The spectrum of DO$_2$ near 60 GHz and the structure of the hydroperoxyl radical

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(Received 29 October 1975)

Spectra for the lowest rotational transition in DO$_2$, $N = 1 \leftarrow 0$, have been observed near 60 GHz. These data have been used to calculate the sum of the rotational constants $B + C$ for DO$_2$ = 60467.7 ± 3 MHz. This result was combined with other measurements on HO$_2$ to compute a structure for the hydroperoxyl radical: r(H–O) = 0.977 × 10^{-10} m, r(O–O) = 1.335 × 10^{-10} m, and < H–O–O = 104.1°. Also we have found for DO$_2$ that $(\epsilon_{bb} + \epsilon_{cc})/2 = -191 \pm 3$ MHz for elements of the electron–spin rotation tensor and a value of −4.2 ± 1.5 MHz for the Fermi contact interaction parameter σ.

INTRODUCTION

The HO$_2$ radical has an interesting history of speculation on its existence, stability, and structure. Although the existence of a transient HO$_2$ species was postulated nearly 50 years ago to explain the mechanism of the H$_2$/O$_2$ reaction,[1] it was not detected in the gas phase until 1953 when the classic mass spectrometer experiment of Foner and Hudson[2] was reported. This work was later extended to determine the thermodynamic stability of HO$_2$.[3]

Walsh predicted in 1953 that the structure of HO$_2$ should be similar to that of HNO.[4] Then, beginning in the 1960's, high speed computers were applied to the problems of the structure and stability of HO$_2$. The quality of these calculations has clearly improved with time and will be discussed in some detail in a later section.

Spectroscopic work on HO$_2$ has increased at an accelerated rate since about 1970, stimulated largely by an interest in the gas chemistry of the radical. Milligan and Jacox[5] and Smith and Andrews[6] have studied HO$_2$ using matrix isolation techniques. In 1972 Paukert and Johnston[7] reported detecting gaseous HO$_2$ in the ultraviolet (near 210 nm) and in the infrared, and Hochanadel *et al.*[8] also detected it in the uv. Recently, Radford *et al.*[9] reported observing Zeeman components of HO$_2$ rotational transitions in the far infrared (near 100 μm) and Hougen *et al.*[10] gave an analysis of these spectra. Hunziker and Wendt[11] have first detected and reported a near infrared absorption spectrum for HO$_2$, which included the discovery of the low energy $^2A'$ excited state at 1.43 μm. Becker *et al.*[12] observed similar transitions in emission. In 1975, Beers and Howard[13] reported measurements of the microwave frequencies of the lowest HO$_2$ rotational transition at 65 GHz. Saito[14] has measured these transitions with improved accuracy, as well as several other transitions at microwave frequencies.

We report here measurements of DO$_2$ spectral lines arising from the change in rotational quantum number, $N = 1 \leftarrow 0$. We have thus obtained a value for the sum of the DO$_2$ rotational constants, $(B + C)$, which combined with the previously obtained rotational constants of

HO$_2$,[10,13,14] allow us to calculate the structural parameters of the hydroperoxyl radical.

EXPERIMENTAL

The apparatus and procedure that were used are essentially the same as described earlier.[13] Minor changes improved the sensitivity. The Zeeman modulation frequency was raised from 4 to 10 kHz. The time constant of the phase sensitive detector was increased from 10 to 30 sec. A specially selected detector crystal was used. Also the klystron used here gave higher power and had a superior frequency stability. Therefore, many of the measurements were made without the phase lock, and thus these could be made much more rapidly.

The DO$_2$ radicals were produced in a discharge-flow system by the reaction of fluorine atoms with D$_2$O$_2$ and DHO$_2$ similar to the method described earlier for HO$_2$.[13] The deuterated peroxide was prepared by mixing about 150 cm^3 of 90% H$_2$O$_2$ solution with about 250 cm^3 of 99.5% deuterated water. This mixture was allowed to stand for an hour or longer to permit the isotopic hydrogen species to exchange in solution. It was then reduced in volume to about 100 cm^3 by vacuum pumping while the solution was heated to about 40 °C to reconcentrate the resulting mixture of peroxide compounds. Since the resulting concentration of deuterated peroxide was less than that of H$_2$O$_2$, the signal-to-noise ratio in the DO$_2$ experiment was somewhat poorer than that in the HO$_2$ experiment.

RESULTS AND DISCUSSION

The $N = 1 \leftarrow 0$ HO$_2$ spectrum consists of two groups of lines roughly 300 MHz apart resulting from transitions from a common $N = 0$, $J = \frac{1}{2}$ lower state to $N = 1$, $J = \frac{1}{2}$ and $\frac{3}{2}$ upper states. The splitting within each group is due to the hyperfine interaction of the hydrogen nucleus. With HO$_2$ there are three lines in each group with a spread of about 30 MHz. Because of its smaller nuclear magnetic moment the splitting would be only about one sixth as large if the deuteron were to have the same nuclear spin of $\frac{1}{2}$ of the proton. However, because the spin is 1, there are five lines with transitions to the

$J = \frac{3}{2}$ upper state and four to the $J = \frac{1}{2}$ upper state. Experimentally these patterns were only partially resolved. In each case only a strong line and one weaker line were observed, but the shapes of the two stronger lines clearly indicated that they are due to two incompletely resolved lines. Zeeman components of the strong lines were observed in both pi and sigma polarizations (microwave electric field parallel and perpendicular to the Zeeman field, respectively), and the frequencies were extrapolated to zero field. However, the Zeeman components of the weak lines could be observed only in the sigma polarization. The slopes of the plots of the Zeeman patterns agreed approximately with those expected from the g_J values of the levels which have been assigned.

Table I compares the observed frequencies to those frequencies that have been calculated from the molecular constants given in Table II. These constants were derived from the spectra using the general methods described earlier.[13] In principle the value of $B + C$ should be corrected by adding the value of the centrifugal distortion constant Δ_N, but since its value[14] is only 0.11 MHz, which is smaller than the assigned error, this effect has been neglected.

Table III gives the structural parameters of the hydroperoxyl radical. The first line of the Table gives parameters that were calculated on the basis of the following information: (1) $B + C$ for DO$_2$ = 60 467.7 ±3 MHz (this work); (2) $B + C$ for HO$_2$ = 65 185.40 ± 0.11 MHz (Ref. 14); and (3) A for HO$_2$ = 610 220 ± 100 MHz (average of values in Refs. 10 and 14). The structural parameters were calculated using the expressions of Gordy and Cook.[15]

The errors associated with these structural parameters which result from the experimental uncertainties in the molecular constants are very small, ±0.0003 ×10^{-10}m, ±0.003×10^{-10}m, and ±0.02° for r(H–O), r(O–O), and < H–O–O, respectively. A much larger uncertainty is introduced by our assumption that the structures of HO$_2$ and DO$_2$ are identical in their ground vibrational states. The differences in vibrational ground state H–O and D–O bond lengths in hydrogen and deuterium substituted hydroxyl and hydrogen peroxide molecules are 0.0035 and 0.015× 10^{-10}m, respectively.[16] In

TABLE II. DO$_2$ molecular constants.

Quantity	Value
$(B+C)$	60 467.7 ± 3 MHz
$(\epsilon_{bb} + \epsilon_{cc})/2$	−191 ± 3 MHz
σ	−4.2 ± 1.5 MHz

addition, there may be a difference in the HO$_2$ and DO$_2$ bond angles up to about 0.6° as found in H$_2$O$_2$ and D$_2$O$_2$.[16] To determine the magnitude of the effect of these differences on our calculation, we have recomputed an HO$_2$ structure from the molecular constants given above and have allowed the D–O bond length to be 0.015 ×10^{-10}m shorter and the D–O–D angle to be 0.6° smaller than the appropriate HO$_2$ parameters. This calculation gave an HO$_2$ structure of r(H–O) = 0.990×10^{-10}m, r(O–O) = 1.331×10^{-10}m, and < HO$_2$ = 106.3°. We feel this structure represents an upper limit and that the true HO$_2$ structure is somewhere between the two limits. It is interesting to note that r(O–O) is not seriously affected as in the case of H$_2$O$_2$ and D$_2$O$_2$.[16]

The results of a number of other predictions of the structure of the HO$_2$ radical are also shown in Table III. Most of these estimates are based on theoretical computations. Obviously there has been a significant improvement in quality with time from the oldest work in 1962 at the bottom of the table to the latest near the top. The work of Boyd was carried out by the SCF-LCAO-MO method using the Roothaan technique. She fixed the (H–O) bond length at 0.958×10^{-10}m and the (O–O) bond length at 1.3×10^{-10}m and then computed the energy of the system for H–O–O angles of 180°, 110°, and 90°. These results were compared to a similar calculation by Furlong and Griffing[18] for an isosceles triangle structure with an angle of 47°. Boyd found that the isosceles structure had the lowest energy and was, therefore, preferred.

Next, Gordon and Pople[19] calculated the equilibrium geometry of the HO$_2$ radical based upon the approximate SCF-MO theory, INDO. The minimum in the energy surface was computed while allowing the bond lengths to vary by increments of 0.01×10^{-10}m and the angle by increments of 0.1°.

In 1971 Liskow *et al.*[20] made a very thorough inves-

TABLE I. Calculated and measured frequencies.

						Calculated		Observed	
N'	J'	F'	N''	J''	F'	Freq. (MHz)	Rel. Int.	Freq. (MHz)	Rel. Int.
1	$\frac{1}{2}$		0	$\frac{1}{2}$		60 658.9 ± 2	No HfS		
1	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	60 653.3	10		
1	$\frac{1}{2}$	$\frac{3}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	60 655.4	80	60 655.4 ± 3	Weak
1	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{3}{2}$	60 659.6	80	60 660.84 ± 0.6	Strong
1	$\frac{1}{2}$	$\frac{3}{2}$	0	$\frac{1}{2}$	$\frac{3}{2}$	60 661.7	100		
1	$\frac{3}{2}$		0	$\frac{1}{2}$		60 372.1 ± 2	No HfS		
1	$\frac{3}{2}$	$\frac{3}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	60 369.3	37	60 368.17 ± 1.5	Weak
1	$\frac{3}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	60 371.4	30	60 371.75 ± 0.8	Strong
1	$\frac{3}{2}$	$\frac{5}{2}$	0	$\frac{1}{2}$	$\frac{3}{2}$	60 372.1	100		
1	$\frac{3}{2}$	$\frac{3}{2}$	0	$\frac{1}{2}$	$\frac{3}{2}$	60 375.6	30		
1	$\frac{3}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{3}{2}$	60 377.7	4		

TABLE III. Structure of HO$_2$.

r(H–O)[a]		r(O–O)[a]	< (HOO)		Reference
0.977	+0.015 −0.005	1.335 ± 0.005	104.1°	+2° −1°	This work
0.96		1.33	104°		McLean and Yoshimine[23]
		1.34 ± 0.02			Hunziker and Wendt[11]
		1.36			Blint and Newton[22]
			113° ± 5°		Gole and Hayes[21]
0.96		1.3	108°		Paukert and Johnston[7]
0.968		1.384	106.8°	(SCF)	Liskow *et al.*[20]
0.973		1.458	104.6°	(CI)	Liskow *et al.*[20]
1.05		1.19	110.7°		Gordon and Pople[19]
			~47°		Boyd[17]

[a]Bond lengths in units of 10^{-10}m (formerly Å).

TABLE IV. Individual rotational constants.

	A MHz	B MHz	C MHz	κ
HO₂	610 221	33 462	31 723	−0.994
DO₂	333 184	31 602	28 864	−0.982

tigation of the geometry and electronic structure of HO₂ using *ab initio* SCF and CI calculations. Both results are given in Table III and agree well with our results.

The structure given by Paukert and Johnston[7] was not determined uniquely but is consistent with the observed rotation–vibration band structure, which was only crudely resolved in their experiment.

Gole and Hayes[21] also computed the structure of HO₂ with an *ab initio* LCAO-MO-SCF and CI calculations. The (H−O) bond length was fixed at 0.96×10^{-10}m and the (O−O) bond at 1.23×10^{-10}m. The calculations were carried out at angle increments of 10° near the minimum, and an angle of about $113 \pm 5°$ is consistent with all their computations.

Blint and Newton[22] in 1973 reported *ab initio* LCAO-MO calculations of the bonding and structure of HO₂.[22] They started with a fixed (H−O) bond length of 0.968 $\times 10^{-10}$m and a fixed angle of 106.8° then calculated the energy of the system at (O−O) bond length increments of 0.01×10^{-10}m.

Hunziker and Wendt[11] also estimated the (O−O) bond length based on their measurement of the (O−O) vibrational frequency in HO₂ and literature vibrational frequency and bond length data for O₂, O₂⁻, and H₂O₂ using Badger's rule.

McLean and Yoshimine[23] have determined the HO₂ potential energy surface from a large scale CI calculation including all single and double excitations from the basic Hartree–Fock wavefunction using a "double-zeta plus polarization" basis set of contracted Gaussian functions.

It can be seen from Table III that the latest calculations of the structure of HO₂ provide excellent agreement with our result.

Using the structural parameters in the first line of Table III, we have computed individual rotational constants and Ray's asymmetry parameter $\kappa = (2A - B - C)/(A - C)$. These are listed in Table IV.

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