HO_2 detected by laser magnetic resonance

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Far-infrared absorption spectra of HO_2 in the gas phase have been detected at six wavelengths of a water vapor laser magnetic resonance spectrometer. The identification of HO_2 as the absorbing molecule is based on a partial analysis of the spectra and on a variety of different chemical methods used to produce the radical. Approximate values of rotational constants and spin doublet separations are derived from the spectra.

INTRODUCTION

Often postulated but seldom observed, the hydroperoxyl radical, HO_2, is a molecule that has offered little reward to spectroscopists. Like other free radical intermediates with short chemical lifetimes, its steady-state concentration in a reacting gas mixture is always low, but there is the further difficulty that HO_2 is an asymmetric molecule with its total spectral intensity divided into a multitude of spectral lines, each of them correspondingly weak. This combination of small concentrations and weak line strengths has prevented any study of the rotational structure of HO_2, although the techniques of photolysis[1,2] and matrix isolation[3,4] have yielded poorly resolved electronic and vibrational spectra. In addition, the concentrations of HO_2 radicals produced in several gaseous reactions have been studied with a molecular beam mass spectrometer.[5]

Using the extremely sensitive technique of laser magnetic resonance (LMR), we have succeeded in detecting several rotational transitions of gaseous HO_2 at far infrared wavelengths. In this paper we describe the spectra, give evidence that they do indeed belong to HO_2, and present a preliminary spectral analysis. Although the spectral analysis is not complete, it is possible to do quantitative chemical measurements of HO_2 in gases, and a study of some important chemical reactions of HO_2 is currently in progress. A more complete analysis of the LMR spectra will yield important data for radio astronomy.

IDENTIFICATION OF HO_2

The 79-μm LMR spectrum, shown in Fig. 1, was first observed when acetylene was mixed in the laser absorption cell with oxygen gas that had passed through a weak microwave discharge. Subsequently, many other gaseous hydrocarbons, when substituted for the acetylene in this reaction, were found to give the same spectrum in varying degrees of intensity; one of the best is ethylene. To identify the atomic constituents of the unknown molecule responsible for the 79-μm spectrum, isotopic substitution experiments were done by monitoring one of the absorption lines while substituting oxygen-18 gas (90% ^{18}O), deuterated ethylene (99% D), and carbon-13 enriched ethylene (88% ^{13}C) for normal oxygen and ethylene. The line intensity was unaffected by the carbon substitution, but was reduced nearly to zero by the oxygen and hydrogen substitutions, thus showing that carbon is not a constituent of the molecule but that oxygen and hydrogen are.

Several other chemically reacting gas mixtures have been found to produce the 79 μm spectrum, including electrically discharged water vapor and reactions of hydrogen atoms with oxygen or fluorine atoms with formaldehyde and hydrogen peroxide. In all of these reactions, discussed further in the next section, the radical HO_2 is an intermediate product which is either observed by other means or securely postulated, and this suggests the working assumption that HO_2 is the particular combination of hydrogen and oxygen responsible for the LMR spectra. OH is also a common product of these reactions, but it can be ruled out because its LMR spectra are well known, and they show no intensity correlation with the present spectra.

The possibility that the molecule is an ion requires consideration, since many of the reactions that produce the spectra involve electric discharges and some of the hydrocarbon–oxygen reactions are known to generate chemi-ionization. The discharge as a source of ionization was eliminated in a study of the $H + O_2$ reaction by using a hot-wire dissociator as an H atom source. In this reaction, the only source of ions would be chemi-ionization, which has not been observed in H_2/O_2 systems even at flame temperatures.[6] The recombination of H and O_2, for example, provides only about 2 eV of energy, far short of the 11.5 eV required to ionize the product HO_2.[5]

Because of the great sensitivity of the LMR technique it is difficult to eliminate, on chemical evidence alone, the possibility that a rare, unfamiliar hydrogen–oxygen molecule has been detected. Water and hydrogen peroxide, for example, although nonparamagnetic in their ground singlet states, may have metastable triplet states in which they would be detectable by the LMR method. The observed spectra, however, show hyperfine struc-

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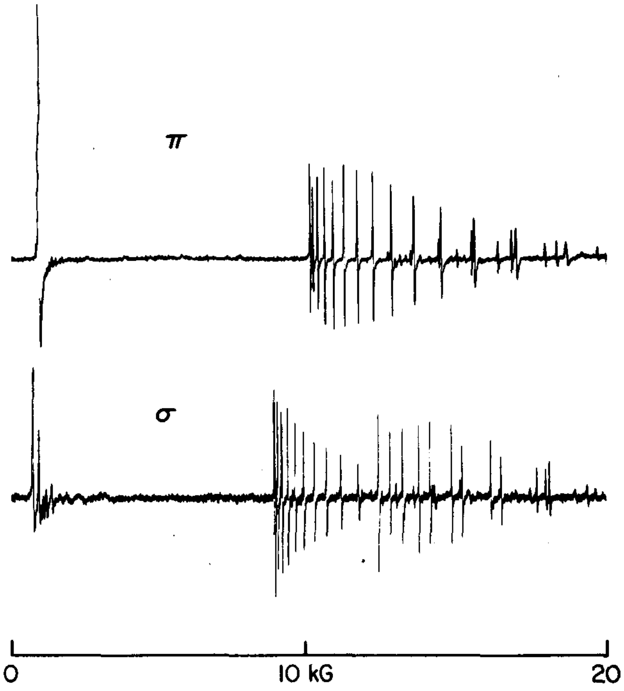

FIG. 1. The 79 μm magnetic resonance spectrum of HO$_2$, in parallel (π) and perpendicular (σ) polarization. Source oscillator: H$_2$O laser. HO$_2$ is produced by reacting fluorine atoms with formaldehyde and oxygen, at a total pressure of 1.2 torr. Zeeman modulation at 100 Hz is used, with a detector time constant of 0.1 sec.

ture (see Fig. 4) that indicates a resultant nuclear spin of 1/2, which is incompatible with any hydrogen–oxygen molecule containing an even number of hydrogen nuclei.

From its chemical behavior and hyperfine structure, then, the molecule is identifiable with reasonable confidence as HO$_2$. The spectral analysis to be described below leads independently to the same conclusion, and thus makes the identification certain.

FORMATION REACTIONS

The general method for forming HO$_2$ radicals consisted of using an electrodeless microwave discharge (2450 MHz) or a thermal dissociator to produce atomic species that initiate a radical reaction sequence. The atoms are reacted with various molecules to eventually form HO$_2$. All of the measurements were made at relatively low pressures (0.2 to 3 Torr) using a flow system to produce the radicals and to introduce them into the LMR absorption cell. An outline of the methods used to produce HO$_2$ is given below.

1. Twenty one different hydrocarbons were tested as HO$_2$ sources in reactions with discharged oxygen (a mixture of O and O$_2$), and all were found to produce the 79-μm spectrum in measurable intensity. The hydrocarbon list includes small aliphatic, olefin, alcohol, aldehyde, ether, acid, aromatic, and ketone molecules. The olefins were the most prolific HO$_2$ sources, possibly because of their great reactivity with atomic oxygen.[7] Specifically, ethylene, propylene, and trans-butene-2 produced about 5 times as much HO$_2$ as did the original source, acetylene. In general the mechanisms of these reactions are not well understood, nevertheless, the observation of HO$_2$ as an intermediate demonstrates its importance in combustion processes.

2. HO$_2$ was detected in a stream of water vapor which was flowing slowly through a microwave discharge. The chemistry of this method is complicated but there have been strong indications that HO$_2$ is produced.[8] The mechanism is likely to involve a reaction sequence such as

$$\mathrm{OH + OH \rightarrow H_2O + O}\ , \tag{1}$$

$$\mathrm{O + OH \rightarrow O_2 + H}\ , \tag{2}$$

$$\mathrm{O_2 + H + M \rightarrow HO_2 + M}\ . \tag{3}$$

The intermediates, H, O, and OH, have been observed as products of a water vapor discharge.[9] This source produced relatively low concentrations of HO$_2$.

3. Another approach to the formation of HO$_2$ was the direct combination of H and O$_2$ [Eq. (3)]. Hydrogen atoms were generated in one of two ways: by using a microwave discharge in H$_2$ (ultrahigh purity) or by passing H$_2$ over a hot tungsten filament. The stream containing H atoms was then mixed with oxygen (ultrahigh purity)

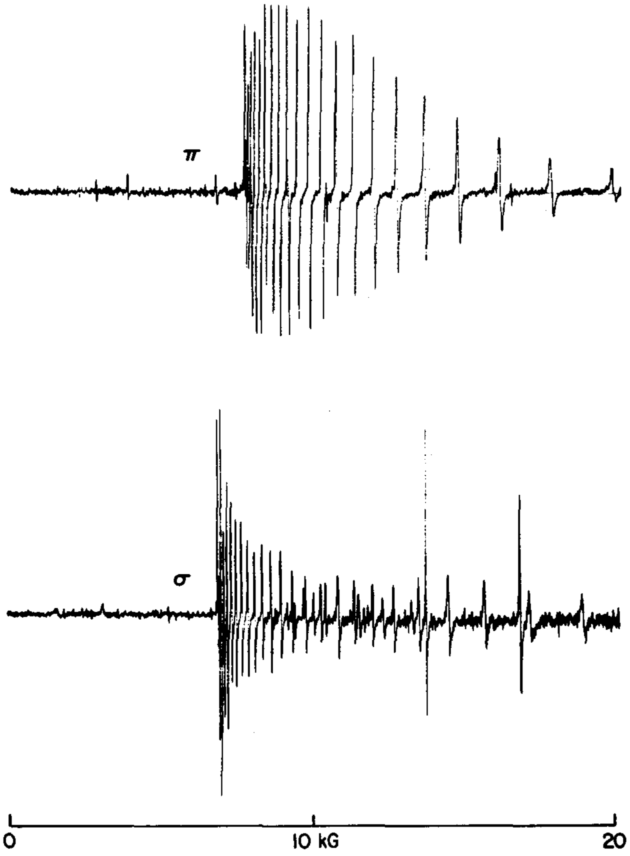

FIG. 2. The 72 μm magnetic resonance spectrum of HO$_2$, in parallel (π) and perpendicular (σ) polarization. Source oscillator: D$_2$O laser. HO$_2$ is produced by reacting a mixture of oxygen atoms and oxygen molecules with ethylene, at a total pressure of 1.2 torr. Zeeman modulation at 100 Hz is used, with a detector time constant of 0.1 sec.

and a large 79 μm absorption signal was observed. The characteristic OH[10] and O_2[11] LMR spectra were also observed, with OH probably being formed in a reaction of hydrogen atoms with HO_2.

4. HO_2 has also been produced by the reaction of molecular oxygen with the formyl radical, HCO, according to

$$O_2 + HCO \rightarrow HO_2 + CO . \tag{4}$$

The HCO radical, which is also detectable by the LMR method,[12] was produced by reacting formaldehyde with atomic fluorine:

$$F + H_2CO \rightarrow HCO + HF , \tag{5}$$

with the fluorine being generated by electric discharge in freon-14 (tetrafluoromethane). To stabilize the discharge and to establish a convenient operating pressure, helium (special analyzed grade) was mixed with the freon-14 in an approximate 10/1 ratio. In practice, reactions (4) and (5) were carried out simultaneously by adding the discharged helium–freon mixture to a mixture of oxygen and formaldehyde, the latter being produced by vaporizing solid paraformaldehyde (USP grade). This method produced as much HO_2 as did the oxygen–olefin reactions, and without the simultaneous production of large amounts of OH.

Reaction (4) is probably also a source of HO_2 in the reactions of electrically discharged oxygen with hydrocarbons, in particular with formaldehyde, where HCO is detectable by its LMR spectrum, and with ethylene and propylene, where HCO is known to be a major product of oxygen atom attack.[13] The reactions that form HCO are

$$O + H_2CO \rightarrow HCO + OH \tag{6a}$$

followed by

$$OH + H_2CO \rightarrow HCO + H_2O \tag{6b}$$

in the case of formaldehyde, and

$$O + C_2H_4 \rightarrow HCO + CH_3 \tag{7}$$

and

$$O + C_3H_6 \rightarrow HCO + C_2H_5 \tag{8}$$

in the case of ethylene and propylene.

5. As a final source of HO_2 the parent hydrogen peroxide molecule, H_2O_2, was tested. The HO_2 radicals were formed in this case by the reaction with fluorine atoms,

$$H_2O_2 + F \rightarrow HO_2 + HF . \tag{9}$$

The H_2O_2 source was a 98% solution which was further enriched by distillation. This source of HO_2 produced a large concentration of HO_2 and few lines from other radicals.

SPECTRA

As in earlier studies of OH,[10] CH,[14] and NO_2,[15] the gaseous absorption sample is pumped continuously through a section of the cavity of a far-infrared cw gas laser, and a magnetic field is varied to bring Zeeman components of molecular absorption lines into resonance with the laser line. A Brewster-angle diaphragm separates the laser gas from the absorbing gas and also reflects a sample of the laser power out to an infrared detector. For greater sensitivity, the Golay cell detector used in earlier work has now been replaced by a liquid helium-cooled germanium bolometer. The spectra of Figs. 1–3, in first-derivative form because of the use of magnetic modulation, are the output of a lock-in amplifier connected to this detector. The laser radiation is linearly polarized by the Brewster-angle diaphragm, and the two tracings in each figure correspond to polarizations of the laser electric field parallel (π) and perpendicular (σ) to the *dc* magnetic field.

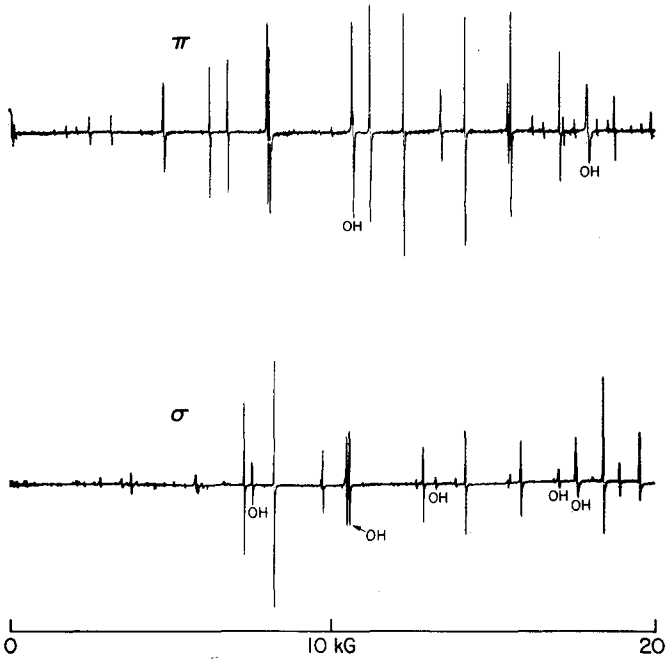

FIG. 3. The 84 μm magnetic resonance spectrum of HO_2, in parallel (π) and perpendicular (σ) polarization. Source oscillator: D_2O laser. HO_2 is produced by reacting fluorine atoms with formaldehyde and oxygen, at a total pressure of 1 torr. Zeeman modulation at 100 Hz is used, with a detector time constant of 0.1 sec.

The spectra of Figs. 1–3 are recorded at an H_2O laser wavelength of 79 μm and D_2O laser wavelengths at 72 and 84 μm, respectively. H_2O wavelengths of 78 and 119 μm and a D_2O wavelength of 108 μm also yield related spectra, but they are either weak or complicated by O_2 and OH lines and are not shown here.

Careful examination of line shapes shows that individual lines in the 79 and 84 μm spectra are partially resolved pairs. Figure 4 shows typical line shapes in the 84 μm spectrum; the splitting is roughly constant in field units, and is masked by the greater width of the high-field lines. We attribute this splitting to magnetic dipole hyperfine structure caused by a nuclear spin of $I = \frac{1}{2}$ and will use this as the starting point for analysis of the spectra.

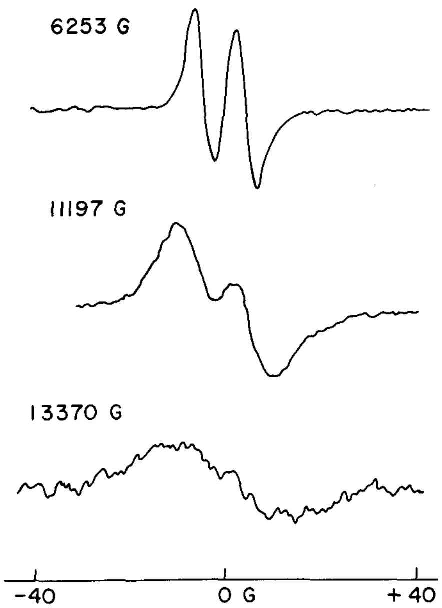

FIG. 4. High-resolution recordings of typical line shapes in the 84 μm (π) spectrum of HO_2. The lines are labelled by the magnetic field strengths at their centers.

The laser frequencies can be shifted by about ± 2 MHz by de-tuning the cavity length, and this provides a way to determine whether the Zeeman sublevels of the absorbing molecular transition are converging or diverging with increasing field strength. In general, convergence is found, with exceptions being the strong low-field line and some of the high-field lines at 79 μm (π and σ), and the two strong high field lines at 72 μm (σ). This information is used in the spectral analysis to determine whether the zero-field frequency of a molecular transition is larger or smaller than the laser line frequency.

ANALYSIS

A hydrogen–oxygen molecule with nuclear spin $I = 1/2$ must contain an odd number of hydrogen nuclei, and hence an odd number of electrons. The energy levels of the ground electronic state will be spin doublets, and the Zeeman effect of such a level depends critically on the size of the doublet splitting. These facts, together with the assumption that the magnetic effects of electron orbital angular momentum are small, which is almost always true for polyatomic molecules, provide the basis of an approximate analysis. We neglect hyperfine structure, K-type doubling, nuclear and rotational magnetism, and any asymmetry of the dominant electron spin magnetism. In this approximation the rotational angular momentum **N** and spin angular momentum **S** add to form the total angular momentum **J**, and the magnetic perturbation operator is $g_s S_z \mu_B H$, where μ_B is the Bohr magneton, g_s is the electron spin g factor, and H is the field strength. From the known matrix elements of S_z,[16] the magnetic energies of a spin doublet are readily found to be

$$E = \pm \tfrac{1}{2}\left[(\Delta\nu)^2 + 2\,\Delta\nu\; g_s m \mu_B H/(N+\tfrac{1}{2}) + (g_s \mu_B H)^2\right]^{1/2} \tag{10a}$$

and for the special case of $m = \pm(N+\frac{1}{2})$,

$$E = \tfrac{1}{2}\Delta\nu \pm \tfrac{1}{2} g_s \mu_B H\,, \tag{10b}$$

a result first derived by Hill.[17] For $H = 0$, Eq. (10a) reduces to $E = \pm\frac{1}{2}\Delta\nu$, from which it is clear that $\Delta\nu$ is the spin doublet splitting, i.e., the separation between the two levels with total angular momentum quantum numbers $J = N+\frac{1}{2}$ and $J = N-\frac{1}{2}$. The magnetic quantum number m can take any half integral value between $N+\frac{1}{2}$ and $-(N+\frac{1}{2})$, with the two extreme values belonging only to the level with $J = N+\frac{1}{2}$.

Only a small part of the far-infrared transition energy can be accounted for by Eq. (10). The most likely way to explain the difference is through a large change in rotational energy, such as is provided by $N', K', J' \leftarrow N'', K'', J''$ transitions of nearly symmetric prolate rotor molecules. According to this interpretation, the three spectra at 72, 79, and 84 μm could be different $N'J' \leftarrow N''J''$ component transitions of the same $K+1 \leftarrow K$ transition. The strongest of these component transitions have $\Delta N = \Delta J = \Delta K$, and so the most likely *a priori* assignment of the spectra is to transitions of the type $N+1, J+1, K+1 \leftarrow N, J, K$.

There is supporting evidence for this assignment in the relative intensities of the lines within each spectrum: although obscured somewhat by the effects of line broadening and overlapping, the intensity patterns of Figs. 1–3 definitely suggest $J+1 \leftarrow J$ transitions. To establish which of the spin doublet levels, $J = N+\frac{1}{2}$ or $J = N-\frac{1}{2}$, is involved, it is sufficient to do a rough calculation with Eq. (10), using the theoretical expectation that $\Delta\nu$ is positive and increases in magnitude with K.[18] The result is that the upper and lower levels of a transition converge with increasing field strength if $J = N+\frac{1}{2}$ for both levels, and the upper and lower levels diverge if $J = N-\frac{1}{2}$ for both levels. It follows from the observations of line shifts with laser tuning that the 72 μm spectrum, the 84 μm spectrum, and the midfield region of the 79 μm spectrum can be assigned to levels with $J = N+\frac{1}{2}$.

Detailed fits of Eq. (10) to the measured spectra were made with a computer least-squares fitting program written by J. M. Moran. This program accepts trial assignment of N, m'', and m' values to a partial listing of the measured line positions, computes best-fit values of the parameters $\Delta\nu''$ and $\Delta\nu'$, the spin splitting of the lower and upper levels of the transition, and of ν_0, the zero-field frequency of the transition, and then predicts the positions of all other lines in the spectrum. Finding the correct assignment of N and m values can be a lengthy process, and it has been done so far only for the 72 and 79 μm spectra. Table I gives the fitted values of $\Delta\nu''$, $\Delta\nu'$, and ν_0 for three trial N assignments to each spectrum, as well as their computed standard errors and the corresponding rms deviations of the calculated line positions from the measured line positions. For the best-fit assignments, $N' = 14 \leftarrow N'' = 13$ and $N' = 19 \leftarrow N'' = 18$, the deviations are comparable to the widths of the sharpest lines in the LMR spectra. It is clear from Table I that the assigned N values of either or both spectra could be increased by 1 without harming the fit greatly. The standard errors in Table I are thus an unrealistic measure of uncertainty in the values of ν_0, $\Delta\nu''$, and $\Delta\nu'$. Until the N values are definitely established, a

TABLE I. Results of least-squares fitting of the 79 and 72 μm spectra for trial assignments of N'' and N'.[a]

Laser frequency (cm^{-1})	$N' \leftarrow N''$	ν_0 (cm^{-1})	$\Delta\nu''$ (cm^{-1})	$\Delta\nu'$ (cm^{-1})	rms dev. (gauss)[b]
	13 ← 12	126.590 ± 0.003	0.762 ± 0.004	1.592 ± 0.023	107
126.432[c]	14 ← 13	126.5740 ± 0.0005	0.778 ± 0.001	1.513 ± 0.004	20
	15 ← 14	126.565 ± 0.001	0.779 ± 0.002	1.454 ± 0.008	41
	18 ← 17	139.103 ± 0.002	0.609 ± 0.004	1.184 ± 0.011	143
138.990[d]	19 ← 18	139.0982 ± 0.0005	0.605 ± 0.001	1.139 ± 0.002	36
	20 ← 19	139.093 ± 0.001	0.599 ± 0.002	1.093 ± 0.005	50

[a] Listed uncertainties are statistical standard errors and do not include systematic errors.

[b] Calculated for the 20 lines that were used as input data in the computer fit.

[c] Inferred from a hetrodyne frequency measurement of the nearby 78 μm line. Uncertainty: ± 0.005 cm^{-1}.

[d] From a wavelength measurement [W. S. Benedict, M. A. Pollack, and W. J. Tomlinson, IEEE J. Quant. Electron. QE-5, 108 (1969)]. Uncertainty: ± 0.02 cm^{-1}.

more conservative estimate of uncertainties would be ± 0.01 cm^{-1} for ν_0, ± 0.02 cm^{-1} for $\Delta\nu''$, and ± 0.06 cm^{-1} for $\Delta\nu'$.

Despite its approximate nature, Eq. (10) fits the observations very well. It accounts for the positions and widths of all the prominent lines of the 72 μm spectrum, excepting only the two strong σ lines that, according to the laser detuning tests, belong to other energy levels. In the 79 μm spectrum the progression of lines beginning at 10 kG in Fig. 1 is accounted for. J. T. Hougen has also analyzed the progression that begins at 13 kG and has shown that this involves levels with the same N values and spin splittings as those found here, but with a slightly different zero-field transition frequency.[19] A satisfactory interpretation is that this doubling of the spectrum, and the difference in zero-field frequency, is due to the K-type doubling of energy levels which is characteristic of slightly asymmetric molecules. A similar doubling of the 72 μm spectrum does not occur, presumably because the other K-type doublet levels are too far from resonance with the laser frequency. The only remaining puzzle in the 79 μm spectrum is the feature at 0.5 kG. It appears to be an unresolved cluster of several lines, and could be a magnetic dipole component of the $N' = 14 \leftarrow N'' = 13$ transition or an entirely different $N'K' \leftarrow N''K''$ transition that also happens to coincide with the laser line.

The value of K'' and K' can be found from the ratio of spin splittings in the two states, since for a nearly symmetric prolate rotor,[18]

$$\Delta\nu \simeq \epsilon_{zz} K^2 (N + \tfrac{1}{2}) / [N(N+1)] , \tag{11}$$

where ϵ_{zz} is a constant. The ratios of the experimental spin splittings of Table I are 1.9 for both the 72 μm spectrum and the 79 μm spectrum, and the only assignment of K values that fits at all is $K'' = 2$, $K' = 3$, for which the expected ratio is 2.1. The difference between the two ratios is probably significant, and due to the ϵ_{xx} and ϵ_{yy} terms neglected in Eq. (11).

To carry the nearly symmetric rotor analysis to its conclusion, one can now use the standard rotational energy formula

$$E \simeq (B + C) N(N+1)/2 + [A - (B + C)/2] K^2 \tag{12}$$

to derive values of the rotational constants A and $(B + C)/2$ from the data of Table I. For the best-fit assignments of $N' \leftarrow N''$, 14 ← 13, and 19 ← 18, the results are $A = 19.4$ cm^{-1} and $(B + C)/2 = 1.26$ cm^{-1}. Other values differing by as much as ± 30% are found when the other possible $N' \leftarrow N''$ assignments 15 ← 14 and 20 ← 19 are considered, and we take this as an estimate of the uncertainty in A and $(B + C)/2$. Further errors, due to the neglect of asymmetry corrections and centrifugal distortion in Eq. (12), should be covered by this ± 30%. Despite these uncertainties, the derived rotational constants predict very precisely the laser-molecule resonance at 84 μm wavelength. From (11) and (12), with $N' = 11$ and $N'' = 10$, the predicted $J' = 11.5 \leftarrow J'' = 10.5$ transition frequency is 118.9 cm^{-1}, as compared to the laser frequency of 118.65 cm^{-1}. The close agreement is perhaps fortuitous, but nonetheless it is satisfying to note that $N' \leftarrow N''$ values found from a preliminary fit of the 84 μm LMR spectrum are indeed 11 ← 10.[19] This tentative identification of the 84 μm spectrum, along with the best-fit identifications of the 79 and 72 μm spectra, is shown in Fig. 5, which is a plot of rotational energy levels calculated from Eq. (12) for K values up to 4 and N values up to 25.

We conclude from this analysis that the molecule is a nearly symmetric prolate rotor with rotational constants of approximately 1 cm^{-1} for $(B + C)/2$ and 20 cm^{-1} for A. For comparison with these values, rotational constants can be computed from the geometrical structure of HO_2, as given by molecular orbital calculations[20] and verified partially by experiment.[1,3] The structure is that of a nearly symmetric prolate rotor with an H–O bond distance of 0.973 Å, and O–O bond distance of 1.458 Å and an H–O–O angle of 104.6°. From this structure we compute the following rotational constants: $A = 21.4$ cm^{-1}, $B = 1.18$ cm^{-1}, $C = 1.11$ cm^{-1}, which are in essential agreement with the values derived from the LMR spectra. The spectral analysis thus leads independently to the same conclusion as does the chemical evidence: the molecule responsible for the LMR spectra is HO_2.

CONCLUSION

By providing a means of detecting HO_2 in gaseous systems, the laser magnetic resonance method can be of immediate help in the study of combustion processes and

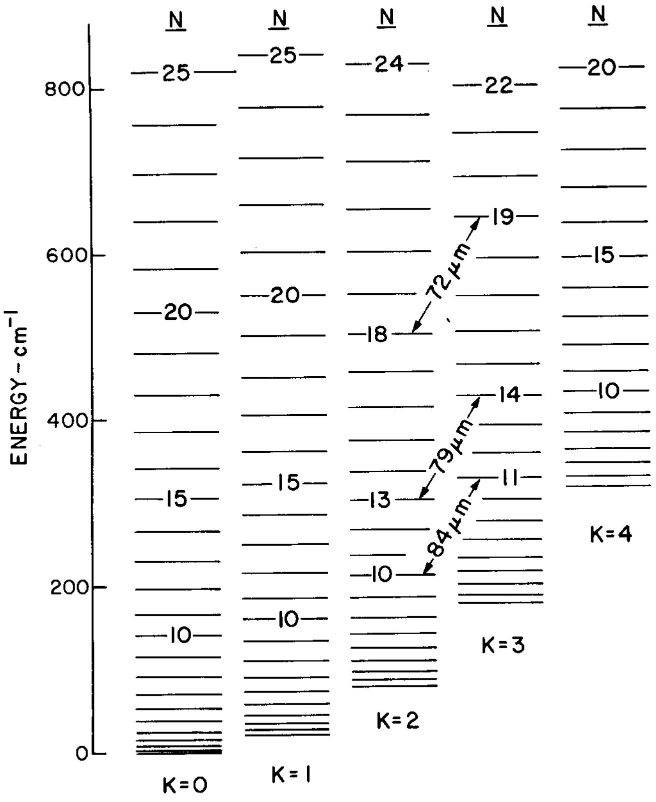

FIG. 5. Rotational energy levels of HO_2, calculated from the nearly symmetric top energy formula, with laser magnetic transitions indicated. The spin doublet splittings, and further small splittings due to molecular asymmetry, the Zeeman effect, and hyperfine structure, are too small to show in this figure.

atmospheric reactions, in which HO_2 figures prominently as an intermediate product. With a single water vapor oscillator it is possible to detect and measure quantitatively the unstable free radicals HO_2, HCO, OH, and CH, as well as the stable free radicals O_2, NO_2, and NO, at very small concentrations in mixed gaseous samples. In the case of OH, for example, we have determined the detection limit to be 2×10^8 molecules/cm^3.

There are a number of ways in which the analysis of the LMR spectra can be improved at little cost in complexity, chiefly by including the effects of nuclear and electronic orbital magnetism, and asymmetry of the electron spin magnetism. The residuals of the computer fits to the 72 and 79 µm spectra show systematic trends, of a type that can be accounted for by a small change in the effective electron spin g factor. By including one additional fitting parameter of this type, we find it possible to reduce the rms deviations of the best-fit cases in Table I by a factor of 5, to 4 G and 9 G for the 79 and 72 µm spectra, respectively. When the physical significance of this parameter is established by detailed theoretical analysis, it should be possible to make a positive assignment of N values to the two spectra and to derive correspondingly more accurate values of the molecular parameters.

A search for HO_2 in the interstellar gas has been prevented by lack of knowledge of its spectral line frequencies. The far-infrared lines measurable by the laser magnetic resonance method may eventually, with improved receivers, become detectable in the interstellar gas, but more likely present candidates for detection are the microwave and millimeter wave lines connecting the lowest rotational levels. Laboratory measurements of these lines can be made once the molecular constants are well determined, and this is one of the chief goals of the further work now in progress on the far-infrared spectrum.

ACKNOWLEDGMENTS

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[1] T. T. Paukert and H. S. Johnston, J. Chem. Phys. **56**, 2824 (1972).
[2] C. J. Hochanadel and J. A. Ghormley, J. Chem. Phys. **56**, 4426 (1972).
[3] D. E. Milligan and M. E. Jacox, J. Chem. Phys. **38**, 2627 (1963); **40**, 605 (1964).
[4] J. F. Olgivie, Spectrochim. Acta, Part A **23**, 737 (1967).
[5] S. N. Foner and R. L. Hudson, J. Chem. Phys. **36**, 2681 (1962).
[6] W. J. Miller, *Oxidation and Combustion Reviews*, edited by C. F. H. Tipper (Elsevier, Amsterdam, The Netherlands, 1968), Vol. 3.
[7] R. J. Cvetanovic, J. Chem. Phys. **30**, 19 (1959).
[8] W. E. Wilson, Jr., J. Phys. Chem. Ref. Data **1**, 535 (1972).
[9] D. H. Howgate, J. Chem. Phys. **36**, 239 (1962).
[10] K. M. Evenson, J. S. Wells, and H. E. Radford, Phys. Rev. Lett. **25**, 199 (1970).
[11] K. M. Evenson and M. Mizushima, Phys. Rev. A **6**, 219 (1972).
[12] C. J. Howard and K. M. Evenson (unpublished results).
[13] J. R. Kanofsky and D. Gutman, Chem. Phys. Lett. **15**, 236 (1972).
[14] K. M. Evenson, H. E. Radford, and J. M. Moran, Appl. Phys. Lett. **18**, 426 (1971).
[15] R. F. Curl, Jr., K. M. Evenson, and J. S. Wells, J. Chem. Phys. **56**, 5143 (1972).
[16] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (University Press, Cambridge, England, 1967), p. 64.
[17] Reported by G. M. Almy, Phys. Rev. **35**, 1495 (1930).
[18] C. C. Lin, Phys. Rev. **116**, 903 (1959).
[19] J. T. Hougen (private communication).
[20] D. H. Liskow, H. F. Schaefer, and C. F. Bender, J. Am. Chem. Soc. **93**, 6734 (1971).