A Study of $\text{H}_2\text{O}_2$ with Threshold Photoelectron Spectroscopy (TPES) and Electronic Structure Calculations: Re-determination of the first Adiabatic Ionization Energy (AIE)

Luca Schio$^{(a)}$, Michele Alagia$^{(a)}$, Antonio A. Dias$^{(b)}$, Stefano Falcinelli$^{(c)}$, Vitali Zhaunerchyk$^{(d)}$, Edmond P.F.Lee$^{(e,f)}$, Daniel K.W.Mok$^{(f)}$, John M. Dyke$^{(e)}$* and Stefano Stranges$^{(g)}$*

(a) IOM-CNR Tasc Laboratory, SS-14, Km 163.5, Area Science Park, 34149 Basovizza, Trieste, Italy
(b) LIBPhys-UNL, Laboratory for Instrumentation, Biomedical Engineering and Radiation Physics; Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Caparica, Portugal
(c) Dipartimento di Ingegneria Civile ed Ambientale, Università di Perugia, 06125 Perugia, Italy
(d) Department of Physics, University of Gothenburg, 41296 Gothenburg, Sweden
(e) School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK
(f) Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Hong Kong
(g) Department of Chemistry and Drug Technologies, Sapienza University, P.le A. Moro 5, 00185 Rome, Italy, and IOM-CNR, Tasc Laboratory, SS-14, Km 163.5, Area Science Park, 34149 Basovizza, Trieste, Italy

Supplementary Information

Geometrical parameters of the ground state of $\text{H}_2\text{O}_2$

In the early infrared work on $\text{H}_2\text{O}_2$ in 1962$^{\text{S11}}$, vibrationally resolved infrared spectra were recorded which gave the following rotational constants for the lowest vibrational level $A'' = 10.068$, $B'' = 0.8740$ and $C'' = 0.8384 \text{ cm}^{-1}$.

$\text{H}_2\text{O}_2$ has four structural parameters which cannot be determined from only three rotational constants. A way forward was found$^{\text{S12}}$ by assuming $r_0(\text{O-H}) = (0.950 \pm 0.005)$ Å.

Using this value, the other $r_0$ parameters were determined from the rotational constants as

$r_0(\text{O-O }) = (1.475 \pm 0.004)$ Å ,
$\angle \text{OOH} = (94.8 \pm 2.0)^\circ$ ,
$\text{HOOH dihedral angle} = (119.8 \pm 3.0)^\circ$

Then, using a computed $r(\text{O-H})$ value of $(0.967 \pm 0.005)$Å , obtained at the MP2 level, Cremer$^{\text{S13}}$ used the rotational constants to re-determine the other $r_0$ parameters as

$r_0(\text{O-O }) = (1.463 \pm 0.004)$ Å ,
$\angle \text{OOH} = (99.3 \pm 2.0)^\circ$ ,

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HOOH dihedral angle = (120.2 ± 3.0)°

Also, in a re-analysis of available infrared and microwave data the following $r_e$ values were proposed$^{SI3, SI4}$, based on an assumed value of $r_e$(O-H) = (0.965 ± 0.005) Å, $r_e$(O-O) = (1.452 ± 0.004) Å, 

$\angle$OOH = (100.0 ± 1.0)°, 

HOOH dihedral angle = (119.2 ± 1.8)°

Summary of Thermodynamic Values with References used to derive $\Delta H_{f,298}$ (H$_2$O$_2$), $D_{0,298}$ (HO-OH) and $D_{0,298}$(H-O$_2$H)

a) $\Delta H_{f,298}$ (H$_2$O$_2$)

Taken as –(32.48 ± 0.05) kcal.mol$^{-1}$ from ref SI4.

b) $D_{0,298}$ (HO-OH)

This is evaluated as (50.26 ± 0.23) kcal.mol$^{-1}$ from $\Delta H_{f,298}$ (OH) = (8.89 ± 0.09) kcal.mol$^{-1}$ (ref SI4 and the above value of $\Delta H_{f,298}$ (H$_2$O$_2$)

c) $D_{0,298}$ (H-O$_2$H)

This is evaluated as (87.9 ± 0.8) kcal.mol$^{-1}$ from $\Delta H_{f,298}$ (HO$_2$) = (3.3 ± 0.8) kcal.mol$^{-1}$, $\Delta H_{f,298}$ (H) = (52.103 ± 0.001) kcal.mol$^{-1}$ (ref SI4) and the above value of $\Delta H_{f,298}$ (H$_2$O$_2$)

References for SI


