

MICROWAVE SPECTROSCOPY OF SHORT-LIVED MOLECULES

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Abstract - Microwave spectroscopy is discussed from a viewpoint of detecting short-lived molecules, especially free radicals. Greater stress is laid on sensitivity of spectrometer, production of molecules and prediction of their transitional frequencies. Some typical examples of the observed short-lived molecules are given in detail with their significance in the related fields such as chemical kinetics, photochemistry and radioastronomy.

INTRODUCTION

Short-lived molecules are produced as intermediates in chemical reactions. They are in some cases the keystones determining how the chemical reactions proceed and how they are affected by physical and chemical factors. A confirmation of the existence of the intermediates in a real process is especially desirable for a deeper understanding of the chemical reaction. The intermediate having one or more unpaired electrons, that is, the free radical, is important in the field of the molecular structural study. The unpaired electron has electromagnetic interactions with the electrons and nuclei of the molecule and acts as a probe revealing the detailed molecular structure which is not obtained in the study of non-paramagnetic molecules. The free radical presents the most interesting and exciting problems to modern high resolution spectroscopy. The first example of the free radical was prepared accidentally by Gomberg (1) in 1900. It was a stable but complicated molecule, triphenyl methyl radical. However, most of simple and fundamental free radicals are very active and have short lifetimes. The production, trapping and detection of the short-lived molecules have been extremely difficult problems (Ref. 2). A great variety of chemical and physical methods has been used to overcome these difficulties. Among them the flash-photolysis combined with high-resolution ultraviolet and visible spectroscopy has been one of the methods achieving the most fruitful results pertinent to molecular structures and chemical kinetics. This method has made clear the existence of many diatomic and polyatomic short-lived molecules and has given information about their molecular constants (Ref. 3-5). The results accumulated by optical spectroscopy have made possible more detailed studies of short-lived molecules by means of recently developed spectroscopic techniques such as molecular beam method, EPR, microwave spectroscopy and LMR. Microwave spectroscopy is one of the most productive methods of observing free radicals. Microwave spectroscopy of free radicals is not straight-forward, but it gives accurate and unique information about the molecules.

THE ESSENTIAL FEATURES OF MICROWAVE SPECTROSCOPY FOR SHORT-LIVED MOLECULES

Generally, the concentrations of short-lived molecules are so low in the absorption cell that it is a rather hard task to detect them. The essential points in microwave spectroscopy of free radicals are sensitivity of the spectrometer, production of molecules and prediction of their transition frequencies.

Sensitivity of the Spectrometer

A high sensitivity is indispensable for detection of short-lived molecules of low concentration. The sensitivity was improved by stabilization of

microwave sources as well as careful selection of detector crystals (Ref. 6). Fig. 1 shows a recorder tracing of the $J = 1 \leftarrow 0$ transition at 11.12 GHz of the $^{18}\text{O}^{12}\text{C}^{34}\text{S}$ molecules in natural abundance. The concentration of this species is about 0.009 %.

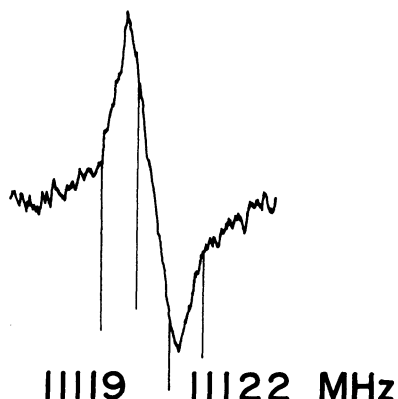


Fig. 1. A recorder tracing of the $J = 1 \leftarrow 0$ transition at 11.12 GHz of the $^{18}\text{O}^{12}\text{C}^{34}\text{S}$ molecules in natural abundance. Experimental conditions: room temperature, 0.07 torr pressure, 1N23G detector, 430 V/cm Stark modulation, 16 sec time constant.

The absorption cell used was made of an X-band waveguide of 3 m in length. The signal to noise ratio of the spectral line is about 25 and its maximum absorption coefficient is $5 \times 10^{-10} \text{ cm}^{-1}$. The sensitivity of our spectrometer, given by the minimum detectable absorption coefficient, $(\gamma_{\text{max}})_{\text{min}}$, is about $2 \times 10^{-11} \text{ cm}^{-1}$ at the X band. This means that the minimum detectable total number of molecules, N_t , is about 5×10^{12} . When the parallel plate type absorption cell designed for observations of short-lived molecules, as is given later (Fig. 2), is used at 60 GHz, $(\gamma_{\text{max}})_{\text{min}}$ is $8 \times 10^{-10} \text{ cm}^{-1}$ and N_t 8×10^{12} . At 120 GHz, $(\gamma_{\text{max}})_{\text{min}}$ is $3 \times 10^{-9} \text{ cm}^{-1}$ and N_t 8×10^{12} . As the peak intensity of a line is proportional to the square of the transition frequency, it becomes stronger in higher frequency. However, the efficiency of microwave detectors decreases in millimeter wave region so that the minimum detectable total number of molecules is not reduced remarkably. If we want to observe the spectrum of a short-lived molecule, we should produce at least 10^{13} molecules in the absorption cell.

Production of short-lived molecules

For production of such a large amount of molecules in the cell, we should use the best chemical reaction suitable for the molecule to be studied. The best method of production differs widely for each molecule. It depends on the lifetime of the molecule.

In the production of molecules of rather long lifetime, 100 msec or more, the parent molecule was discharged or pyrolyzed at about 20 cm upstream of the absorption cell (Fig. 2) and the reaction products were pumped through the cell.

When the lifetime of the molecule becomes shorter, the molecule cannot survive through the full length of the cell or cannot reach to the cell. The molecule of shorter lifetime has to be generated just inside the parallel plates. The parent gas was discharged in the reaction tube. The second reacting gas was mixed with the discharged products through the shower nozzle just between the edges of the parallel plates (Fig. 2). It is important to use a large linear velocity of gas flow. The gas mixture was pumped out from the absorption cell with the linear velocity of 10 m/sec.

This means that a molecule having the lifetime of 10 msec can survive a path of 10 cm. The molecule of a lifetime as short as 10⁻⁶ msec can be observed by the use of our spectrometer described below.

Prediction of the transitions

When a short-lived molecule has no unpaired electrons, its rotational levels are the same as those of the stable molecule (Ref. 7). The problem is how a reasonable geometrical structure can be estimated for the molecule.

The rotational levels of the free radical having unpaired electrons vary greatly with its electronic state. The rotational levels split and shift in a complicated way according to the electromagnetic interactions among the angular momenta due to the electron orbital motion, electron spin, rotation and nuclear spin.

If we want to try to detect a new free radical, it is important to look over its predicted spectrum and pick up the transitions most suitable for spectroscopy. The intensity of each transition, the sensitivity of the spectrometer, the optimum voltages of Stark modulation and dc bias, and reliability of predicted transition frequencies have to be considered.

For example, the spectra of the molecule in the $^2\Pi_{3/2}$ or $^1\Delta$ electronic state show the first-order Stark effect because of its Λ -type degeneracy. Small Stark modulations do not give serious leakage of modulation power to the amplifier. Small dc biases do not bring about an electric breakdown between the parallel electrodes so that the sensitivity of the spectrometer can be maintained at higher levels. The NCO($^2\Pi_1$) (Ref. 8), SO($^1\Delta$) (Ref. 9) and IO($^2\Pi_{3/2}$) (Ref. 10) radicals were observed under these conditions. When the molecule in the $^3\Sigma$ state has a large spin-spin interaction, its spectrum deviates greatly from the well-known rotational spectral pattern. The linear molecule in the $^2\Sigma$ state or the nonlinear molecule in the doublet state having a large spin-rotation interaction shows a similar deviated spectrum.

The rotational levels of the light molecules in the $^2\Pi_{1/2}$ state generally split into large Λ -type doublets. It is rather difficult to predict these spectra precisely.

Information from other spectroscopic methods is indispensable for a good prediction of the transition frequencies of short-lived molecules. In some cases, the rotational constants have been determined by studies of high-resolution optical spectroscopy (Ref. 3-5). However, the parameters of fine and hyperfine structures have been rarely reported by these methods. Gas-phase EPR spectroscopy which also sees the rotational levels of paramagnetic molecules has succeeded in detecting many diatomic and triatomic free radicals. (Ref. 11.). It uses the high-Q cavity resonator of small volume which is advantageous to detection of short-lived free radicals. Furthermore, the magnetic fields to be searched for are predictable on the basis of the quantum state of the molecule. Recently developed laser magnetic resonance (LMR) is bringing about the more reliable molecular constants of short-lived free radicals because it is extremely sensitive and its accuracy is high.

MICROWAVE SPECTROMETER FOR SHORT-LIVED MOLECULES

The microwave spectrometer used was a conventional 100 kHz Stark modulated system of high sensitivity (Ref. 6) with some modifications required for spectroscopy of short-lived molecules. The schematic diagram of a typical absorption cell is shown in Fig. 2.

It was made of a pair of gold plated parallel plates 40 cm long. Microwave discharge was made in the quartz tube by a modified Evenson-Broida 2450 MHz cavity (Ref. 12.). The microwave power dissipated in the cavity was within 100 W. The gas mixture was pumped out from the cell by a mechanical booster pump with a pumping speed of 3300 l/min followed by two liquid nitrogen traps and by a rotary pump of 600 l/min.

Microwave power sources up to 138 GHz were mainly the OKI klystrons. In the frequency region above 130 GHz, a harmonic generator, T5707, was employed as the power source. The output frequency of the klystrons was determined with accuracy of about 10^{-6} - 10^{-7} by monitoring a beat of their output with the X-band output of a Hewlett-Packard K10-8400B phase-locked microwave sweep oscillator. The beat was generated by a mixer equipped with an 1N78 and was

detected with an all-wave receiver.

The detector crystals used were carefully selected as described above. Above 80 GHz, a GaAs Schottky barrier diode mixer, W3420A, was used. The microwave spectrometer using these power sources and detectors combined with the parallel-plate absorption cell is satisfactorily usable up to 170 GHz (Ref. 13)

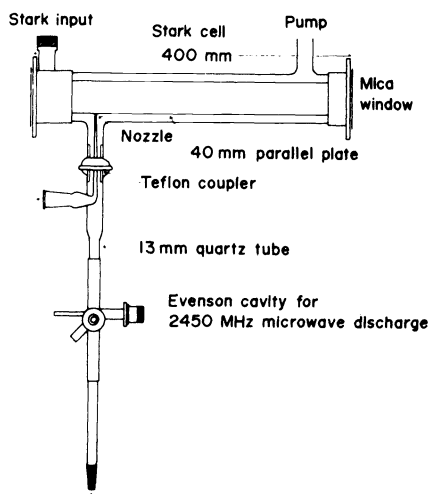


Fig. 2. The schematic diagram of the absorption cell and the microwave-discharge quartz tube.

MICROWAVE SPECTRUM OF SHORT-LIVED MOLECULES

We observed the microwave spectra of several free radicals and unstable molecules by using the method and principle discussed above. The results obtained are typical examples of the rotational spectra of the molecules in the various electronic states. Some results have considerable significance in related fields such as chemical kinetics, photochemistry and radioastronomy. The main features of each molecule observed are as follows:

- IO(${}^2\Pi_{3/2}$). The last homologue of the halogen monoxide radical. Short lifetime (~10 msec). Large hyperfine interactions.
- SO(${}^1\Delta$). The first example of the electronically excited molecule studied by microwave spectroscopy. Significant to chemical reactions analogous to those of $O_2(X^3\Sigma_g^-)$ and $O_2({}^1\Delta_g)$.
- NCO(${}^2\Pi_1$). The first example of the linear triatomic radical having Renner effect. One of the rare cases where all the hyperfine coupling constants were determined with high accuracy.
- HCO(${}^2A'$). $1_{01} \leftarrow 0_{00}$ was observed. Identified as an interstellar molecule. Significant to the kinetics in hydrocarbon flame.
- HO $_2$ (${}^2A''$). Most of the transitions up to 140 GHz were observed. The off-diagonal component of the spin-rotation interaction tensor was obtained. Highly important to many fundamental chemical reactions.
- HNO(${}^1A'$). The spin multiplicity of the ground electronic state was derived from the microwave spectrum.
- CH $_2$ =CHOH. The stable existence of vinyl monomer was confirmed for the first time by means of microwave spectroscopy. Long lifetime.

The detailed results for some of these molecules will be discussed below.

SO(${}^1\Delta$) (Ref. 9)

It is well known that the oxygen molecule in the first electronically excited state, the so-called singlet oxygen, can be easily produced in a large amount by microwave or rf discharge of gaseous oxygen (Ref. 14), and has a long lifetime. The ${}^1\Delta_g$ state of oxygen is metastable at 7918 cm^{-1} above the ${}^3\Sigma_g^-$ ground state (Ref. 15). This is because the transition between the ${}^1\Delta_g$ state and the ${}^3\Sigma_g^-$ ground state is triply forbidden. The SO radical,

analogous to the molecular oxygen, has a low-lying metastable excited state, $^1\Delta$, located at about 6350 cm^{-1} above the $^3\Sigma^-$ ground state (Ref. 16). Since the population of the molecules in the electronically excited states is nearly zero due to the Boltzmann distribution law, the molecule in the excited state could be hardly observed by conventional microwave spectroscopy.

Carrington, Levy, and Miller (Ref. 17) observed the EPR spectrum of the $^1\Delta$ SO and obtained the molecular constants of the $^1\Delta$ SO (Ref. 18).

We have observed the lowest rotational transition of the SO radical in the $^1\Delta$ state. This is the first observation of the rotational transition for a molecule in an electronically excited state. The SO radical in the $^1\Delta$ state was produced by mixing OCS with the product of microwave discharge in molecular oxygen (Ref. 19). A line observed at 127770.47 ± 0.15 MHz showed a paramagnetic behavior, indicated the first-order Stark effect which is a characteristic of the Λ degeneracy and was resolved into four well-separated components at higher Stark dc bias, as shown in Fig. 3.



Fig. 3. The $J = 3 + 2$ transition of the SO radical in the $^1\Delta$ electronic state: Stark dc bias = 55.3 V/cm ; Stark ac modulation = 2.3 V/cm , $\nu_0 = 127770.47\text{ MHz}$.

This is just expected from the $J = 3 + 2$ transition of the $^1\Delta$ molecule composed of the nuclei of zero spins. The rotational constants, the SO bond length and the dipole moment determined are listed in Table 1 where the molecular constants of the SO molecule in the ground state are given for comparison.

It should be noted that the SO distance of the $^1\Delta$ state is slightly longer than that of the $^3\Sigma^-$ state whereas the situation is reverse for the dipole moments of both states. These features present interesting information for molecular orbital calculation.

Now that both the spectra of the triplet and singlet SO are known, it would be interesting (Ref. 20-23) to discuss the chemical reactions of the SO radical from the viewpoint of spin multiplicity of the reactants as has been done for many important reactions of O_2 .

The lifetime of the free radical becomes shorter as the number of the atoms constituting it increases. This hampers observations of polyatomic free radicals by microwave spectroscopy. Only a few polyatomic free radicals have been studied so far. We observed three of such radicals. One is a linear triatomic radical, NCO (Ref. 8). The others are bent unsymmetrical triatomic molecules, HCO (Ref. 24) and HO_2 (Ref. 13).

HCO($^2A'$) (Ref. 24)

HCO is one of the most fundamental molecules to molecular spectroscopy, chemical kinetics and radioastronomy. It has been frequently postulated and is known as an important intermediate in many chemical reactions such as

hydrocarbon flame (Ref. 25). HCO has been expected to exist in appreciable amount in interstellar space because hydrogen, oxygen and carbon have relatively high cosmic abundances.

Table 1. Molecular Constants of the SO molecule

Constant	$X^3\Sigma^-$	$a^1\Delta$
T_e (cm^{-1})	0	$\sim 6350^a$
ω_e (cm^{-1})	1148.19^b	
B (MHz)	21609.55 ± 0.15^c	21295.1 ± 0.7^d
r (Å)	1.48108 ± 0.00005^c	1.49198 ± 0.00002^d
μ (D)	1.55 ± 0.02^e	1.336 ± 0.045^d

a. Ref. 21. b. R. G. Norrish and C. A. Oldershaw, Proc. Roy. Soc. Lond. A, 249, 498 (1959). c. B_e and r_e : T. Amano, E. Hirota, and Y. Morino, J. Phys. Soc. Japan, 22, 399 (1967). d. This work. e. F. X. Powell and D. R. Lide, Jr., J. Chem. Phys. 41, 1413 (1964).

Its related molecules, H_2CO and CO, were found to be widely distributed in interstellar space (Ref. 26). Jefferts et al. (Ref. 27) searched for the $1_{01} \leftarrow 0_{00}$ transition of the interstellar formyl radical on the basis of the rotational constants determined from optical absorption spectra (Ref. 28), but they could not detect it in molecular clouds showing strong lines of H_2CO and CO. Some low-J K-type doubling transitions of HCO were first observed in laboratory by Carrington and his group (Ref. 29-31) using EPR spectroscopy and then by Austin et al. (Ref. 32). The formyl radical was produced by a reaction of H_2CO with the product of a microwave discharge in CF_4 . The strongest component of the $1_{01} \leftarrow 0_{00}$ transition of HCO is shown in Fig. 4.

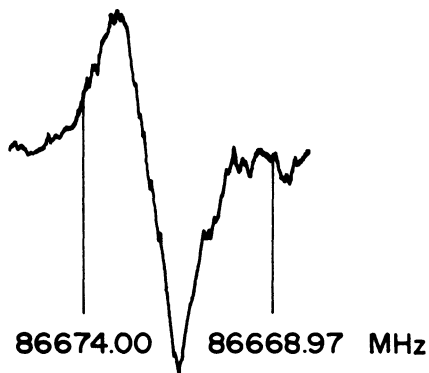


Fig. 4. The $F=2 \leftarrow 1$ component of the $J=3/2 \leftarrow 1/2$, $1_{01} \leftarrow 0_{00}$ transition of the HCO radical.

The deuterated species DCO was produced by the reaction of D_2CO .

As the formyl radical has an odd number of electrons and resultant electronic spin, each rotational level is split in two by the interaction of the electron spin with molecular rotation. Each split level is further split by the interaction of the electron spin with the nuclear spin of the hydrogen or

deuterium, such as Fermi interaction and magnetic dipole-dipole interaction. As a result, there may be six hyperfine components for the $1_{01} \leftarrow 0_{00}$ transition of HCO and nine for that of DCO corresponding to $\Delta J = 0, \pm 1$, and $\Delta F = 0, \pm 1$ selection rules. We observed four components for HCO and seven for DCO. The observed spectra were analyzed with consideration for spin-rotation, Fermi and dipole-dipole interactions (Ref. 33). The molecular constants obtained are shown in Table 2,

Table 2. The Molecular Constants of HCO and DCO (MHz)

Constants	HCO	DCO
$B_0 + C_0$	86718.07 ± 0.10 (86796) ^a	73533.9 ± 0.2 (73521) ^a
$E_{bb} + E_{cc}$	-187.3 ± 0.40	-168.4 ± 0.4
a_F	393 ± 8 (± 303.9) ^b	58.7 ± 0.2 (± 58.0) ^b
$T_{bb} + T_{cc}$	-11.8 ± 0.5	-1.4 ± 0.4

a. Ref. 28. b. F. J. Adrian, E. L. Cochran, and V. A. Bowers, J. Chem. Phys. 36, 1661 (1962).

where E , a_F and T are the coupling constants of spin-rotation, Fermi contact and magnetic dipole-dipole interactions, respectively. It is noted that there is a discrepancy of about 78 MHz between the $B_0 + C_0$ values of HCO obtained by this study (Ref. 24) and by optical spectroscopy (Ref. 28). On the basis of the observed frequencies for the component shown in Fig. 4, Snyder et al. (Ref. 34) detected the interstellar HCO in some particular moderate-density molecular clouds containing ionized carbon.

HO₂(²A") (Ref. 12)

The hydroperoxyl radical HO₂ is also fundamental to chemical kinetics.

It is an often quoted intermediate in reactions containing oxygen and hydrogen atoms (Ref. 35) or in hydrocarbon oxidation (Ref. 25). Recently it turns out that HO₂ takes part in main photochemical reactions in the upper atmosphere.

However, because of its short lifetime, accurate spectroscopic studies of this radical have become possible only very recently. Radford et al. (Ref. 36) succeeded in detecting the LMR spectra of several rotational transitions of HO₂ in the far infrared region. Based on the molecular constants determined by LMR (Ref. 37), Beers and Howard observed all of the fine and hyperfine structures of the $1_{01} \leftarrow 0_{00}$ transition for HO₂ (Ref. 38) and DO₂ (Ref. 39) by using a Zeeman modulated cavity microwave spectrometer.

The HO₂ radicals were produced by a reaction of allyl alcohol with the product of a microwave discharge in the oxygen. All the a-type $N = 2 \leftarrow 1$ transitions and four b-type transitions were observed with rather good signal-to-noise ratios. The observed spectra were analyzed on the basis of the following Hamiltonian:

$$\mathcal{H} = \mathcal{H}_r + \mathcal{H}_{sr} + \mathcal{H}_{hfs} \quad (1)$$

where \mathcal{H}_r is the ordinary rotational Hamiltonian, \mathcal{H}_{sr} the electron spin-rotation interaction, and \mathcal{H}_{hfs} the magnetic hyperfine interaction. The effective expressions for \mathcal{H}_{sr} and \mathcal{H}_{hfs} are as follows:

$$\mathcal{H}_{sr} = E_{aa} N_a S_a + E_{bb} N_b S_b + E_{cc} N_c S_c + (E_{ab} + E_{ba})(N_a S_b + S_a N_b)/2 \quad (2)$$

$$\mathcal{H}_{hfs} = a_F \mathbf{S} \cdot \mathbf{I} + \mathbf{S} \cdot \mathbf{T} \cdot \mathbf{I} \quad (3)$$

The matrix elements of \mathcal{H}_{sr} and \mathcal{H}_{hfs} were discussed in detail by Curl and Kinsey (Ref. 33), by Raynes (Ref. 40), and more recently Bowater et al. (Ref. 30).

In the analysis of the observed spectra the off-diagonal component of the spin-rotation coupling tensor, $E_{ab} + E_{ba}$, was included though its contributions to transition frequencies are small. This was carried out by

taking into account the second-order perturbation terms of $\epsilon_{ab} + \epsilon_{ba}$ in the analysis of the spin doublings. Since the energy differences between the rotational levels of N_{ON} and $(N-1)_{1,(N-2)}$ are minimum and change their signs around $N = 9$ and 10 as shown in Fig. 5, the second-order contributions to the $9_{09} \leftarrow 8_{18}$, $J = 17/2 \leftarrow 15/2$ and $10_{0,10} \leftarrow 9_{19}$, $J = 19/2 \leftarrow 17/2$ transitions are especially large and opposite in signs.

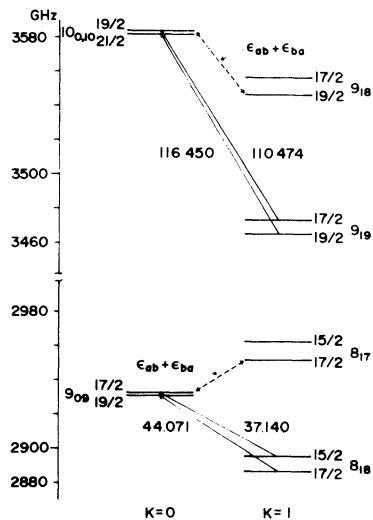


Fig. 5. The energy levels of HO_2 , concerned with the remarkable second-order perturbation of $\epsilon_{ab} + \epsilon_{ba}$. Observed transitions are shown by solid arrows and their frequencies are given in GHz.

In fact, if the second-order terms are not included in the analysis of the spin doublings, the spin doublings calculated for the $9_{09} \leftarrow 8_{18}$ and $10_{0,10} \leftarrow 9_{19}$ transitions deviate from the observed values by -19 and 13 MHz, respectively. However, when the second-order terms are taken into account in the analysis, the agreement between the observed and calculated values of the spin doublings is satisfactory. The molecular constants obtained are listed in Table 3 where those determined from the LMR spectra are also given for comparison. The agreement is good.

All the hyperfine constants of HO_2 were obtained for the first time. The magnitude of the Fermi contact parameter is small, -28 MHz. This leads to the conclusion that the unpaired electron of the HO_2 radical occupies a π -type orbital. Adrian, Cochran, and Bowers (41) observed the ESR spectrum of HO_2 in argon matrix and concluded that the isotropic hyperfine constant, a_F , is -10.2 Oe (-28.6 MHz) and the out-of-plane component of the anisotropic part of the hyperfine tensor, T_{cc} , is -4.4 Oe (-12.3 MHz). These are in good agreement with the corresponding values obtained in this study. Also all the principal components of the tensor were determined separately in this study. This result will be useful for the detailed studies of the Zeeman effect of HO_2 because the principal components of the spin g tensor can be calculated from the principal components of the ϵ tensor through Curl's relation (Ref. 42). The observed transitional frequencies as well as the molecular constants given above have now been used for the study of HO_2 in other related fields. Astronomical searches for the b-type transitions were made in some molecular clouds with the 6 m telescope at the Tokyo Astronomical Observatory (Ref. 43). Radford of Harvard College Observatory (Ref. 44) also made searches for the $N = 2 \leftarrow 1$ transitions at 130 GHz in likely astronomical sources. Both the results were negative. HO_2 is of particular interest to stratospheric chemistry and its atmospheric searches are now in progress (Ref. 45 & 46).

The molecules so far given are paramagnetic. There have been known many non-paramagnetic molecules of short lifetime, which play an important role in the

fundamental chemical reactions. Some of them may be considered as free radicals after the definition by Herzberg (Ref. 5). We have studied two of such unstable molecules, HNO (Ref. 47-49) and $\text{CH}_2=\text{CHOH}$ (Ref. 50).

Table 3. Molecular Constants of HO_2 (MHz)^a

Constants	Mw ^b	LMR ^c
A	610257±35	610318±225
B	33511.95±0.60	33514±38
C	31673.46±0.60	31679±38
D _N	0.112±0.068	0.126±0.060
D _{NK}	3.47±0.48	3.6±0.75
D _K	123 ^e	123±23
ε _{aa} ^d	-49546.1±5.8 ^f	-49292±650
ε _{bb}	-431.9±3.3	-486±200
ε _{cc}	17.6±3.3	54±200
$ \epsilon_{ab} + \epsilon_{ba} /2$	189±30	
a _F	-27.6±1.4	
T _{aa}	-8.1±1.1	
T _{bb}	19.5±1.1	
T _{cc}	-11.4±1.1	

a. The error quoted for each molecular constant is 2.5 times the standard deviation. b. This work. c. Ref. 36. d. An effective ϵ_{bb} (b) obtained from the b-type transitions is -417.9±1.5 MHz. e. Assumed. d. The value for the K=1 levels.

HNO(¹A') (Ref. 47-49)

HNO is isoelectronic with molecular oxygen so that the linear HNO should have an electronic structure similar to O_2 . However, as the HNO angle becomes smaller, the ¹Δ state splits into two states, ¹A' and ¹A'', and the ¹A' state goes down energetically according to Walsh diagram (Ref. 51). Hence, there had been some discussions (Ref. 4.) on the ground electronic state of HNO: which is the ground electronic state of HNO, singlet or triplet. The electronic absorption spectrum of HNO was first observed by Dalby (Ref. 52) using the flash photolysis method. He assigned the transition to ¹A'' - ¹A' and determined the molecular constants in both states, but there is a possibility that the triplet state must lie very low and might even be the true ground state. Triplet states of HNO have not been observed. DNO was produced by the reaction of NO with the D atom generated by a microwave discharge in the deuterium gas. The a-type $1_{01} \leftarrow 0_{00}$ and three K-type doubling transitions, and two b-type R and P branch transitions were observed. Some of the transitions showed the hyperfine structure due to the quadrupole interaction of the nitrogen nucleus. They were not due to stable molecules such as DNO₂, DNO₃, NH₂D, NHD₂, D₂O, and N₂O nor to paramagnetic molecules such as NO₂. The rotational constants determined agreed with those of DNO in the lower electronic state ¹A' determined by Dalby (Ref. 52) within the error limits as shown in Table 4. Subsequently the microwave spectrum of the H species was observed by the use of reactions of NO with the H atom. The molecular constants obtained are also given in Table 4. Moreover, the lifetime of the molecule giving the spectra was found to range from 1 to 40 sec depending upon the conditions. This long lifetime can be understood from the fact that all the halogen derivatives of nitroxyl are rather stable compounds. Thus the molecular species observed was assigned to the HNO molecule, and its ground electronic state was determined to be ¹A'. HNO has been also expected to exist in interstellar space. After many unsuccessful searches (Ref. 53&54), the $1_{01} \leftarrow 0_{00}$ transition of HNO was detected in emission from the directions of Sagittarius B2 and NGC2024

(Ref. 55). The most significant aspect of this result is that HNO is the first interstellar molecule containing the NO bond. This will inevitably lead to an improvement or and extension of the ion-molecule reaction theory explaining the formation of various interstellar molecules.

Table 4. Molecular Constants of HNO and DNO (MHz)

Constant	HNO	DNO
A	553903.0±2.7 (553994 ±15) ^a	315496.5±2.3 (315449 ±21) ^a
B	42308.52±0.10 (42316 ±6) ^a	38732.16±0.10 (38734 ±12) ^a
C	39169.46±0.10 (39187 ±6) ^a	34353.68±0.10 (34364 ±12) ^a
Δ_o^b	0.04489±0.00006	0.06116±0.00008
χ_{aa}	0.36±0.40	1.03±0.40
χ_{bb}	-5.46±0.40	-6.13±0.26
χ_{cc}	5.10±0.26 ^c	5.10±0.26
μ_a	1.03±0.01 D	1.18±0.04 D
μ_b	1.31±0.02 D	1.22±0.04 D
μ_{total}	1.67±0.03 D	1.70±0.05 D

a. Ref. 52. b. amuA². c. Assumed.

Vinyl Alcohol, CH₂=CHOH (Ref. 50)

Vinyl alcohol, a tautomer of acetaldehyde, has been suggested to be an intermediate of reactions leading to the formation of acetaldehyde (Ref. 56-59). In 1973, Blank and Fisher (Ref. 60) observed the NMR spectrum of presumable vinyl alcohol, highly enhanced by CIDNP during photolysis of acetaldehyde and of 2-hydroxybutane-3-one (acetoin). The observation has, however, been carried out only in the liquid phase, and the existence of vinyl alcohol in the gas phase has never been recognized.

On the other hand, it is well known that various derivatives of vinyl alcohol such as methyl vinyl ether, vinyl acetate, and especially poly(vinyl alcohol) are very stable. This may be explained from the equilibrium of the keto-enol tautomerization, favourable to the existence of acetaldehyde (Ref. 61). Vinyl alcohol was produced by a dehydration reaction of ethylene glycol. Ethylene glycol was introduced into a 6 mm quartz tube, heated to 700 - 1000 degree centigrade. Pyrolyzed sample was pumped through the parallel plate absorption cell. An appreciable amount of acetaldehyde and a small amount of ethylene oxide as well as unreacted ethylene glycol were identified in the reaction products by monitoring their microwave spectra. In addition to the spectra of known stable molecules, a series of strong and sharp lines were observed at 50 to 70 GHz with the optimum intensity at about 900°C. The lines were assigned to a series of the b-type Q branch transitions by means of well-resolved Stark patterns. The rotational constants preliminarily obtained were consistent with a structure of vinyl alcohol in the syn form. The inertia defect derived from the rotational constants was positive and small. This strongly supported that the molecule is planar. The conclusion was definitely confirmed by the observation of the spectrum of CH₂=CHOD, which was produced by the dehydration of CH₂ODCH₂OD.

The lifetime of vinyl alcohol was measured by monitoring its lines on CRO. The reaction products were stored in a conventional absorption cell of an X-band waveguide 3 m long at room temperature. The half-life was found to be about 4 sec. On the other hand, the half-life of vinyl alcohol was about 30 minutes, when stored in a Pyrex flask of 500 cm³ equipped with a hydrocarbon-greased stopcock. Vinyl alcohol is nearly stable in the glass ware. It is

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