table 8. Gas phase enthalpies of formation $\Delta_f H^\circ(298.15\text{ K})$ for HO_3

$\Delta_f H^\circ$ (kJ mol ⁻¹)	Uncert (kJ mol ⁻¹)	Reference	Method	Notes
Evaluation				
22.0	0.6	This work	Selected	2011BEA/LES [158]
27.8	0.7	2013RUS2 [134]	Thermo network	$\Delta_f H^\circ(0\text{ K})=32.7\text{ kJ/mol}$
18.1	6.2	2011SAN/ABB [14]	Review	$\Delta_f H^\circ(0\text{ K})=21.8\text{ kJ/mol}$
19.3	0.5	2010SMI/LEP [157]	Review	
Experimental				
22.0	0.5	2011BEA/LES [158]	Reevaluation	$D_0=1004(24)\text{ cm}^{-1}$ $\Delta_f H^\circ(0\text{ K})=25.26\text{ kJ/mol}$ Reevaluated 2010LEP/TIZ [160] using accurate torsion potential ($\Delta\Delta_f H^\circ(298\text{ K})=-3.3\text{ kJ/mol}$) [159]
19.3	0.5	2010LEP/TIZ [160]	Kinetics/Equil	$D_0=12.3(0.3)\text{ kJ/mol}; 1030(30)\text{ cm}^{-1}$ $\Delta_f H^\circ(0\text{ K})=24.9\text{ kJ/mol}$ ($\Delta\Delta_f H^\circ(298\text{ K})\equiv -5.6\text{ kJ/mol}$)
>10.4		2009MUR/DER [161]	Vib predissoc	$D_0<1860\text{ cm}^{-1}; <22.3\text{ kJ/mol}$
>10.5		2008DER/SEC [162]	Vib predissoc	$D_0<1856\text{ cm}^{-1}; <22.2\text{ kJ/mol}$
>7.1		2007MUR/DER [163]	Vib predissoc	$D_0<2140\text{ cm}^{-1}; <25.6\text{ kJ/mol}$ $\Delta_f H^\circ(298\text{ K})=7.1\text{ kJ/mol}$ ($\Delta\Delta_f H^\circ(298\text{ K})\equiv -4.5\text{ kJ/mol}$)
>6.3		2007DER/MUR [164]	Vib predissoc	$D_0<2208\text{ cm}^{-1}; <26.4\text{ kJ/mol}$
-4.2	21	1996SPE [165]	Ion cycle	IE=1059(17) kJ/mol
Calculation				
29.5		2014SPR/IRI [125]	CC-F12	$\Sigma D_0=923.3\text{ kJ/mol}$ $\Delta\Delta_f H^\circ(0\text{ K})=33.33\text{ kJ/mol}$
28.9	8	2014BUR [166]	G3B3	
21.1		2013ZHO/HU [167]	MRCI+Q/AV5Z	$D_e=21.9\text{ kJ/mol}$ $D_0=10.5\text{ kJ/mol}$
20.4	0.4	2012VAR [168]	MRCI+Q/cbs	$D_e=19.7\text{ kJ/mol}$ $D_0=11.3\text{ kJ/mol}$
21.6	0.4	2011VAR [169]	MRCI+Q/cbs	$D_e=19.8\text{ kJ/mol}$ $D_0=10.0\text{ kJ/mol}$
19.0		2010ANG/OLI [170]	CASPT2	$D_e=24.3\text{ kJ/mol}$ $D_0=12.6\text{ kJ/mol}$
21.3		2009VAR/HAR [171]	CC/cbs	$D_0=10.3\text{ kJ/mol}$
17.6	4.2	2009GRA/DIX [89]	CC/cbs	$\Delta_f H^\circ(0\text{ K})=21.3\text{ kJ/mol}$
23.0	4.2	2009DEN/ORN [143]	CC/cbs iso	$\Delta\Delta_f H^\circ(298\text{ K})=-4.4\text{ kJ/mol}$
5.8		2008BRA/YU [172]	DFT(HCTH)	$D_0=2153\text{ cm}^{-1}$
11.6		2008SEM/KHU [173]	DFT(PBE0)	$D_0=20\text{ kJ/mol}$
31.5		2008DEN/ORN [174]	CC/cbs	
23.0		2007MAN/ANG [175]	CASPT2	$D_0=8.6\text{ kJ/mol}$
32.9		2006JAN/FAB [176]	W1U	
15.3		2005SUM/SUM [177]	MRCI	$D_0=16.3\text{ kJ/mol}$
21.2		2005FAB/KAL [178]	MR-ACPF/cbs	$\Delta_f H^\circ(0\text{ K})=26.1\text{ kJ/mol}$
32.9		2005FAB/KAL [178]	CC/cbs	
28.5		2003DEN/KIE [179, 180]	CBS-APNO	
33.5		2003DEN/KIE [179, 180]	CBS-QB3	
35.6		2003DEN/KIE [179, 180]	G3	
36.8		2003DEN/KIE [179, 180]	CC/cbs	
24.9		2002XU/GOD [181]	B3LYP/cc-pVTZ	
19.3		2000SET/SAT [182]	CASSCF/MRMP2	$D_0=12.3\text{ kJ/mol}$
17.2		1998MCK/WRI [99]	G2MP2	$D_0=14.4\text{ kJ/mol}$
26.8		1996JUN/SEI [132]	CBS-Q/APNO	$D_0=4.8\text{ kJ/mol}$
91.2		1979NAN/BEN [183]	Empirical	

of formation of HO₃ with an acceptable level of uncertainty. Beames et al. (2011) [158] have since revised the dissociation energy D_0 from Le Picard et al. measurements by treating the torsional potential correctly in computing thermochemical functions [156] (see also Sec. 3.2.1). Since then there have been a number of high level quantum chemical calculations that confirmed the experimentally-derived value to within about (2 to 3) kJ mol⁻¹. The earlier “high” enthalpies of formation from theory were because of the inability of the single reference methods employed to properly treat HO₃ due to significant spin contamination and the multi-reference character of the wavefunctions (see discussion in references in Table 8). With the use of multi-reference configuration interaction methods and other treatments this problem was apparently solved. Thus, both the experimental and quantum chemical methods have converged to similar values for the enthalpy of formation of HO₃.

We selected an enthalpy of formation using the revised D_0 from Beames et al. and using a thermal correction from an enthalpy H° calculated treating the molecule as a rigid rotor harmonic oscillator (RRHO), plus using the scaled torsional potential of Beames et al. to compute the contribution of the hindered rotor (see Sec. 3.2.1 for more details). We also increased slightly the uncertainty assigned by Beames et al. (from 0.5 kJ mol⁻¹ to 0.6 kJ mol⁻¹) to reflect the uncertainty (est. 0.3 kJ mol⁻¹) in the contribution of the torsion to the free energy (considering uncertainties in both enthalpy H° and entropy S°).

We note that the quantum chemical calculations used a wide range of ZPEs (about 500 cm⁻¹ \equiv 6 kJ mol⁻¹) and this contributes to some of the spread in the theoretical values (see Sec. 3.1 and Table 11). In Table 11, we suggest the use of the ZPE from Grant et al. (2009) [89], which is an average of experimental fundamental and computed harmonic frequencies.

2.9 H₂O₃ (hydrogen trioxide)

There are no experimental determinations for the gas phase enthalpy of formation of H₂O₃. Hence, we have selected an enthalpy of formation based on the high level ab initio calculations of Grant et al. (2009) [89]. We have assigned an estimated (liberal) uncertainty of 1.2 kJ mol⁻¹ considering the uncertainties in the quantum chemical calculations (see Table 9 for the range of computed values), zero point energies, and the contribution to the enthalpy from the torsions. We have corrected the Grant et al. value slightly using the anharmonic ZPE computed by Hollman and Schaefer (2012) [200] and treating the torsions as hindered rotors (Grant et al. treated them as vibrations). These corrections increased the ZPE (and $\Delta_f H^\bullet$ at 0 K) by about 0.5 J/mol and the enthalpy $H^\circ(298.15\text{ K})$ by about 0.3 kJ mol⁻¹ for an increase in $\Delta_f H^\bullet(298.15\text{ K})$ of about 0.8 kJ mol⁻¹ relative to value provided by Grant et al. (There is also a substantial change in entropy S° and thus, in free energy $\Delta_f G^\bullet$ and the equilibrium constant/stability of H₂O₃). See Sec. 3.2.2 for more details.

2.10 Summary of Selected Values for Gas Phase Enthalpies of Formation

Table 10 is a summary of the selected values for the gas phase enthalpies of formation for each hydrogen-oxygen H_xO_y species as outlined in previous sections.

The gas phase enthalpies of formation of H atom, O atom, OH, H₂O, and O₃ have uncertainties of less than 0.1 kJ mol⁻¹. Compared to uncertainties associated with the values in the JANAF [1] and Gurvich et al. [2] thermochemical tables, the updated values in Table 10 are (50-100) times more precise for H atom, O atom, and O₃ and about 7 times more precise for OH. The precision for H₂O is only slightly better (about 33 %). For all of these species (except O₃), the values from quantum chemical calculations also agree to within 0.1 kJ mol⁻¹. In the case of ozone (O₃), the quantum chemical calculations agree to within the uncertainty of the calculations (estimated at 1.6 kJ mol⁻¹). This is excellent, and likely fortuitously, agreement given the unpaired electrons in ozone (requiring multiconfigurational calculational approaches).

The gas phase enthalpy of formation of H₂O₂ is also known relatively well (to less than 0.2 kJ mol⁻¹) being derived largely from a spectroscopic measurement of the $D_0(\text{HO-OH})$ dissociation energy (with a precision of about 3 cm⁻¹). The precision is only slightly better (about 25 %) compared to values in the JANAF and Gurvich thermochemical tables which are largely based on the calorimetric measurements of decades ago for the decomposition of H₂O₂ by Matheson and Maas (1929) [142] and Giguere et al. (1955) [140].

Table 9. Gas phase enthalpies of formation $\Delta_f H^\circ(298.15\text{ K})$ for H_2O_3

$\Delta_f H^\circ$ (kJ mol^{-1})	Uncert (kJ mol^{-1})	Reference	Method	Notes
Evaluation				
-88.1	1.2	This work	Selected	2009GRA/DIX [89] Also this work see text
-90.5	0.9	2011RUS [148]	Thermo network	$\Delta_f H^\circ(0\text{ K})=-81.4\text{ kJ/mol}$
-90.0		2011SAN/ABB [14]	Review	$\Delta_f H^\circ(0\text{ K})=-81.1\text{ kJ/mol}$
Calculation				
-89.4		2014BUR [166]	G3B3	
-92.6		2011MAR/ANG [184]	CC/pVQZ	
-88.1		2009GRA/DIX [89]	CC/cbs	$\Delta_f H^\circ(0\text{ K})=-79.8\text{ kJ/mol}$ Revised in this work
-89.1		2009GRA/DIX [89]	CC/cbs	$\Delta_f H^\circ(0\text{ K})=-80.3\text{ kJ/mol}$
-90.0		2009DEN/ORN [143]	CC/cbs iso	
-95.0		2002KRA/CRE [185]	CC/6-311G	
-83.3		2003DEN/KIE [179, 180]	G3	
-90.4		2003DEN/KIE [179, 180]	CC/cbs	
-88.3		2003DEN/KIE [179, 180]	CBS-APNO	
-98.3		2003DEN/KIE [179, 180]	CBS-QB3	
-96.2		1997LAY/BOZ [186]	G2 iso	
-83.1		2001LAN/WHE [187]	CC/pVTZ	$\text{H}_2\text{O}_3 + \text{H}_2 \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ $\Delta_f H(0\text{ K})=-294.1\text{ kJ/mol}$
-99.1		1998MCK/WRI [99]	G2MP2	$D_0(\text{HO}_2\text{-OH})=141.9\text{ kJ/mol}$
-105.9		1998MCK/WRI [99]	G2MP2	$D_0(\text{HO}_3\text{-H})=14.4\text{ kJ/mol}$

Table 10. Selected Gas Phase Enthalpies of Formation ($\Delta_f H^\circ$)

Species	$\Delta_f H^\circ(298.15\text{ K})$ (kJ mol^{-1})	$\Delta_f H^\circ(0\text{ K})$ (kJ mol^{-1})	Uncert (kJ mol^{-1})	Reference
H	217.9979	216.0340	0.0001	2004ZHA/CHE [22]
O	249.229	246.844	0.002	2014RUS/FEL [9]
OH	37.51	37.27	0.03	2013BOY/KOS [76]
H_2O	-241.831	-238.928	0.026	2013RUS [100]
HO_2	12.30	15.21	0.35	2006RUS/PIN [73]
H_2O_2	-135.51	-129.50	0.16	1992LUO/FLE [138]
O_3	141.73	144.39	0.04	2004RUS/PIN [6]
HO_3	22.0	25.3	0.6	2011BEA/LES [158]
H_2O_3	-88.1	-79.8	1.2	2009GRA/DIX [89] revised in this work

The uncertainty in the gas phase enthalpy of formation for hydroperoxyl radical HO_2 is somewhat larger – about 0.4 kJ mol^{-1} . The energies of neutral and ion reactions involving HO_2 have uncertainties of about $(1.5\text{ to }2.5)\text{ kJ mol}^{-1}$, while high level quantum chemical calculations have (estimated) uncertainties of about $(0.2\text{ to }0.4)\text{ kJ mol}^{-1}$. The selected value for the enthalpy of formation for HO_2 is now about 10 times more precise than the values in the JANAF and Gurvich et al. thermochemical tables.

The gas phase enthalpies of formation of the HO_3 radical and for H_2O_3 , which are important species in atmospheric chemistry, are not found in prior evaluation. We provide recommended values here, as well as supplementary data consisting of molecular geometries, vibrational frequencies, and torsional potentials for these species in Sec. 3.2. These data can be used to compute thermochemical functions (C_p , S° , H° , and $\Delta_f H^\circ$) for these species.

For many years, the enthalpy of formation of the HO₃ radical was elusive both from an experimental and theoretical point of view. The experimental values were “too low” by (10 to 20) kJ mol⁻¹ (compared to the now accepted value), while the theoretical values were “too high” by (10 to 15) kJ mol⁻¹. In the last 5 years (since 2010), both the experimental and quantum chemical methods converged to similar values – the experimental value (derived from a spectroscopic kinetic/equilibrium measurement) has an uncertainty of about (0.5 to 0.8) kJ mol⁻¹ and the quantum chemical values are known to about (2 to 3) kJ mol⁻¹.

There are no experimental measurements for the enthalpy of formation of H₂O₃. However, different high level quantum chemical methods predict similar values. We assigned a liberal (and estimated) uncertainty of about 1.2 kJ mol⁻¹ to the selected value considering the uncertainties in the contribution of the torsions to the enthalpy H° , zero point energy (ZPE), and the quantum chemical calculations.

3. Supplementary Data

3.1 Zero Point Energies and Vibrational Frequencies

Table 11 and Table 12 provide zero point energies (ZPEs) and vibrational frequencies, respectively, for the hydrogen-oxygen species. ZPEs are necessary for correcting electronic total atomization energies ΣD_e to ground state total atomization energies ΣD_0 (at T=0 K). The ZPEs are derived from vibrational frequencies including anharmonic terms.

The zero point energies (ZPEs) given in cm⁻¹ (standard spectroscopic units) for the hydrogen-oxygen species are given in Table 11. For the selected values, the ZPEs in kJ mol⁻¹ are given, along with uncertainties (2σ) (in parenthesis). The ZPEs for the diatomics H₂, O₂, and OH come from the review and analysis by Irikura [193, 194] and that for H₂O from the evaluation by Irikura et al. [195]. These ZPEs for H₂, O₂, OH, and H₂O are derived from experimental spectroscopic constants.

The ZPEs compiled in Table 11 used by different workers consist of a mix from experimental fundamental frequencies, computed harmonic frequencies, scaled computed harmonic frequencies (equivalent to fundamental frequencies), and averages of the harmonic and anharmonic frequencies (a relatively good approximation). In some cases anharmonic ZPEs were computed (more accurately) using the vibrational configuration interaction (VCI) [188] or second-order vibrational perturbation theory (VPT2) [189] methods. Some discussion regarding uncertainties in computed ZPEs can be found in work by Barone (2004) [190], Irikura et al. (2009) [195], Kesharwanti et al. (2015) [191], and references contained therein.

For each species in Table 11, for reference purposes, we have also provided ZPEs computed directly from the experimental fundamental frequencies ($ZPE_f = \frac{1}{2}\Sigma v_i$) and from the computed harmonic frequencies ($ZPE_h = \frac{1}{2}\Sigma \omega_e$). We have also computed an empirical estimate of anharmonic ZPEs using the relationship $ZPE_{emp} = (1/2)(ZPE_h + ZPE_f) + (1/8)(ZPE_h - ZPE_f)$ (the average of harmonic and anharmonic frequencies plus a correction) from the work of Csonka et al. (2005) [192] who found that the anharmonic ZPEs for a series of polyatomic molecules obeyed this relationship to about 7 cm⁻¹ (0.08 kJ mol⁻¹). We have used these values to screen our selected ZPE values and find a MAD (mean absolute deviation) of about 11 cm⁻¹ (0.13 kJ mol⁻¹) for this set of molecules – consistent with that estimated by Csonka et al.

Table 12 provides vibrational frequencies for the species. The first line for each species lists the experimental fundamental frequencies (ν) for that species [note: the ν_2 mode of HO₃ is the only mode derived from a quantum calculation]. The second line for each species lists the harmonic frequencies (ω_e) for that species. For most of these species the harmonic frequencies are derived from experimental spectroscopic rotational-vibrational lines, while for H₂O₂, HO₃, and H₂O₃ the harmonic frequencies are derived from ab initio calculations.

Table 11. Zero Point Energies (ZPE)

Species	ZPE (cm ⁻¹)	ZPE (kJ mol ⁻¹)	Reference
H ₂	2179.3(0.1)	26.07	2007IRI [193, 194]
O ₂	787.380(0.006)	9.42	2007IRI [193, 194]
OH	1850.69(0.05)	22.14	2007IRI [193, 194]
	1856		2015GAN/CSO [71]
	1857		2004TAJ/SZA [129]
	1860		2008HAR/VAZ [91]
H ₂ O	4636(10)	55.46(0.12)	2009IRI/JOH [195]
	4634		1991GRE/JAN [196]
	4645		2015GAN/CSO [71]
	4639		2013PFE/RAU [197]
	4723		2009KLO/RUS [198]
	4664		2008HAR/VAZ [91]
	4638		2006BAR/SHI [199]
	4659		2004TAJ/SZA [129]
	[f] 4504		Fundamental ½Σv _i
	[h] 4712		Harmonic ½Σω _e
	4634		Empirical (see text)
HO ₂	3068(16)	36.70(0.2)	2014SPR/IRI [125]
	3082		2015GAN/CSO [71]
	3095		2009KAR/PAR [126]
	3086		2008HAR/VAZ [91]
	3097		2004TAJ/SZA [129]
	3095		2004FLO/SZA [128]
	[h] 3117		2014SPRI/IRI
	[f] 2963		Fundamental ½Σv _i
	[h] 3105		Harmonic ½Σω _e
	3052		Empirical (see text)
H ₂ O ₂	5714(33)	68.35(0.4)	2014SPR/IRI [125]
	5685		2012HOL/SCH [200]
	5705		2009KAR/PAR [126]
	5726		2009KLO/RUS [198]
	5750		2009DEN/ORN [143]
	5750		2008FEL/PET [92]
	5751		2008HAR/VAZ [91]
	5748		2004TAJ/SZA [129]
	5726		2002MLA [201]
	5685		1999KUH/RIZ [147]
	[h] 5811		1999KUH/RIZ [147]
	[h] 5811		2012HOL/SCH [200]
	[h] 5814		2014SPR/IRI [125]
	[f] 5554		Fundamental ½Σv _i
	[h] 5837		Harmonic ½Σω _e
	5686		Empirical (see text)
O ₃	1451(8)	17.36(0.1)	2006KAR/RAB [202]
			2002BAR/CHI [203]
	1464		2014SPR/IRI [125]
	1476		2013PFE/RAU [197]
	1452		2010HOL/SZA [154]
	1471		2009KLO/RUS [198]
	1448		2008FEL/PET [92]
	[f] 1423		Fundamental ½Σv _i
	[h] 1470		Harmonic ½Σω _e
	1452		Empirical (see text)

HO ₃	3428(32)	41.0(0.4)	2009GRA/DIX [89]
	3541		2013SUM/SUM [204]
	3342		2012VAR [168]
	3590		2010ANG/OLI [170]
	3614		2009VAR/HAR [171]
	4092		2007MAN/ANG [175]
	3824		2000SET/SAT [182]
	3846		1996JUN/SEI [132]
	[a] 3661		2005FAB/KAL [178]
	[h] 3682		2014SPR/IRI [125]
	[h] 3588		2013ZHO/HU [167]
	[h] 3640		2010ANG/OLI [170]
	[h] 3834		2005FAB/KAL [178]
	[f] 3324		Fundamental $\frac{1}{2}\Sigma v_i$
	[h] 3590		Harmonic $\frac{1}{2}\Sigma \omega_e$
	3424		Empirical (see text)
H ₂ O ₃	6514(22)	77.92(0.3)	2012HOL/SCH [200]
	6474		2009GRA/DIX [89]
	6554		2009DEN/ORN [143]
	[hf] 6474		1993JAC [205]
	[f] 6302		Fundamental $\frac{1}{2}\Sigma v_i$
	[h] 6664		Harmonic $\frac{1}{2}\Sigma \omega_e$
		6528	
Notes			
h	ZPE _h = $\frac{1}{2}\Sigma \omega_e$ [harmonic frequencies]		
a	ZPE _a = $\frac{1}{2}\Sigma v_a$ [computed anharmonic]		
f	ZPE _f = $\frac{1}{2}\Sigma v_i$ [experimental fundamentals]		
hf	ZPE _{hf} = $\frac{1}{2}(ZPE_h + ZPE_f)$ [harmonic and fundamentals]		
Empirical	ZPE _{emp} = ZPE _{hf} + $\frac{1}{8}(ZPE_h - ZPE_f)$ [see Ref. [192]]		

Table 12. Vibrational Frequencies

Species	ν – Fundamental Frequencies (cm ⁻¹) ω_e – Harmonic Frequencies (cm ⁻¹)	Reference
H ₂	4161.0 4401.2	1955DIE [209] 2007IRI [193]
O ₂	1556.388 1580.161	1992ROU/MIL [210] 2007IRI [193]
OH	2988.6 3737.8	1956BAR [84] 2007IRI [193]
H ₂ O	3657.1, 1594.7, 3755.9 3832.2, 1648.5, 3942.5	2001TEN/ZOB [211] 1967PLI/SPI [212]
HO ₂	3436, 1392, 1098 3663, 1431, 1116	2013JAC/THO [213] 2007XU/JIA [214]
H ₂ O ₂	3610, 1383, 866(a), 371(b), 3611, 1266 3800, 1448, 915, 380(b), 3800, 1331	1988OLS/HUN [215] 2012HOL/SCH [200]
O ₃	1103.1, 700.9, 1042.1 1134.9, 716.0, 1089.2	1987STE/ADL [216] 1974BAR/SEC [217]
HO ₃	3569, 1225(c), 998, 482, 244, 129 3726, 1372, 1129, 533, 275, 144	2008DER/SEC2 [218] 2010ANG/OLI [170]
H ₂ O ₃	3530, 1347, 821, 509, 346, 3530, 1359, 776, 387 3750, 1397, 909, 531, 361, 3747, 1406, 811, 415	2002ENG/NEL [219] 2012HOLSCH [200]
(a) 1992CAM/FLA [220] (b) see text (c) no experimental fundamental, scaled harmonic frequency by 0.893, the average of other non-hydrogen frequencies in the molecule		

Experimental values for the vibrational frequencies for HO₂ and H₂O₂ can be found in the review by Jacox [206, 207]. There is a single high resolution measurement of the vibrational frequencies of H₂O₃ by Engdahl and Nelander [219]. Much earlier, Arnau and Giguere [208] measured ν_3 , ν_4 , and ν_8 for H₂O₃ at 857,400, and 755 cm⁻¹, respectively – about a 21 cm⁻¹ mean deviation from the values of Engdahl and Nelander.

There is some uncertainty in the vibrational modes (and thus in computed ZPEs) for two of the molecules – H₂O₂ and HO₃.

The torsion potential in H₂O₂ is a double well with two torsional frequencies 371 cm⁻¹ (ungerade) and 255 cm⁻¹ (gerade). For the other modes, there is good agreement between the computed anharmonic frequencies and the observed fundamental frequencies (mean absolute deviation of 11 cm⁻¹). For the torsional mode, however, there is a discrepancy where the computed anharmonic and harmonic frequencies are 316 cm⁻¹ and 380 cm⁻¹, respectively. That is, the harmonic frequency is comparable to the fundamental frequency (9 cm⁻¹ higher) when one might expect it to be (20 to 35) cm⁻¹ higher. In addition, the computed anharmonic frequency is substantially different than the measured fundamental frequency. See Sec. 3.2.2 for more discussion.

The torsional potential in HO₃ is a double well with a *cis* form about (0.9 to 1.2) kJ mol⁻¹ less stable than *trans* form and a *trans*-to-*cis* barrier of about (3 to 4) kJ mol⁻¹ – or $\Delta E=(75 \text{ to } 100) \text{ cm}^{-1}$ and $V=(250 \text{ to } 330) \text{ cm}^{-1}$, respectively. Beames et al. (2011) [158] have computed the torsional potential. The experimental torsional frequency for the *trans* form is 129 cm⁻¹ and the computed value for the *cis* form is slightly lower at 122 cm⁻¹. Accurate representation of this torsional potential is necessary to properly compute the thermochemical functions (particularly the entropy) at low temperatures (100 to 300) K which are relevant to atmospheric chemistry. See Sec. 3.2.1 for more discussion.

3.2 Supplementary Data for HO₃ and H₂O₃

In this section, we provide and discuss supplementary data for HO₃ and H₂O₃ consisting of molecular geometries, vibrational frequencies, and torsional potentials. These data are not provided in prior evaluations and can be used to compute thermochemical functions (C_p , S° , H° , and $\Delta_f H^\circ$). Both HO₃ and H₂O₃ are important species in atmospheric chemistry. HO₃ is considered to be a key intermediate, but is difficult to detect.

3.2.1 Data for HO₃

Suma et al. (2005) [177] derived a molecular geometry for HO₃ from rotational spectra yielding $r_0(\text{OO}^*)=1.225 \text{ \AA}$, $r_0(\text{OO})=1.688 \text{ \AA}$, $\theta_0(\text{OOO})=111.02^\circ$, $r_0(\text{OH})=0.972 \text{ \AA}$, and $\theta_0(\text{OOH})=90.04^\circ$ for the *trans* (most stable) form assuming a planar geometry. More recently, McCarthy et al. (2012) [221] similarly derived a molecular structure and found $r_0(\text{OO}^*)=1.235(4) \text{ \AA}$, $r_0(\text{OO})=1.684(3) \text{ \AA}$, $\theta_0(\text{OOO})=110.7(3)^\circ$, $r_0(\text{OH})=0.913(26) \text{ \AA}$, and $\theta_0(\text{OOH})=92.4(14)^\circ$. Their measured rotational constants correspond to moments of inertia $\{I_a, I_b, I_c\} = \{57.76, 50.60, 7.140\} \text{ amu \AA}^2$ or $\{9.59, 8.40, 1.186\} \times 10^{-46} \text{ kg m}^2$ in SI units. We utilize the molecular structure from the work of McCarthy et al. We note that later Suma et al. (2013) [204] derived values for equilibrium structure (r_e , θ_e) using the isotopic rotational constants from their earlier work and that of McCarthy et al. plus theoretically-derived vibration-rotation interaction constants.

Experimental vibrational frequencies for HO₃ come from the work of Derro et al. (2008) [218] except they did not observe ν_2 . Anglada et al. (2010) [141] computed harmonic vibrational frequencies using the CASSCF(19,15) level of theory. In this work, we used a scaled harmonic ν_2 from Anglada (see vibrational frequencies table in Sec. 3.1). The experimental fundamental and computed harmonic vibrational frequencies are given in Table 12.

The most stable form of HO₃ is a *trans* geometry. A number of workers have computed the difference in energy between the *cis* and *trans* forms. Braams and Yu (2008) [146] using the density functional method (DFT) HCTH computed that the *cis* form was 4.6 kJ mol⁻¹ higher with barrier-to-rotation of 8.8 kJ mol⁻¹. Beames et al. (2011) [158] using the EOMIP-CCSD/ANO method computed a torsional potential where the *cis* form was about 49 cm⁻¹ (0.59 kJ mol⁻¹) higher and there was a *trans*-to-*cis* classical barrier-to-rotation of 255 cm⁻¹ (3.05 kJ mol⁻¹). They utilized a scaling factor of 1.35 with the *ab initio*

potential to produce a torsional potential of 132 cm^{-1} that roughly agrees with the experimental torsional frequency of 129 cm^{-1} . Varandas (2012, 2011) [143, 222] using CCSD(T) and MRCI-Q methods with cc-pVnZ basis sets extrapolated to the complete basis set limit and including higher order corrections calculated the *cis* form to be (0.5 to 0.6) kJ/mol higher with a barrier-to-rotation of about (3.3 to 4.8) kJ mol⁻¹. Although Varandas computed the torsional potential as a function of torsional angle, unfortunately it is not provided in numerical form for use by others. Hoy et al. (2013) [223] using the 2-RDM density functional method computed that *cis*-HO₃ was about 7.4 kJ mol⁻¹ higher with a barrier-to-rotation of about 8.5 kJ mol⁻¹ (only slightly higher than the *cis* form).

We recommend using the scaled torsional potential of Beames et al. (2011) [158] to compute thermochemical functions for HO₃ (treating the rest of the molecule as a rigid rotor harmonic oscillator). In our work, RRHO calculations were performed using the program ChemRate [224] and hindered rotor thermochemical functions were computed using the program FGH1D (Fourier Grid Hamiltonian 1-D) [225]. We suggest employing a rotational constant of $B=22.93\text{ cm}^{-1}$ to generate a hindered rotor with a *trans* form with torsional frequency of 129 cm^{-1} and a *cis* form that was 84 cm^{-1} higher with a torsional frequency of 146 cm^{-1} . We also computed thermochemical functions for the hindered rotor using a simpler analytical torsional potential employing $V_n\cos(n\theta)$ terms with $V_1=54\text{ cm}^{-1}$ and $V_2=257\text{ cm}^{-1}$. This torsional potential gives a classical barrier of 288 cm^{-1} with the *cis* form at 49 cm^{-1} (0.6 kJ mol⁻¹) relative to the *trans* form and a torsional frequency of 129 cm^{-1} (we used a rotational constant of $B=22.93\text{ cm}^{-1}$ from the molecular geometry). We found small differences in the thermochemical functions relative to that computed using the scaled torsional potential of Beames et al.: entropies S° differing by about 0.1-0.4 J mol⁻¹ K⁻¹ and enthalpies H° differing by 0.2-0.4 kJ mol⁻¹ at temperatures of 300 K to 1000 K.

3.2.2 Data for H₂O₃

Suma et al. (2005) [226] derived a molecular geometry for H₂O₃ from rotational transitions yielding $r_0(\text{OO})=1.428\text{ \AA}$, $\theta_0(\text{OOO})=107.0^\circ$, $r_0(\text{OH})=0.963\text{ \AA}$, $\theta_0(\text{OOH})=101.1^\circ$, and $\phi_0(\text{OOOH})=81.8^\circ$. This structure was derived from rotational constants $B_a=1.706\text{ cm}^{-1}$, $B_b=0.351\text{ cm}^{-1}$, and $B_c=0.312\text{ cm}^{-1}$. These correspond to moments of inertia $\{I_a, I_b, I_c\} = \{9.88, 47.28, 54.02\}\text{ amu \AA}^2$ or $\{1.64, 7.85, 8.97\}\times 10^{-46}\text{ kg m}^2$ in SI units. By comparing the measured rotational constants to those derived from structures from their ab initio calculations, they determined that the *trans* form was more stable than the *cis* form. We note that the first molecular structures for H₂O₃ calculated by Blint and Newton (1973) [227] and Cremer (1978) [228] using quantum chemical methods are in fairly good agreement with those experimentally determined by Suma et al.

Engdahl and Nelander [219] measured all of the vibrational frequencies for H₂O₃ (see Table 12). Earlier, Arnau and Giguere (1974) [208] measured three frequencies: ν_3 , ν_4 , and ν_8 . Hollman and Schaefer (2012) [200] computed anharmonic and harmonic frequencies (the latter are given in Table 12). Jackel (1993) [205] has also computed harmonic frequencies.

The most stable rotational conformer of H₂O₃ is a *trans* form. Su et al. (2002) [229] calculated the *cis* form to be 10.0 kJ mol⁻¹ higher a barrier-to-isomerization of 21.8 kJ mol⁻¹. We note that the first quantum chemical calculations (MP2) of the rotational potential of this molecule were done by Cremer (1978) [228] and predicted the *cis* form to be about 15.9 kJ mol⁻¹ less stable and that there was a very high barrier-to-isomerization of 46.4 kJ mol⁻¹.

To compute thermochemical functions for H₂O₃, we recommend treating the molecule as a rigid rotor harmonic oscillator (RRHO) with the two torsions treated as hindered rotors, and employing the molecular structure of Suma et al. and the vibrational frequencies of Engdahl and Nelander.

We note that in order to correctly compute the hindered rotor partition functions one would need to treat them as two coupled rotors and account for the difference between the *trans* and *cis* forms. This is a difficult problem that we cannot solve here. We have treated it as the sum of two identical 1-D rotors. We estimated the uncertainty in the free energy $G^\circ(298.15\text{ K})$ to be about 0.3 kJ mol⁻¹ to account for this approximate treatment (considering uncertainties in both enthalpy H° and entropy S°).

Using the FGH1D program [225], we reproduced the *cis-trans* energy difference and barrier-to-rotation of 10.0 kJ mol⁻¹ (836 cm^{-1}) and 22.1 kJ mol⁻¹ (1847 cm^{-1}), respectively, using $V_n\cos(n\theta)$ functions with $V_1=860\text{ cm}^{-1}$ and $V_2=1580\text{ cm}^{-1}$ employing a rotational constant of $B=21.09\text{ cm}^{-1}$ (from the molecular structure). This yielded fundamental frequencies for the *trans* and *cis* conformers of 369 cm^{-1} and

313 cm^{-1} . This frequency for the *trans* conformer is very close to the average of the symmetric torsional ($\nu_9=346 \text{ cm}^{-1}$) and asymmetric torsional modes ($\nu_8=387 \text{ cm}^{-1}$).

The enthalpy of formation that we selected for H_2O_3 was derived from the quantum chemical calculations of Grant et al. (2009) [89] (there are no experimental measurements). We have corrected their value slightly using the anharmonic ZPE computed by Hollman and Schaefer (2012) [200] and treated the torsions as hindered rotors (Grant et al. treated them as vibrations). They used a ZPE of 6474 cm^{-1} (see Table 11) based on an average of the experimental fundamental frequencies (ν) and computed harmonic frequencies (ω_e). We have employed the anharmonic ZPE of 6514 cm^{-1} computed by Hollman and Schaefer (a difference of $+0.47 \text{ kJ mol}^{-1}$) and our computed enthalpy H° of $13.00 \text{ kJ mol}^{-1}$ (a difference of $+0.45 \text{ kJ mol}^{-1}$).

Xu and Goddard (2002) [181] reported on a chemical mechanism for the formation of H_2O_3 from $\text{H}_2 + \text{O}_3$ based on quantum chemical calculations [229] and analysis of experimental data from Engdahl and Nelander (2002) [219] and Goddard and coworkers (2001,2002) [229-231]. They found that the reaction $\text{H}_2\text{O}_2 + \text{O}_3 \rightarrow \text{H}_2\text{O}_3 + \text{O}_2$ occurs via a set of complex reactions with ring intermediates. The barrier-to-addition of O_3 to H_2O_2 to form an OOOH-OOH adduct is about 6.3 kJ mol^{-1} and the reaction overall to form H_2O_3 is about 135 kJ mol^{-1} exothermic. H_2O_3 is formed in a *cis* configuration (from decomposition of a ring). They calculated that *cis* form was about 10.0 kJ mol^{-1} (836 cm^{-1}) higher in energy than the *trans* form and that the barrier-to-isomerization from *trans*-to-*cis* was about 22.1 kJ mol^{-1} (1847 cm^{-1}).

Goddard and coworkers calculated vibrational frequencies for H_2O_3 both *cis* and *trans* using the B3LYP/6-31G** method. They found excellent agreement between the experimental values of Engdahl and Nelander using average scaling factor (expt/theory) of 0.985. The vibrational frequencies of the *cis* form in general were very similar to the *trans* form differing by about (0.5 to 1)%. However, the symmetric torsion ν_9 for the *cis* form was 190 cm^{-1} or much lower than the experimental and calculated values of 346 cm^{-1} and 347 cm^{-1} , respectively. The ratio of the experimental asymmetric torsion ν_8 (387 cm^{-1}) to the symmetric torsion ν_9 (346 cm^{-1}) of 1.12 is consistent with slightly different (20 %) rotational constants for the two (opposite) modes on the same potential energy surface. The very low calculated symmetric torsion ν_9 for the *cis* form implies that the two motions are highly coupled (energetically) and that use of a simple 1-D torsion potential energy surface is not fully adequate.

3.3 Ion Energetics

In Table 13, ion reaction energetics, such as ionization energies, electron affinities, and appearance energies, are provided, along with uncertainties. These quantities are utilized to compute enthalpies of formation for a number of the hydrogen-oxygen species using thermochemical cycles involving ion processes. This compilation is of the most precise values available (not all reported values are included). The values are given both in their original reported units and converted to kJ mol^{-1} . The conversion factors employed are given in Sec. 1 “Introduction.”

Table 13. Ion Reactions

Species	Quantity	Energy (orig units)	Energy (kJ mol^{-1})	Reference
H	IE	0.9994665083441(43) Ry	1312.04948(6)	2015YER/SHA [232]
	IE	109678.77174307(10) cm^{-1}	1312.04948(6)	2015KRA/RAL [233] 2005JEN/KOT [234]
	IE	109678.7717(na) cm^{-1}	1312.04948	2005SAN/MAR [235]
	IE	109678.771196(5) cm^{-1}	1312.04948(6)	1985JOH/SOF [236]
	IE	109678.764(na) cm^{-1}	1312.04939	1970MOO [237]
	IE	109678.758(na) cm^{-1}	1312.04932	1966WIE/SMI [238]
	IE	109678.764(na) cm^{-1}	1312.04939	1965GAR/MAC [239]
	EA	6082.99(15) cm^{-1}	72.769(2)	1991LYK/MUR [240]
	EA	6083.0958(na) cm^{-1}	72.770	1962PEK [241]
H_2	IE	124417.49113(37) cm^{-1}	1488.363722(4)	2009LIU/SAL [20]
	IE	124417.476(12) cm^{-1}	1488.36354(14)	2002DEL/REI [242]
	IE	124417.491 cm^{-1}	1488.36372	1995WOL [37] (quantum)
	IE	124417.507(12) cm^{-1}	1488.36391(14)	1993SHI/GIL [243]

	IE	124417.501(17) cm ⁻¹	1488.36384(20)	1992JUN/DAB [244, 245]
	IE	124417.507(18) cm ⁻¹	1488.36391(22)	1992GIL/EYL [246]
	IE	124417.524(15) cm ⁻¹	1488.36412(18)	1989MCC/GIL [247]
	IE	124417.61(7) cm ⁻¹	1488.3651(8)	1987GLA/HES [248]
	IE	124417.2(4) cm ⁻¹	1488.360(5)	1972HER/JUN [249]
	AE(H+)	18.078(3) cm ⁻¹	1744.3(3)	1994WEI/MAH [250]
	IPF(H+,H-)	139714.8(1.0) cm ⁻¹	1671.361(10)	2000SHI/HU [251]
	IPF(H+,H-)	139714.0(0.2) cm ⁻¹	1671.351(2)	1992PRA/MCC [252]
	IPF(H+,H-)	17.3223(2) eV	1671.35(2)	1975CHU/DEH [253]
O	IE	109837.02(6) cm ⁻¹	1313.9426(7)	1976MOO [254]
	EA	11784.676(7) cm ⁻¹	140.9760(1)	2005BLO/CHA [255]
	EA	11784.648(6) cm ⁻¹	140.9761(1)	1995BLO [256]
	EA	11784.645(6) cm ⁻¹	140.9757(1)	1985NEU/LYK [257]
	EA	11784.675(6) cm ⁻¹	140.9760(1)	1985NEU/LYK [257] revised by 2005BLO/CHA [255]
OH	IE		1255.95(4)	2015GAN/CSO [71]
	IE	104989(2) cm ⁻¹	1255.95(2)	1992WIE/TON [81]
	EA	14740.982(7) cm ⁻¹	176.3413(1)	2005GOL/DRA [258]
	EA	14741.02(3) cm ⁻¹	176.3418(4)	1997SMI/KIM [259]
H ₂ O	IE	101766.8(1.2) cm ⁻¹	1217.401(14)	1998MER/SIG [260]
	IE	101766(2) cm ⁻¹	1217.392(24)	1991TON/WIE [261]
	IE	101772(2) cm ⁻¹	1217.463(24)	1990CHI/JUN [262]
	AE(OH+)	18.1182(9) eV	1748.14(9)	2014BOD/CSO [263]
	AE(OH+)	146117(24) cm ⁻¹	1747.95(29)	2002RUS/WAG [74]
	AE(OH+)	18.115(4) eV	1747.8(4)	2001RUS/FEL [79]
	AE(OH+)	18.115(8) eV	1747.8(8)	1976MCC [82]
O ₂	IE	97345(4) cm ⁻¹	1164.505(48)	1999SON/EVA [264]
	IE	97352.2(1.2) cm ⁻¹	1164.591(14)	1998MER/SIG [260]
	IE	97347(1.3) cm ⁻¹	1164.529(16)	1994KON/HEP [265]
	IE	97348(2) cm ⁻¹	1164.54(2)	1989TON/WIN [266]
	IE	12.071(1) eV	1164.67(10)	1975SAM/GAR [267]
	EA	0.448(6) eV	43.2(6)	2003ERV/ANU [268]
	EA	0.451(7) eV	43.5(7)	1989TRA/COW [269]
	EA	0.440(8) eV	42.5(8)	1972CEL/BEN [270]
	IPF(O ⁺ ,O ⁻)	139319.1(7) cm ⁻¹	1666.627(8)	1997MAR/HEP [53]
	IPF(O ⁺ ,O ⁻)	139312.6(9.7) cm ⁻¹	1666.515(12)	1975DEH/CHU [59]
O ₂ ⁺	AE(O+)	18.73(1) eV	1807.2(1.0)	1985RIC/DUT [271]
	AE(O+)	18.734(1) eV	1807.56(0.10)	1981BLY/POW [56]
HO ₂	IE		1095.71(0.45)	2015GAN/CSO [71]
	IE	11.352(7) eV	1095.3(0.7)	1998LIT/RUS [112]
	IE	11.35(1) eV	1096(1)	1981DYK/JON [272]
	EA		103.88(0.44)	2015GAN/CSO [71]
	EA	1.078(6) eV	104.0(0.6)	2002RAM/BLA [110]
	EA	1.089(6) eV	105.1(0.6)	1998CLI/WEN [111]
	EA	1.078(17) eV	104.0(1.6)	1985OAK/HAR [114]
H ₂ O ₂	IE	10.631(7) eV	1025.7(0.7)	1998LIT/RUS [112]
	AE(HO ₂ +)	15.112(35) eV	1458.1(3.4)	1998LIT/RUS [112]
	AE(OH+)	15.174(4) eV	1464.1(0.4)	1998LIT/RUS [112]
	AE(H+)		1575.3(2.1)	2002RAM/BLA [110]
O ₃	IE		1208.47(6)	2005WIL/INN [273]
	IE	12.519(4) eV	1207.9(4)	1977WEI/BER [274]
	EA	2.103(4) eV	202.9(4)	1994ARN/XU [275]
	EA	2.1028(25) eV	202.89(24)	1979NOV/ENG [276]

4. Glossary

Notations, acronyms, and abbreviations referred to in this work are provided in Table 14 along with a short description for each. References are also provided for the quantum chemical methods for more information.

Table 14. Notations and Descriptions

Notation	Description	Reference
Absorp limit	Absorption limit	
AE	Appearance Energy	
Calorim decomp	Calorimetric decomposition	
Dissoc continuum	Dissociation continuum	
EA	Electron Affinity	
Empirical	Estimated using empirical trends	
Equilibrium	Determined from equilibrium	
Heat combustion	Determined from heat of combustion.	
Heat reaction	Determined from heat of reaction.	
IE	Ionization Energy	
Ion cycle	Derived using thermochemical cycles using ion energetics	
Ion pair dissoc	Ion pair dissociation	
Ioniz threshold	Ionization threshold	
Ioniz/Quantum	Ionization threshold combined with quantum (see text for H atom)	
IPF	Ion Pair Formation	
Kinetics	Measured using a kinetic method and forward and reverse barriers to reaction	
Kinetics/Equil	Measured using kinetics along with equilibrium measurements	
Review	Recommend value based on a review/evaluation	
PEPICO	Photoelectron photoion coincidence spectroscopy	
Photodissoc	Photodissociation	
Photofrag spec	Photofragment spectroscopy	
Photofragment	Photofragmentation	
Spec dissoc limit	Spectroscopic dissociation limit	
Thermo network	Thermochemical network	
Vib predissoc	Vibrational predissociation	
Quantum Chemical Methods		
B3LYP	Becke Three Parameter method with LYP Hybrid Functionals	1993BEC [277]
CASPT2	Complete active space (second order perturbation) method.	1998FIN/MAL [278]
CASSCF	Complete active space self-consistent field method	1985KNO/WER [279]
CBS-APNO	Complete basis set-quadratic CI model with atomic pair natural orbitals	1996OCH/PET [280]
CBS-Q	Complete basis set-quadratic CI model using QCISD(T) and large basis sets	1996OCH/PET [281]
CBS-QB3	CBS-Q method with B3LYP DFT geometries and frequencies	1999MON/FRI [282]
CC	Use of one of a number of coupled cluster methods. Could be CCSD (single and double excitations), CCSD(T) (approximate triples), CCSDQ (quintuplets), etc.	1978BAR/PUR [283]
CC-F12	Coupled cluster method with F12 corrections/correlations	2009KNI/ADL [284]
CC-R12	Coupled cluster method with R12 corrections/correlations	1994NOG/KUT [285]
CCSD(T)	CC with single and double excitation and approximate triples	
CISD	Configuration interaction method with single and double excitations	1977POP/SEE [286]
DFT(HCTH)	Density functional method using the HCTH functional	1998HAM/COH [287]
DFT(PBE0)	Density functional method using the PBE0 functional	1999ADA/BAR [288]
EOMIP	Equation of motion ionization problem	1994STA/GAU [289]
FCI	Full configuration interaction method	1984KNO/HAN [290]
FCI(CEEIS)	FCI method with correlation energy extrapolation by intrinsic scaling	2005BYT/RUE [66]
FCI(SCI)	FCI method with selected configuration interaction truncation	2006BUN [291]
G2	Gaussian-2 quantum chemical method	1991CUR/RAG [292]
G2MP2	Approximate G2 method using MP2 energies	
G3	Gaussian-3 quantum chemical method	1999CUR/RAG [98]
G3B3	G3 method using B3LYP DFT geometries and frequencies	
G3MP2	Approximate G3 method using MP2 energies	

G3MP2B3	G3 method using MP2 energies and B3LYP geometries	
HEAT	High accuracy extrapolated ab initio thermochemistry method	2004TAJ/SZA [129]
iso	Use of an ab initio method with energies corrected using isodesmic reactions	
MR-ACPF	Multireference theory with averaged coupled pair functional	1988GDA/AHL [293]
MRCI	Multireference configuration interaction approach	1978BUE/PEY [294]
MRCI+Q	MRCI method with Davidson correction	1974LAN [295]
MRSDCI	MRCI approach with singlet and doublet excitation	
MRMP2	Use of multireference MP2 energy differences	1992HIR [296]
MR-CISD	Multireference with CISD method	
NEAT	Network of Computed Reaction Enthalpies to Atom-Based Thermochemistry method.	2010CSA/FUR [87]
QCI	Use of a quadratic configuration method	1987POP/HEA [297]
Quantum	Use of a quantum chemical method (unspecified)	
W1	W1 quantum chemical method	1999MAR/DEO [298]
W1U	Variant of W1 quantum chemical method	
W2	W2 quantum chemical method	1999MAR/DEO [298]
W4	W4 quantum chemical method	2006KAR/RAB [202]
Quantum Chemical Basis Sets		
/AV5Z	Use of an aug-cc-pV5Z type basis set	
/cbs	Use of correlation consistent basis sets (e.g., aug-cc-pVnZ) extrapolated to the complete basis set limit.	1998TRU [299] 1999FEL/PET [300]
/DZ	Use of a double zeta type basis set	
/pVTZ	Use of a cc-pVTZ type basis set (may include diffuse functions)	
/pVQZ	Use of a cc-pVQZ type basis set (may include diffuse functions)	
/pV6Z	Use of a cc-pV6Z type basis set (may include diffuse functions)	

5. References

- [1] M. W. Chase Jr., "NIST-JANAF Thermochemical Tables, Fourth Edition," *J. Phys. Chem. Ref. Data, Monograph 9*, 1-1951 (1998).
- [2] L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances. Volume 1*, Hemisphere Pub. Co., New York, (1989).
- [3] B. N. Taylor and C. E. Kuyatt, *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, NIST Technical Note 1297, National Institute of Standards and Technology, Gaithersburg, MD (1994).
- [4] P. J. Mohr, B. N. Taylor, and D. B. Newell, "CODATA recommended values of the fundamental physical constants: 2010," *J. Phys. Chem. Ref. Data* **41**, 043109 (2012). <http://dx.doi.org/10.1063/1.4724320>
- [5] B. Ruscic, R. E. Pinzon, M. L. Morton, G. von Laszewski, S. Bittner, S. G. Nijsure, K. A. Amin, M. Minkoff, and A. F. Wagner, "Active Thermochemical Tables Software and Associated Data Libraries," Argonne National Laboratory, Argonne, IL, 2002-2004.
- [6] B. Ruscic, R. E. Pinzon, M. L. Morton, G. von Laszewski, S. J. Bittner, S. G. Nijsure, K. A. Amin, M. Minkoff, and A. F. Wagner, "Introduction to active thermochemical tables: Several "key" enthalpies of formation revisited," *J. Phys. Chem. A* **108**, 9979 (2004). <http://dx.doi.org/10.1021/Jp047912y>
- [7] B. Ruscic, R. E. Pinzon, G. von Laszewski, D. Kodeboyina, A. Burcat, D. Leahy, D. Montoya, and A. F. Wagner, "Active Thermochemical Tables: thermochemistry for the 21st century," *J. Phys. Conf. Ser.* **16**, 561 (2005). <http://dx.doi.org/10.1088/1742-6596/16/1/078>
- [8] B. Ruscic, J. E. Boggs, A. Burcat, A. G. Csaszar, J. Demaison, R. Janoschek, J. M. L. Martin, M. L. Morton, M. J. Rossi, J. F. Stanton, P. G. Szalay, P. R. Westmoreland, F. Zabel, and T. Berces, "IUPAC critical evaluation of thermochemical properties of selected radicals," *J. Phys. Chem. Ref. Data* **34**, 573 (2005). <http://dx.doi.org/10.1063/1.1724828>
- [9] B. Ruscic, D. Feller, and K. A. Peterson, "Active Thermochemical Tables: dissociation energies of several homonuclear first-row diatomics and related thermochemical values," *Theor. Chem. Acct.* **133**, 1415 (2014). <http://dx.doi.org/10.1007/S00214-013-1415-Z>
- [10] B. Ruscic, "Uncertainty quantification in thermochemistry, benchmarking electronic structure computations, and Active Thermochemical Tables," *Int. J. Quant. Chem.* **114**, 1097 (2014). <http://dx.doi.org/10.1002/qua.24605>
- [11] B. Ruscic, Active Thermochemical Tables (ATcT), <http://atct.anl.gov> [Accessed August 31, 2015].
- [12] E. Goos, A. Burcat, and B. Ruscic, Extended Third Millennium Ideal Gas Thermochemical Database with Updates from Active Thermochemical Tables, <http://burcat.technion.ac.il/dir/BURCAT.THR> [Accessed August 31, 2015].
- [13] D. Sprecher, C. Jungen, W. Ubachs, and F. Merkt, "Towards measuring the ionisation and dissociation energies of molecular hydrogen with sub-MHz accuracy," *Faraday Discuss.* **150**, 51 (2011). <http://dx.doi.org/10.1039/C0fd00035c>

- [14] S. P. Sander, J. Abbatt, J. R. Barker, J. B. Burkholder, R. R. Friedl, D. M. Golden, R. E. Huie, C. E. Kolb, M. J. Kurylo, G. K. Moortgat, V. L. Orkin, and P. H. Wine, Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17 (JPL Publication 10-6), Jet Propulsion Laboratory, Pasadena (2011). <http://jpldataeval.jpl.nasa.gov> [Accessed August 12, 2015].
- [15] B. P. Stoicheff, "On the dissociation energy of molecular hydrogen," *Can. J. Phys.* **79**, 165 (2001). <http://dx.doi.org/10.1139/cjp-79-2-3-165>
- [16] J. D. Cox, D. D. Wagman, and V. A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere Publishing Corp., New York (1989).
- [17] W. C. Stwalley, "The dissociation energy of the hydrogen molecule using long-range forces," *Chem. Phys. Lett.* **6**, 241 (1970). [http://dx.doi.org/10.1016/0009-2614\(70\)80t-5](http://dx.doi.org/10.1016/0009-2614(70)80t-5)
- [18] B. deB. Darwent, "Bond dissociation energies in simple molecules," Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.) 31 (1970).
- [19] B. Jeziorski and W. Kotos, "On the ionization potential of H₂," *Chem. Phys. Lett.* **3**, 677 (1969). [http://dx.doi.org/10.1016/0009-2614\(69\)87007-7](http://dx.doi.org/10.1016/0009-2614(69)87007-7)
- [20] J. J. Liu, E. J. Salumbides, U. Hollenstein, J. C. J. Koelemeij, K. S. E. Eikema, W. Ubachs, and F. Merkt, "Determination of the ionization and dissociation energies of the hydrogen molecule," *J. Chem. Phys.* **130**, 174306 (2009). <http://dx.doi.org/10.1063/1.3120443>
- [21] J. Liu, D. Sprecher, F. Merkt, E. J. Salumbides, and W. Ubachs, "Determination of the ionization and dissociation energies of H₂ and He₂," *AIP. Conf. Proc.* **1504** (2012). <http://dx.doi.org/10.1063/1.4771748>
- [22] Y. P. Zhang, C. H. Cheng, J. T. Kim, J. Stanojevic, and E. E. Eyler, "Dissociation energies of molecular hydrogen and the hydrogen molecular ion," *Phys. Rev. Lett.* **92**, 203003 (2004). <http://dx.doi.org/10.1103/PhysRevLett.92.203003>
- [23] A. Balakrishnan, V. Smith, and B. P. Stoicheff, "Dissociation energies of the hydrogen and deuterium molecules," *Phys. Rev. A* **49**, 2460 (1994). <http://dx.doi.org/10.1103/PhysRevA.49.2460>
- [24] E. E. Eyler and N. Melikechi, "Near-threshold continuum structure and the dissociation-energies of H₂, HD, and D₂," *Phys. Rev. A* **48**, R18 (1993). <http://dx.doi.org/10.1103/PhysRevA.48.R18>
- [25] A. Balakrishnan, V. Smith, and B. P. Stoicheff, "Dissociation Energy of the hydrogen molecule," *Phys. Rev. Lett.* **68**, 2149 (1992). <http://dx.doi.org/10.1103/PhysRevLett.68.2149>
- [26] E. F. McCormack and E. E. Eyler, "Perturbed structure of molecular hydrogen near the 2nd dissociation limit," *Phys. Rev. Lett.* **66**, 1042 (1991). <http://dx.doi.org/10.1103/PhysRevLett.66.1042>
- [27] G. Herzberg, "Dissociation energy of hydrogen molecule," *J. Mol. Spectrosc.* **33**, 147 (1970). [http://dx.doi.org/10.1016/0022-2852\(70\)90060-3](http://dx.doi.org/10.1016/0022-2852(70)90060-3)
- [28] G. Herzberg and A. Monfils, "The dissociation energies of the H₂, HD, and D₂ molecules," *J. Mol. Spectrosc.* **5**, 482 (1960). [http://dx.doi.org/10.1016/0022-2852\(61\)90111-4](http://dx.doi.org/10.1016/0022-2852(61)90111-4)
- [29] H. Beutler and H. O. Junger, "The binding strength in the H₂ molecule," *Z. Phys.* **101**, 304 (1936). <http://dx.doi.org/10.1007/BF01342327>
- [30] O. W. Richardson and P. M. Davidson, "The spectrum of H₂ - The bands analogous to the parhelium line spectrum - Part II," *Proc. Roy. Soc. Lond. A* **123**, 466 (1929). <http://dx.doi.org/10.1098/rspa.1929.0079>
- [31] G. H. Dieke and J. J. Hopfield, "The structure of the ultra-violet spectrum of the hydrogen molecule," *Phys. Rev.* **30**, 400 (1927). <http://dx.doi.org/10.1103/PhysRev.30.400>
- [32] I. Isanrdi, "Concerning the thermal conduction in dissociated gas and concerning dissociation of water material in an atom," *Z. Elektrochem.* **21**, 405 (1915). <http://dx.doi.org/10.1002/bbpc.19150211701>
- [33] K. Wohl, "The dissociation of chlorine and hydrogen in the atom 2 Part - The dissociation of hydrogen," *Z. Elektrochem.* **30**, 49 (1924). <http://dx.doi.org/10.1002/bbpc.19240300301>
- [34] I. Langmuir, "The dissociation of hydrogen into atoms. Part II. Calculation of the degree of dissociation and the heat of formation," *J. Am. Chem. Soc.* **37**, 417 (1915). <http://dx.doi.org/10.1021/ja02168a002>
- [35] I. Langmuir, "Flames of hydrogen," *General Electric Review* **29**, 153 (1926).
- [36] K. Piszczatowski, G. Lach, M. Przybytek, J. Komasa, K. Pachucki, and B. Jeziorski, "Theoretical determination of the dissociation energy of molecular hydrogen," *J. Chem. Theory Comput.* **5**, 3039 (2009). <http://dx.doi.org/10.1021/Ct900391p>
- [37] L. Wolniewicz, "Nonadiabatic energies of the ground-state of the hydrogen molecule," *J. Chem. Phys.* **103**, 1792 (1995). <http://dx.doi.org/10.1063/1.469753>
- [38] W. Kolos and J. Rychlewski, "Improved theoretical dissociation-energy and ionization-potential for the ground-state of the hydroge molecule," *J. Chem. Phys.* **98**, 3960 (1993). <http://dx.doi.org/10.1063/1.464023>
- [39] L. Wolniewicz, "Relativistic energies of the ground-state of the hydrogen molecule," *J. Chem. Phys.* **99**, 1851 (1993). <http://dx.doi.org/10.1063/1.465303>
- [40] C. Schwartz and R. J. Leroy, "Nonadiabatic eigenvalues and adiabatic matrix-elements for all isotopes of diatomic hydrogen," *J. Mol. Spectrosc.* **121**, 420 (1987). [http://dx.doi.org/10.1016/0022-2852\(87\)90059-2](http://dx.doi.org/10.1016/0022-2852(87)90059-2)
- [41] W. Kolos, K. Szalewicz, and H. J. Monkhorst, "New Born-Oppenheimer potential-energy curve and vibrational energies for the electronic ground-state of the hydrogen molecule," *J. Chem. Phys.* **84**, 3278 (1986). <http://dx.doi.org/10.1063/1.450258>
- [42] L. Wolniewicz, "The X¹Σ_g⁺ state vibration-rotational energies of the H₂, HD, and D₂ molecules," *J. Chem. Phys.* **78**, 6173 (1983). <http://dx.doi.org/10.1063/1.444580>
- [43] D. M. Bishop and L. M. Cheung, "Rigorous theoretical investigation of ground-state of H₂," *Phys. Rev. A* **18**, 1846 (1978). <http://dx.doi.org/10.1103/PhysRevA.18.1846>
- [44] W. Kolos and L. Wolniewicz, "Improved potential-energy curve and vibrational energies for electronic ground-state of hydrogen molecule," *J. Mol. Spectrosc.* **54**, 303 (1975). [http://dx.doi.org/10.1016/0022-2852\(75\)90083-1](http://dx.doi.org/10.1016/0022-2852(75)90083-1)
- [45] P. R. Bunker, "Breakdown of Born-Oppenheimer approximation for a diatomic molecule," *J. Mol. Spectrosc.* **42**, 478 (1972). [http://dx.doi.org/10.1016/0022-2852\(72\)90224-X](http://dx.doi.org/10.1016/0022-2852(72)90224-X)

- [46] W. Kolos and L. Wolniewicz, "Improved theoretical ground-state energy of hydrogen molecule," *J. Chem. Phys.* **49**, 404 (1968). <http://dx.doi.org/10.1063/1.1669836>
- [47] G. Hunter, "Adiabatic dissociation energies for the ground states of the H₂, HD, and D₂ molecules," *J. Chem. Phys.* **45**, 3022 (1966). <http://dx.doi.org/10.1063/1.1728057>
- [48] W. Kolos and L. Wolniewicz, "Accurate computation of vibronic energies and of some expectation values for H₂, D₂, and T₂," *J. Chem. Phys.* **41**, 3674 (1964). <http://dx.doi.org/10.1063/1.1725797>
- [49] W. Kolos and C. C. J. Roothaan, "Accurate electronic wave functions for the H₂ molecule," *Rev. Mod. Phys.* **32**, 219 (1960). <http://dx.doi.org/10.1103/RevModPhys.32.219>
- [50] H. M. James and A. S. Coolidge, "The ground state of the hydrogen molecule," *J. Chem. Phys.* **1**, 825 (1933). <http://dx.doi.org/10.1063/1.1749252>
- [51] C. E. Moore, Tables of Spectra of Hydrogen, Carbon, Nitrogen, and Oxygen Atoms and Ions, CRC Press, Boca Raton, FL (1993).
- [52] P. C. Cosby and D. L. Huestis, "On the dissociation-energy of O₂ and the energy of the O₂(+)⁴B₄Σ_g State," *J. Chem. Phys.* **97**, 6108 (1992). <http://dx.doi.org/10.1063/1.463720>
- [53] J. D. D. Martin and J. W. Hepburn, "Electric field induced dissociation of molecules in Rydberg-like highly vibrationally excited ion-pair states," *Phys. Rev. Lett.* **79**, 3154 (1997). <http://dx.doi.org/10.1103/PhysRevLett.79.3154>
- [54] S. T. Gibson, B. R. Lewis, K. G. H. Baldwin, and J. H. Carver, "Rotational features in the fluorescence excitation spectrum of O(1D₂) from vacuum ultraviolet-laser photodissociation of O₂," *J. Chem. Phys.* **94**, 1060 (1991). <http://dx.doi.org/10.1063/1.460062>
- [55] B. R. Lewis, L. Berzins, J. H. Carver, and S. T. Gibson, "Decomposition of the photoabsorption continuum underlying the Schumann-Runge bands of 16O₂. I. Role of the B₃Σ_u⁻ state - a new dissociation limit," *J. Quant. Spectrosc. Radiative Transfer* **33**, 627 (1985). [http://dx.doi.org/10.1016/0022-4073\(85\)90031-7](http://dx.doi.org/10.1016/0022-4073(85)90031-7)
- [56] R. G. C. Blyth, I. Powis, and C. J. Danby, "Competing pre-dissociations of O₂⁺," *Chem. Phys. Lett.* **84**, 272 (1981). [http://dx.doi.org/10.1016/0009-2614\(81\)80343-0](http://dx.doi.org/10.1016/0009-2614(81)80343-0)
- [57] C. Pernot, J. Durup, J. B. Ozenne, J. A. Beswick, P. C. Cosby, and J. T. Moseley, "Angular-distributions and separation energies of predissociation photofragments of O₂⁺," *J. Chem. Phys.* **71**, 2387 (1979). <http://dx.doi.org/10.1063/1.438644>
- [58] D. L. Albritton, J. T. Moseley, P. C. Cosby, and M. Tadjeddine, "Dissociation-energy of O₂," *J. Mol. Spectrosc.* **70**, 326 (1978). [http://dx.doi.org/10.1016/0022-2852\(78\)90169-8](http://dx.doi.org/10.1016/0022-2852(78)90169-8)
- [59] P. M. Dehmer and W. A. Chupka, "High resolution study of photoionization processes in O₂," *J. Chem. Phys.* **62**, 4525 (1975). <http://dx.doi.org/10.1063/1.430359>
- [60] C. J. Danby and J. H. D. Eland, "Photoelectron-photoion coincidence spectroscopy: II. Design and performance of a practical instrument," *Int. J. Mass Spectrom. Ion Phys.* **8**, 153 (1972). [http://dx.doi.org/10.1016/0020-7381\(72\)80005-6](http://dx.doi.org/10.1016/0020-7381(72)80005-6)
- [61] P. Brix and G. Herzberg, "Fine structure of the Schumann-Runge bands near the convergence limit and the dissociation energy of the oxygen molecule," *Can. J. Phys.* **32**, 110 (1954). <http://dx.doi.org/10.1139/p54-013>
- [62] D. Feller, K. A. Peterson, and B. Ruscic, "Improved accuracy benchmarks of small molecules using correlation consistent basis sets," *Theor. Chem. Acc.* **133**, 1407 (2014). <http://dx.doi.org/10.1007/s00214-013-1407-z>
- [63] H. Liu, D. H. Shi, J. F. Sun, Z. L. Zhu, and Z. Shulin, "Accurate calculations on the 22 electronic states and 54 spin-orbit states of the O₂ molecule: Potential energy curves, spectroscopic parameters and spin-orbit coupling," *Spectrochim Acta A* **124**, 216 (2014). <http://dx.doi.org/10.1016/j.saa.2014.01.003>
- [64] L. Bytautas, N. Matsunaga, and K. Ruedenberg, "Accurate ab initio potential energy curve of O₂. II. Core-valence correlations, relativistic contributions, and vibration-rotation spectrum," *J. Chem. Phys.* **132**, 074307 (2010). <http://dx.doi.org/10.1063/1.3298376>
- [65] A. J. C. Varandas, "Accurate global ab initio potentials at low-cost by correlation scaling and extrapolation to the one-electron basis set limit," *Chem. Phys. Lett.* **443**, 398 (2007). <http://dx.doi.org/10.1016/j.cplett.2007.06.061>
- [66] L. Bytautas and K. Ruedenberg, "Correlation energy extrapolation by intrinsic scaling. IV. Accurate binding energies of the homonuclear diatomic molecules carbon, nitrogen, oxygen and fluorine," *J. Chem. Phys.* **122**, 154110 (2005). <http://dx.doi.org/10.1063/1869493>
- [67] K. A. Peterson, A. K. Wilson, D. E. Woon, and T. H. Dunning Jr., "Benchmark calculations with correlated molecular wave functions XII. Core correlation effects on the homonuclear diatomic molecules B₂-F₂," *Theor. Chem. Acc.* **97**, 251 (1997). <http://dx.doi.org/10.1007/s002140050259>
- [68] A. G. Csaszar and W. D. Allen, "The effect of 1s correlation on De, re, and ωe of first-row diatomics," *J. Chem. Phys.* **104**, 2746 (1996). <http://dx.doi.org/10.1063/1.471008>
- [69] S. J. Cole, M. Hasan, and B. Kirtman, "Single-Reference Coupled-Cluster Calculations of the Triplet Ground-State O₂ Dissociation Potential," *Isr. J. Chem.* **31**, 303 (1991). <http://dx.doi.org/10.1002/ijch.199100035>
- [70] S. L. Guberman, "Accurate ab initio potential curve for ground state O₂," *J. Chem. Phys.* **67**, 1125 (1977). <http://dx.doi.org/10.1063/1.434963>
- [71] A. Ganyecz, J. Csontos, B. Nagy, and M. Kallay, "Theoretical and thermochemical network approaches to determine the heats of formation for HO₂ and its ionic counterparts," *J. Phys. Chem. A* **119**, 1164 (2015). <http://dx.doi.org/10.1021/jp5104643>
- [72] B. Ruscic, Active Thermochemical Tables. ATcT B. Version 1.110 Core Argonne 30.5.2010. Available at <http://atct.anl.gov/Thermochemical Data/version 1.110> and <http://burcat.technion.ac.il/dir/Archives/BURCAT2010.THR> [Accessed July 30, 2015].
- [73] B. Ruscic, R. E. Pinzon, M. L. Morton, N. K. Srinivasan, M. C. Su, J. W. Sutherland, and J. V. Michael, "Active thermochemical tables: Accurate enthalpy of formation of hydroperoxyl radical, HO₂," *J. Phys. Chem. A* **110**, 6592 (2006). <http://dx.doi.org/10.1021/jp056311j>
- [74] B. Ruscic, A. F. Wagner, L. B. Harding, R. L. Asher, D. Feller, D. A. Dixon, K. A. Peterson, Y. Song, X. M. Qian, C. Y. Ng, J. B. Liu, W. W. Chen, and D. W. Schwenke, "On the enthalpy of formation of hydroxyl radical and gas-phase bond dissociation energies of water and hydroxyl," *J. Phys. Chem. A* **106**, 2727 (2002). <http://dx.doi.org/10.1021/jp013909s>

- [75] J. A. Joens, "The dissociation energy of OH and the enthalpy of formation of OH, ClOH, and BrOH from thermochemical cycles," *J. Phys. Chem. A* **105**, 11041 (2001). <http://dx.doi.org/10.1021/jp011833u>
- [76] O. V. Boyarkin, M. A. Koshelev, O. Aseev, P. Maksyutenko, T. R. Rizzo, N. F. Zobov, L. Lodi, J. Tennyson, and O. L. Polyansky, "Accurate bond dissociation energy of water determined by triple-resonance vibrational spectroscopy and ab initio calculations," *Chem. Phys. Lett.* **568**, 14 (2013). <http://dx.doi.org/10.1016/j.cplett.2013.03.007>
- [77] P. Maksyutenko, T. R. Rizzo, and O. V. Boyarkin, "A direct measurement of the dissociation energy of water," *J. Chem. Phys.* **125**, 181101 (2006). <http://dx.doi.org/10.1063/1.2387163>
- [78] J. T. Herbon, R. K. Hanson, D. M. Golden, and C. T. Bowman, "A shock tube study of the enthalpy of formation of OH," *Proc. Combust. Inst.* **29**, 1201 (2002). [http://dx.doi.org/10.1016/S1540-7489\(02\)80149-3](http://dx.doi.org/10.1016/S1540-7489(02)80149-3)
- [79] B. Ruscic, D. Feller, D. A. Dixon, K. A. Peterson, L. B. Harding, R. L. Asher, and A. F. Wagner, "Evidence for a lower enthalpy of formation of hydroxyl radical and a lower gas-phase bond dissociation energy of water," *J. Phys. Chem. A* **105**, 1 (2001). <http://dx.doi.org/10.1021/jp003711s>
- [80] S. A. Harich, D. W. H. Hwang, X. Yang, J. J. Lin, X. Yang, and R. N. Dixon, "Photodissociation of H₂O at 121.6 nm: A state-to-state dynamical picture," *J. Chem. Phys.* **113**, 10073 (2000). <http://dx.doi.org/10.1063/1.1322059>
- [81] R. T. Wiedmann, R. G. Tonkyn, M. G. White, K. H. Wang, and V. McKoy, "Rotationally resolved threshold photoelectron spectra of OH and OD," *J. Chem. Phys.* **97**, 768 (1992). <http://dx.doi.org/10.1063/1.463179>
- [82] K. E. McCulloh, "Energetics and mechanisms of fragment ion formation in the photoionization of normal and deuterated water and ammonia," *Int. J. Mass Spectrom. Ion Phys.* **21**, 333 (1976). [http://dx.doi.org/10.1016/0020-7381\(76\)80131-3](http://dx.doi.org/10.1016/0020-7381(76)80131-3)
- [83] C. Carlone and F. W. Dalby, "Spectrum of hydroxyl radical," *Can. J. Phys.* **47**, 1945 (1969). <http://dx.doi.org/10.1139/p69-245>
- [84] R. F. Barrow, "The B²Σ⁺-A²Σ⁺ band systems of OH and OD," *Ark. Fys.* **11**, 281 (1956).
- [85] R. J. Dwyer and O. Oldenberg, "The dissociation of H₂O into H + OH," *J. Chem. Phys.* **12**, 351 (1944). <http://dx.doi.org/10.1063/1.1723957>
- [86] O. Riechmeier, H. Senftleben, and H. Pastorff, "Über die Energieverhältnisse bei der Dissoziation des Wasserdampfmoleküls in seine Atome," *Ann. d. Phys.* **411**, 202 (1934). <http://dx.doi.org/10.1002/andp.19344110206>
- [87] A. G. Csaszar and T. Furtenbacher, "From a Network of Computed Reaction Enthalpies to Atom-Based Thermochemistry (NEAT)," *Chem. Eur. J.* **16**, 4826 (2010). <http://dx.doi.org/10.1002/chem.200903252>
- [88] A. G. Csaszar, E. Matyus, T. Szidarovszky, L. Lodi, N. F. Zobov, S. V. Shirin, O. L. Polyansky, and J. Tennyson, "First-principles prediction and partial characterization of the vibrational states of water up to dissociation," *J. Quant. Spectr. Radiat. Transfer* **111**, 1043 (2010). <http://dx.doi.org/10.1016/j.jqsrt.2010.02.009>
- [89] D. J. Grant, D. A. Dixon, J. S. Francisco, D. Feller and K. A. Peterson, "Heats of formation of the H_{1,2}O_mSn (m, n=0-3) molecules from electronic structure calculations," *J. Phys. Chem. A* **113**, 11343 (2009). <http://dx.doi.org/10.1021/Jp905847e>
- [90] M. Grechko, O. V. Boyarkin, T. R. Rizzo, P. Maksyutenko, N. F. Zobov, S. V. Shirin, L. Lodi, J. Tennyson, A. G. Csaszar, and O. L. Polyansky, "State-selective spectroscopy of water up to its first dissociation limit," *J. Chem. Phys.* **131**, 221105 (2009). <http://dx.doi.org/10.1063/1.3273207>
- [91] M. E. Harding, J. Vazquez, B. Ruscic, A. K. Wilson, J. Gauss, and J. F. Stanton, "High-accuracy extrapolated ab initio thermochemistry. III. Additional improvements and overview," *J. Chem. Phys.* **128**, 114111 (2008). <http://dx.doi.org/10.1063/1.2835612>
- [92] D. Feller, K. A. Peterson, and D. A. Dixon, "A survey of factors contributing to accurate theoretical predictions of atomization energies and molecular structures," *J. Chem. Phys.* **129**, 204105 (2008). <http://dx.doi.org/10.1063/1.3008061>
- [93] H. T. Ma, W. S. Bian, S. J. Zheng, and L. P. Meng, "Highly accurate quantum chemical study of the OH radical," *Acta Chim. Sin.* **63**, 263 (2005).
- [94] L. R. Peebles and P. Marshall, "High-accuracy coupled-cluster computations of bond dissociation energies in SH, H₂S, and H₂O," *J. Chem. Phys.* **117**, 3132 (2002). <http://dx.doi.org/10.1063/1.1493175>
- [95] R. Janoschek and M. J. Rossi, "Thermochemical properties of free radicals from G3MP2B3 calculations," *Int. J. Chem. Kinet.* **34**, 550 (2002). <http://dx.doi.org/10.1002/kin.10082>
- [96] J. M. L. Martin, "A fully ab initio potential curve of near-spectroscopic quality for OH⁻ ion: importance of connected quadruple excitations and scalar relativistic effects," *Spectrochim. Acta A* **57**, 875 (2001). [http://dx.doi.org/10.1016/S1386-1425\(00\)00450-9](http://dx.doi.org/10.1016/S1386-1425(00)00450-9)
- [97] L. A. Curtiss, K. Raghavachari, P. C. Redfern, and B. B. Stefanov, "Assessment of complete basis set methods for calculation of enthalpies of formation," *J. Chem. Phys.* **108**, 692 (1998). <http://dx.doi.org/10.1063/1.475442>
- [98] L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, "Gaussian-3 (G3) theory for molecules containing first and second-row atoms," *J. Chem. Phys.* **109**, 7764 (1998). <http://dx.doi.org/10.1063/1.477422>
- [99] D. J. McKay and J. S. Wright, "How long can you make an oxygen chain?," *J. Am. Chem. Soc.* **120**, 1003 (1998). <http://dx.doi.org/10.1021/ja971534b>
- [100] B. Ruscic, "Active Thermochemical Tables: water and water dimer," *J. Phys. Chem. A* **117**, 11940 (2013). <http://dx.doi.org/10.1021/jp403197t>
- [101] R. C. King and G. T. Armstrong, "Constant pressure flame calorimetry with fluorine. 2. Heat of formation of oxygen difluoride," *J. Res. Nat. Bur. Stand. Sect. A* **72**, 113 (1968). <http://dx.doi.org/10.6028/jres.072A.012>
- [102] F. D. Rossini, "Heat and free energy of formation of water and of carbon monoxide," *J. Res. Nat. Bur. Stand.* **22**, 407 (1939). <http://dx.doi.org/10.6028/jres.022.029>
- [103] F. D. Rossini, "The heat of formation of water," *J. Res. Nat. Bur. Stand.* **6**, 1 (1931). <http://dx.doi.org/10.6028/jres.006.001>
- [104] F. D. Rossini, "The heat of formation of water and the heats of combustion of methane and carbon monoxide. A correction," *J. Res. Nat. Bur. Stand.* **7**, 329 (1931). <http://dx.doi.org/10.6028/jres.007.017>
- [105] C. X. Almora-Diaz, "Highly correlated configuration interaction calculations on water with large orbital bases," *J. Chem. Phys.* **140**, 184302 (2014). <http://dx.doi.org/10.1063/1.4874319>
- [106] D. Feller and K. A. Peterson, "High level coupled cluster determination of the structure, frequencies, and heat of formation of water," *J. Chem. Phys.* **131**, 154306 (2009). <http://dx.doi.org/10.1063/1.3246353>

- [107] L. Bytautas and K. Ruedenberg, "Correlation energy extrapolation by intrinsic scaling. V. Electronic energy, atomization energy, and enthalpy of formation of water," *J. Chem. Phys.* **124**, 174304 (2006). <http://dx.doi.org/10.1063/1.2194542>
- [108] T. Helgaker, W. Klopper, H. Koch, and J. Noga, "Basis set convergence of the molecular electric dipole moment," *J. Chem. Phys.* **106**, 9639 (1997). <http://dx.doi.org/10.1063/1.473863>
- [109] L. G. S. Shum and S. W. Benson, "Review of the heat of formation of the hydroperoxyl radical," *J. Phys. Chem.* **87**, 3479 (1983). <http://dx.doi.org/10.1021/j100241a025>
- [110] T. M. Ramond, S. J. Blanksby, S. Kato, V. M. Bierbaum, G. E. Davico, R. L. Schwartz, W. C. Lineberger, and G. B. Ellison, "Heat of formation of the hydroperoxyl radical via negative ion studies," *J. Phys. Chem. A* **106**, 9641 (2002). <http://dx.doi.org/10.1021/jp014614h>
- [111] E. P. Clifford, P. G. Wenthold, R. Gareyev, W. C. Lineberger, C. H. DePuy, V. M. Bierbaum, and G. B. Ellison, "Photoelectron spectroscopy, gas phase acidity, and thermochemistry of tert-butyl hydroperoxide: Mechanisms for the rearrangement of peroxy radicals," *J. Chem. Phys.* **109**, 10293 (1998). <http://dx.doi.org/10.1063/1.477725>
- [112] M. Litorja and B. Ruscic, "A photoionization study of the hydroperoxyl radical, HO₂, and hydrogen peroxide," H₂O₂. *J. Electr. Spectr. Rel. Phenom.* **97**, 131 (1998). [http://dx.doi.org/10.1016/S0368-2048\(98\)00264-3](http://dx.doi.org/10.1016/S0368-2048(98)00264-3)
- [113] E. R. Fisher and P. B. Armentrout, "Heat of formation of the hydroperoxyl radical HO₂. A direct determination from guided ion beam studies of oxygen-methane [O₂+ + CH₄] reaction," *J. Phys. Chem.* **94**, 4396 (1990). <http://dx.doi.org/10.1021/j100374a007>
- [114] J. M. Oakes, L. B. Harding, and G. B. Ellison, "The photoelectron spectroscopy of HO₂," *J. Chem. Phys.* **83**, 5400 (1985). <http://dx.doi.org/10.1063/1.449709>
- [115] A. J. Hills and C. J. Howard, "Rate coefficient temperature dependence and branching ratio for the OH+ClO reaction," *J. Chem. Phys.* **81**, 4458 (1984). <http://dx.doi.org/10.1063/1.447414>
- [116] L. G. S. Shum and S. W. Benson, "Mechanism and thermochemistry of oxidation of HCl and HBr at high temperatures. The heat of formation of HO₂," *Int. J. Chem. Kinet.* **15**, 341 (1983). <http://dx.doi.org/10.1002/kin.550150404>
- [117] Y. P. Lee and C. J. Howard, "Temperature dependence of the rate constant and the branching ratio for the reaction Cl + HO₂," *J. Chem. Phys.* **77**, 756 (1982). <http://dx.doi.org/10.1063/1.443892>
- [118] L. A. Khachatryan, O. M. Niazyan, A. A. Mantashyan, V. I. Vedenev, and M. A. Teitel'Boim, "Experimental determination of the equilibrium constant of the reaction CH₃ + O₂ = CH₃O₂ during the gas-phase oxidation of methane," *Int. J. Chem. Kinet.* **14**, 1231 (1982). <http://dx.doi.org/10.1002/kin.550141107>
- [119] C. J. Howard, "Kinetic study of the equilibrium HO₂ + NO = OH + NO₂ and the thermochemistry of HO₂," *J. Am. Chem. Soc.* **102**, 6937 (1980). <http://dx.doi.org/10.1021/ja00543a006>
- [120] K. Glanzer and J. Troe, "HO₂ formation in shock heated HNO₃-NO₂ mixtures," *Ber. Bunsenges, Phys. Chem.* **79**, 465 (1975). <http://dx.doi.org/10.1002/bbpc.19750790514>
- [121] V. F. Kochubei and J. B. Moin, "Determination of HO₂ radical formation heat by kinetic method," *Dokl. Akad. Nauk SSSR* **219**, 141 (1974).
- [122] S. N. Foner and R. L. Hudson, "Mass spectrometry of HO₂ free radical," *J. Chem. Phys.* **36**, 2681 (1962). <http://dx.doi.org/10.1063/1.1732352>
- [123] W. A. Rosser Jr. and H. Wise, "The kinetics of oxidation of HBr," *J. Phys. Chem.* **63**, 1753 (1959). <http://dx.doi.org/10.1021/j150580a044>
- [124] S. N. Foner and R. L. Hudson, "Ionization potential of the free HO₂ radical and the H-O₂ bond dissociation energy," *J. Chem. Phys.* **23**, 1364 (1955). <http://dx.doi.org/10.1063/1.1742299>
- [125] M. K. Sprague and K. K. Irikura, "Quantitative estimation of uncertainties from wavefunction diagnostics," *Theor. Chem. Acc.* **133**, 1544 (2014). <http://dx.doi.org/10.1007/s00214-014-1544-z>
- [126] A. Karton, S. Parthiban, and J. M. Martin, "Post-CCSD(T) ab Initio thermochemistry of halogen oxides and related hydrides XO_x, XO₂, HO_x, XO_n, and HXO_n, (X = F, Cl), and evaluation of DFT methods for these systems," *J. Phys. Chem. A* **113**, 4802 (2009). <http://dx.doi.org/10.1021/jp8087435>
- [127] Y. J. Bomble, J. Vazquez, M. Kallay, C. Michauk, P. G. Szalay, A. G. Csaszar, J. Gauss, and J. F. Stanton, "High-accuracy extrapolated ab initio thermochemistry. II. Minor improvements to the protocol and a vital simplification," *J. Chem. Phys.* **125**, 064108 (2006). <http://dx.doi.org/10.1063/1.2206789>
- [128] B. A. Flowers, P. G. Szalay, J. F. Stanton, M. Kallay, J. Gauss, and A. G. Csaszar, "Benchmark thermochemistry of the hydroperoxyl radical," *J. Phys. Chem. A* **108**, 3195 (2004). <http://dx.doi.org/10.1021/jp037347j>
- [129] A. Tajti, P. G. Szalay, A. G. Csaszar, M. Kallay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vazquez, and J. F. Stanton, "HEAT: High accuracy extrapolated ab initio thermochemistry," *J. Chem. Phys.* **121**, 11599 (2004). <http://dx.doi.org/10.1063/1.1811608>
- [130] D. A. Dixon, D. Feller, C. G. Zhan, and J. S. Francisco, "Decomposition pathways of peroxytrifluoroacetic acid: gas-phase and solution energetics," *J. Phys. Chem. A* **106**, 3191 (2002). <http://dx.doi.org/10.1021/jp013783z>
- [131] S. P. Karkach and V. I. Osherov, "Ab initio analysis of the transition states on the lowest triplet H₂O₂ potential surface," *J. Chem. Phys.* **110**, 11918 (1999). <http://dx.doi.org/10.1063/1.479131>
- [132] T. P. W. Jungkamp and J. H. Seinfeld, "The enthalpy of formation of trioxy radicals ROOO (R=H, CH₃, C₂H₅). An ab initio study," *Chem. Phys. Lett.* **257**, 15 (1996). [http://dx.doi.org/10.1016/0009-2614\(96\)00520-9](http://dx.doi.org/10.1016/0009-2614(96)00520-9)
- [133] C. W. Bauschlicher Jr. and H. Partridge, "An accurate determination of the HO₂ heat of formation," *Chem. Phys. Lett.* **208**, 241 (1993). [http://dx.doi.org/10.1016/0009-2614\(93\)89069-T](http://dx.doi.org/10.1016/0009-2614(93)89069-T)
- [134] B. Ruscic, "Active Thermochemical Tables (ATcT). ATcT D - version 1.110 Core ARGONNE 30.12.2013," <http://atct.anl.gov> [Accessed August 12, 2015].
- [135] O. V. Dorofeeva, V. S. Iorish, V. P. Novikov, and D. B. Neumann, "NIST-JANAF thermochemical tables. II. Three molecules related to atmospheric chemistry. HNO₃, H₂SO₄, and H₂O₂," *J. Phys. Chem. Ref. Data* **323**, 879 (2003). <http://dx.doi.org/10.1063/1.1547435>
- [136] P. A. Giguere and I. D. Liu, "Recommended values for the thermodynamic properties of hydrogen and deuterium peroxides," *J. Am. Chem. Soc.* **77**, 6477 (1955). <http://dx.doi.org/10.1021/ja01629a012>

- [137] F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of Individual Substances*, Reinhold Pub. Corp, New York (1936).
- [138] X. Luo, P. R. Fleming, and T. R. Rizzo, "Vibrational overtone spectroscopy of the $4\nu\text{OH} + \nu\text{OH}$ combination level of HOOH via sequential local mode–local mode excitation," *J. Chem. Phys.* **96**, 5659 (1992). <http://dx.doi.org/10.1063/1.462665>
- [139] W. Forst, "Second-order unimolecular kinetics in the thermal decomposition of hydrogen peroxide vapor," *Can. J. Chem.* **36**, 1308 (1958).
- [140] P. A. Giguere, B. G. Morissette, A. W. Olmos, and O. Knop, "Hydrogen peroxide and its analogues. 7. Calorimetric properties of the systems H₂O–H₂O₂ and D₂O–D₂O₂," *Can. J. Chem.* **33**, 804 (1955). <http://dx.doi.org/10.1139/v55-098>
- [141] O. Maass and W. H. Hatcher, "The properties of pure hydrogen peroxide. I," *J. Am. Chem. Soc.* **42**, 2548 (1920). <http://dx.doi.org/10.1021/ja01457a013>
- [142] G. L. Matheson and O. Maass, "The properties of pure hydrogen peroxide. VI," *J. Am. Chem. Soc.* **51**, 674 (1929). <http://dx.doi.org/10.1021/ja01378a004>
- [143] P. A. Denis and F. R. Ornellas, "Theoretical characterization of hydrogen polyoxides: HOOH, HOOOH, HOOOOH, and HOOO," *J. Phys. Chem. A* **113**, 499 (2009). <http://dx.doi.org/10.1021/jp808795e>
- [144] S. R. Selvevag, Y. Georgievskii, and J. A. Miller, "Kinetics of the gas-phase recombination reaction of hydroxyl radicals to form hydrogen peroxide," *J. Phys. Chem. A* **113**, 4457 (2009). <http://dx.doi.org/10.1021/jp8110524>
- [145] S. Parthiban and J. M. L. Martin, "Assessment of W1 and W2 theories for the computation of electron affinities, ionization potentials, heats of formation, and proton affinities," *J. Chem. Phys.* **114**, 6014 (2001). <http://dx.doi.org/10.1063/1.1356014>
- [146] S. J. Blanksby, T. M. Ramond, G. E. Davico, M. R. Nimlos, S. Kato, V. M. Bierbaum, W. C. Lineberger, G. B. Ellison, and M. Okumura, "Negative-ion photoelectron spectroscopy, gas-phase acidity, and thermochemistry of the peroxy radicals CH₃OO and CH₃CH₂OO," *J. Am. Chem. Soc.* **123**, 9585 (2001). <http://dx.doi.org/10.1021/ja010942j>
- [147] B. Kuhn, T. R. Rizzo, D. Luckhaus, M. Quack, and M. A. Suhm, "A new six-dimensional analytical potential up to chemically significant energies for the electronic ground state of hydrogen peroxide," *J. Chem. Phys.* **111**, 2565 (1999). <http://dx.doi.org/10.1063/1.479534>
- [148] B. Ruscic, Active Thermochemical Tables. ATcT C. Version 1.112 Core Argonne 4.2.2011. Bromine Species. Data available in <http://burcat.technion.ac.il/dir/Archives/BURCAT2014.THR> [Accessed July 30, 2015].
- [149] N. Taniguchi, K. Takahashi, Y. Matsumi, S. M. Dylewski, J. D. Geiser, and P. L. Houston, "Determination of the heat of formation of O₃ using vacuum ultraviolet laser-induced fluorescence spectroscopy and two-dimensional product imaging techniques," *J. Chem. Phys.* **111**, 6350 (1999). <http://dx.doi.org/10.1063/1.479939>
- [150] K. Takahashi, M. Kishigami, N. Taniguchi, Y. Matsumi, and M. Kawasaki, "Photofragment excitation spectrum for O(D1) from the photodissociation of jet-cooled ozone in the wavelength range 305–329 nm," *J. Chem. Phys.* **106**, 6390 (1997). <http://dx.doi.org/10.1063/1.473629>
- [151] M. A. A. Clyne, D. J. McKenney, and B. A. Thrush, "Rate of Combination of Oxygen Atoms with Oxygen Molecules," *Trans Faraday Soc* **61**, 2701 (1965). <http://dx.doi.org/10.1039/Tf9656102701>
- [152] P. Gunther, E. Wassmuth, and L. A. Schryver, "The formation warmth of ozones," *Z. Phys. Chem. A* **158**, 297 (1932).
- [153] A. Kailan and S. Jahn, "Articles on the knowledge of the ozone V. The heat hues of the decomposition," *Z. Anorg. Chem.* **68**, 243 (1910). <http://dx.doi.org/10.1002/zaac.19100680122>
- [154] F. Holka, P. G. Szalay, T. Muller, and V. G. Tyuterev, "Toward an improved ground state potential energy surface of ozone," *J. Phys. Chem. A* **114**, 9927 (2010). <http://dx.doi.org/10.1021/jp104182q>
- [155] P. Fleurat-Lessard, S. Y. Grebenshchikov, R. Siebert, and R. Schinke, "Theoretical investigation of the temperature dependence of the O + O₂ exchange reaction," *J. Chem. Phys.* **118**, 610 (2003). <http://dx.doi.org/10.1063/1.1525255>
- [156] Le Picard et al. (2010) in supplementary material for the paper indicate that they used an enthalpy of formation $\Delta_f H^\circ(298.15\text{ K})$ for OH of 37.2 kJ/mol instead of the currently accepted value of 37.5 kJ/mol (see Table 3). They also indicated that they calculated the vibrational partition function $Q_{\text{vib}}(\text{HO}_3)$ using the four lowest frequency vibrations taken from Derro et al. (2008). Using this partition function, we compute that H° at 298 K is about 0.3 kJ/mol lower than our computed value and that ΔS° is about 1.5 kJ/mol. Employing their computed thermofunctions, we derive a thermal correction $\Delta\Delta_f H(298.15\text{ K})$ of about -5.4 kJ/mol (their reported $\Delta_f H(298.15\text{ K})$ and D_0 correspond to about $\Delta\Delta_f H(298.15\text{ K}) = -5.6$ kJ/mol). This compares to our computed value (treating the torsion as a torsion) of $\Delta\Delta_f H(298.15\text{ K}) = -3.27$ kJ mol⁻¹ (see Sec. 3.2.2) – a difference of about (2.1 to 2.3) kJ mol⁻¹.
- [157] I. W. M. Smith, S. D. Le Picard, M. Tizniti, A. Canosa, and I. R. Sims, "The Quest for the Hydroxyl-Peroxy Radical," *Z. Phys. Chem.* **224**, 949 (2010). <http://dx.doi.org/10.1524/zpch.2010.6135>
- [158] J. M. Beames, M. I. Lester, C. Murray, M. E. Varner, and J. F. Stanton, "Analysis of the HOOO torsional potential," *J. Chem. Phys.* **134**, 044304 (2011). <http://dx.doi.org/10.1063/1.3518415>
- [159] See text in this section, reference 156 (an endnote), Sec. 3.2.1 for details.
- [160] S. D. Le Picard, M. Tizniti, A. Canosa, I. R. Rims, and I. W. M. Smith, "The thermodynamics of the elusive HO₃ radical," *Science* **328**, 1258 (2010). <http://dx.doi.org/10.1126/Science.1184459>
- [161] C. Murray, E. L. Derro, T. D. Sechler, and M. I. Lester, "Weakly bound molecules in the atmosphere: a case study of HOOO," *Acct. Chem. Res.* **42**, 419 (2009). <http://dx.doi.org/10.1021/ar8001987>
- [162] E. Derro, T. D. Sechler, C. Murray, and M. I. Lester, "Infrared action spectroscopy of the OD stretch fundamental and overtone transitions of the DOOO radical," *J. Phys. Chem. A* **112**, 9269 (2008). <http://dx.doi.org/10.1021/jp801232a>
- [163] C. Murray, E. L. Derro, T. D. Sechler, and M. I. Lester, "Stability of the hydrogen trioxy radical via infrared action spectroscopy," *J. Phys. Chem. A* **111**, 4727 (2007). <http://dx.doi.org/10.1021/jp071473w>
- [164] E. L. Derro, C. Murray, T. D. Sechler, and M. I. Lester, "Infrared action Spectroscopy and dissociation dynamics of the HOOO radical," *J. Phys. Chem. A* **111**, 11592 (2007). <http://dx.doi.org/10.1021/jp0760915>
- [165] M. Speranza, "Structure, stability, and reactivity of cationic hydrogen trioxides and thermochemistry of their neutral analogs. A fourier-transform ion cyclotron resonance study," *Inorg. Chem.* **35**, 6140 (1996). <http://dx.doi.org/10.1021/ic960549s>

- [166] A. Burcat, unpublished results. Available at <http://burcat.technion.ac.il/dir/Archives/BURCAT2014.THR> [Accessed July 30, 2015].
- [167] Y. Zhou, H. Hu, L. Li, H. Hou, and B. Wang, "Ab initio study of the elusive HO₃ radical and the HO + O₂ = HO₃ reaction," *Comput. Theor. Chem.* **1026**, 24 (2013). <http://dx.doi.org/10.1016/j.comptc.2013.10.010>
- [168] A. J. C. Varandas, "Ab initio treatment of bond-breaking reactions: accurate course of HO₃ dissociation and revisit to isomerization," *J. Chem. Theory Comput.* **8**, 428 (2012). <http://dx.doi.org/10.1021/ct200773b>
- [169] A. J. C. Varandas, "On the stability of the elusive HO₃ radical," *Phys. Chem. Chem. Phys.* **13**, 15619 (2011). <http://dx.doi.org/10.1039/c1cp20791a>
- [170] J. M. Anglada, S. Olivella, and A. Sole, "On the Dissociation of Ground State trans-HOOO Radical: A Theoretical Study," *J. Chem. Theory Comput.* **6**, 2743 (2010). <http://dx.doi.org/10.1021/ct100358e>
- [171] M. E. Varner, M. E. Harding, J. Vazquez, J. Gauss, and J. F. Stanton, "Dissociation Energy of the HOOO Radical," *J. Phys. Chem. A* **113**, 11238 (2009). <http://dx.doi.org/10.1021/jp907262s>
- [172] B. J. Braams and H. G. Yu, "Potential energy surface and quantum dynamics study of rovibrational states for HO₃," *Phys. Chem. Chem. Phys.* **10**, 3150 (2008). <http://dx.doi.org/10.1039/b801928b>
- [173] D. G. Semes'ko and S. L. Khursan, "Quantum-chemical calculations of the structure of trioxyl radicals," *Russ. J. Phys. Chem. A* **82**, 1277 (2008). <http://dx.doi.org/10.1134/S0036024408080074>
- [174] P. A. Denis and F. R. Ornellas, "Spin contamination in XOO radicals X=F,Cl,Br,HO: how is the investigation of the HOOO radical affected," *Chem. Phys. Lett.* **464**, 150 (2008). <http://dx.doi.org/10.1016/j.cplett.2008.09.025>
- [175] A. Mansergas, J. M. Anglada, S. Olivella, M. F. Ruiz-Lopez, and M. Martins-Costa, "On the nature of the unusually long OO bond in HO₃ and HO₄ radicals," *Phys. Chem. Chem. Phys.* **9**, 5865 (2007). <http://dx.doi.org/10.1039/b711464h>
- [176] R. Janoschek and W. M. F. Fabian, "Enthalpies of formation of small free radicals and stable intermediates: Interplay of experimental and theoretical values," *J. Mol. Struct.* **780-81**, 80 (2006). <http://dx.doi.org/10.1016/j.molstruc.2005.04.050>
- [177] K. Suma, Y. Sumiyoshi, and Y. Endo, "The rotational spectrum and structure of the HOOO radical," *Science* **308**, 1885 (2005). <http://dx.doi.org/10.1126/Science.1112233>
- [178] W. M. F. Fabian, J. Kalcher, and R. Janoschek, "Stationary points on the energy hypersurface of the reaction O₃+H=O₃H=O₂+OH and thermodynamic functions of O₃H at G3MP2B3, CCSD(T)-CBS(W1U) and MR-ACPF-CBS levels of theory," *Theor. Chem. Acct.* **114**, 182 (2005). <http://dx.doi.org/10.1007/s00214-005-0659-7>
- [179] P. A. Denis, M. Kieninger, O. N. Ventura, R. E. Cachau, and G. H. F. Diercksen, "Erratum to: 'Complete basis set and density functional determination of the enthalpy of formation of the controversial HO₃ radical. A discrepancy between theory and experiment' [Chem. Phys. Lett. 365 (2002) 440-449]," *Chem. Phys. Lett.* **377**, 483 (2003). [http://dx.doi.org/10.1016/S0009-2614\(03\)01078-9](http://dx.doi.org/10.1016/S0009-2614(03)01078-9)
- [180] P. A. Denis, M. Kieninger, O. N. Ventura, R. E. Cachau, and G. H. F. Diercksen, "Complete basis set and density functional determination of the enthalpy of formation of the controversial HO₃ radical: a discrepancy between theory and experiment," *Chem. Phys. Lett.* **365**, 440 (2002). [http://dx.doi.org/10.1016/S0009-2614\(02\)01432-X](http://dx.doi.org/10.1016/S0009-2614(02)01432-X)
- [181] X. Xu and W. A. Goddard, "Peroxone chemistry: Formation of H₂O₃ and ring-(HO₂)(HO₃) from O-3/H₂O₂," *Proc. Natl. Acad. Sci. U.S.A.* **99**, 15308 (2002). <http://dx.doi.org/10.1073/pnas.202596799>
- [182] O. Setokuchi, M. Sato, and S. Matuzawa, "A theoretical study of the potential energy surface and rate constant for an O(3P) + HO₂ reaction," *J. Phys. Chem. A* **104**, 3204 (2000). <http://dx.doi.org/10.1021/jp993573a>
- [183] P. S. Nangia, P. S., and S. W. Benson, "Thermochemistry of organic polyoxides and their free radicals," *J. Phys. Chem.* **83**, 1138 (1979). <http://dx.doi.org/10.1021/j100472a006>
- [184] M. Martins-Costa, J. M. Anglada, and M. F. Ruiz-López, "Structure, stability, and dynamics of hydrogen polyoxides," *Int. J. Quant. Chem.* **111**, 1543 (2011). <http://dx.doi.org/10.1002/qua.22695>
- [185] E. Kraka, D. Cremer, J. Koller, and B. Plesnicar, "Peculiar structure of the HOOO⁻ anion," *J. Am. Chem. Soc.* **124**, 8462 (2002). <http://dx.doi.org/10.1021/ja012553v>
- [186] T. H. Lay and J. W. Bozzelli, "Enthalpies of formation and group Additivity of alkyl peroxides and trioxides," *J. Phys. Chem. A* **101**, 9505 (1997). <http://dx.doi.org/10.1021/jp972103i>
- [187] Y. Lan, S. E. Wheeler, and K. N. Houk, "Extraordinary Difference in Reactivity of Ozone (OOO) and Sulfur Dioxide (OSO): A Theoretical Study," *J. Chem. Theory Comput.* **7**, 2104 (2011). <http://dx.doi.org/10.1021/ct200293w>
- [188] M. Neff and G. Rauhut, "Toward large scale vibrational configuration interaction calculations," *J. Chem. Phys.* **131**, 124129 (2009). <http://dx.doi.org/10.1063/1.3243862>
- [189] V. Barone, "Anharmonic vibrational properties by a fully automated second-order perturbative approach," *J. Chem. Phys.* **122**, 014108 (2005). <http://dx.doi.org/10.1063/1.1824881>
- [190] V. Barone, "Vibrational zero-point energies and thermodynamic functions beyond the harmonic approximation," *J. Chem. Phys.* **120**, 3059 (2004). <http://dx.doi.org/10.1063/1.1637580>
- [191] M. K. Kesharwani, B. Brauer, and J. M. L. Martin, "Frequency and Zero-Point Vibrational Energy Scale Factors for Double-Hybrid Density Functionals (and Other Selected Methods): Can Anharmonic Force Fields Be Avoided?," *J. Phys. Chem. A* **119**, 1701 (2015). <http://dx.doi.org/10.1021/jp508422u>
- [192] G. I. Csonka, A. Ruzsinszky, and J. P. Perdew, "Estimation, computation, and experimental correction of molecular zero-point vibrational energies," *J. Phys. Chem. A* **109**, 6779 (2005). <http://dx.doi.org/10.1021/jp0519464>
- [193] K. K. Irikura, "Experimental vibrational zero-point energies: Diatomic molecules," *J. Phys. Chem. Ref. Data* **36**, 389 (2007). <http://dx.doi.org/10.1063/1.2436891>
- [194] K. K. Irikura, "Erratum: Experimental Vibrational Zero-Point Energies: Diatomic Molecules [*J. Phys. Chem. Ref. Data* **36**, 389-397 (2007)]," *J. Phys. Chem. Ref. Data* **38**, 749 (2009). <http://dx.doi.org/10.1063/1.3167794>
- [195] K. K. Irikura, R. D. Johnson III, R. N. Kacker, and R. Kessel, "Uncertainties in scaling factors for ab initio vibrational zero-point energies," *J. Chem. Phys.* **130**, 114102 (2009). <http://dx.doi.org/10.1063/1.3086931>
- [196] R. S. Grev, C. L. Janssen, and H. F. Schaefer III, "Concerning zero-point vibrational energy corrections to electronic energies," *J. Chem. Phys.* **95**, 5128 (1991). <http://dx.doi.org/10.1063/1.461680>

- [197] F. Pfeiffer, G. Rauhut, D. Feller, and K. A. Peterson, "Anharmonic zero point vibrational energies: Tipping the scales in accurate thermochemistry calculations?," *J. Chem. Phys.* **138**, 044311 (2013). <http://dx.doi.org/10.1063/1.4777568>
- [198] W. Klopper, B. Ruscic, D. P. Tew, F. A. Bischoff, and S. Wolfsegger, "Atomization energies from coupled-cluster calculations augmented with explicitly-correlated perturbation theory," *Chem. Phys.* **356**, 14 (2009). <http://dx.doi.org/10.1016/j.chemphys.2008.11.013>
- [199] P. Barletta, S. V. Shirin, N. F. Zobov, O. L. Polyansky, J. Tennyson, E. F. Valeev, and A. G. Csaszar, "CVRQD ab initio ground-state adiabatic potential energy surfaces for the water molecule," *J. Chem. Phys.* **125**, 204307 (2006). <http://dx.doi.org/10.1063/1.2378766>
- [200] D. S. Hollman and H. F. Schaefer III, "In search of the next Holy Grail of polyoxide chemistry: Explicitly correlated ab initio full quartic force fields for HOOH, HOOOH, HOOOOH, and their isotopologues," *J. Chem. Phys.* **136**, 084302 (2012). <http://dx.doi.org/10.1063/1.3684231>
- [201] M. Mladenovic, "Discrete variable approaches to tetraatomic molecules: part II: application to H₂O₂ and H₂CO," *Spectrochim. Acta A* **58**, 809 (2002). [http://dx.doi.org/10.1016/S1386-1425\(01\)00670-9](http://dx.doi.org/10.1016/S1386-1425(01)00670-9)
- [202] A. Kanton, E. Rabinovich, J. M. L. Martin, and B. Ruscic, "W4 theory for computational thermochemistry: In pursuit of confident sub-kJ/mol predictions," *J. Chem. Phys.* **125**, 144108 (2006). <http://dx.doi.org/10.1063/1.2348881>
- [203] A. Barbe, A. Chichery, T. Cours, V. G. Tyuterev, and J. J. Plateaux, "Update of the anharmonic force field parameters of the ozone molecule," *J. Mol. Struct.* **616**, 55 (2002). [http://dx.doi.org/10.1016/S0022-2860\(02\)00183-7](http://dx.doi.org/10.1016/S0022-2860(02)00183-7)
- [204] K. Suma, Y. Sumiyoshi, and Y. Endo, "Force-field calculation and geometry of the HOOO radical," *J. Chem. Phys.* **139**, 094301 (2013). <http://dx.doi.org/10.1063/1.4819323>
- [205] C. F. Jackels, "The vibrational spectrum of H₂O₃ – an ab initio investigation," *J. Chem. Phys.* **99**, 5768 (1993). <http://dx.doi.org/10.1063/1.465928>
- [206] M. E. Jacox, "Vibrational and electronic energy levels of polyatomic transient molecules. Supplement B," *J. Phys. Chem. Ref. Data* **32**, 1 (2003). <http://dx.doi.org/10.1063/1.1497629>
- [207] M. E. Jacox, "Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P. J. Linstrom and W. G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, <http://webbook.nist.gov>, (retrieved August 13, 2015). [Accessed August 13, 2015].
- [208] J. L. Arnau and P. A. Giguere, "Vibrational analysis and molecular structure of the hydrogen polyoxides, H₂O₃, H₂O₄, D₂O₃, and D₂O₄," *J. Chem. Phys.* **60**, 270 (1974). <http://dx.doi.org/10.1063/1.1680779>
- [209] G. H. Dieke, "The molecular spectrum of hydrogen and its isotopes," *J. Mol. Spec.* **2**, 494 (1958). [http://dx.doi.org/10.1016/0022-2852\(58\)90095-X](http://dx.doi.org/10.1016/0022-2852(58)90095-X)
- [210] G. Rouille, G. Millot, R. Saint-Loup, and H. Berger, "High-resolution stimulated Raman spectroscopy of O₂," *J. Mol. Spectr.* **154**, 372 (1992). [http://dx.doi.org/10.1016/0022-2852\(92\)90215-A](http://dx.doi.org/10.1016/0022-2852(92)90215-A)
- [211] J. Tennyson, N. F. Zobov, R. Williamson, O.L. Polyanski, and P. F. Bernath, "Experimental energy levels of the water molecule," *J. Phys. Chem. Ref. Data* **30**, 735 (2001). <http://dx.doi.org/10.1063/1.1364517>
- [212] J. Pliva, V. Spirko, and D. Papousek, "Anharmonic potential functions of polyatomic molecules *: Part VII. Iterational calculation of anharmonic corrections to fundamental frequencies," *J. Mol. Spectr.* **23**, 331 (1967). [http://dx.doi.org/10.1016/S0022-2852\(67\)80022-5](http://dx.doi.org/10.1016/S0022-2852(67)80022-5)
- [213] M. E. Jacox and W. E. Thompson, "Infrared spectra of products of the reaction of H atoms with O₂ trapped in solid neon: HO₂, HO₂(+), HOHOH(-), and H₂O(HO)," *J. Phys. Chem. A* **117**, 9380 (2013). <http://dx.doi.org/10.1021/jp310849s>
- [214] C. X. Xu, B. Jiang, D. Q. Xie, S. C. Farantos, S. Y. Lin, and H. Guo, "Analysis of the HO₂ vibrational spectrum on an accurate ab initio potential energy surface," *J. Phys. Chem. A* **111**, 10353 (2007). <http://dx.doi.org/10.1021/jp072319c>
- [215] W. B. Olson, R. H. Hunt, B. W. Young, A. G. Maki, and J. W. Braut, "Rotational constants of the lowest torsional component (0G) of the ground state and lowest torsional component (1G) of the first excited torsional state of hydrogen peroxide," *Mol. Spectrosc.* **127**, 12 (1988). [http://dx.doi.org/10.1016/0022-2852\(88\)90004-5](http://dx.doi.org/10.1016/0022-2852(88)90004-5)
- [216] J. I. Steinfeld, S. M. Adler-Golden, and J. W. Gallagher, "Critical survey of data on the spectroscopy and kinetics of ozone in the mesosphere and thermosphere," *J. Phys. Chem. Ref. Data* **16**, 911 (1987). <http://dx.doi.org/10.1063/1.555796>
- [217] A. Barbe, C. Secroun, and P. Jouve, "Infrared spectra of 16O₃ and 18O₃: Darling and Dennison resonance and anharmonic potential function of ozone," *J. Mol. Spectr.* **49**, 171 (1974). [http://dx.doi.org/10.1016/0022-2852\(74\)90267-7](http://dx.doi.org/10.1016/0022-2852(74)90267-7)
- [218] E. L. Derro, T. D. Sechler, C. Murray, and M. I. Lester, "Observation of $\nu_1 + \nu_n$ combination bands of the HOOO and DOOO radicals using infrared action spectroscopy," *J. Chem. Phys.* **128**, 244313 (2008). <http://dx.doi.org/10.1063/1.2945872>
- [219] A. Engdahl and B. Nelander, "The vibrational spectrum of H₂O₃," *Science* **295**, 482 (2002). <http://dx.doi.org/10.1126/Science.1067235>
- [220] C. Camy-Peyret, J. M. Flaud, J. W. C. Johns, and M. Noel, "Torsion-vibration interaction in H₂O₂: First high-resolution observation of ν_3 ," *J. Mol. Spectrosc.* **155**, 84 (1992). [http://dx.doi.org/10.1016/0022-2852\(92\)90550-8](http://dx.doi.org/10.1016/0022-2852(92)90550-8)
- [221] M. C. McCarthy, V. Lattanzi, D. Kokkin, O. Martinez Jr., and J. F. Stanton, "On the molecular structure of HOOO," *J. Chem. Phys.* **136**, 034303 (2012). <http://dx.doi.org/10.1063/1.3673875>
- [222] A. J. C. Varandas, "Is HO₃ minimum cis or trans? An analytic full-dimensional ab initio isomerization path," *Phys. Chem. Chem. Phys.* **13**, 9796 (2011). <http://dx.doi.org/10.1039/c1cp20221a>
- [223] E. P. Hoy, C. A. Schwerdtfeger, and D. A. Mazziotti, "Relative energies and geometries of the cis- and trans-HO₃ radicals from the parametric 2-electron density matrix method," *J. Phys. Chem. A* **117**, 1817 (2013). <http://dx.doi.org/10.1021/jp3105562>
- [224] V. Mokrushin, V. Bedanov, W. Tsang, M. Zachariah, and V. Knyazev, ChemRate, Version 1.5, National Institute of Standards and Technology, Gaithersburg, Maryland (2008).
- [225] R. D. Johnson III, FGH1D Program for one-dimensional solution of the Schrodinger equation. Version 1.01, National Institute of Standards and Technology, Gaithersburg, Maryland (1999).
- [226] K. Suma, Y. Sumiyoshi, and Y. Endo, "The rotational spectrum and structure of HOOH," *J. Am. Chem. Soc.* **127**, 14998 (2005). <http://dx.doi.org/10.1021/ja0556530>

- [227] R. J. Blint and M. D. Newton, "Ab initio studies of interoxygen bonding in O₂, HO₂, H₂O₂, O₃, HO₃, and H₂O₃," *J. Chem. Phys.* **59**, 6220 (1973). <http://dx.doi.org/10.1063/1.1680001>
- [228] D. Cremer, "Theoretical determination of molecular structure and conformation. II. Hydrogen trioxide—a model compound for studying the conformational modes of geminal double rotors and five membered rings," *J. Chem. Phys.* **69**, 4456 (1978). <http://dx.doi.org/10.1063/1.436435>
- [229] X. Xu, R. P. Muller, and W. A. Goddard III, "The gas phase reaction of singlet dioxygen with water: A water-catalyzed mechanism," *Proc. Natl. Acad. Sci. U.S.A.* **99**, 3376 (2002). <http://dx.doi.org/10.1073/pnas.052710099>
- [230] P. Wentworth Jr., L. H. Jones, A. D. Wentworth, X. Y. Zhu, N. A. Larsen, I. A. Wilson, X. Xu., W. A. Goddard III, K. D. Janda, A. Eschenmoser, and R. A. Lerner, "Antibody catalysis of the oxidation of water," *Science* **293**, 1806 (2001). <http://dx.doi.org/10.1126/Science.1062722>
- [231] D. Datta, N. Vaidehi, X. Xu, and W. A. Goddard III, "Mechanism for antibody catalysis of the oxidation of water by singlet dioxygen," *Proc. Natl. Acad. Sci. U.S.A.* **99**, 2636 (2002). <http://dx.doi.org/10.1073/pnas.052709399>
- [232] V. A. Yerokhin and V. M. Shabaev, "Lamb shift of n=1 and n=2 states of hydrogen-like atoms, 1<=Z<=110," *J. Phys. Chem. Ref. Data* **44**, 033103 (2015). <http://dx.doi.org/10.1063/1.4927487>
- [233] A. Kramida, Yu. Ralchenko, and J. Reader, NIST Atomic Spectra Database (ver. 5.2), [Online]. Available: <http://physics.nist.gov/asd> [2015, August 5]. National Institute of Standards and Technology, Gaithersburg, MD. [Accessed August 12, 2015].
- [234] U. D. Jentschura, S. Kotochigova, E. O. Le Bigot, P. J. Mohr, and B. N. Taylor, "Precise calculation of transition frequencies of hydrogen and deuterium based on a least-squares analysis," *Phys. Rev. Lett.* **95**, 163003 (2005). <http://dx.doi.org/10.1103/PhysRevLett.95.163003>
- [235] J. E. Sansonetti and W. C. Martin, "Handbook of basic atomic spectroscopic data," *J. Phys. Chem. Ref. Data* **34**, 1559 (2005). <http://dx.doi.org/10.1063/1.1800011>
- [236] W. R. Johnson and G. Soff, "The Lamb shift in hydrogen-like atoms, 1<=Z<=110," *At. Data Nucl. Tab.* **33**, 405 (1985). [http://dx.doi.org/10.1016/0092-640X\(85\)90010-5](http://dx.doi.org/10.1016/0092-640X(85)90010-5)
- [237] C. E. Moore, "Ionization potentials and ionization limits derived from the analyses of optical spectra," *Nat. Stand. Ref. Data Ser., NSRDS-NBS* **34**, 22p (Nat. Bur. Stand. U.S., 1970).
- [238] W. L. Wiese, M. W. Smith, and B. M. Glennon, "Atomic Transition Probabilities. Volume 1. Hydrogen through Neon." NSRDS-NBS 4 (National Bureau of Standards, U. S. Government Printing Office, 1966).
- [239] J. D. Garcia and J. E. Mack, "Energy level and line tables for 1-electron atomic spectra," *J. Opt. Soc. Am.* **55**, 654 (1965). <http://dx.doi.org/10.1364/JOSA.55.000654>
- [240] K. R. Lykke, K. K. Murray, and W. C. Lineberger, "Threshold Photodetachment of H-," *Phys. Rev. A* **43**, 6104 (1991). <http://dx.doi.org/10.1103/PhysRevA.43.6104>
- [241] C. L. Pekeris, "1 2S, 2 1S, and 2 3S states of H- and of He," *Phys. Rev.* **126**, 1470 (1962). <http://dx.doi.org/10.1103/PhysRev.126.1470>
- [242] A. de Lange, E. Reinhold, and W. Ubachs, "Spectroscopy on some g symmetry states in H₂ and determination of the ionization potential," *Phys. Rev. A* **65**, 064501 (2002). <http://dx.doi.org/10.1103/PhysRevA.65.064501>
- [243] D. Shiner, J. M. Gilligan, B. M. Cook, and W. Lichten, "H₂, D₂, and HD ionization potentials by accurate calibration of several iodine lines," *Phys. Rev. A* **47**, 4042 (1993). <http://dx.doi.org/10.1103/PhysRevA.47.4042>
- [244] Ch. Jungen, I. Dabrowski, G. Herzberg, and M. Vervloet, "The ionization potential of D₂," *J. Mol. Spectrosc.* **153**, 11 (1992). [http://dx.doi.org/10.1016/0022-2852\(92\)90452-T](http://dx.doi.org/10.1016/0022-2852(92)90452-T)
- [245] Ch. Jungen, I. Dabrowski, G. Herzberg, and W. Kendall, "High orbital angular momentum states in H₂ and D₂. II. The 6h–5g and 6g–5f transitions," *J. Chem. Phys.* **91**, 3926 (1989). <http://dx.doi.org/10.1063/1.456824>
- [246] J. M. Gilligan and E. E. Eyler, "Precise determinations of ionization potentials and EF-state energy levels of H₂, HD, and D₂," *Phys. Rev. A* **46**, 3676 (1992). <http://dx.doi.org/10.1103/PhysRevA.46.3676>
- [247] E. McCormack, J. M. Gilligan, C. Cornaggia, and E. E. Eyler, "Measurement of high Rydberg states and the ionization potential of H₂," *Phys. Rev. A* **39**, 2260 (1989). <http://dx.doi.org/10.1103/PhysRevA.39.2260>
- [248] W. L. Glab and J. P. Hessler, "Multiphoton excitation of high singlet np Rydberg states of molecular hydrogen: Spectroscopy and dynamics," *Phys. Rev. A* **35**, 2102 (1987). <http://dx.doi.org/10.1103/PhysRevA.35.2102>
- [249] G. Herzberg and Ch. Jungen, "Rydberg series and ionization potential of the H₂ molecule," *J. Mol. Spectrosc.* **41**, 425 (1972). [http://dx.doi.org/10.1016/0022-2852\(72\)90064-1](http://dx.doi.org/10.1016/0022-2852(72)90064-1)
- [250] K. M. Weitzel, J. Mahnert, and M. Penno, "ZEKE-PEPICO investigations of dissociation energies in ionic reactions," *Chem. Phys. Lett.* **224**, 371 (1994). [http://dx.doi.org/10.1016/0009-2614\(94\)00567-2](http://dx.doi.org/10.1016/0009-2614(94)00567-2)
- [251] R. C. Shiell, X. K. Hu, Q. C. J. Hu, and J. W. Hepburn, "Threshold ion-pair production spectroscopy (TIPPS) of H₂ and D₂," *Farad. Disc.* **115**, 331 (2000). <http://dx.doi.org/10.1039/a909428h>
- [252] S. T. Pratt, E. F. McCormack, J. L. Dehmer, and P. M. Dehmer, "Field-induced ion-pair formation in molecular hydrogen," *Phys. Rev. Lett.* **68**, 584 (1992). <http://dx.doi.org/10.1103/PhysRevLett.68.584>
- [253] W. A. Chupka, P. M. Dehmer, and W. T. Jivery, "High resolution photoionization study of ion-pair formation in H₂, HD, and D₂," *J. Chem. Phys.* **63**, 3929 (1975). <http://dx.doi.org/10.1063/1.431833>
- [254] C. E. Moore, "Selected Tables of Atomic Spectra, Atomic Energy Levels and Multiplet Tables – O I," *Nat. Stand. Ref. Data Ser., NSRDS-NBS* **3** (Sect. 7), 33 pp. (Nat. Bur. Stand., U.S., 1976).
- [255] C. Blondel, W. Chaibi, C. Delsart, C. Drag, F. Goldfarb, and S. Kroger, "The electron affinities of O, Si, and S revisited with the photodetachment microscope," *Eur. Phys. J. D* **33**, 335 (2005). <http://dx.doi.org/10.1140/epjd/e2005-00069-9>
- [256] C. Blondel, "Recent experimental achievements with negative ions," *Physica Scripta* **T58**, 31 (1995). <http://dx.doi.org/10.1088/0031-8949/1995/T58/004>
- [257] D. M. Neumark, K. R. Lykke, T. Andersen, and W. C. Lineberger, "Laser photodetachment measurement of the electron affinity of atomic oxygen," *Phys. Rev. A* **32**, 1890(1985). <http://dx.doi.org/10.1103/PhysRevA.32.1890>

- [258] F. Goldfarb, C. Drag, W. Chaibi, S. Kroger, C. Blondel, and C. Delsart, "Photodetachment microscopy of the P, Q, and R branches of the OH($v=0$) to OH($v=0$) detachment threshold," *J. Chem. Phys.* **122**, 014308 (2005). <http://dx.doi.org/10.1063/1.1824904>
- [259] J. R. Smith, J. B. Kim, and W. C. Lineberger, "High-resolution threshold photodetachment spectroscopy of OH $^-$," *Phys. Rev. A* **55**, 2036 (1997). <http://dx.doi.org/10.1103/PhysRevA.55.2036>
- [260] F. Merkt, R. Signorell, H. Palm, A. Osterwalder, and M. Sommariva, "Towards resolving the hyperfine structure in ions by photoelectron spectroscopy," *Mol. Phys.* **95**, 1045 (1998). <http://dx.doi.org/10.1080/002689798166657>
- [261] R. G. Tonkyn, R. Wiedmann, E. R. Grant, and M. G. White, "Rotationally resolved photoionization of H $_2$ O," *J. Chem. Phys.* **95**, 7033 (1991). <http://dx.doi.org/10.1063/1.461431>
- [262] M. S. Child and Ch. Jungen, "Quantum defect theory for asymmetric tops: Application to the Rydberg spectrum of H $_2$ O," *J. Chem. Phys.* **93**, 7756 (1990). <http://dx.doi.org/10.1063/1.459355>
- [263] A. Bodi, J. Csontos, M. Kallay, S. Borkar, and B. Sztaray, "On the protonation of water," *Chem. Sci.* **5**, 3057 (2014). <http://dx.doi.org/10.1039/c4sc00791c>
- [264] Y. Song, M. Evans, C. Y. Ng, C. W. Hsu, and G. K. Jarvis, "Rotationally resolved pulsed field ionization photoelectron bands of O $_2^+$ in the energy range of 12.05–18.15 eV," *J. Chem. Phys.* **111**, 1905 (1999). <http://dx.doi.org/10.1063/1.479459>
- [265] W. Kong and J. W. Hepburn, "Rotationally resolved threshold photoelectron spectroscopy of O $_2$ using coherent XUV: formation of vibrationally excited ions in the Franck–Condon gap," *Can. J. Phys.* **72**, 1284 (1994). <http://dx.doi.org/10.1139/p94-164>
- [266] R. G. Tonkyn, J. W. Winniczek, and M. G. White, "Rotationally resolved photoionization of O $_2$ near threshold," *Chem. Phys. Lett.* **164**, 137 (1989). [http://dx.doi.org/10.1016/0009-2614\(89\)85005-5](http://dx.doi.org/10.1016/0009-2614(89)85005-5)
- [267] J. A. R. Samson and J. L. Gardner, "On the ionization potential of molecular oxygen," *Can. J. Phys.* **53**, 1948 (1975). <http://dx.doi.org/10.1139/p75-244>
- [268] K. M. Ervin, W. Anusiewicz, P. Skurski, J. Simons, and W. C. Lineberger, "The only stable state of O $_2^-$ is the X $_2$ state and it (still!) has an adiabatic electron detachment energy of 0.45 eV," *J. Phys. Chem. A* **107**, 8521 (2003). <http://dx.doi.org/10.1021/jp0357323> □g ground
- [269] M. J. Travers, D. C. Cowles, and G. B. Ellison, "Reinvestigation of the Electron Affinities of O $_2$ and NO," *Chem. Phys. Lett.* **164**, 449 (1989). [http://dx.doi.org/10.1016/0009-2614\(89\)85237-6](http://dx.doi.org/10.1016/0009-2614(89)85237-6)
- [270] R. J. Celotta, R. A. Bennett, J. L. Hall, M. W. Siegel, and J. Levine, "Molecular photodetachment spectrometry. II. The electron affinity of O $_2$ and the structure of O $_2^-$," *Phys. Rev. A* **6**, 631 (1972). <http://dx.doi.org/10.1103/PhysRevA.6.631>
- [271] M. Richard-Viard, O. Dutuit, M. Lavallee, T. Govers, P. M. Guyon, and J. Durup, "O $_2^+$ ions dissociation studied by threshold photoelectron–photoion coincidence method," *J. Chem. Phys.* **82**, 4054 (1985). <http://dx.doi.org/10.1063/1.448846>
- [272] J. M. Dyke, N. B. H. Jonathan, A. Morris, and M. J. Winter, "Vacuum ultraviolet photoelectron spectroscopy of transient species. Part 13. Observation of the X $_3$ A state of HO $_2$," *Mol. Phys.* **44**, 1059 (1981). <http://dx.doi.org/10.1080/00268978100103011>
- [273] S. Willitsch, F. Innocenti, J. M. Dyke, and F. Merkt, "High-resolution pulsed-field-ionization zero-kinetic-energy photoelectron spectroscopic study of the two lowest electronic states of the ozone cation O $_3^+$," *J. Chem. Phys.* **122**, 024311 (2005). <http://dx.doi.org/10.1063/1.1829974>
- [274] M. J. Weiss, J. Berkowitz, and E. H. Appelman, "Photoionization of ozone: Formation of O $_4^+$ and O $_5^+$," *J. Chem. Phys.* **66**, 2049 (1977). <http://dx.doi.org/10.1063/1.434164>
- [275] D. W. Arnold, C. S. Xu, E. H. Kim, and D. M. Neumark, "Study of low-lying electronic states of ozone by anion photoelectron spectroscopy of O $_3^-$," *J. Chem. Phys.* **101**, 912 (1994). <http://dx.doi.org/10.1063/1.467745>
- [276] S. E. Novick, P. C. Engelking, P. L. Jones, J. H. Futrell, and W. C. Lineberger, "Laser photoelectron, photodetachment, and photodestruction spectra of O $_3^-$," *J. Chem. Phys.* **70**, 2652 (1979). <http://dx.doi.org/10.1063/1.437842>
- [277] A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *J. Chem. Phys.* **98**, 5648 (1993). <http://dx.doi.org/10.1063/1.464913>
- [278] J. Finley, P. A. Malmqvist, B. O. Roos, and L. Serrano-Andres, "The multi-state CASPT2 method," *Chem. Phys. Lett.* **288**, 299 (1998). [http://dx.doi.org/10.1016/S0009-2614\(98\)00252-8](http://dx.doi.org/10.1016/S0009-2614(98)00252-8)
- [279] P. J. Knowles and H. J. Werner, "An efficient second-order MC SCF method for long configuration expansions," *Chem. Phys. Lett.* **115**, 259 (1985). [http://dx.doi.org/10.1016/0009-2614\(85\)80025-7](http://dx.doi.org/10.1016/0009-2614(85)80025-7)
- [280] J. A. Montgomery Jr., J. W. Ochterski, and G. A. Petersson, "A complete basis set model chemistry. IV. An improved atomic pair natural orbital method," *J. Chem. Phys.* **101**, 5900 (1994). <http://dx.doi.org/10.1063/1.467306>
- [281] J. W. Ochterski, G. A. Petersson, and J. A. Montgomery Jr., "A complete basis set model chemistry .5. Extensions to six or more heavy atoms," *J. Chem. Phys.* **104**, 2598 (1996). <http://dx.doi.org/10.1063/1.470985>
- [282] J. A. Montgomery, M. J. Frisch, J. W. Ochterski, and G. A. Petersson, "A complete basis set model chemistry. VI. Use of density functional geometries and frequencies," *J. Chem. Phys.* **110**, 2822 (1999). <http://dx.doi.org/10.1063/1.477924>
- [283] R. J. Bartlett and G. D. Purvis III, "Many-body perturbation-theory, coupled-pair many-electron theory, and importance of quadruple excitations for correlation problem," *Int. J. Quant. Chem.* **14**, 561 (1978). <http://dx.doi.org/10.1002/qua.560140504>
- [284] G. Knizia, T. B. Adler, and H. J. Werner, "Simplified CCSD(T)-F12 methods: theory and benchmarks," *J. Chem. Phys.* **130**, 054104 (2009). <http://dx.doi.org/10.1063/1.3054300>
- [285] J. Noga and W. Kutzelnigg, "Coupled cluster theory that takes care of the correlation cusp by inclusion of linear terms in the interelectronic coordinates," *J. Chem. Phys.* **101**, 7738 (1994). <http://dx.doi.org/10.1063/1.468266>
- [286] J. A. Pople, R. Seeger, and R. Krishnan, "Variational configuration interaction methods and comparison with perturbation theory," *Int. J. Quant. Chem. Suppl.* **Y-11**, 149 (1977). <http://dx.doi.org/10.1002/qua.560120820>
- [287] F. A. Hamprecht, A. J. Cohen, D. J. Tozer, and N. C. Handy, "Development and assessment of new exchange-correlation functionals," *J. Chem. Phys.* **109**, 6264 (1998). <http://dx.doi.org/10.1063/1.477267>
- [288] C. Adamo and V. Barone, "Toward reliable density functional methods without adjustable parameters: The PBE0 model," *J. Chem. Phys.* **110**, 6158 (1999). <http://dx.doi.org/10.1063/1.478522>

- [289] J. F. Stanton and J. Gauss, "Analytic energy derivatives for ionized states described by the equation of motion coupled cluster method," *J. Chem. Phys.* **101**, 8938 (1994). <http://dx.doi.org/10.1063/1.468022>
- [290] P. J. Knowles and N. C. Handy, "A new determinant-based full configuration interaction method," *Chem. Phys. Lett.* **111**, 315 (1984). [http://dx.doi.org/10.1016/0009-2614\(84\)85513-X](http://dx.doi.org/10.1016/0009-2614(84)85513-X)
- [291] C. F. Bunge, "Selected configuration interaction with truncation energy error and application to the Ne atom," *J. Chem. Phys.* **125**, 014107 (2006). <http://dx.doi.org/10.1063/1.2207620>
- [292] L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, "Gaussian-2 theory for molecular energies of 1st row and 2nd row compounds," *J. Chem. Phys.* **94**, 7221 (1991). <http://dx.doi.org/10.1063/1.460205>
- [293] R. J. Gdanitz and R. Ahlrichs, "The averaged coupled-pair functional (ACPF): A size-extensive modification of MRCI(SD)," *Chem. Phys. Lett.* **143**, 413 (1988). [http://dx.doi.org/10.1016/0009-2614\(88\)87388-3](http://dx.doi.org/10.1016/0009-2614(88)87388-3)
- [294] R. J. Buenker, S. D. Peyerimhoff, and W. Butscher, "Applicability of the multi-reference double-excitation CI (MRD-CI) method to the calculation of electronic wavefunctions and comparison with related techniques," *Mol. Phys.* **35**, 771 (1978). <http://dx.doi.org/10.1080/00268977800100581>
- [295] S. R. Langhoff and E. R. Davidson, "Configuration interaction calculations on the nitrogen molecule," *Int. J. Quantum Chem.* **8**, 61 (1974). <http://dx.doi.org/10.1002/qua.560080106>
- [296] K. Hirao, "Multireference Moller-Plesset method," *Chem. Phys. Lett.* **190**, 374 (1992). [http://dx.doi.org/10.1016/0009-2614\(92\)85354-D](http://dx.doi.org/10.1016/0009-2614(92)85354-D)
- [297] J. A. Pople, M. Head-Gordon, and K. Raghavachari, "Quadratic configuration interaction - a general technique for determining electron correlation energies," *J. Chem. Phys.* **87**, 5968 (1987). <http://dx.doi.org/10.1063/1.453520>
- [298] J. M. L. Martin and G. de Oliveira, "Towards standard methods for benchmark quality ab initio thermochemistry - W1 and W2 theory," *J. Chem. Phys.* **111**, 1843 (1999). <http://dx.doi.org/10.1063/1.479454>
- [299] D. G. Truhlar, "Basis set extrapolation," *Chem. Phys. Lett.* **294**, 45 (1998). [http://dx.doi.org/10.1016/S0009-2614\(98\)00866-5](http://dx.doi.org/10.1016/S0009-2614(98)00866-5)
- [300] D. Feller and K. A. Peterson, "Re-examination of atomization energies for the Gaussian-2 set of molecules," *J. Chem. Phys.* **110**, 8384 (1999). <http://dx.doi.org/10.1063/1.478747>

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