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NOTE

Improved Molecular Constants for the Ground State of HO_2

Molecular constants for the ground state of HO_2 were recently published by some of us (*1*). These constants were based on measurements of the frequencies of 17 transitions in the region 2.5 to 5.9 THz combined with previously measured microwave and millimeter-wave measurements. Unfortunately it has been found that there was a small error in the computer program used; the off-diagonal spin–rotation matrix element $\langle NK|H_{SR}|N-1K\rangle$ included a term $\Delta^S_{NK}N(N+1)(K/2)(N^2-K^2)^{1/2}\phi(N)$ instead of the correct $\Delta^S_{NK}N^2(K/2)(N^2-K^2)^{1/2}\phi(N)$. This error particularly affected the values fitted for b_s, Δ^s_{NK}, δ^s_K, and T^2_1. Table 1 gives the molecular constants obtained after this correction. In the meantime, a rotational analysis of the 000–000 band of the $\tilde{A}^2A' \rightarrow \tilde{X}^2A''$ electronic transition in the region of 7000 cm^{-1} (*2*) revealed systematic discrepancies between observed and calculated ground state combination differences at high values of N and K_a. The terahertz, microwave, and millimeter-wave measurements encompassed rotational levels up to $N = 26$ and $K_a = 5$ but the near-infrared measurements extended to $N = 31$ and $K_a = 9$. The magnitude of the discrepancy for predicting combination differences involving $K_a = 7$–9 was 0.01–0.04 cm^{-1}.

A revised set of molecular constants is obtained by combining both sets of data with appropriate weightings, where the combination differences are assigned uncertainties of 0.002–0.003 cm^{-1}, and refitting to the parameterized Hamiltonian. Combination differences (133), involving values of N and K_a found only in the near infrared band, and 173 rotational transitions are used in the final fitting. The weighted RMS of the fit is 1.1. The revised constants are given in Table 2.

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TABLE 1

Corrected Molecular Constants for the HO_2 Ground State (MHz) from Simultaneous Fit of 173 Lines from 27 GHz to 5.9 THz

Constant	Value	σ	Constant	Value	σ
$A-(B+C)/2$	577 680.504	0.031	a_0	16 662.215	0.069
$(B+C)/2$	32 592.7334	0.0017	a_s	16 455.075	0.050
$(B-C)/4$	462.5330	0.0088	b_s	215.819	0.025
Δ_N	0.116 902	0.000 011	d_s	194.20	0.18
Δ_{NK}	3.445 80	0.000 29	Δ^S_K	23.696	0.027
Δ_K	123.5978	0.0061	Δ^S_{NK}	0.2942	0.0023
$\delta_N \times 10^3$	6.1433	0.0028	δ^S_K	0.150	0.013
δ_K	2.0097	0.0090	$\Phi^S_K \times 10^2$	-3.17	0.12
$\Phi_{NK} \times 10^5$	1.834	0.049	a_F	-27.533	0.075
$\Phi_{KN} \times 10^3$	1.103	0.015	T^2_0	-4.153	0.045
Φ_K	0.101 01	0.000 40	T^2_1	-6.4	1.4
$L_K \times 10^4$	-1.854	0.079	T^2_2	6.427	0.026

TABLE 2

Revised Molecular Constants for the HO_2 Ground State (MHz) Including Combination Differences from $\tilde{A}^2A' \rightarrow \tilde{X}^2A''$

Constant	Value	σ	Constant	Value	σ
$A-(B+C)/2$	577 680.377	0.025	a_0	16 662.064	0.065
$(B+C)/2$	32 592.7291	0.0016	a_s	16 454.971	0.046
$(B-C)/4$	462.5018	0.0073	b_s	215.841	0.025
Δ_N	0.116 865	0.000 010	d_s	194.39	0.18
Δ_{NK}	3.445 31	0.000 24	Δ^s_K	23.664	0.021
Δ_K	123.5724	0.0035	Δ^s_{NK}	0.2911	0.0022
$\delta_N \times 10^3$	6.1499	0.0026	δ^s_K	0.159	0.012
δ_K	1.9779	0.0075	$\Phi^s_K \times 10^2$	-3.039	0.092
$\Phi_{NK} \times 10^5$	1.936	0.044	a_F	-27.518	0.075
$\Phi_{KN} \times 10^3$	1.060	0.013	T^2_0	-4.160	0.045
$\Phi_K \times 10^2$	9.914	0.018	T^2_1	-6.3	1.4
$L_K \times 10^4$	-1.387	0.018	T^2_2	6.428	0.026

For definition of the constants, see (1)

REFERENCES

1. K. V. Chance, K. Park, K. M. Evenson, L. R. Zink, and F. Stroh, *J. Mol. Spectrosc.* **172,** 407–420 (1995).
2. E. H. Fink and D. A. Ramsay, to be published.

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