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High Resolution Spectroscopy

High Resolution Spectroscopy

A GENERAL DISCUSSION
ON
High Resolution Spectroscopy

13th, 14th and 15th April, 1981

A GENERAL DISCUSSION on High Resolution Spectroscopy was held at the University of Bristol on 13th, 14th and 15th April, 1981. The President of the Faraday Division, Professor J. S. Rowlinson, F.R.S., was in the chair: about 150 Fellows of the Faraday Division and visitors from overseas attended the meeting. Among the overseas visitors were:

Dr. J. A. Beswick, *France*
Dr. P. Brechignac, *France*
Prof. H. Burger, *West Germany*
Dr. G. Cazzilo, *Italy*
Dr. C. Cossart, *France*
Prof. J. A. Coxon, *Canada*
Mrs. C. Demuynck, *France*
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Dr. F. Engelke, *West Germany*
Dr. K. M. Evenson, *U.S.A.*
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CONTENTS

CONTENTS

Spiers Memorial Lecture

Far-infrared Laser Magnetic Resonance*

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Far-infrared laser magnetic resonance (l.m.r.) is now a laboratory spectroscopic technique used in at least six laboratories throughout the world, and some 50 papers on l.m.r. spectroscopy have been published.[1-50] L.m.r. is an extremely sensitive technique for finding rotational Zeeman spectra in paramagnetic atoms and molecules. Some 31 species have been detected, some of which had never been discovered before. L.m.r. is now also used in a number of laboratories to study the reaction rates of these paramagnetic free radicals.[37] The field of mid-infrared l.m.r. using CO and CO_2 lasers has also expanded rapidly and is summarized in McKellar's paper[51] at this meeting.

A review of far-infrared l.m.r. was presented a little over one year ago.[37] The purpose of the present report is to bring that comprehensive paper up to date and to point out some recent results in the field of laser frequency measurements which are leading the way to a redefinition of the metre.

In this publication, I will list all of the far-infrared l.m.r. spectrosopic papers chronologically;[1-50] give a list of all the species observed with references, describe the design of a new l.m.r. spectrometer in the N.B.S. Boulder Laboratories; present some new ideas on the sensitivity of intracavity absorption; and finally show how recent laser frequency measurements are leading to a new definition of the metre in terms of the second, thus fixing the value of the speed of light.

FAR-INFRARED PARAMAGNETIC FREE RADICALS

The first 50 entries in the bibliography are a current chronological list of the l.m.r. spectroscopic papers. In table 1 a list of all the far-infrared l.m.r. molecules identified up to now is presented. The far-infrared l.m.r. spectra of 26 different species, 5 metastable electronic states and several vibrationally excited states have been observed. Some of the observed species are not " well-behaved ", that is, the spin decouples from the orbital angular momentum at low field, and the l.m.r. spectrum is not observable at fields of more than a few hundredths of a tesla (a few hundred gauss). Species exhibiting this behaviour are: CCH, CH_2F and CH_2OH. These weakly coupled molecules contrast with strongly coupled molecules such as OH, where spectra have been observed to 5 T (50 kG).[9] Generally most spectra are observed below 2 T. The rate of new entries may be slower in the future because the " easier " radicals have already been observed.

TABLE 1.—ATOMS AND MOLECULES DETECTED BY FAR-INFRARED LASER MAGNETIC RESONANCE

species	state	reference	species	state	reference
atoms			triatomics		
O	$3p$	28, 34	NO_2	$^2A_1$	6
C	$3p$	42	HO_2	$^2A''$	12, 15, 16
			HCO	$^2A'$	17
diatomics					
O_2	$^3\Sigma^-$	1, 8, 10, 13	PH_2	$^2B_1$	21, 36
NO	$^2\Pi$	7	NH_2	$^2B_1$	18
CH	$^2\Pi$	5, 27	CH_2	$^3B_1$	38
PH	$^3\Sigma^-$	20	CCH	$^2\Sigma^+$	53
NH	$^3\Sigma^-$	19	polyatomics		
ClO	$^2\Pi$	52	CH_3O		24, 40
CF	$^2\Pi$	50	CH_2F		26
OH	$^2\Pi$	9, 32, 33,	CH_2OH		45
	$v = 0, 1, 2, 3 \ldots$	47, 49			
OD	$^2\Pi$	41, 49	metastables		
	$v = 0, 1, 2, 3 \ldots$		O_2	$^1\Delta_u$	48
SeH	$^2\Pi$	29	PH	$^1\Delta$	20
SeD	$^2\Pi$	44	HO_2	$^2A'$?	16
SH	$^2\Pi$	30	CO	$a^3\Pi$	54
			NF	$'\Delta$	46
ions					
HBr^+	$^2\Pi$	35			
DBr^+	$^2\Pi$	35			

EXPERIMENTAL DETAILS

A new far-i.r. l.m.r. spectrometer has been constructed in our N.B.S. Boulder laboratory which should be more sensitive, allow more lines to lase, and which will be significantly easier to operate.   The new spectrometer is shown in fig. 1.   A new com-
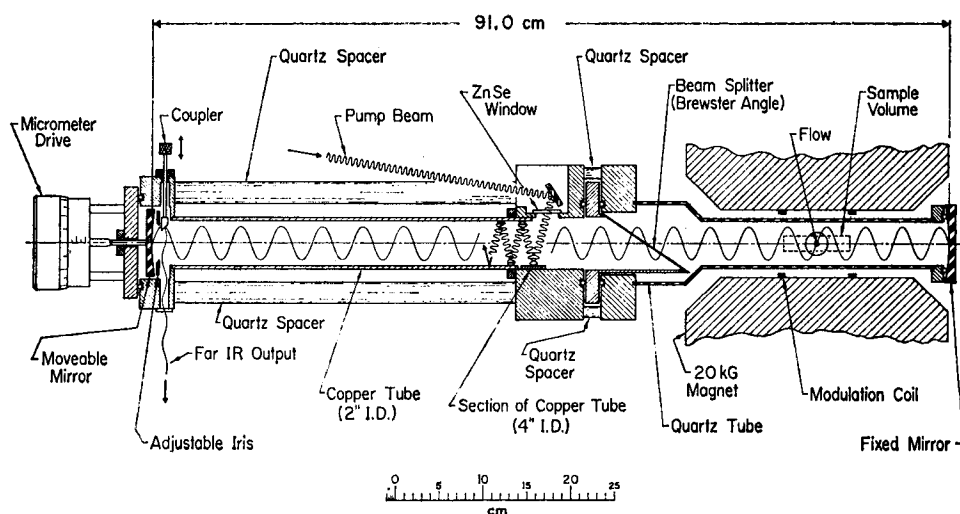

FIG. 1.—Laser magnetic resonance spectrometer, 40-1000 μm.

puter-controllable 15 in. electromagnet with ring-shimmed Hyperco pole caps pro-
duces a 7.5 cm homogeneous field region 5 times longer than that of our previous
spectrometer;[37] hence, it should be five times more sensitive.   The new f.i.r. cavity
is 25 cm shorter and should oscillate to well over 1000 μm.   Better overlap between
pump and f.i.r. laser yields a lower threshold of oscillation and consequently a larger
number of f.i.r. lines.   The improved overlap was accomplished with a nearly con-
focal mirror geometry, the insertion of the CO_2 pump at the beam waist and the use of a
cylindrical copper tube as the CO_2 reflector.   This cylindrical copper tube was found
to double the output power in a f.i.r. laser compared with the use of flat side mirrors.
A section of 4 in. I.D. copper tube is used as the first cylindrical CO_2 beam focuser to
begin a series of consecutive refocuses of the pump beam.   Quartz is used as the
spacers in the spectrometer to provide better thermal stability.   For ease of operation,
the micrometer, coupler, detector, CO_2 laser grating, and gas-handling system are all
available from one side of the magnet.   The beam splitter is rotatable about the
laser axis so the polarization can be rotated.

INTRA-CAVITY SENSITIVITY

Measurements of the sensitivity of our previous intracavity far-infrared l.m.r.
spectrometer indicated an enhancement of sensitivity by about a factor of 20 over
what one would expect from a passive cavity.[37]   Recently, Radford and Rohbeck[55]
used a simple expression of Rigrod's[56] for the saturated c.w. gain of a homogeneously
broadened laser.   The expression may explain the enhanced sensitivity.   Rigrod's
expression is

$$\text{gain} = \frac{2gL}{1 + P_{in}/P_s}$$

where g is the low-signal gain per unit length, L is the length of the gain cell, P_{in} is the
power density in the laser cavity, and P_s is the self-saturation power level.   Then,
letting

$$\text{gain} = \text{loss}$$

where the loss is given by $t + a$, with t the fractional coupling, a the round-trip
cavity loss, P the power output of the laser, and

$$P = \frac{tP_{in}}{2}$$

one obtains:

$$P = \frac{tP_s}{2}\left(\frac{2gL}{t + a} - 1\right). \tag{1}$$

For an additional small absorption αl, where α is the absorption coefficient and l is
absorption length, the signal is given by

$$\Delta P = P(a + 2\alpha l) - P(a);$$

and substituting in eqn (1), one obtains:

$$\Delta P = \frac{tP_s}{2}\left(\frac{2gL}{t + a}\right)\left(\frac{2\alpha l}{t + a}\right). \tag{2}$$

Now, we would like to find $\Delta P = f(P)$, so we will eliminate g between eqn (1) and (2);
thus

$$\Delta P = \left(P + \frac{tP_s}{2}\right)\left(\frac{2\alpha l}{t + a}\right). \tag{3}$$

We have found that the maximum sensitivity occurs with the spectrometer oscillating well above threshold, and this expression seems to be in agreement with the experimental results: (i) the sensitivity is nearly independent of P, $i.e.$ $tP_s/2 > P$, (ii) the sensitivity is some 20 times more than one would expect from a passive cavity, $i.e.$ $tP_s/2 \approx 20P$, (iii) $\Delta P \propto 2\alpha l$ (the spectrometer is linear), (iv) $\Delta P \propto$ cavity Q [$i.e.$ $\Delta P \propto 1/(t + a)$], (v) $\Delta P \propto$ pressure of lasing gas ($i.e.$ $\Delta P \propto P_s$). However, before a positive confirmation can be made, further experimental verification is needed.

RADIO ASTRONOMY

Radio-astronomical observations ($i.e.$ with heterodyne techniques) have recently been extended well into the far-infrared region.[57,58] These observations are made at high altitudes in the NASA Kuiper Airborne Observatory or from the top of Mauna Kea in Hawaii. Radio-astronomical searches require an accurate knowledge of the frequencies of the atom or molecule sought. This accuracy generally cannot be supplied with optical data, but can be supplied from l.m.r. data. In fact, the discovery of atomic carbon[57] in Orion was made possible from l.m.r. measurements of atomic carbon which yielded the fine-structure separations[42] good to better than 1 MHz and some 100 times more accurate than optical data.

The measurements of the l.m.r. spectrum of OH[47] also yielded improved rotational frequencies of OH and hence more accurate Doppler shifts in the recent astronomical observations of OH.[59] These astronomical measurements were made with interferometric techniques and hence did not require high-accuracy data for the astronomical detection.

The first terrestrial detection of CCH was performed with far-infrared l.m.r.[53] following the radio-astronomical detection of the $N = 0 \rightarrow 1$ transition.[60] A precise fit of the l.m.r. data has yielded separate values for B and D and thus accurate $N = 2 \rightarrow 3$ transition frequencies.[53] These transitions have just been observed with radio techniques.[61]

With these successes in the last two years it seems likely that the measurement of other free radicals should lead to their detection in interstellar space. In fact, NASA is now supporting our spectroscopy for exactly this purpose.

ACCURATE DETERMINATION OF MOLECULAR CONSTANTS FROM L.M.R. DATA

To determine more accurately structural constants of paramagnetic molecules, Brown et $al.$,[47] have fitted all the l.m.r. data of OH to an effective Zeeman Hamiltonian in order to obtain a highly accurate set of rotational constants. With these constants, predictions of the zero-field term values to $ca.$ 3 MHz was possible. Although this determination is $ca.$ 3 times less accurate than the atomic carbon numbers, it is quite comparable when one considers that the two atomic carbon transitions were determined with 10 different laser frequencies. Thus, we see that the Zeeman theory for diatomics is approximately as accurate as it is for atoms. That is, the uncertainties are mainly caused by uncertainties in the experimental data, notably from measurements of the magnetic field and the laser frequency.

The Zeeman theory of polyatomics is, in general, not as accurate. One of the best examples of a " successful " Zeeman theory of a triatomic is with HO_2. The abundant and regular l.m.r. spectrum of HO_2 was fitted very nicely to the theory of Hougen.[15] In contrast, CH_2 exhibits sparse and irregular spectra,[38] and the spectra have not yet been assigned. A crucial test of the Zeeman theory of triatomics will

be made in fitting these data to find a set of rotational constants for this elusive molecule.[38] We feel that more l.m.r. data are needed than are now at hand. A few of the lower levels of CH_2 will certainly be of interest to radio astronomers, and work is continuing on this molecule.

One of the recent outstanding achievements in far-infrared l.m.r. spectroscopy and Zeeman theory is the observation of a previously speculated molecule CH_3O,[24] and the subsequent fit of its l.m.r. spectrum[40] yielding the rotational constants of this polyatomic radical.

The successful fits of l.m.r. data have been to radicals in which the spin remains coupled to the rotation of the molecule. However, the success with fitting the CCH spectrum indicates that some of these too may be amenable to analysis.

THE FUTURE OF L.M.R.

Most of the ground states of the more common paramagnetic hydrides have been observed. A few of the more elusive ones such as SiH still elude the experimentalist. However, hundreds of metastables and polyatomic radicals and many paramagnetic ions remain to be discovered by l.m.r.; therefore, I predict that this highly sensitive tool will be used to measure dozens of new and exciting free radicals in the next few years.

FAR-INFRARED LASERS, FREQUENCY MEASUREMENT AND THE REDEFINITION OF THE METRE

The number of c.w. far-infrared lasing lines reported in Knight's recent tabulation[62] is 1350. Of these, about one-quarter oscillate in conventional l.m.r. spectrometers, and about one-half of these have been accurately (frequency) measured. In the operation of the spectrometer, the f.i.r. laser is tuned to the centre frequency of the lasing molecule by maximizing the laser power in single-mode operation. This adjustment is reproducible to *ca.* $\pm 5 \times 10^{-7}$, and does not drift outside this range during a spectral search.

The frequencies of these f.i.r. lasers are measured in separate experiments by synthesizing a frequency within a radiofrequency difference either from harmonics of microwave radiation or from difference frequencies between two CO_2 laser lines and possibly an additional X-band oscillator. It is this latter technique we have used[63] because it covers the entire far-infrared spectral region. A tungsten–nickel point-contact diode[64] is used as the non-linear element. The radiation from the f.i.r. laser, the two CO_2 lasers and the microwave oscillator (when needed) all radiate the tungsten antenna and electrons tunnel across the nickel oxide layer to the nickel base generating a radiofrequency difference. The far-infrared frequency difference, $\nu_{f.i.r.}$, is

$$\nu_{f.i.r.} = n(\nu_1 - \nu_2) \pm m\nu_\mu \pm \nu_b$$

where n is the harmonic of the CO_2 difference frequency, ν_1 is one CO_2 laser frequency, ν_2 is the other CO_2 laser frequency, m is the microwave harmonic, ν_μ is the microwave frequency and ν_b is the r.f. difference frequency.

The uncertainty in this measurement is due to the uncertainty in finding the centre of the gain curve of the lasing medium $\pm 5 \times 10^{-7}$. Other uncertainties in determining $\nu_{f.i.r.}$ are significantly less in most cases. To find the appropriate CO_2 lines, the frequency is first determined to an accuracy of <1 GHz by a wavelength measurement, made by measuring a number of half-wavelengths with the calibrated micrometer on the f.i.r. laser.
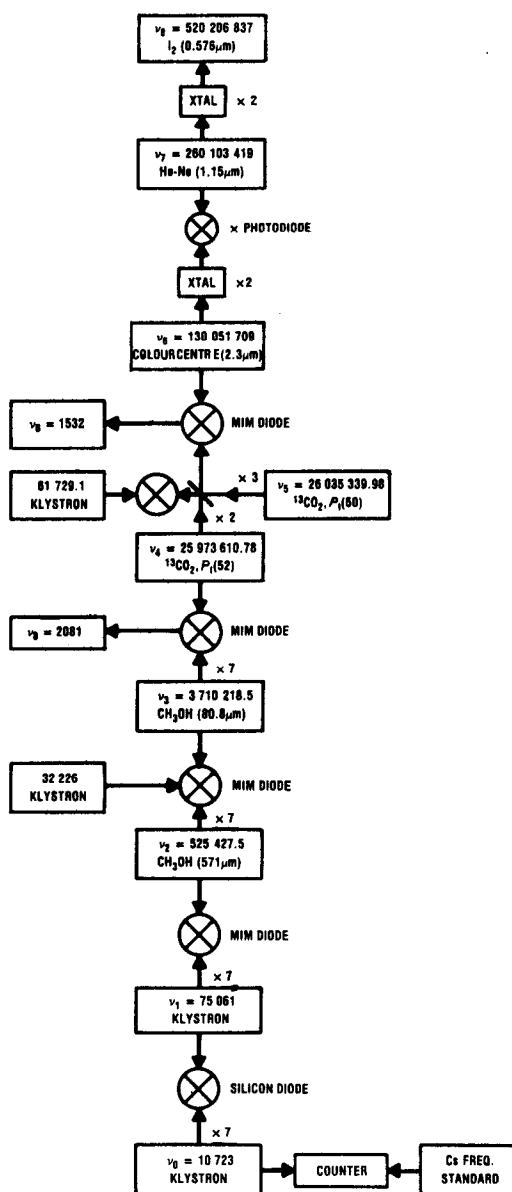
FIG. 2.—Laser frequency synthesis chain (to the visible).   All frequencies in MHz.

The overall result is that the uncertainty in the f.i.r. laser frequency is *ca.* $\pm 7 \times 10^{-7}$. The uncertainty of 5×10^{-7} in setting the laser to the top of the gain curve is multiplied by $2^{\frac{1}{2}}$ because the laser must be adjusted to the top of its gain curve two times: once when the frequency is measured, and once when the l.m.r. spectrometer is adjusted. We have not yet found it necessary to stabilize the f.i.r. cavity to the top of the gain curve.

While I am discussing laser frequency measurements, I would like to point out that

the frequency of visible light has recently been measured.[65] Frequencies can be measured orders of magnitude more accurately than wavelengths; therefore, the entire electromagnetic spectrum up to the visible is now accessible with ultra-high-resolution and extremely accurate frequency metrology. These events stimulated the Comité Consultatif Pour La Définition du Métre in 1979 to propose a new definition of the metre: " The metre is the length equal to the distance travelled in a time interval of 1/299 792 458th of a second by plane electromagnetic waves in vacuum." This recommendation will be acted upon by the general conference of weights and measures in 1984.

The metre will be realized from this definition *via* a vacuum wavelength obtained from any stabilized laser whose frequency has been measured. The vacuum wavelength is, of course, the "fixed" value of c (299 792 458 ms^{-1}) divided by the measured frequency of that laser. It is therefore important that accurate frequencies of visible lasers be made. The first measurement of the frequency of visible light[65] was not of sufficient accuracy for realizing the " new " metre. Hence, more accurate measurements are now underway.

To extend frequency measurements to lasers, a series of steps are used in which harmonics of the radiation of one laser are heterodyned with the radiation from a higher-frequency laser to obtain a radiofrequency difference. The previously mentioned measurement of the frequency of visible light consisted of a " chain " of such harmonically related lasers connecting the caesium standard with the frequency of an iodine absorption in the visible. We are presently at work on a simpler and more accurate chain shown in fig. 2, connecting the caesium frequency with the same iodine frequency. The accuracy ultimately is limited by the accuracy of the caesium standard itself, $\pm 1 \times 10^{-13}$.

[1] K. M. Evenson, H. P. Broida, J. S. Wells, R. J. Mahler and M. Mizushima, *Phys. Rev. Lett.*, 1968, **21**, 1038.
[2] J. S. Wells and K. M. Evenson, *Rev. Sci. Instr.*, 1970, **41**, 227.
[3] K. M. Evenson and J. S. Wells, *IEEE J. Quantum Electron.*, 1970, QE6, 184.
[4] K. M. Evenson, J. W. Wells, and H. E. Radford, *Phys. Rev. Lett.*, 1970, **25**, 199.
[5] K. M. Evenson, H. E. Radford, and M. M. Moran Jr, *Appl. Phys. Lett.*, 1971, **18**, 426.
[6] R. F. Curl, Jr, K. M. Evenson and J. S. Wells, *Chem. Phys.*, 1972, **56**, 5144.
[7] M. Mizushima, K. M. Evenson and J. S. Wells, *Phys. Rev. A*, 1972, **5**, 2276.
[8] M. Mizushima, J. S. Wells, K. M. Evenson and W. M. Welch, *Phys. Rev. Lett.*, 1972, **29**, 831.
[9] T. Kasuya and K. Shimoda, *Jpn J. Appl. Phys.*, 1972, **11**, 1571.
[10] K. M. Evenson and M. Mizushima, *Phys. Rev. A*, 1972, **6**, 2197.
[11] K. M. Evenson and C. J. Howard, *Laser Spectroscopy*, ed. R. G. Brewer and A. Moorodian (Plenum Press, New York, 1975), p. 535.
[12] H. E. Radford, K. M. Evenson and C. J. Howard, *J. Chem. Phys.*, 1974, **60**, 3178.
[13] L. Tomuta, M. Mizushima, C. J. Howard and K. M. Evenson, *Phys. Rev. A*, 1975, **12**, 974.
[14] P. B. Davies and K. M. Evenson, *Proc. 2nd Int. Conf. Laser Spectrosc.*, ed. S. Haroche, J. C. Pebay-Peyroula, T. W. Hänsch and S. E. Harris (Springer-Verlag, Berlin, 1975), p. 132.
[15] Jon T. Hougen, *J. Mol. Spectrosc.*, 1975, **54**, 447.
[16] Jon T. Hougen, H. E. Radford, K. M. Evenson and C. J. Howard, *J. Mol. Spectrosc.*, 1975, **56**, 210.
[17] J. M. Cook, K. M. Evenson, C. J. Howard and R. F. Curl Jr, *J. Chem. Phys.*, 1976, **64**, 1381.
[18] P. B. Davies, D. K. Russell, B. A. Thrush and F. D. Wayne, *J. Chem. Phys.*, 1975, **62**, 3739.
[19] H. E. Radford and M. M. Litvak, *Chem. Phys. Lett.*, 1975, **34**, 561.
[20] P. B. Davies, D. K. Russell and B. A. Thrush, *Chem. Phys. Lett.*, 1975, **36**, 280.
[21] P. B. Davies, D. K. Russell and B. A. Thrush, *Chem. Phys. Lett.*, 1976, **37**, 43.
[22] F. D. Wayne and H. E. Radford, *Mol. Phys.*, 1976, **32**, 1407.
[23] P. B. Davies, D. K. Russell, B. A. Thrush and H. E. Radford, *Proc. R. Soc. London, Ser. A*, 1978, **353**, 299.
[24] H. E. Radford and D. K. Russell, *J. Chem. Phys.*, 1977, **66**, 2223.
[25] K. M. Evenson, D. A. Jennings, F. R. Peterson, J. A. Mucha, J. J. Jimenez, R. M. Charlton and C. J. Howard, *IEEE J. Quantum Electron.*, 1977, QE13, 442.

[26] J. A. Mucha, D. A. Jennings, K. M. Evenson and J. T. Hougen, *J. Mol. Spectrosc.*, 1977, **68**, 122.

[27] J. T. Hougen, J. A. Mucha, D. A. Jennings and K. M. Evenson, *J. Mol. Spectrosc.*, 1978, **72**, 463.

[28] P. B. Davies, B. J. Handy, E. K. Murray-Lloyd and D. R. Smith, *J. Chem. Phys.*, 1978, **68**, 1135.

[29] P. B. Davies, B. J. Handy, E. K. Murray-Lloyd and D. K. Russell, *J. Chem. Phys.*, 1978, **68**, 3377.

[30] P. B. Davies, B. J. Handy, E. K. Murray-Lloyd and D. K. Russell, *Mol. Phys.*, 1978, **36**, 1005.

[31] P. B. Davies, D. K. Russell, D. R. Smith and B. A. Thrush, *J. Can. Phys.*, 1979, **57**, 522.

[32] P. B. Davies, W. Hack, A. W. Preuss and F. Temps, *Chem. Phys. Lett.*, 1979, **64**, 94.

[33] J. P. Burrows, D. J. Cliff, P. B. Davies, G. W. Harris, B. A. Thrush and J. P. T. Wilkinson, *Chem. Phys. Lett.*, 1979, **65**, 197.

[34] R. J. Saykally and K. M. Evenson, *J. Chem. Phys.*, 1979, **71**, 1564.

[35] R. J. Saykally and K. M. Evenson, *Phys. Rev. Lett.*, 1979, **43**, 515.

[36] P. B. Davies, D. K. Russell, B. A. Thrush and H. E. Radford, *Chem. Phys.*, 1979, **44**, 421.

[37] K. M. Evenson, R. J. Saykally, D. A. Jennings, R. F. Curl Jr and J. M. Brown, *Proc. Yamada Conf. III on Free Radicals*, ed. Y. Morina, I. Tanaka, E. Hirota, K. Obi and S. Saito (Association for Science Documents, 1979), p. 159.

[38] J. A. Mucha, K. M. Evenson, D. A. Jennings, G. B. Ellison and C. J. Howard, *Chem. Phys. Lett.*, 1979, **66**, 244.

[39] K. M. Evenson and R. J. Saykally, *Interstellar Molecules*, ed. B. H. Andrews (International Astronomical Union, 1980), p. 239.

[40] D. K. Russell and H. E. Radford, *J. Chem. Phys.*, 1980, **72**, 2750.

[41] J. S. Geiger, D. R. Smith and J. D. Bonnett, *Chem. Phys. Lett.*, 1980, **70**, 600.

[42] R. J. Saykally and K. M. Evenson, *Astrophys. J.*, 1980, **238**, L107.

[43] K. M. Evenson, R. J. Saykally, D. A. Jennings, R. F. Curl Jr and J. M. Brown, *Chemical and Biochemical Applications of Lasers*, ed. C. B. Moore (Academic Press, New York, 1980), p. 95.

[44] D. I. Cliff, P. B. Davies, B. J. Handy, B. A. Thrush and E. K. M. Lloyd, *Chem. Phys. Lett.*, 1980, **75**, 9.

[45] H. E. Radford, K. M. Evenson and D. A. Jennings, *Chem. Phys. Lett.*, 1981, **78**, 589.

[46] P. B. Davies and F. Temps, *J. Chem. Phys.*, in press.

[47] J. M. Brown, C. M. L. Kerr, F. D. Wayne, K. M. Evenson and H. E. Radford, *J. Mol. Spectrosc.*, 1981, **86**, 544.

[48] A. Scalabrin, R. J. Saykally, K. M. Evenson, H. E. Radford and M. Mizushima, *J. Mol. Spectrosc.*, to be published.

[49] P. B. Davies, W. Hack and J. G. Wagner, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 15.

[50] R. J. Saykally, K. G. Lubic, A. Scalabrin and K. M. Evenson, in preparation.

[51] R. W. McKellar, High Resolution Spectroscopy, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 63.

[52] Y. P. Lee, R. M. Stimpfle, R. A. Perry, J. A. Mucha, K. M. Evenson, D. A. Jennings and C. J. Howard, in preparation.

[53] R. J. Saykally, D. C. Reuter and K. M. Evenson, in preparation.

[54] R. J. Saykally and K. M. Evenson, in preparation.

[55] H. E. Radford and W. Rohbeck, personal communication.

[56] W. W. Rigrod, *J. Appl. Phys.*, 1963, **34**, 2602.

[57] T. G. Phillips, P. J. Huggins, T. B. H. Kuiper and R. E. Miller, *Astrophys. J. Lett.*, 1980, **238**, L103.

[58] H. R. Fetterman, G. Koepf, P. F. Goldsmith, B. J. Clifton, D. Buhl, N. R. Erickson, D. D. Peck, N. McAroy, P. E. Tannenwald, *Science*, 1981, **211**, 580.

[59] J. W. V. Storey, C. H. Townes and D. M. Watson, *Astrophys. J. Lett.*, 1981, **244**, L27.

[60] K. D. Tucker, M. L. Kutner and P. Thaddeus, *Astrophys. J. Lett.*, 1974, **193**, L115.

[61] L. M. Zuirys, R. J. Saykally, R. N. Plambeck and N. Erickson, in preparation.

[62] D. J. E. Knight, National Physical Laboratory, Teddington, Middlesex, U.K., NPL Report QU-45 (1981).

[63] F. R. Petersen, K. M. Evenson, D. A. Jennings, J. S. Wells, K. Goto and J. J. Jiminez, *IEEE J. Quantum Electron.*, 1975, **QE11**, 838.

[64] A. Sanchez, C. F. Davis Jr, K. C. Liu and A. Javan, *J. Appl. Phys.*, 1978, **49**, 5270.

[65] K. M. Baird, K. M. Evenson, G. R. Haines, D. A. Jennings and F. R. Peterson, *Opt. Lett.*, 1979, **4**, 263.

Far-infrared Laser Magnetic Resonance Spectra of Vibrationally Excited OH and OD

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Several new far-infrared laser magnetic resonance spectra of OH and OD have been detected in the reactions of H or D atoms with ozone. The strongest spectra have been assigned to rotational transitions in $v = 6$ OH and $v = 4$ OD of the $X\,^2\Pi_{3/2}$ state.

The OH radical is one of the most widely studied of all transient gaseous species, and is of fundamental importance in spectroscopy and in reaction kinetics and dynamics. Spectroscopic studies have ranged from the radiofrequency to the ultraviolet yielding a large amount of structural information which has been used to test *ab initio* calculations. Of particular interest in the present work are the rotational transitions of the $X\,^2\Pi$ electronic state both in the ground and excited vibrational levels. Rotational term values were first tabulated by Dieke and Crosswhite[1] for levels up to $v = 3$ based on the analysis of the $A\,^2\Sigma \rightarrow X\,^2\Pi$ system. Data on the higher vibrational levels have come from studies of the vibration–rotation Fourier transform spectrum.[2]

Recently, Coxon[3] has determined optimum molecular constants for OH based on the wealth of data available from optical, vibration–rotation and microwave spectra. His tabulated term values for OH from $v = 0$ to 5 are much more accurate than the earlier data and provide an excellent data set for calculating rotational transition wavenumbers. However, these term values exclude data based on the measurement of the rotational transitions themselves. Work by Clyne *et al.*[4a] on the A–X system of OD is a useful starting point for predicting approximate frequencies in the lower vibrational levels. However, much higher quality data have recently been published[4b] from a simultaneous fit to vibration–rotation, electronic and microwave spectra.

The transitions within the $X\,^2\Pi_i$ manifold of OH and OD that are amenable to study by far-infrared laser magnetic resonance (l.m.r.) can be approximately classified as: (i) pure rotational transitions within the $\Omega = 1/2$ or $3/2$ states and (ii) transitions where $\Delta\Omega = \pm 1$, which are forbidden electric dipole transitions in the limit of a pure Hund's case (a) molecule. However, although relatively weak the latter were among the first l.m.r. transitions discovered and assigned.[5] Early work on the ground vibrational state at 79.1 μm was later extended to $v = 1$, 2 and 3 at 78.4 and 79.1 μm.[6] Based on precisely measured or calculated g-factors these studies yielded accurate values of the $^2\Pi_{3/2}$, $J = \frac{3}{2} \leftrightarrow {}^2\Pi_{1/2}$, $J = \frac{1}{2}$ fine-structure spacing with change in vibrational quantum state. In contrast the allowed rotational transitions (i) are much stronger and in particular the OH $^2\Pi_{3/2}$ $v = 0$ $J = \frac{3}{2} \rightarrow \frac{5}{2}$ l.m.r. transition around 118 μm is one of the most common and widely used in kinetics.[7] However, because the

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rotational interval changes markedly with v, for the pure rotational transitions, it is difficult to obtain l.m.r. spectra arising from more than one vibrational state with a single laser line.   Several examples of both types of transition have recently been described by Geiger *et al.* for $v = 0$ OD$(X\ ^2\Pi)$.[8]

Fortunately there is a convenient and efficient source of vibrationally excited OH and OD radicals, namely the reaction of H or D atoms with ozone.[9]   At short reaction times it is relatively easy to generate considerable concentrations of vibrationally excited molecules at pressures of 1.3 mbar or less by this reaction.   In the present work we describe an extension of earlier studies[6] on vibrationally excited OH at 78.4 and 79.1 μm to pure rotational transitions in vibrationally excited OH and OD using other water-vapour laser lines.

The l.m.r. studies complement earlier electron paramagnetic resonance measurements[9–12] of vibrationally excited OH and OD which provide useful tests of the theoretical accuracy of the g-factors necessary to calculate the Zeeman parameters.

EXPERIMENTAL

The far-infrared laser magnetic resonance spectrometer has been described in detail elsewhere.[13]   The fast flow system used to generate OH† was similar to that employed in the earlier studies[6] but modified to maximise the effective sample volume by displacing the entrance and exit ports of the flow system in the magnetic-field region.   The nominal pumping speed was 4000 dm^3 min^{-1}.   Optimum signals of OH† were produced by discharging He (99.996 %), which had been passed through Teflon tubing slightly porous to air, in a 2450 MHz discharge and mixing the discharge products with ozone as close to the laser axis as possible.   Ozone was prepared by passing pure O_2 through a commercial ozoniser (Argentox mbH), storing on silica gel ($-78\ ^\circ$C) and displacing it from the trap as required with a flow of pure He.

The concentration of vibrationally excited OH was found to be critically dependent on the amount of H_2 present in accord with the known rapid relaxation[14] of OH† by H_2.   The addition of H_2 to the discharge was only of marginal value in increasing [OH†] and often yielded considerably smaller concentrations.   Vibrationally excited OD was produced by discharging D_2 + He mixtures and reacting the products with O_3.   For both OH and OD, concentrations of vibrationally excited species were relatively inert to pressure between 0.4 and 0.9 mbar.

Laser lines used in this study were those from H_2O and D_2O gas discharge lasers, namely:

$$H_2O \qquad 78.4,\ 79.1\ \text{and}\ 118.6\ \mu\text{m}$$

$$D_2O \qquad 84,\ 108\ \text{and}\ 171\ \mu\text{m}.$$

The frequencies of these lines are accurately known (± 1 MHz) with the exception of the D_2O line at 171 μm.   This line does not appear to have been used before in published l.m.r. work and Benedict *et al.*[16] give its wavenumber as 58.25 cm^{-1}.   Interchange between laser lines and suppression of higher order modes was greatly facilitated by incorporating an intracavity iris.   The magnetic field was calibrated by measuring the positions of other well-known spectra.   Examples of the strongest spectra obtained, with a He cooled bolometer detector, field modulation at 90 Hz and phase-sensitive detection are shown in fig. 1, 2 and 3 and discussed below.

RESULTS

ASSIGNMENT AND ZERO-FIELD SPACINGS

The assignment of the new spectra reported here to " pure " rotational transitions within the $^2\Pi_{3/2}$ manifold of OH and OD is relatively straightforward.   Allowed rotational transitions for levels up to $v = 5$ were first derived from Coxon's[3] term