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COLLEGE ON ATOMIC AND MOLECULAR PHYSICS: PHOTON ASSISTED COLLISIONS IN ATOMS AND MOLECULES

(30 January - 24 February 1989)

HIGH RESOLUTION SPECTROSCOPY OF ATOMIC OXYGEN: A CASE STORY

Lecture 4

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Napoli
Italy

M. INGUSCIO LECTURE N. 4

HIGH RESOLUTION SPECTROSCOPY
O ATOMIC OXYGEN : A CASE STORY

a) COLLISIONAL PRODUCTION AND DESTRUCTION OF THE ATOM. FLUORESCENCE AND OPTOGALVANIC SPECTRA. HIGH RESOLUTION INTERMODULATED SPECTROSCOPY

b) FINE STRUCTURE RESOLUTION

c) ISOTOPE EFFECT MEASUREMENTS.

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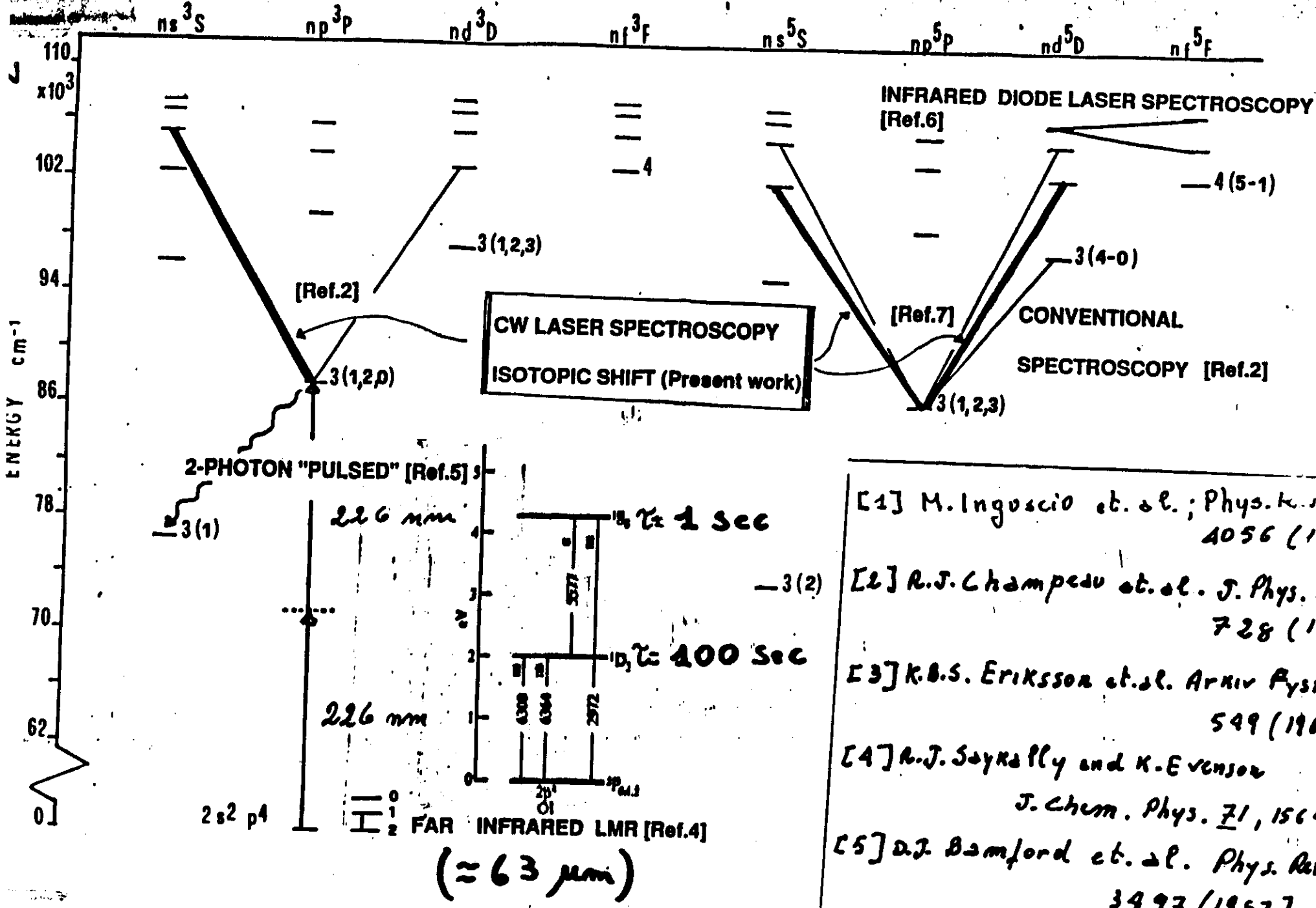


[1] M. Inguscio et. al.; Phys. Rev. A 37, 4056 (1988)

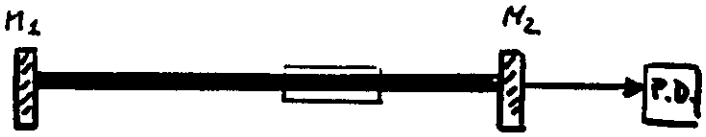
[2] R.J. Champeau et. al. J. Phys. B 8, 728 (1975)

[3] K.B.S. Eriksson et. al. Arkiv Fysik 29, 549 (1963)

[4] R.J. Saykally and K. Evenson J. Chem. Phys. 71, 1564 (1979)

[5] D.J. Bamford et. al. Phys. Rev. A 36, 3497 (1987)

[6] P.R. Brown et. al Chem. Phys. ...



$P_{in} = P_{out} \cdot \frac{1}{T_2}$

Intracavity Spectroscopy

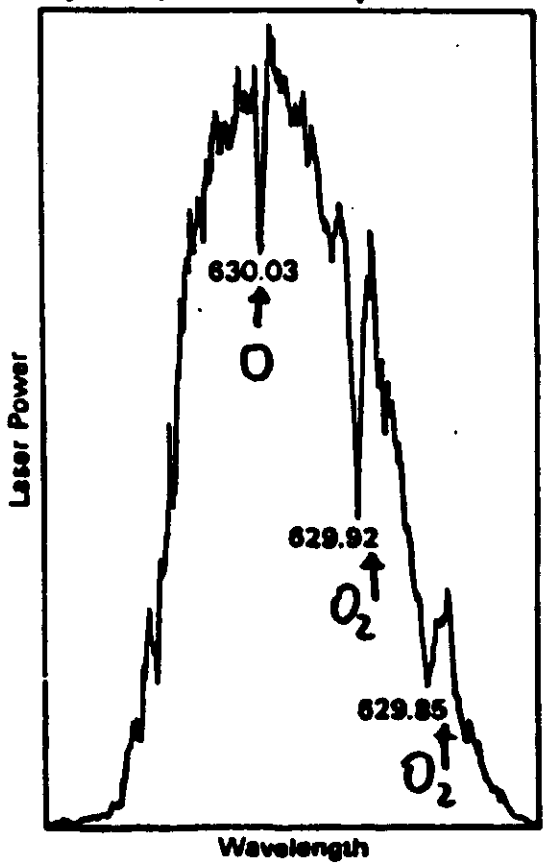
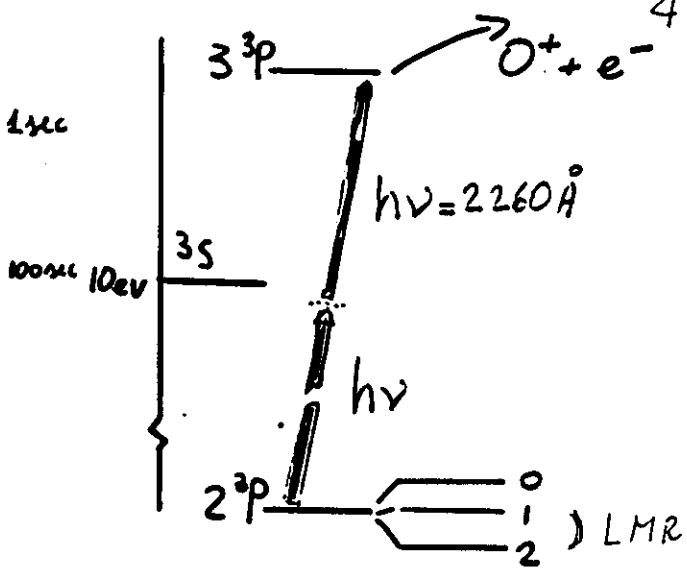


Fig. 1. Intracavity spectrum of the $O(^3P_2) \rightarrow O(^1D)$ transition at 630.03 nm, centered in the laser's spectral profile. A pair of O_2 lines at 629.92 and 629.85 nm is also present. The pumping power is about twice threshold ($P^* = 2$). The tuning element is a tuning wedge.

FORBIDDEN TRANSITIONS

Goldsmith J Chem Phys 78, 1610 (83)

TWO PHOTON



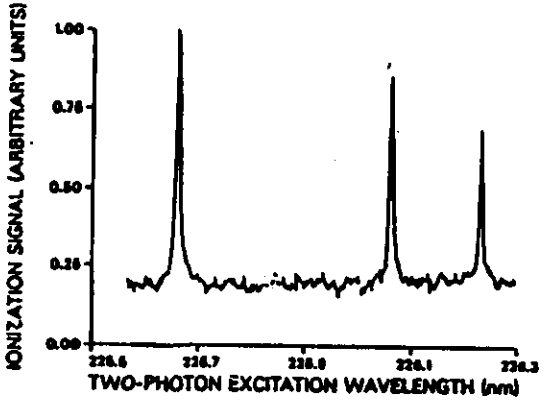
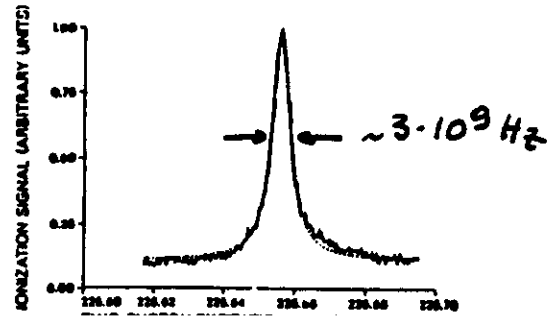


FIG. 1. Ionization signal from atomic oxygen recorded in an atmospheric pressure stoichiometric hydrogen/oxygen/argon flame. There are three peaks because of fine-structure splitting of the 2^3P state.



TWO PHOTON

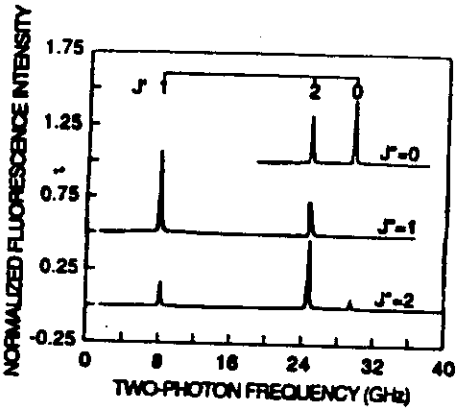


FIG. 1. Doppler-free spectra for the $3p\ ^3P_{J'} \leftarrow 2p\ ^3P_{J''}$ two-photon transitions in atomic oxygen. The level of two-photon excitation is monitored using fluorescence from the $3p\ ^3P_{J'} \rightarrow 3s\ ^3S_1$ transition at 845 nm, normalized to the square of the laser intensity. Doppler-limited absorption forms a broad pedestal underneath each peak. Each spectrum has the same integrated area. The middle and top spectra are displaced from the bottom one by 0.5 and 1.0 vertical units, respectively.

TABLE I. Experimental and theoretical (in parentheses, from Ref. 5) integrated two-photon cross sections for the $3p\ ^3P_{J'} \leftarrow 2p\ ^3P_{J''}$ transition in atomic oxygen.

		$\sigma^{(2)}(J' \leftarrow J'')$		
J''	J'	Absolute (10^{-36} cm^4)[a]		Relative[b]
2	2	13.2	(9.42)	0.706 ± 0.077(0.714)
2	1	3.63	(2.61)	0.194 ± 0.043(0.198)
2	0	1.87	(1.16)	0.100 ± 0.040(0.088)
1	2	6.98	(4.34)	0.373 ± 0.067(0.329)
1	1	11.7	(8.86)	0.627 ± 0.067(0.671)
1	0	0	(0)	0 (0)
0	2	9.01	(5.79)	0.482 ± 0.045(0.439)
0	1	0	(0)	0 (0)
0	0	9.69	(7.41)	0.518 ± 0.045(0.561)

[a]These numbers must be multiplied by a line-shape factor $g(\omega - \omega_{J'})$ to get the effective cross section at any given two-photon radial frequency, ω. If the line-shape function is a 300-K Doppler profile $g(0) = 1.81 \times 10^{-11}$ sec.
[b]Experimental error limits are $\pm 1\sigma$, where σ is the sample standard deviation.

Meccanismi di produzione / distruzione di ossigeno atomico

$$\left.\begin{array}{l} Ne^+ + O_2 \rightarrow (O_2^+)^* + e^- + Ne \\ O_2^+ + e^- \rightarrow O^* + O \end{array}\right\} \text{PRODUZIONE}$$

$$\left.\begin{array}{l} O^* + O_2 \rightarrow 3O \end{array}\right\} \text{DISTRUZIONE}$$

Volume 120, number 3

COLLISIONS WITH METASTABLE NOBLE GASES IN A DISCHARGE.

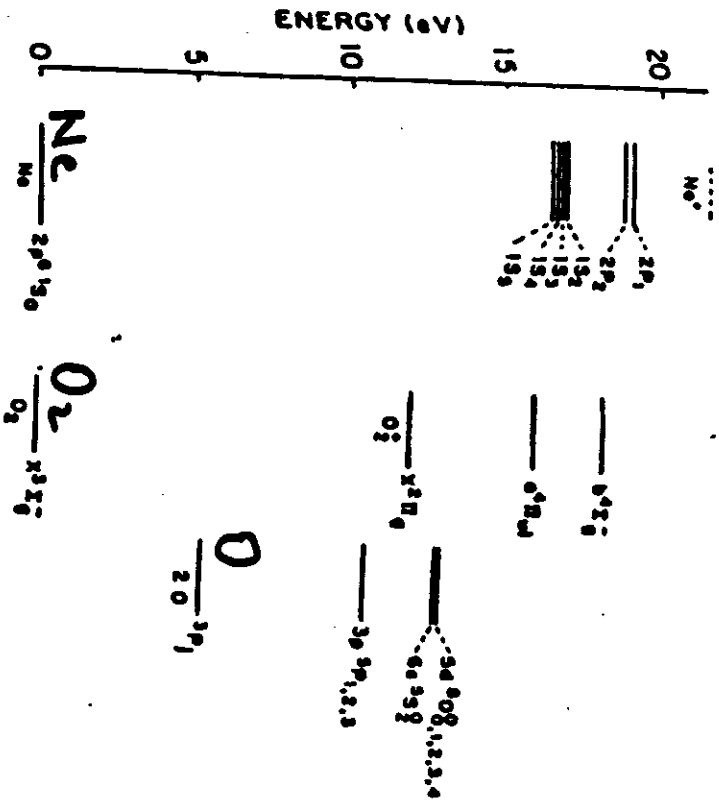


Fig. 2. Relevant energy levels for a Ne/O_2 plasma. See table 1

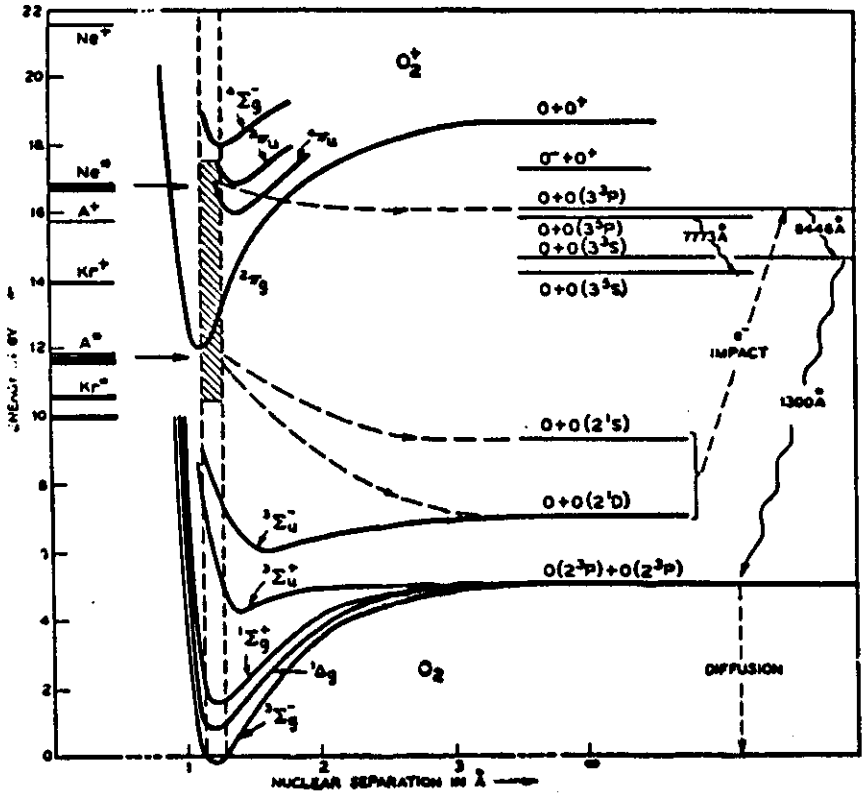


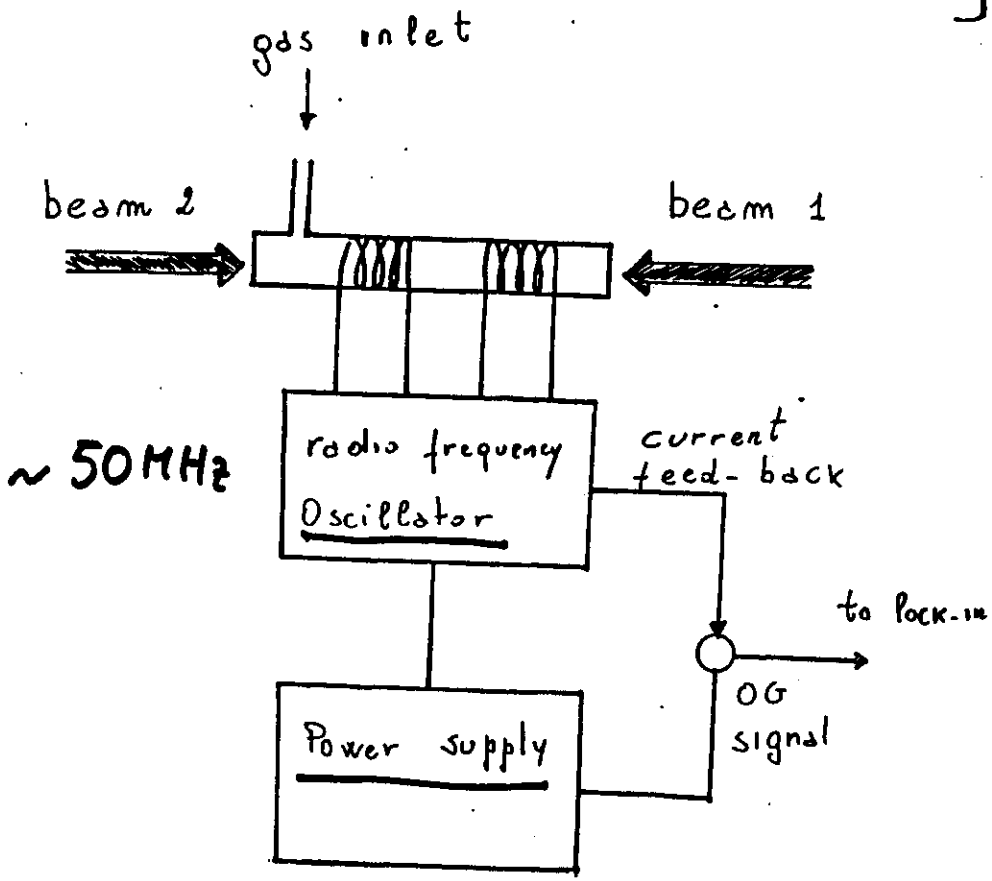
FIG. 1. Relevant energy levels. Oscillation occurs on the 8446 Å line of atomic oxygen. The paths of excitation in the Ne-O_2 and Ar-O_2 masers are shown by the arrows.

$$\begin{cases} Ne^* + O_2 \longrightarrow Ne + O + O^* \\ O^* + O_2 \longrightarrow 3O \\ O + O + Ne \longrightarrow O_2 + Ne^* \end{cases}$$

$$[O^*] \propto \frac{[Ne]\,[O_2]}{\alpha\beta\,[O_2]^2 + \text{const}\,[O_2]}$$

$$[Ne^*] = \frac{\text{const}\,[Ne]}{\beta[O_2] + \text{const}}$$

PRESENCE OF O_2^+

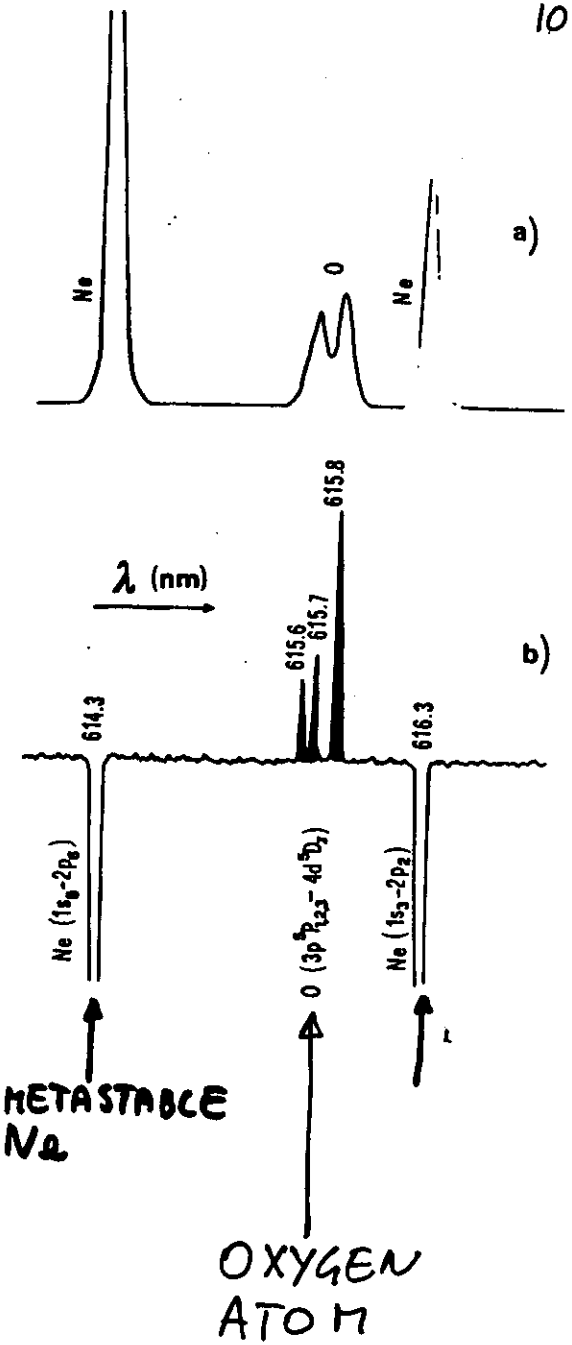


MOGS detection scheme

in a r.f. discharge.
(NO INTERNAL ELECTRODES)

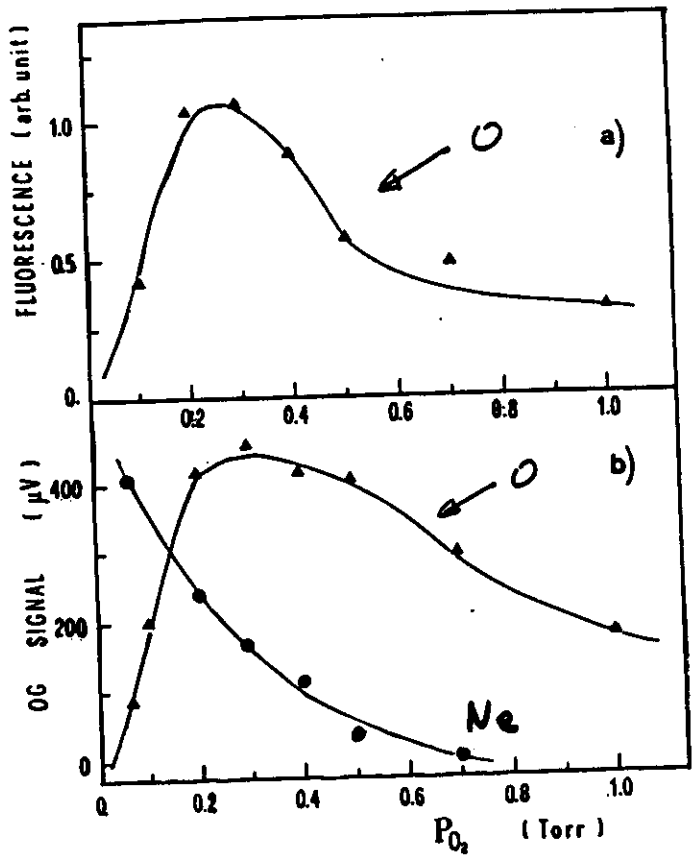
FLUORESC.
O_2 .1 Torr
Ne 10 Torr

O. G.



FL

O4



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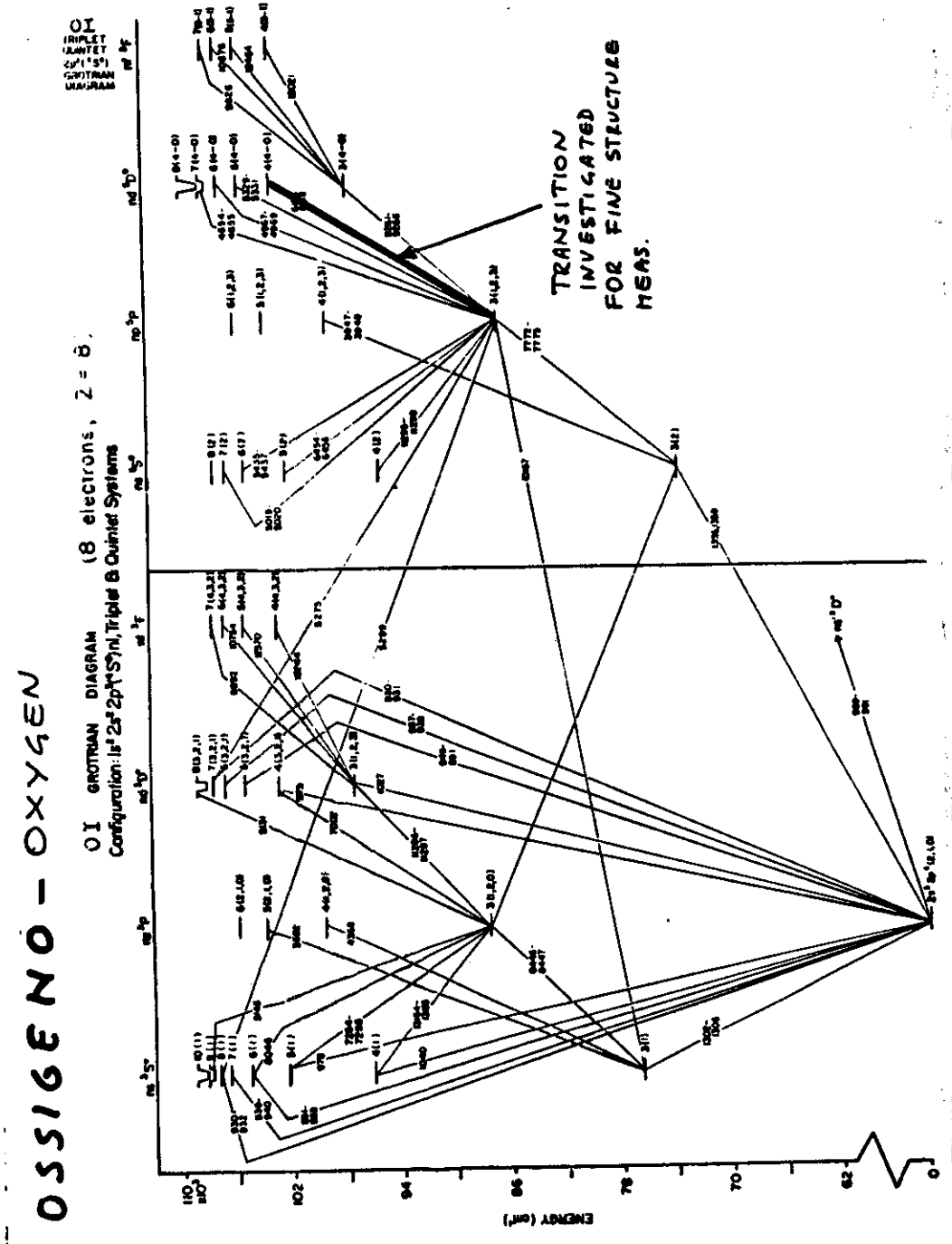
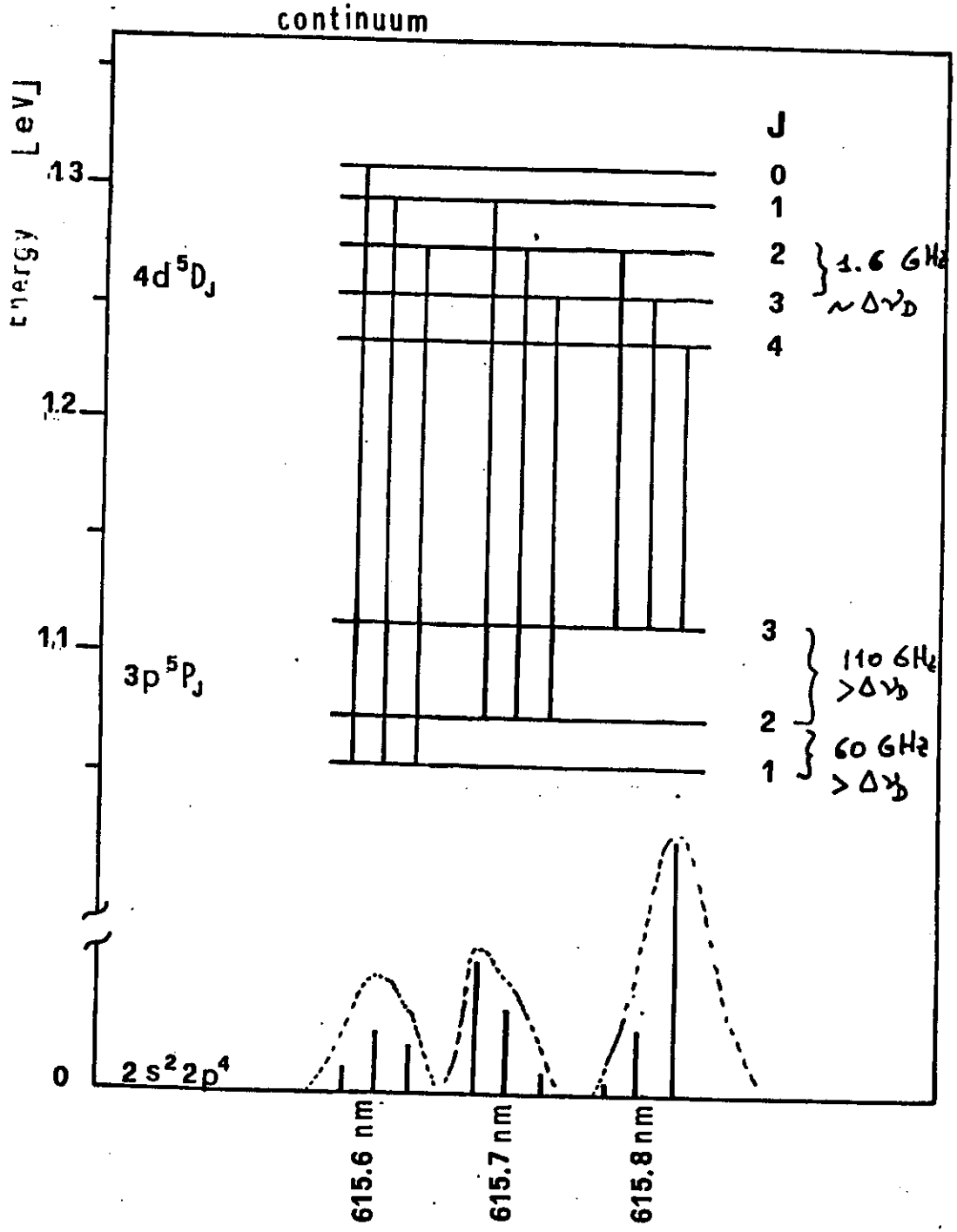
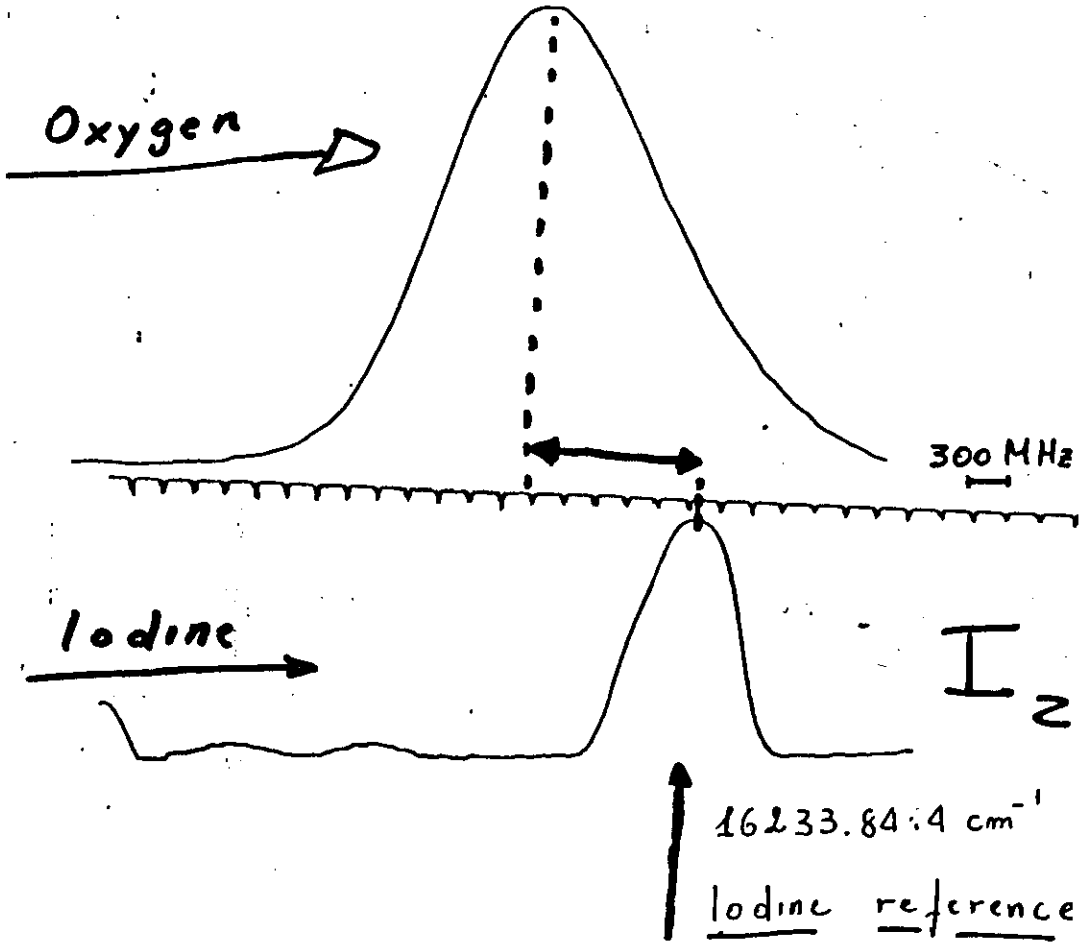




Doppler profile of 6158.19 Å transition

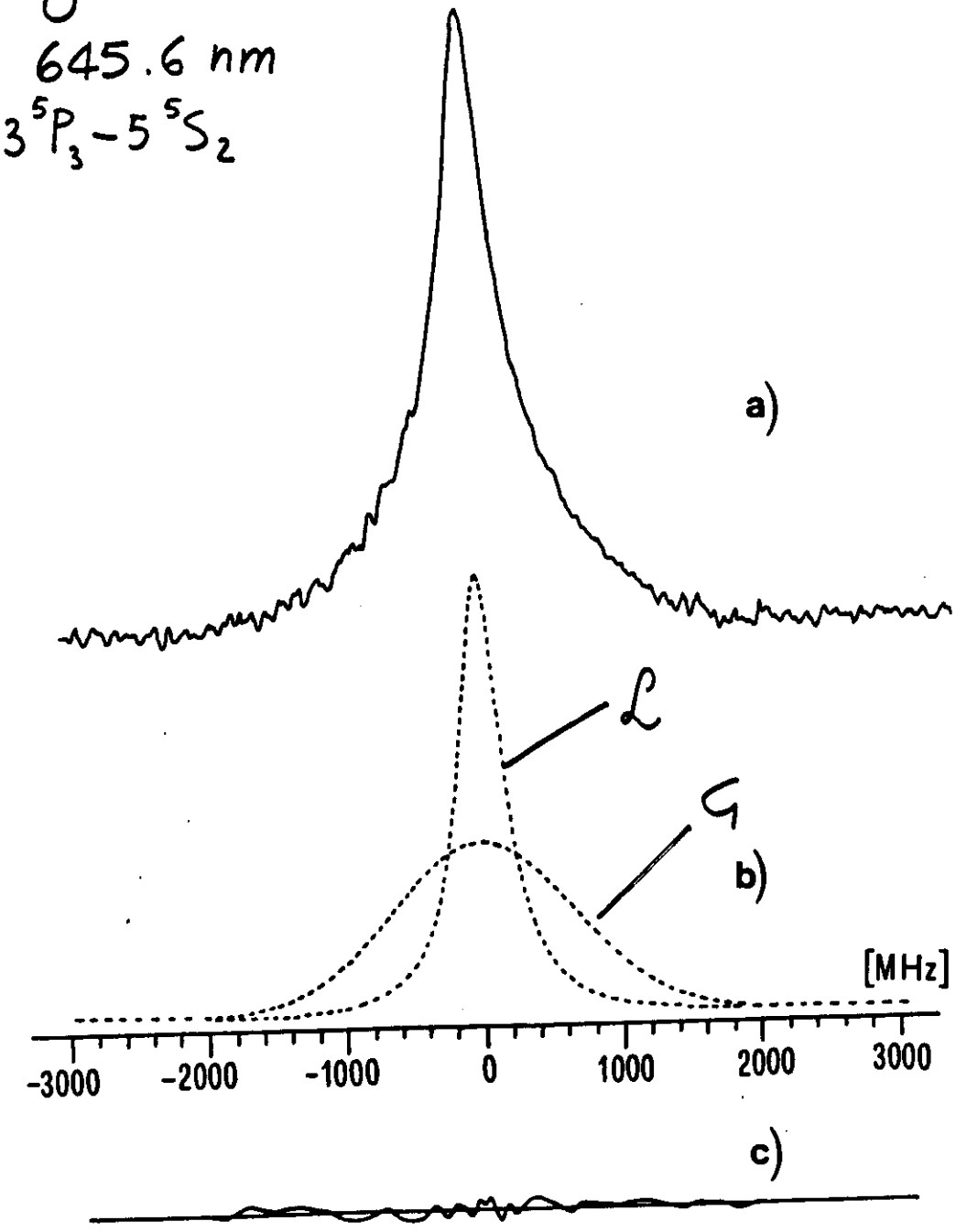


FIT TO THE SUM OF THREE "VOIGT" PROFILES

Fig. 4

APPARATUS FOR HIGH RESOLUTION.

O
645.6 nm
$3^5P_3 - 5^5S_2$



$$A\left[\frac{\gamma^2/4}{\gamma^2/4+(\nu-\nu_0)^2}+C\exp\left(-\frac{\nu^2\nu_0}{\delta\nu_D}\right)^2\right]\otimes G$$

$$C = 2\sqrt{\pi \ln 2}\,\frac{\Gamma\gamma}{\delta\Delta_D}$$

O_2/Ar (.1/5 Torr)

$\Delta\nu_D = 2$ GHz (520 °K)

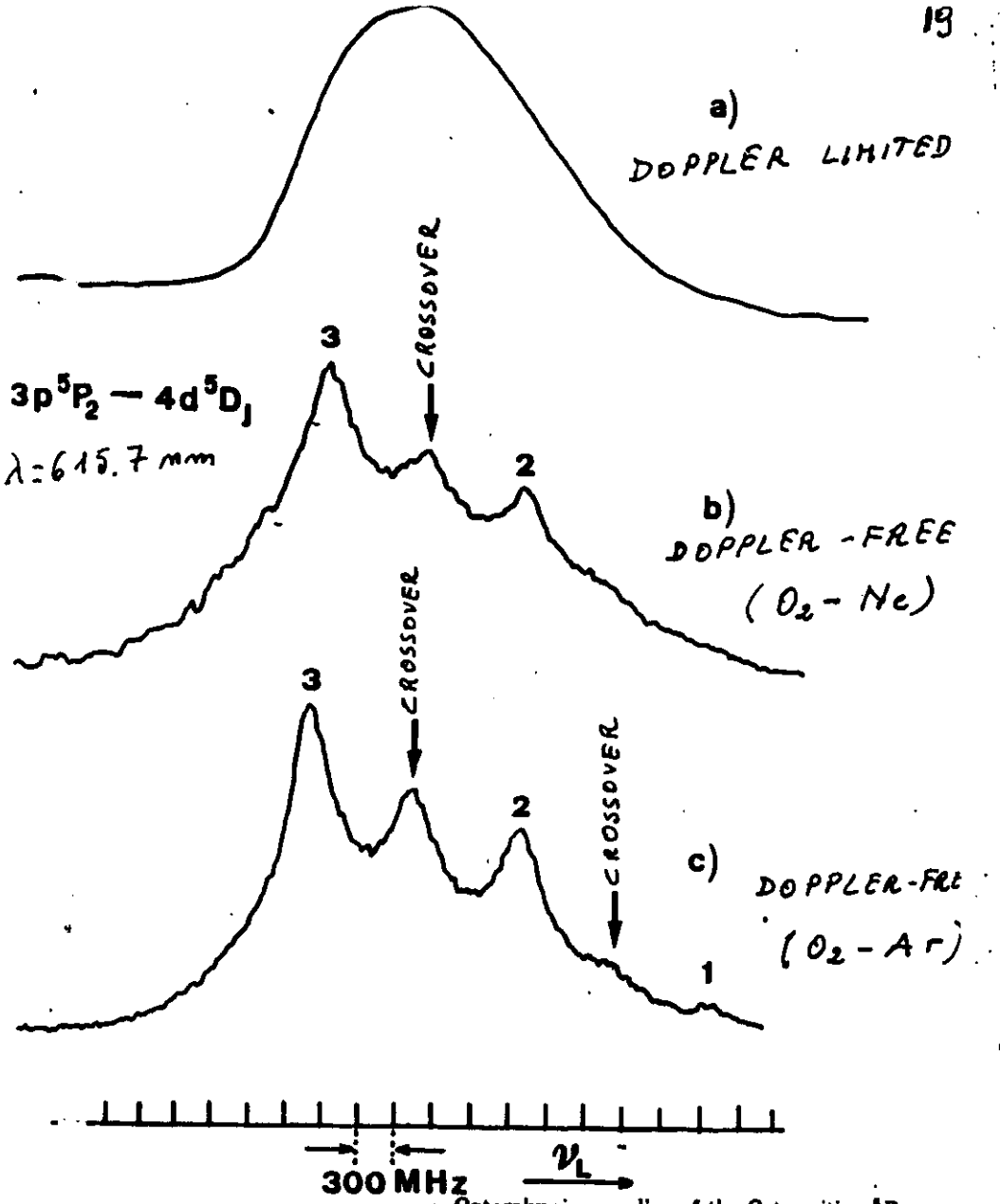
$\gamma = \Delta\nu_{hom} = 386$ MHz (FWHM)

$C = 0.39$

O_2–Ar (.1–5 Torr) $\quad G = 2(\pi \ln 2)^{1/2}\,\frac{\Gamma\gamma}{\delta\Delta D}$

$\Delta\nu_D = 2$ GHz (520 K)

$\gamma = 386$ MHz (FWHM)



Optogalvanic recording of the O transition $^5P_2 \rightarrow {}^5D_{3,2,1}$ using a single mode dye laser. The Doppler broadened signal is shown in a) while the intermodulated scheme is used in b) and c). Different gas mixtures were used, namely O_2/Ne in b) and O_2/Ar in c). The total scan for the Doppler registration is 2.7 times broader than the Doppler-free recordings. Arrow denote the cross-over peaks.

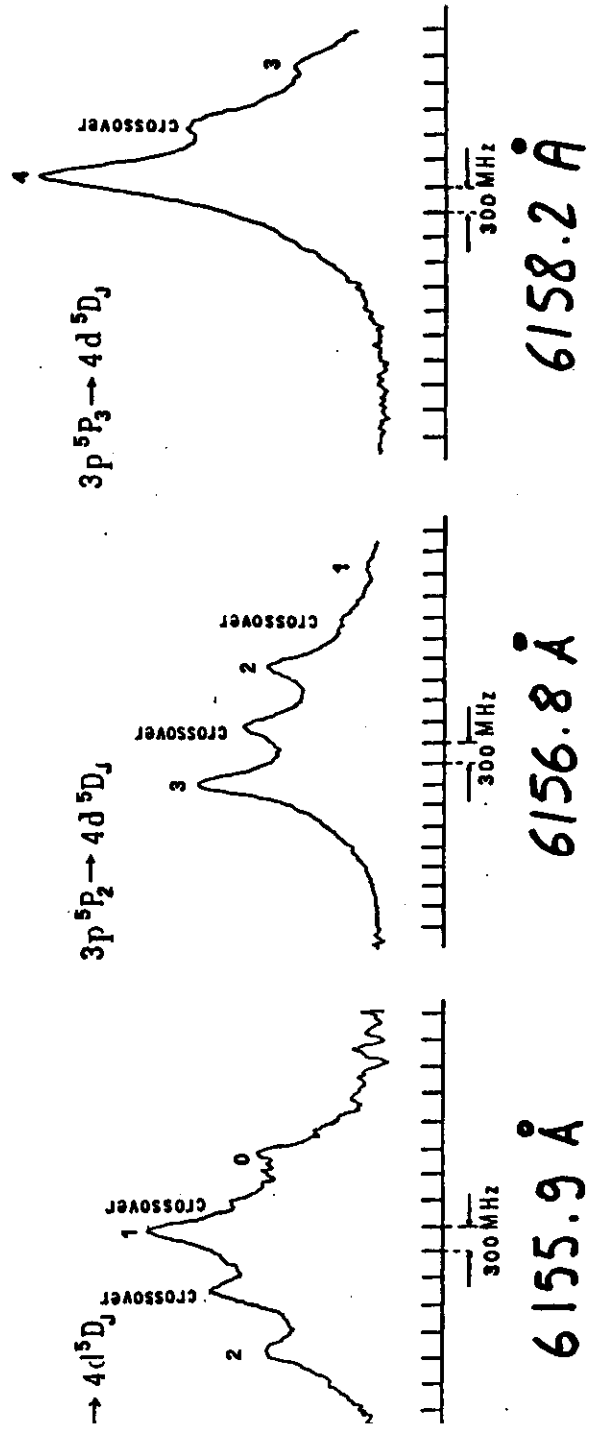


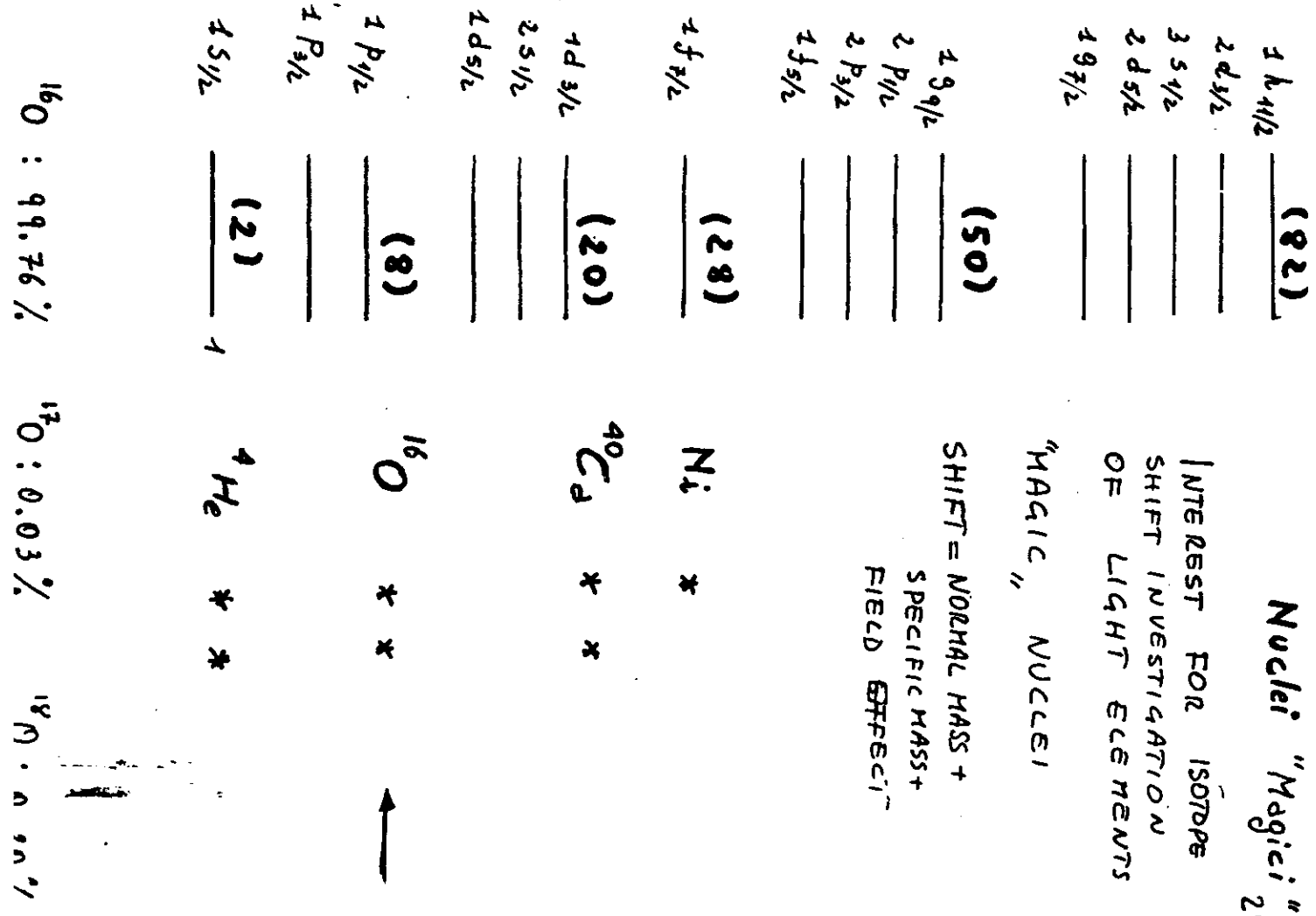
Fig. 3

Δ_{ij}	Our results [MHz] [1] Exp.	Theor.	[2]	[3]
$1\,^5D_{4,3,2,1,0}$ Δ_{01}	735 (20)	752	786 (51)	720 (200)
Δ_{12}	1360 (20)	1341	1416 (24)	1469 (200)
Δ_{23}	1594 (20)	1605	1680 (24)	1769 (200)
Δ_{34}	1382 (20)	1380	1407 (30)	1229 (200)
$^5P_{1,2,3}$ Δ_{12}	59.3 (0.2) GHz			60.6 GHz
Δ_{23}	110.3 (0.2) "			110.2 "

[1] M. INGUSCIO et al. Phys. Rev. A 37, 4056 (1988)

[2] R.J. CHAMPEAU et al. J. Phys. B 8, 728 (1975)

[3] K.B.S. ERIKSSON et al. Arkiv Physik 24, 549 (1963)

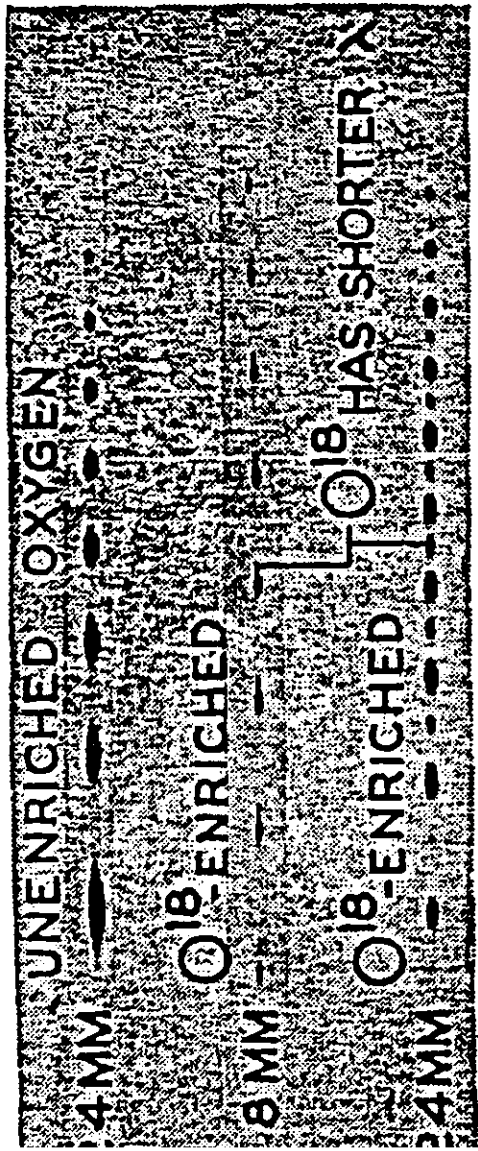


CLASSICAL SPECTROSCOPY INVESTIGATION

L OF THE OPTICAL SOCIETY OF AMERICA VOLUME 43, NUMBER 2 FEBRUARY, 1953

Isotope Shift In Neutral Oxygen*†

LEE W. PARRETT AND JOHN R. HOLMES
University of Southern California, Los Angeles, California
(Received October 14, 1952)



i. 1. Interferometric patterns of the singlet line λ8820, showing isotope structure. 24 mm and 8 mm spacers.

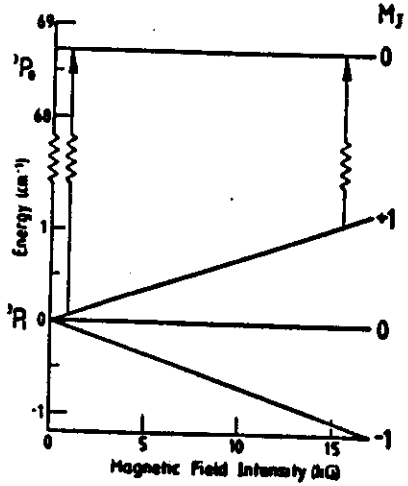
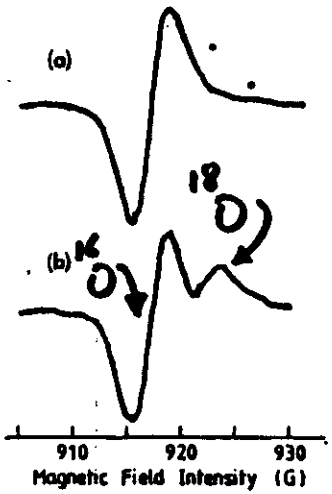


FIG. 1. LMR lines at 917 and 15443 G obtained with the CH_3OD and CH_3NH_2 lasers respectively, and their assignment to the (J, M_J) 0, 0 — 1, +1 transition in O^3P_J.

ISOTOPE SHIFT ON $^3P_1 - {}^3P_0$



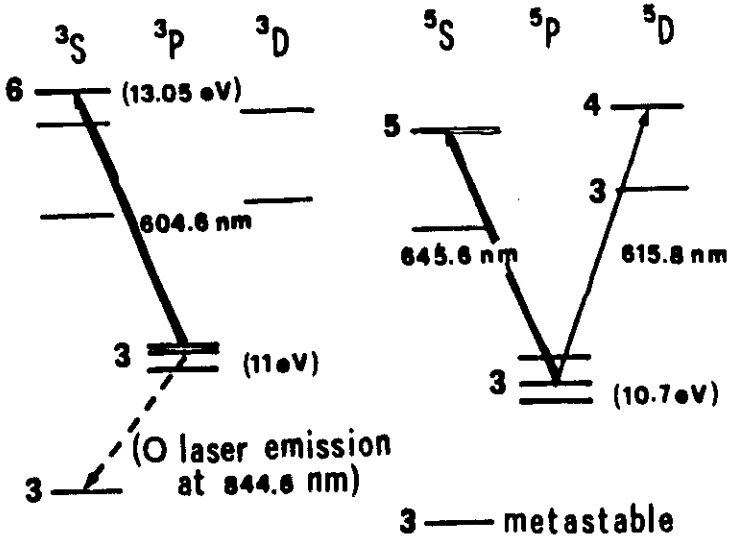
natural ^{16}O

enriched (20% ^{18}O

FIG. 2. LMR spectrum of $O(^3P)$ with the CH_3OD laser at 145.7 μm (a) microwave discharge in $^{16}O_2$; (b) discharge in O_2 enriched with 20% $^{18}O_2$.

8, No. 3, 1 February 1978

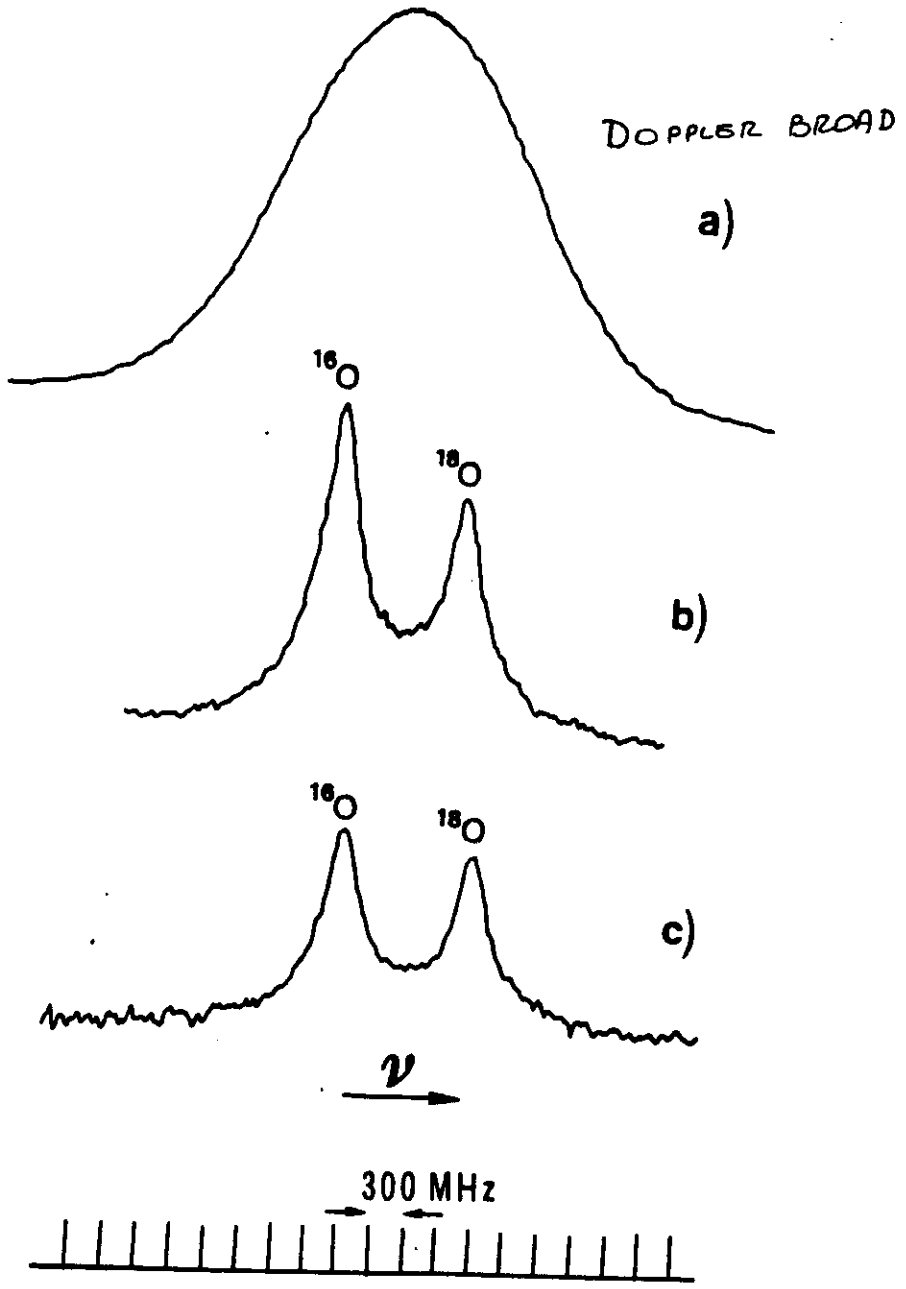
I.S. = 10.5 MHz



TRANSITIONS USED FOR THE SUBDOPPLER MEASUREMENT OF I.S.

Fig. 1

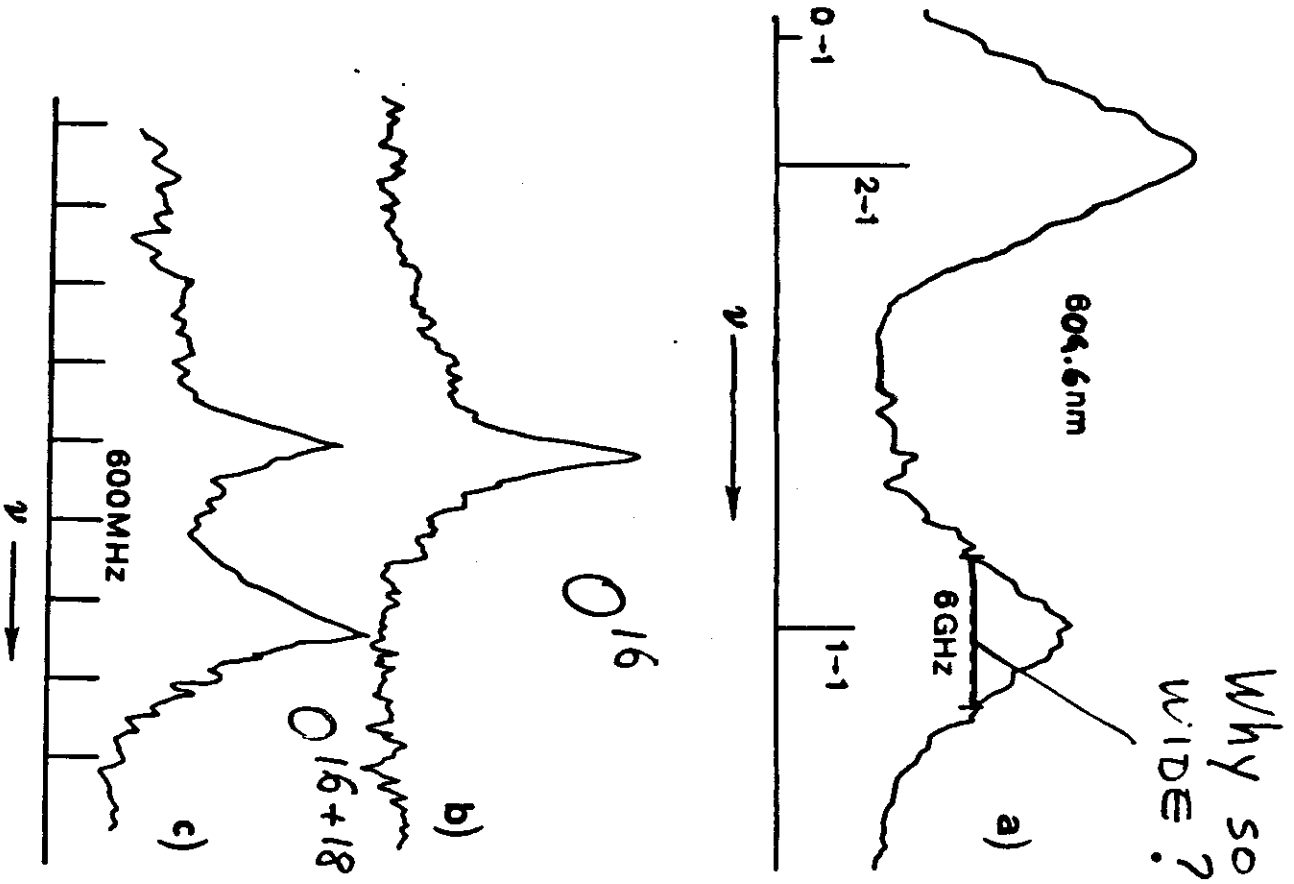
$\lambda = 645.6$ nm



L.W. Parker and J.R. Holmes
J. Opt. Soc. Am. 43, 103 (1953)

ope

Transition	Wavelength (nm)	Isotopic shift present work (MHz)	Previous data [8] (MHz)
$3p\ ^5P_3 - 4d\ ^5D_4$	615.8	1310 (40)	< 900
$3p\ ^5P_2 - 5s\ ^5S_2$	645.5	1160 (20)	—
$3p\ ^5P_3 - 5s\ ^5S_2$	645.6	1160 (20)	< 600
$3p\ ^3P_2 - 6s\ ^3S_1$	604.6	1350 (40)	—



• • • effect of the collisional energy transfer ?

WORK IN PROGRESS

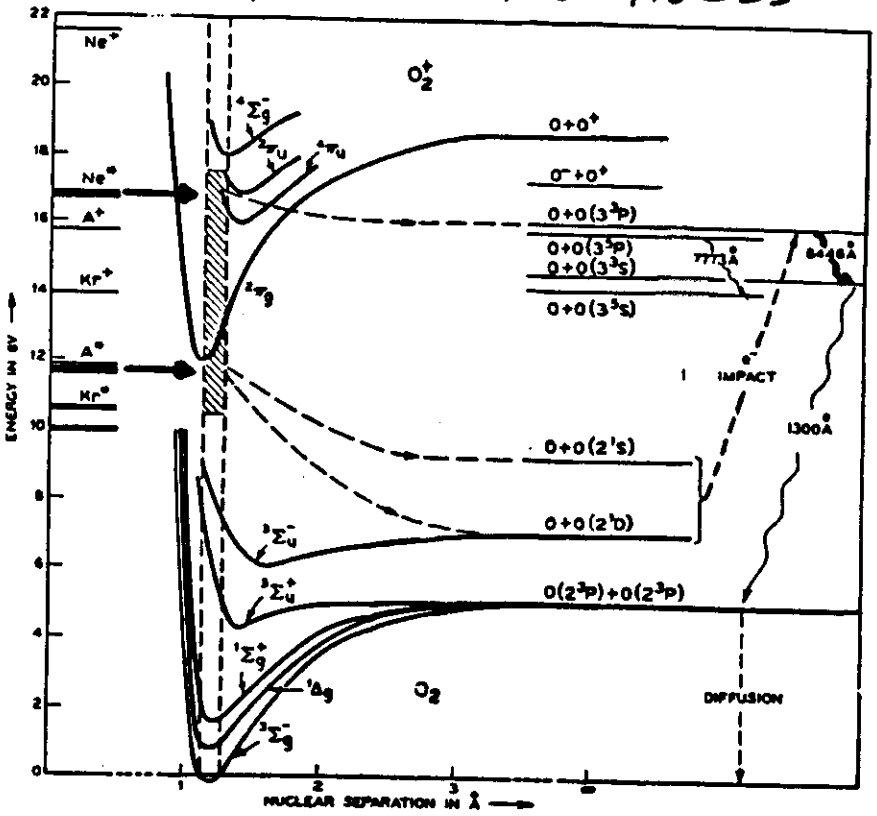


FIG. 1. Relevant energy levels. Oscillation occurs on the 8446Å line of atomic oxygen. The paths of excitation in the Ne–O_2 and Ar–O_2 masers are shown by the arrows.

$$Ne^* + O_2 \rightarrow O_2^+ + e^- \rightarrow O^* + O$$

$$Ar^* + O_2 \rightarrow O_2^+ + e^- \rightarrow O(2^1S) + O + \tilde{\lambda}$$

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High-resolution optical spectroscopy of atomic oxygen

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AMERICAN INSTITUTE OF PHYSICS

High-resolution optical spectroscopy of atomic oxygen

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Dipartimento di Scienze Fisiche, Università di Napoli, 80125 Napoli, Italy
(Received 8 December 1987)

We report sub-Doppler laser spectroscopy of atomic oxygen. The atom is detected as a trace in a noble-gas radio-frequency discharge by means of optogalvanic effect. The fine structure of the $2p^3 3p\ ^5P_{1,2,3} \rightarrow 2p^3(4S^0)4d\ ^5D_{4,3,2,1,0}$ transitions is fully resolved and preliminary values for the upper level splittings are: $\Delta_{4,3}=1382(20)$ MHz, $\Delta_{3,2}=1594(20)$ MHZ, $\Delta_{2,1}=1360(20)$ MHz, and $\Delta_{1,0}=735(20)$ MHz. The best values so far derived from conventional spectroscopy are one order of magnitude less accurate and in marginal agreement with our data.

Modern laser techniques, such as saturation or intermodulated spectroscopy, have proved to be very efficient in eliminating Doppler broadening. A multitude of atomic species and transitions have been carefully investigated, especially after the demonstration of possible combination with unconventional schemes like optogalvanic detection.[1]

Atomic oxygen has so far been elusive to any high-resolution investigation, which on the contrary would be highly desirable. Indeed, this atom is an important intermediate in fundamental physical and chemical processes; it is the third abundant element after hydrogen and helium. Its spectral features, of fundamental interest in the upper atmosphere, are relatively faint in the solar spectrum, in part masked by H_2O absorptions, and accurate laboratory measurements could expedite identification.

The lack of high-resolution investigations of oxygen is caused by the fact that, like for many other light atoms, the resonance lines are in the vacuum ultraviolet (VUV) region, where tunable radiation of high intensity and spectral purity is hard to produce. The use of pulsed sources, which are well suitable for lifetime measurements[2] or time-resolved spectroscopy, is often necessary. However, the pulsed linewidths limit the precision of the determination of spectral features.[3,4] The ground-state fine-structure splittings are the only high-accuracy data available for oxygen since they could be directly measured at far infrared frequencies[5,6] where Doppler effect is negligible. The very low probability transitions in the red from the ground state were detected by cw laser intracavity configuration[7] but with no high resolution. Rydberg transitions were observed in the infrared.[8]

In this Rapid Communication, we describe the first Doppler-free investigation of atomic oxygen. It is performed in the visible and it promises to be a powerful tool for studying optical transitions in oxygen, including those involving high-lying states.

We produce atomic oxygen by dissociation of O_2 mol cule in a moderate power radio-frequency dischar (about 50 W at 60 MHz). The discharge is substained b a buffer noble gas (Ne or Ar) at rather high pressure (4- mbar) with the addition of O_2 at low partial pressure (few parts in 10^3). As we shall discuss later, the hig buffer gas pressure causes significant inhomogeneous v locity changing effects, but does not prevent sub-Dopp resolution with homogeneous linewidths at least one ord of magnitude narrower than the Doppler ones. Th discharge sample configuration naturally leads to a dete tion scheme based on the change of impedance under res nant absorption of photons (optogalvanic spectroscopy[9] We have studied the $3p\ ^5P_{1,2,3} \rightarrow 4d\ ^5D_{4,3,2,1,0}$ multip transitions at 616 nm. Nine fine-structure componen are originated, as shown schematically in Fig. 1. Doppler-limited spectroscopical investigations, only t splittings of the lower ^5P state are sufficiently large to resolved and only three separated lines can be observed 6158.19, 6156.78, and 6155.99 Å. Indeed, the ^5P separ tions are known[10] with the typical uncertainty of a fe hundred MHz.

In our experiment, tunable radiation is provided by a actively stabilized rhodamine 6-G ring dye las (Coherent 699-21). The laser beam is split into tw beams of roughly equal intensity. One beam is chopped a frequency of 350 Hz and the other at 490 Hz by t same mechanical chopper which provides separate refe ence signals at each of the two frequencies and at the su frequency of 840 Hz. The two beams counterpropaga through the discharge cell. This is a Pyrex tube 150 m long containing the oxygen–noble-gas mixture and plac inside two sets of coils of the same diameter of the cell mm). The discharge is maintained by an oscillator fed b

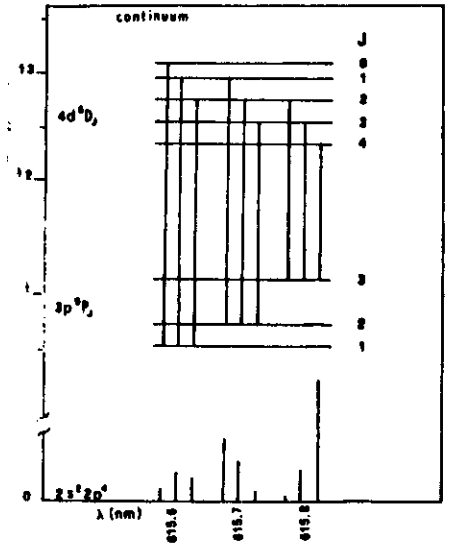

FIG. 1. Partial oxygen-atom level scheme with the transitions ed to demonstrate sub-Doppler resolution. In the lower part, : relative oscillator strengths are shown.

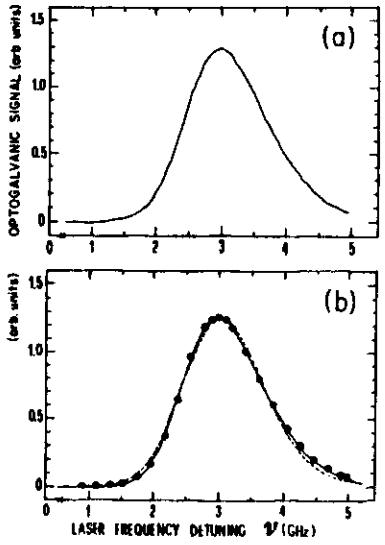

FIG. 2. Doppler-broadened line shape of the $^5P_3 \rightarrow D_{4,3,2}$ overlapping transitions. In (a) the experimental optogalvanic recording is reported. In (b) the experimental recording is fitted to the existing data from conventional spectroscopy (dashed line). A better fit (solid line) is obtained using for the parameters of the three overlapping Gaussians the values directly obtained from the present sub-Doppler investigation.

current stabilized power supply. At the resonance, the ange in the impedance of the discharge is recorded with gh sensitivity by monitoring the change of the feedback ;nal on the stabilized power supply. The laser wave- ıgth is determined by recording the absorption from a I_2 ll, while the frequency scan is calibrated by means of e markers from a 300-MHz free spectral range confocal ıbry-Perot interferometer.

A Doppler-broadened recording, obtained blocking one the two counterpropagating beams, is shown in Fig. a) for the unresolved triplet $^5P_3 \rightarrow {}^5D_{4,3,2}$ at 6158.2 Å. ;-Ne mixture in the ratio of 5×10^{-3} for a total pressure 9 mbar was used. The recording signal to noise ratio is good as 100:1 with a time constant of 1 s.

The fine-structure multiplets are directly resolved by using the intermodulated scheme of detection[1] and the results are shown in Fig. 3 for all the components originating from the ^5P levels. These measurements were performed using a O_2-Ar (1:45; total pressure 4.6 mbar) mixture. Total signals with Ar were comparable with those with Ne, but the contrast between the Doppler-free contribution and the broad pedestal was higher. The observed homogeneous linewidth of about 250 MHz is due primarily to pressure broadening, while a power broadening cannot be excluded since the laser intensity could not be reduced to less than 10 W/cm^2. In addition to the

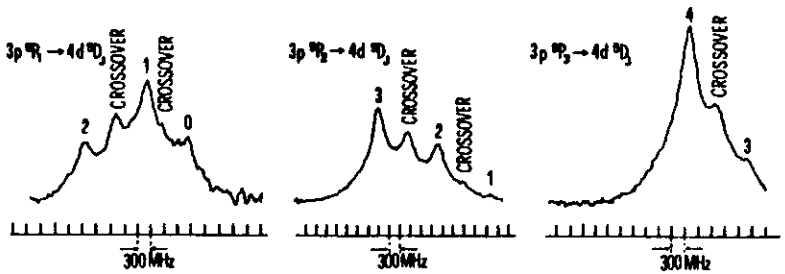

FIG. 3. Doppler-free recording of the oxygen $^5P \rightarrow {}^5D_{4,3,2,1,0}$ transitions at 6155.99, 6156.78, and 6158.19 Å using intermodulated dio-frequency optogalvanic technique.

fine-structure components, also the associated crossovers are recorded with comparable intensity. This last feature seems to be common to measurements in relatively high-pressure discharge[1] and it is possibly suggestive of a contribution of the velocity changing collisions also to the crossover signals.

A quantitative analysis of the line shapes has been performed following the model introduced earlier in Ref. 11 and then extended in Ref. 12 to take into account the case of "weak" collisions. In the hypothesis of a homogeneous width γ much smaller than the Doppler one $\Delta\nu_D$, each intermodulated component line shape can be assumed to a good approximation as the superposition of a Lorentzian $L(\nu)$ (Doppler-free signal) and a Gaussian pedestal $G(\nu)$ caused by velocity changing collisions:

$$S = A[L(\nu) + CG(\nu)] \qquad (1)$$

where S denotes signal, L has the width γ and G the width $\Delta\nu_D/\sqrt{2}$, A is a normalization constant, and C represents the weight of the collisional pedestal. Under our experimental conditions, involving rather high gas pressures, C is found to range from 0.1 to 0.5.

By fitting the experimental data, we obtain values for the relative positions of the maxima only slightly different (less than 2%) from those directly inferred from the recorded spectra. Moreover, no appreciable deviations have been found when the fits have been performed with Voigt profiles (γ comparable to $\Delta\nu_D$) instead of Gaussian functions. The ^5D sublevel separations in some cases (e.g., the $\Delta J_{1,2}$) can be obtained in two independent ways from the recordings, using transitions originating from different ^5P sublevels. In this case, the internal consistency is of a few percent for the individual measurements. By repeating the measurements several times, also changing the buffer gas, and fitting all the data we can give for the fine-structure splitting the values in Table I, with quoted uncertainties of 1 standard deviation. In general, the present accuracy is better than 1% except for the 0-1 separation which can be deduced from only one multiplet (6155.99 Å) and in addition is the weakest component of that multiplet. In Ref. 10 the accuracy is given only for levels directly measured (120 MHz), while it is not clearly stated for unresolved fits. The 200-MHz estimate in Table I seems to us to be a reasonable assumption.

The comparison with the data from conventional spectroscopy analysis is interesting not only for the improvement in the accuracy but also in view of verifying the assumptions made in that analysis.[10] In order to fit the line shape to the sum of three overlapping and unresolved Doppler-broadened Gaussians in Ref. 10, it had to be assumed the relative values between the fine-structure intervals in the high ^5D terms to be the same as for the $3d\,^5D$, the only ones directly observable. The present direct measurements show, for the splitting ratios, a deviation ranging from 2% to 25%. This is stimulating in view of extending similar measurements on even higher ^5D multiplets with $n = 5,6,\ldots$, still accessible to dye lasers and investigating the actual dependence of the splittings at present only postulated to be proportional to n^{-3}. Also, the relative intensity of the resolved components is found to follow the assumptions according to LS coupling[10] only within a few tens of a percent. The better spectral knowledge now available can be qualitatively evidenced also in the Doppler limited measurements that in Fig. 2(b) are fitted using Voigt profile to the previous (dashed line) and present parameters (solid line). The width of the Gaussians obtained from the fit is about 2 GHz, corresponding to the Doppler broadening at 520 K, and the Lorentzian contribution to the linewidth results of 230 MHz.

TABLE I. Fine-structure splittings in the atomic oxygen $2p^3(4S^0)4d\,^5D_{4,3,2,1,0}$ levels as obtained from sub-Doppler spectroscopy. For comparison the data deduced in conventional spectroscopy are reported. Ratios between adjacent splittings are also compared.

Δ_{ij}	Our results (MHz)	Ref. 10 (MHz)
$\Delta_{0,1}$	735(20)	720(200)
$\Delta_{1,2}$	1360(20)	1469(200)
$\Delta_{2,3}$	1594(20)	1769(200)
$\Delta_{3,4}$	1382(20)	1229(200)
$\Delta_{0,1}/\Delta_{1,2}$	0.54	0.49
$\Delta_{1,2}/\Delta_{2,3}$	0.85	0.83
$\Delta_{2,3}/\Delta_{3,4}$	1.15	1.44

Our experiment could not improve the accuracy of the splittings in the ^5P level because each component position could only be evaluated relative to Doppler-broadened iodine lines, used for laser wavelength calibration.

The present results demonstrate that atomic oxygen can be produced in enough amount even in highly excited states and still under environmental conditions well suitable for high-resolution spectroscopy. Intermodulated radio-frequency optogalvanic spectroscopy has been used for the sub-Doppler recording of $3p\,^5P \rightarrow 4d\,^5D$ transitions. Improvements in the sensitivity, for instance, using heterodyne technique,[13] could allow a narrowing of the linewidth. However, the present resolution is already sufficient to increase the knowledge of this fundamental atom. Further developments can be made not only in the direction of a systematic investigation of the fine structure for a light and theoretically still tractable atom, but also of the isotope shifts of the optical transitions. This last possibility seems important because the ^{16}O nucleus is doubly magic and the high resolution now accessible should allow investigation of the nuclear structure via the relatively small contribution of the volume change to the isotopic shift.

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OPTICS LETT

Laser Measurement of the ^{16}O - ^{18}O Isotope Shift at Optical Frequencies

by

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Abstract

We demonstrate the full resolution of isotope shifts in atomic oxygen by means of sub-Doppler laser spectroscopy of ^{18}O enriched samples. Measurements are performed with a few percent accuracy on four transitions ranging from 605 to 646 nm. Previous values from conventional spectroscopy are either not available or one order magnitude less accurate and in marginal agreement with our data.

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The fundamental configuration $1s^2\,2s^2\,2p^4$ of atomic oxygen, generates levels coupled by highly forbidden transitions in the visible, while the first level of the excited configuration lies at more than nine electronvolts in energy. Mainly for these reasons, until very recently the optical spectrum of this fundamental atom has been elusive to high resolution laser investigations. In ref. [1], excited oxygen atoms could be conveniently produced in moderate power radiofrequency discharges and optogalvanic detection allowed the first optical sub-Doppler laser spectroscopy to be perfo.ned. As a consequence, this fundamental importance atom is now available for precise investigations of its spectrum. Isotope shift effects are among those it is worth exploring, also considered that the only existing experimental investigation of this effect on atomic oxygen dates back to more than tirthy-five years ago [2].

The interest in isotope shift of optical transitions of atoms originates from both practical purposes and possible comparisons between theory and experiments. The latter aspect relies on the cross-relations between nuclear structure and electronic configuration and is particularly interesting for a light and still theoretically tractable atom. As is well known [3], the isotope shift in an atomic transition can be written as the sum of mass and field components.The mass effect is the result of a "normal" contribution, $\Delta\nu_N$, easy to be computed and equivalent to that for hydrogen-like systems, and of a "specific" contribution, which takes into account electron cross-interactions and is difficult to be accurately evaluated. The field contribution, originated by the change in the nuclear charge distribution, is very small for light elements and its observation is more likely to occur for a "magic number" nucleus. In fact, the "doubly closed shell isotopes" of calcium are the lightest elements for which deviations from mass effect have been unambigously detected [4]. Also the n.cl'us of

^{16}O is "doubly magic", hence making stimulating the investigation of the isotope effect. Purpose of the present work is to demonstrate the feasibility of accurate isotope shift measurements by using a ^{18}O enriched sample, while for possibly evidencing field effects a further investigation will be necessary using also ^{17}O. On the other hand, data on ^{18}O are also interesting by themselves: for instance in astrophysics ^{18}O seems to play an important role in the galactic nucleosynthesis of neutron-rich isotopes [5].

In our experimental apparatus, as discussed in [1], the atom is produced by dissociation of O_2 molecules in a radiofrequency discharge substained by a noble gas. The sample is contained in a sealed-off pyrex tube (6mm internal diameter), placed inside a set of coils fed by a radiofrequency oscillator. Tunable radiation from an actively stabilized ring dye laser (Coherent 699-21), operating with rhodamine 6G or DCM, is sent throught the cell. At resonance, the discharge impedance is affected and it is possible to detect a change on the feedback signal to the current - stabilized power supply which feeds the oscillator. This sensitive optogalvanic scheme [6] allows the detection of excited oxygen atoms which can be produced only from O_2 in trace amounts, because of the quenching role also plaied by the molecules [7]. Sub-Doppler recording of homogeneous lineshapes are obtained by splitting the laser radiation into two counterpropagating beams of nearly equal intensity. The two beams are chopped at two different frequencies by the same mechanical chopper which provides separate reference signals at the two frequencies and at the sum one. The latter is used for spectroscopic recordings in intermodulated configuration [8].

The oxygen transitions used for the present investigation are schematically shown in Fig.1. They all are transitions starting from the first excited triplet or quintet P levels, which however are at more than ten electronvolts in energy. As a consequence the upper levels of the optical transitions are close to the ionization limit (13.6 eV). Optogalvanic recordings could be performed with good signal to noise ratio for all the investigated transitions, using neon or argon as gases substaining the discharge. Signals, in general stronger for the transitions involving quintet states, were larger of nearly a factor four with argon in comparison with neon. The sensitivity was always high enough to perform sub-Doppler measurements in intermodulated configuration.

A typical intermodulated spectroscopy recording is shown in Fig. 2 a) for the $3p^5P_3$ - $5s^5S_2$ transition at 645.6 nm. The Doppler-free signal is superimposed on a broader pedestal caused by the velocity-changing collisions. In the case of a homogeneous width γ much smaller than the Doppler one $\Delta\nu_D$ (FWHM), the resulting lineshape is given [9] by the sum of a Lorentzian and a Gaussian, as shown in the figure. The separated contribution of the Lorentzian and of the Gaussian is plotted in Fig. 2 b), while the deviation of the computed from the experimental lineshape is reported in Fig. 2 c). The "weight" of the collisional pedestal is given by a factor $C = 2\,(\pi \log 2)^{1/2}\,\Gamma\gamma / \delta\,\Delta\nu_D$, where δ is the decay rate of the longer effective lifetime level of the transition and Γ is its cross-relaxation rate. In the present experiment, the forced use of rather high noble gas pressures implies relatively large values of C. For the recording of Fig. 2 it is $C = 0.39$, we also obtain $\gamma = 386$ MHz (FWHM) and $\Delta\nu_D = 2$ GHz (FWHM). The observed homogeneous linewidth is due primarly to pressure broadening and power broadening, while the Doppler width, also directly obtained from the Voigt profile in single laser beam interaction, corresponds to a temperature of about 570K. This value is a little larger than that obtained [1] for other transitions sharing a common lower level but recorded using neon instead of argon. Later on we shall discuss how for the corresponding triplet-levels transition the width comes out to be anomalously

larger. However also the width of 2 GHz is large enough to mask any isotope effect. This is illustrated in Fig.3, for measurements performed using a ^{18}O enriched (~ 50%) sample. Recordings a) and b) refer to the same transition of Fig.2, while recording c) is from a weaker fine structure component. The isotope shift is resolved for both the transitions and the measured values are reported in TABLE 1, together with those of other transitions investigated in the present work. Within our present experimental accuracy we are not able to estimate any difference in the isotope shift of the two fine structure components originating from $^5P_3$ and $^5P_2$ levels. The difference should be of the order of 10 MHz or less and could be possibly evidenced directly measuring the fine structure transition. This has been done [10] for the ground state $^3P_1$ - $^3P_2$ fine structure transition at far infrared frequencies.

As for the other quintet transitions, multiplet at 615.8nm, the shift could be measured only for the $^5P_3$ - $^5D_4$ component, because of the overlap with the fine structure which in the ^5D level is comparable with the isotope effect [1]. This overlap also reflects on the worse accuracy of obtained value.

In Table 1, in addition to the experimental values and to the previous, much less accurate data, we report also the normal mass isotope shift which is easy to be computed. The residual effect is determined mostly by the specific mass effect and porsibly by the volume effect. However a quantitative evaluation of these contributions will be possible only when independent measurements on another isotope pair, say ^{16}O - ^{17}O, will be available.

In view of demonstrating the feasibility of a broad spectral investigation of the isotope effect in oxygen, we decided to perform measurements on the weaker triplet transitions. In particular we investigated the 3p $^3P_{0,2,1}$ - 6s $^3S_1$ multiplet at 604.6 nm. A result at first surprising was given by the observation of an extremely large Doppler effect, when argon was used to substain the discharge. A Doppler broadening recording of the entire multiplet is shown in Fig.4 a). The large width prevents from the observation of three separated components in spite of a fine structure splittings in the $^3P_{0,2,1}$ level of 4.8 (0→2) and 16.2 (2→1) GHz respectively. Differently from the quintet transitions case, here the lineshapes are not very accurately fitted by a Voigt profile. This is probably due to the superposition of more than one Gaussian, even though much higher signal to noise ratio should be necessary for a careful investigation of the actual shape. However, by fitting the isolated $^3P_1$ - $^3S_1$ component to a Voigt profile, we obtain a Doppler width of 5.7 GHz, corresponding to a temperature of about 4500 K, i.e. nearly one order of magnitude larger than that observed for the other quintet transitions investigated in the present work. This anomalous behaviour with the temperature can be understood according to the model discussed in [11] to explain the peculiar effects observed in the O laser emission at 844.6 nm [12], sharing the ^3P excited level with the transition at 604.6 nm, as shown in Fig.1. The energy defect in the dissociation of O_2^+ ions, produced by Penning collisions with metastable Ar atoms, should be responsible for the production of excited atoms with a wide velocity distribution. Our present technique seems suitable for a wider investigation of the phenomenon, over different oxygen transitions and by changing collisional partners, which could bring to a deeper understanding of the energy transfer processes, particularly complex in this case [7]. However, the present work is devoted to the measurement of isotope shifts and this is actually done also in the case of this anomously broadened lines. Figure 4 b) shows an intermodulated spectroscopy measurement of the $^3P_2$ - $^3S_1$ component for oxygen in natural abundance. In Fig. 4 c) the same measurement is repeated with the ^{18}O enriched sample. Sub-Doppler signals are recorded with enough signal to noise ratio and

resolution to measure the isotope shift, as reported in Table 1.

In conclusion, we have demonstrated that it is possible to systematically investigate isotope effect in atomic oxygen, over a large variety of transition strengths and widths. The accuracy of the measurements, at present limited by the rather high noble gas pressure necessary for a stable discharge operation, seems good enough to possibly evidence "field effects". At this purpose the extension to ^{17}O, when available, will be necessary in order to separate the specific mass contribution. However it is worth noting that the measurements on the ^{18}O isotope itself are interesting also by themselves. At this purpose it will be useful to extend present measurements at different wavelengths (288.4 and 423.3 nm) where from conventional investigation [2] shifts much larger than the Doppler broadening are expected, making the data also of astrophysical interest.

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FIGURE CAPTIONS

FIG.1 Partial scheme of some of lowest excited levels of neutral atomic oxygen. The transitions for which we investigate the isotope shift are also shown. Ionization limit is 13.6 eV.

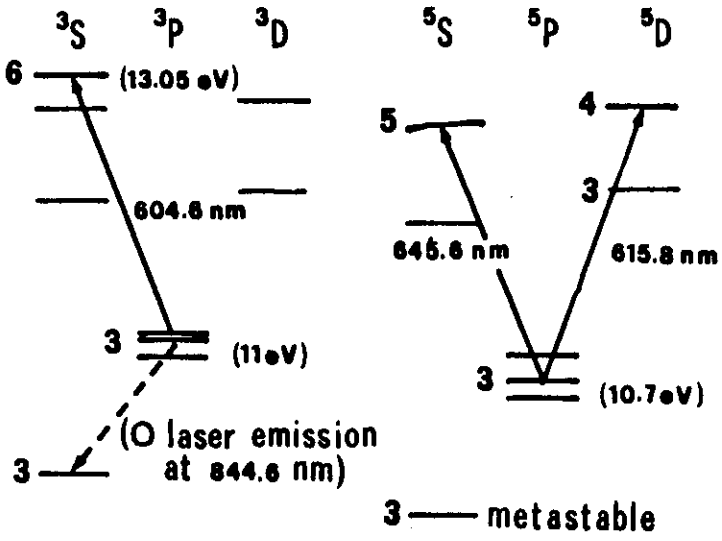
FIG. 2 a) Intermodulated optogalvanic recording of the ^{16}OI 3p $^5P_3$-5s $^5S_2$ transition at 645.6 nm as obtained in a O_2 / Ar radiofrequency discharge (partial pressures 0.1 / 5 Torr). The lineshape is given by the superposition of a Lorentzian and a Gaussian (dashed lines) as explained in the text. The separated contribution of the two curves is shown in b). The difference between the experimental curve and the fitted one is reported in c) (Note the vertical scale here is amplified by a factor of four).

FIG. 3 Measurements performed using a $^{18}O_2$ enriched sample in a O_2/Ar mixture (0.05/2.3 Torr), with a total laser power of about 400 mwatts.
a) and b) refer to the ^{16,18}OI 3p $^5P_3$ - 5s $^5S_2$ transition at 645.6 nm, respectively Doppler -limited and Doppler-free. c) refers to the Doppler-free recording of the other fine structure $^5P_2$ - $^5S_2$ component at 645.5 nm.

FIG. 4 a)Doppler-broadened optogalvanic recording of the $3p^3P_{0,1,2}$ - $6s^3S_1$ multiplet at 604.6 nm. Natural abundance oxygen was mixed with Ar (partial pressures O_2/Ar = 0.05/3.7 Torr).
b) and c) are intermodulated sub-Doppler recordings of the $^3P_2$ - $^3S_1$ component. Partial pressures: O_2/Ar = 0.07/3.7 Torr. Natural abundance oxygen is used in b) and ^{18}O enriched in c).

TABLE 1 : Measured $\nu_{18} - \nu_{16}$ shifts for various transitions of atomic oxygen. The computed $\Delta\nu_N$ normal mass shift value and the residual contributions are also reported.

TRANSITION	WAVELENGTH (nm)	I.S. (MHz)	$\Delta\nu_N$ (MHz)	I.S. - $\Delta\nu_N$ (MHz)	I.S.[Ref.2] (MHz)
$3p^5P_3$ - $4d^5D_4$	615.8	1310 (40)	1844	- 534	< 900
$3p^5P_3$ - $5s^5S_2$	645.6	1160 (20)	1759	- 599	< 600
$3p^5P_2$ - $5s^5S_2$	645.4	1160 (20)	1760	- 600	
$3p^3P_2$ - $6s^3S_1$	604.6	1350 (30)	1878	- 528	


^3S ^3P ^3D
6
(13.05 eV)
604.6 nm
3
(11eV)
3
(O laser emission at 844.6 nm)
^5S ^5P ^5D
5
4
3
645.6 nm
615.8 nm
3
(10.7eV)
3 — metastable

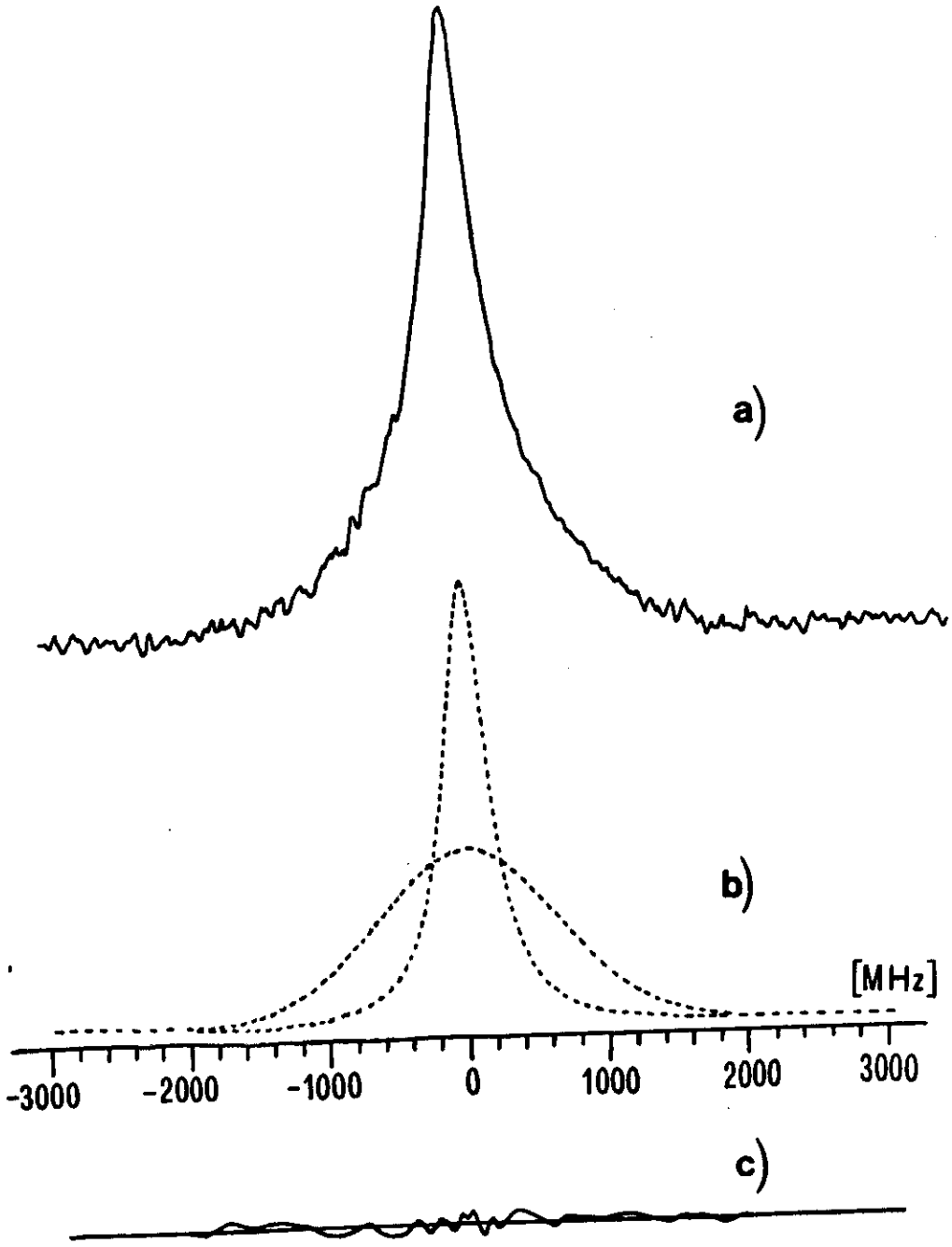
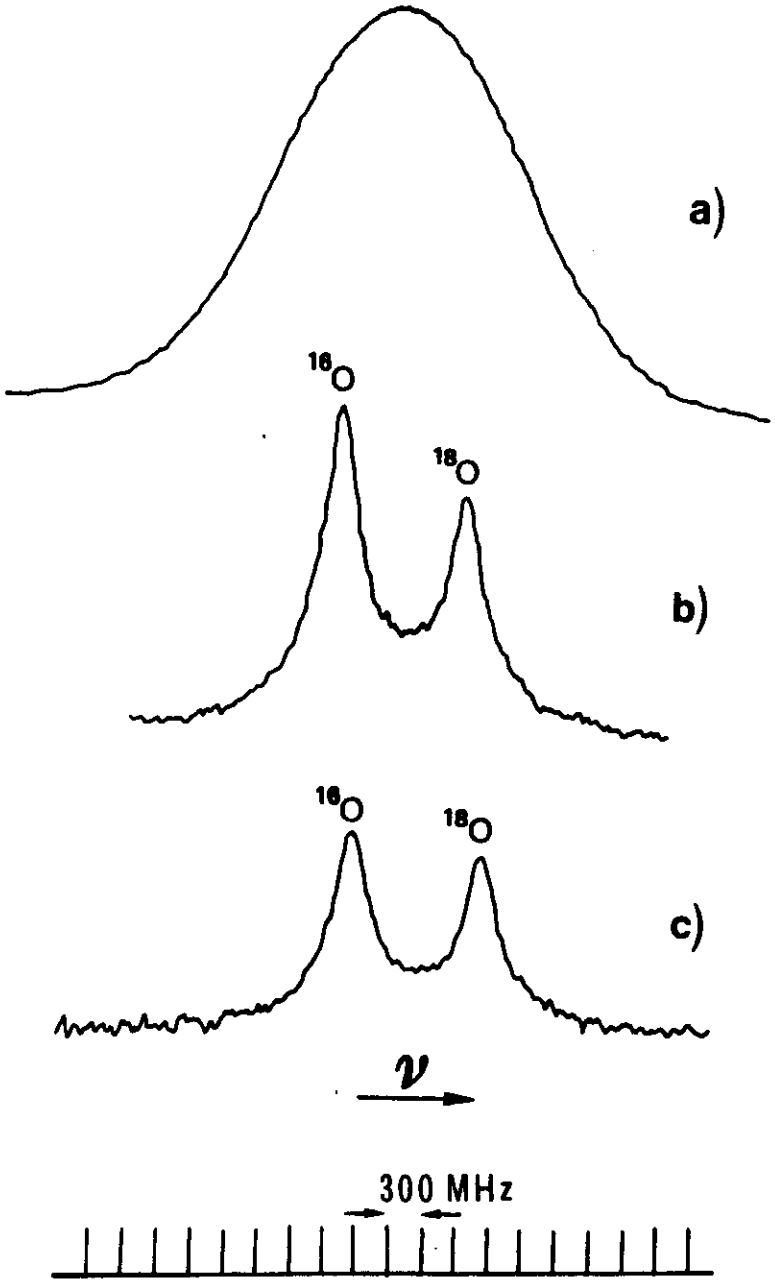
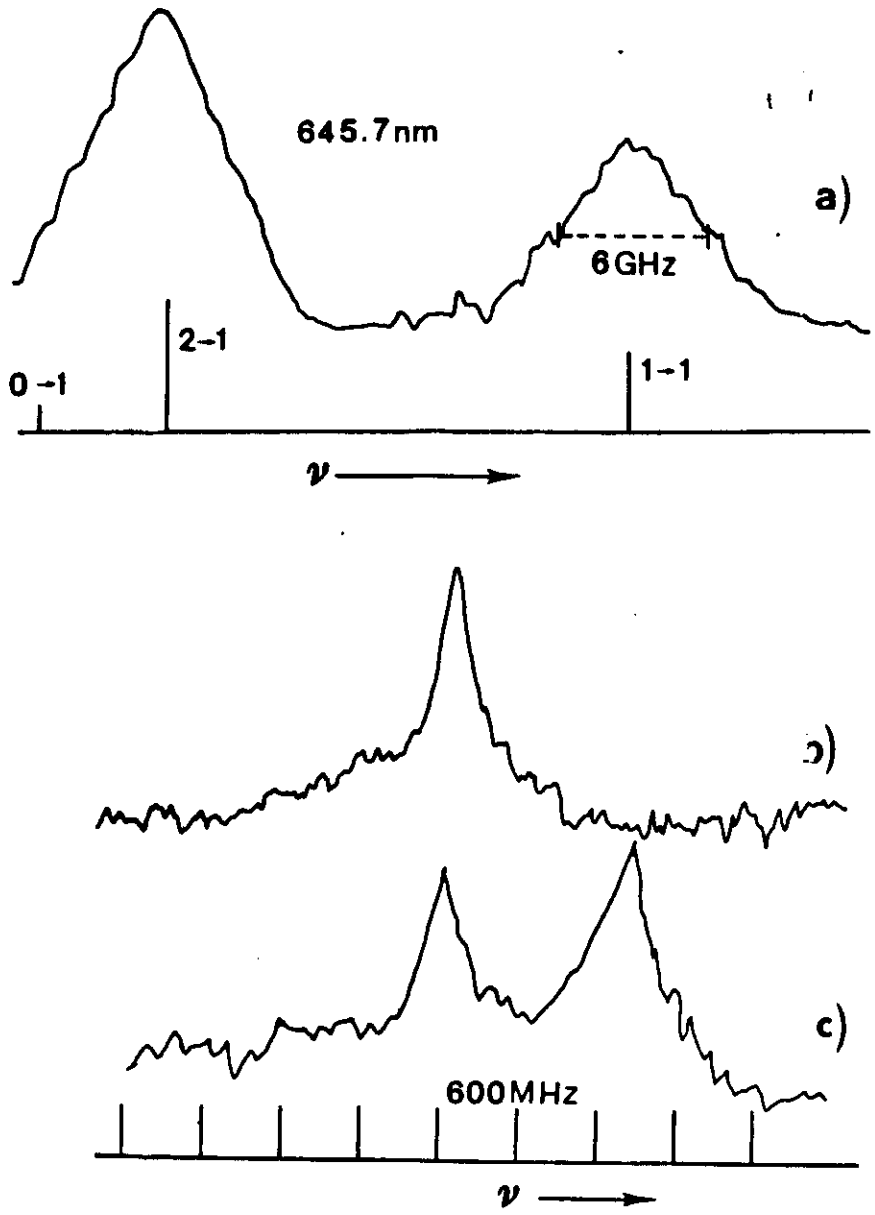

a)
b)
[MHz]
-3000
-2000
-1000
0
1000
2000
3000
c)

Fig. 1


a)
^{16}O
^{18}O
b)
^{16}O
^{18}O
c)
ν
300 MHz


645.7nm
a)
6GHz
2–1
0–1
1–1
ν
b)
c)
600MHz
ν