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LASER EXCITATION OF OPTICAL SPECTRA

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BACKGROUND MATERIAL

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ABSTRACT

A brief description is given of the characteristics and types of lasers available. The use of lasers for the excitation of molecular spectra, especially resonance fluorescence spectra, is illustrated with examples. The technique of saturation spectroscopy, or "inverse Lamb-dip" spectroscopy, as a means for achieving ultrahigh resolution is discussed. The application of high-powered lasers to the observation of two-photon spectra, both with and without Doppler broadening, is also discussed.

I. CHARACTERISTICS AND TYPES OF LASERS

The main characteristics of optical lasers are:

(i) high monochromaticity
(ii) high power
(iii) coherence.

Both CW and pulsed lasers are available for most of the optical region of the spectrum. We will consider a few specific examples.

I.A. CW Lasers

He-Ne, A^+ and Kr^+ lasers are readily available with powers ranging from milliwatts to a few tens of watts. An argon ion laser with an output of 1 watt in the 4800 Å line produces ∿2.5×10^{18} photons/sec in a line with a width of ∿0.01 cm^{-1}. Such lasers are essentially fixed frequency lasers although they can sometimes be tuned over very narrow frequency ranges.

Dye lasers have the advantage that they can be tuned over much larger wavelength ranges. The most commonly used CW dye laser is the Rhodamine-6G dye laser pumped by an argon ion laser. The useful wavelength range is from 5600 to 6300 Å and typical output powers are ∿20% of the pumping powers. The normal band width of the output radiation is ∿0.1 cm^{-1} but with an etalon inside the cavity the band width can be reduced to ∿0.001 cm^{-1} (30 MHz).

I.B. Pulsed Lasers

The first optical laser was a flash lamp-pumped ruby laser and such lasers are still in common use. The output is essentially fixed frequency (6943 Å) but a small degree of tuning (±5 Å) can be achieved by varying the temperature of the ruby. Many other solid state lasers are available and pulses up to 100 MW can be obtained for short durations, e.g. a few nanoseconds. The outputs can also be frequency-doubled by using suitable materials, e.g. KH_2PO_4.

Pulsed dye lasers are available throughout the visible region of the spectrum (4000-7000 Å). The pump source may either be a flash lamp with a low repetition rate (e.g. 1/sec-1/min) or a pulsed N_2 laser with repetition rates up to 10^2/sec. With a 300 kW N_2 laser operating at 20 pulses/sec, a dye laser would typically have output pulses of 5-20 kW lasting for a few nanoseconds and having a band width of ∿0.1 Å. By using an etalon in the cavity the band width can be reduced to ∿0.001 Å with some sacrifice in peak power.

II. EXCITATION OF MOLECULAR SPECTRA

Two examples will be considered, both taken from work in our own laboratory.

II.A. Band Spectra

The emission spectrum of glyoxal can be readily excited using the various lines of a 1W argon ion laser. The emission contains bands of the first singlet-singlet system ($^1A_u-^1A_g$) and of the corresponding triplet-singlet system ($^3A_u-^1A_g$) (Fig. 1). The relative intensities of the bands depend on the exciting line used. With the 4880 Å laser line some new bands were excited and could not be fitted into the above systems. These new bands were subsequently shown to be produced by cis glyoxal which is present in glyoxal at room temperature to the extent of a few percent (Holzer and Ramsay 1970, Currie and Ramsay 1971, Dong and Ramsay 1973).

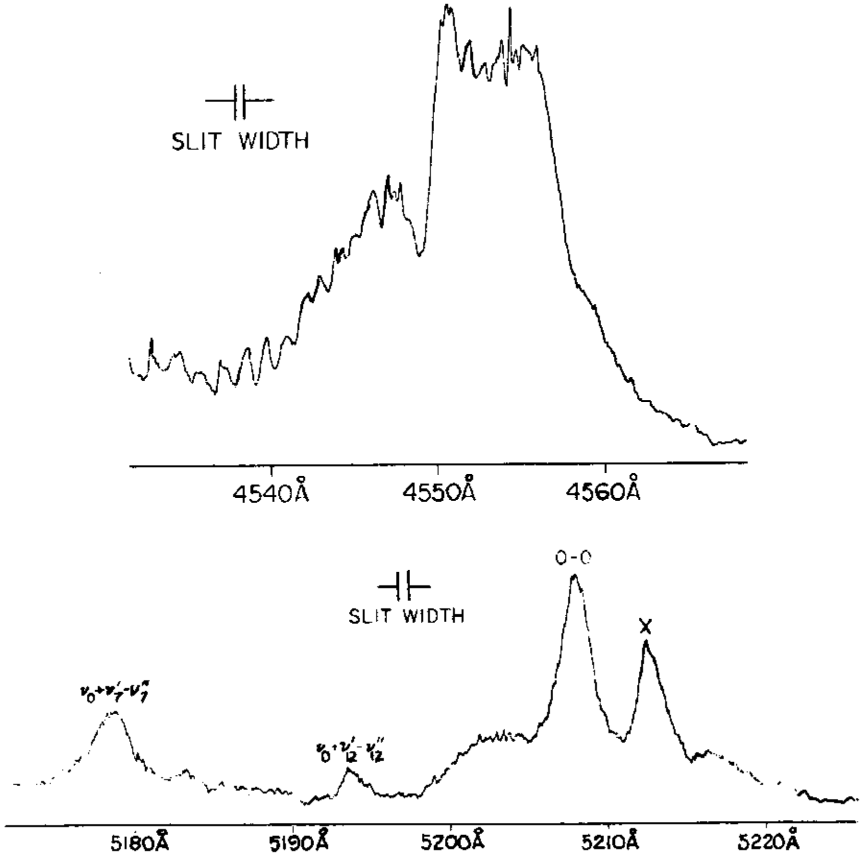

Fig. 1. The upper trace shows the 0-0 band of the $^1A_u-^1A_g$ system of glyoxal excited by the 4765 Å line of an argon ion laser.

The lower trace shows bands of the $^3A_u-^1A_g$ system of glyoxal excited by the 4880 Å line of an argon ion laser. The band marked with an X is a band of cis glyoxal.

The 4880 Å line overlaps the 0-0 band of the first singlet-singlet system ($^1B_1-^1A_1$) of cis glyoxal which is thereby selectively excited. In this way cis glyoxal was first identified experimentally.

The vibrational assignments for the bands of trans glyoxal were straightforward, since the absorption spectrum had been studied in considerable detail and furthermore all the ground state frequencies were well-known. However, new information was obtained for some of the vibrational frequencies of the cis isomer.

II.B. Resonance Fluorescence

The emission spectrum of the NH_2 free radical can be readily excited by means of a tunable dye laser. Kroll (1975) prepared NH_2 radicals in a flow system by reacting H atoms with N_2H_4 and observed the excitation spectrum by tuning a Rhodamine-6G dye laser through the rotational lines of the absorption spectrum (Fig. 2). When the laser was tuned to a single absorption line the emission spectrum was predominantly a resonance fluorescence spectrum, i.e. the lines observed had a common upper level connected to different rotational and vibrational levels in the lower state. In this way the 100, 110, 020 and 040 levels of the ground state were identified for the first time and preliminary rotational constants determined for these levels.

In addition to the resonance fluorescence spectrum, other lines were observed with increasing relative intensity as the pressure increased. Such lines originate in additional rotational levels of the excited state populated by collisional processes. In this way some information on rotational selection rules for collision processes was obtained.

III. SATURATION SPECTROSCOPY

The factor which limits the resolution which can be achieved in conventional high resolution spectroscopy of simple gases, is usually the Doppler width of an individual rotational line. This limit depends on the molecular weight and temperature of the gas, but Doppler widths for lines in the visible region of the spectrum are usually $\sim 0.05\ \mathrm{cm}^{-1}$. Laser lines, however, can be considerably narrow, e.g. $\sim 0.001\ \mathrm{cm}^{-1}$.

Let us consider the interaction of a laser beam with an individual line in the spectrum of a gas. If the frequency of the laser, ν_L, is equal to the center frequency of the absorption line, ν_o, then laser power can be absorbed only by those molecules which are moving transversely to the laser beam. If the laser frequency is slightly detuned from the center frequency, then laser power can be absorbed only by those molecules which have a velocity component $\underline{v}$ along the laser direction (and away from the laser), such that

$$\nu_L = \nu_o \left(1 - \frac{v}{c}\right). \qquad (1)$$

If the laser beam is sufficiently intense, then the population of

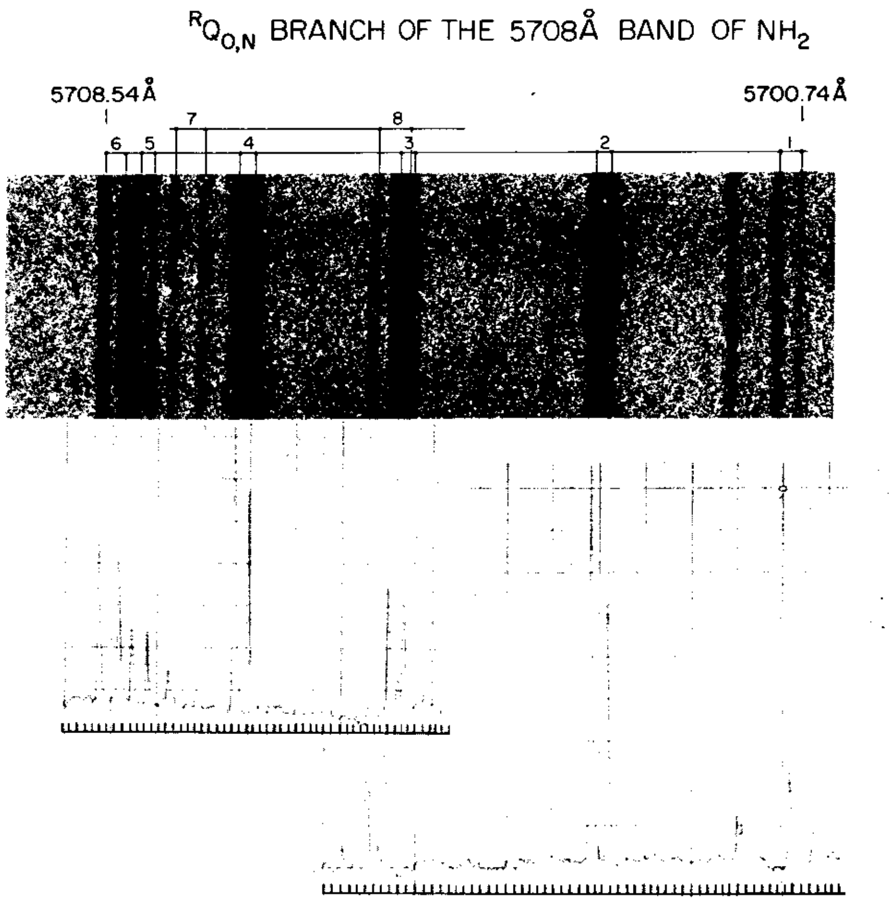

Fig. 2. The upper photograph shows a part of the NH_2 spectrum photographed in absorption during the flash photolysis of ammonia.

The lower traces show the spectrum of NH_2 excited by a tunable dye laser.

the group of molecules with velocity component $\underline{v}$ will be depleted in the lower state and increased in the upper state.

Consider now the experimental arrangement shown in Fig. 3. Suppose that the intense laser beam interacts with molecules which have a velocity component +v in the direction of the laser beam. Then the weaker reflected beam will interact with a different group of molecules having the same velocity component $\underline{v}$ but moving in the opposite direction. If the frequency of the laser is varied over the width of the absorption line, then the reflected beam can be used to monitor the profile of the absorption line. A normal Doppler profile will be obtained except at the center of the line where a "dip" in the absorption will be recorded, since the population of the group of molecules with $\underline{v} = 0$ was depleted by the incident beam. Center frequencies of lines can therefore be determined with precisions depending on the widths of the laser lines.

As an example of the increased resolution which can be obtained using the technique of saturated absorption ('inverse Lamb-dip') spectroscopy, Hanes, Lapierre, Bunker and Shotton (1971) have resolved the 21 nuclear hyperfine components of the P(33) line in the 6-3 band of the $B \leftarrow X$ system of I_2 and have measured the relative positions of the components with a precision of 0.36 MHz (0.000012 cm^{-1}).

IV. TWO-PHOTON SPECTROSCOPY

The basic theory of two-photon processes was given by Göppert-Meyer (1929, 1931) more than forty years ago, yet only comparatively recently have these processes been studied in the optical region of the spectrum. The main reason was the lack of sufficiently intense light sources to observe the phenomena until the advent of the laser in the early 1960's.

The probability I_{ik} for two photons of the same frequency ω to cause a transition between an initial state $\underline{i}$ and a final state $\underline{k}$ is given by

$$I_{ik} \; \alpha \; \left| \sum_j \frac{<i|M|j><j|M|k>}{\omega-\omega_{ij}} \right|^2 , \tag{2}$$

where M is the dipole moment operator, ω_{ij} is the frequency of an "intermediate" transition, and the summation extends over all other states $\underline{j}$. The probability is considerably enhanced if there are strongly allowed single-photon transitions between the intermediate state j and the initial and final states $\underline{i}$ and $\underline{k}$, and also if $\omega \sim \omega_{ij}$. The selection rules are different from those for single-photon processes and the possibility exists for observing new excited states by two-photon absorption. For example, in a molecule with a center of symmetry the selection rules for two-photon transitions ($g \leftrightarrow g$, $u \leftrightarrow u$, $g \not\leftrightarrow u$) are the reverse of those for single-photon transitions.

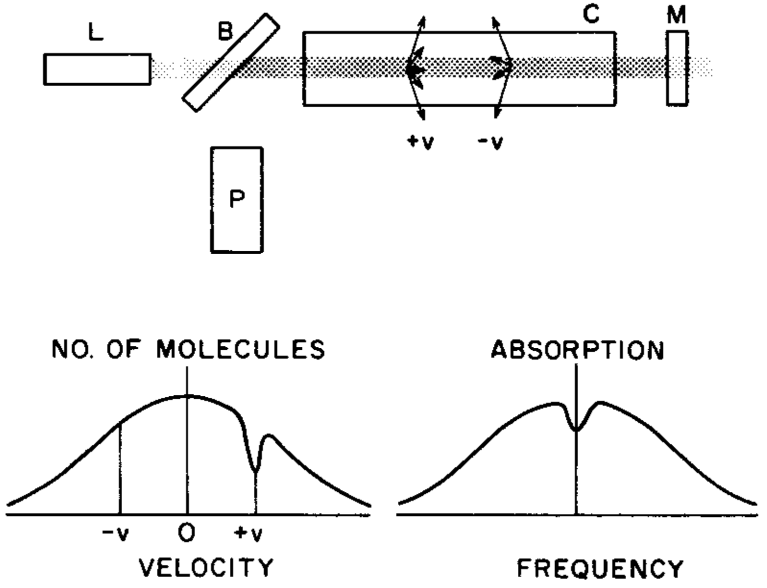

Fig. 3. Apparatus for observing "inverse-Lamb dip" effects: L-laser, B-beam splitting mirror, C-cell containing absorbing gas, M-partially reflecting mirror, P-photodetector. The velocity vectors of molecules interacting with the forward beam (+v) and with the weaker returning beam (-v) are indicated.

Bottom left - Velocity profile showing the molecules which interact with the intense incident beam (+v) and the weaker reflected beam (-v).

Bottom right- Absorption profile obtained with the reflected beam, showing the inverse Lamb-dip at the center frequency.

IV.A. Detection of Two-Photon Processes

One method for detecting two-photon absorption spectra involves monitoring the emission from the final state. In the apparatus shown in Fig. 4 light pulses from a dye laser pumped by a pulsed N_2 laser, are focussed into a cell containing the absorbing molecule. Emission in the ultraviolet is monitored using a photomultiplier with filters to eliminate scattered light from the dye laser and from the pulsed N_2 laser. The spectrum is scanned by rotating the grating in the laser cavity. Using this type of apparatus Hochstrasser, Sung and Wessel (1973) have observed two-photon spectra in benzene both in the crystal and vapor and have observed eight out of the ten ungerade fundamentals in the $^1B_{2u}$ excited state. Bray, Hochstrasser and Wessel (1974) have also observed rotational fine structure in the two-photon excitation spectrum of the $A^2\Sigma^+ - X^2\Pi$ transition of NO and have observed two new branches, O ($\Delta J=-2$) and S($\Delta J=+2$), which are permitted by the two-photon selection rules. We have observed a two-photon excitation spectrum in thiophosgene ($CSCl_2$) in the vapor (Hillier and Ramsay 1975). In all cases it has been verified that the intensity of the two-photon spectrum varies as the square of the intensity of the incident radiation.

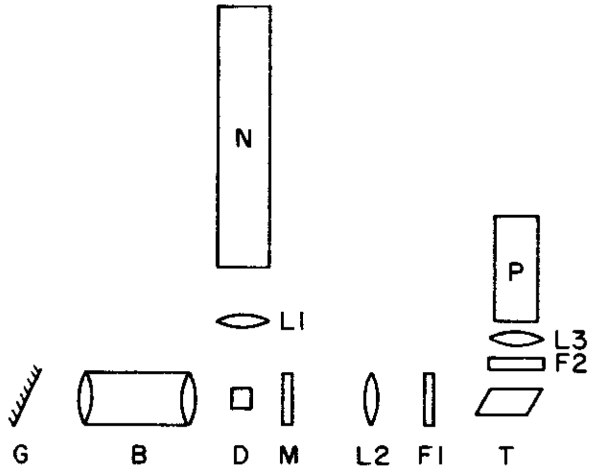

Fig. 4. Apparatus for observing two-photon excitation spectra: N-nitrogen laser, L1, L2 and L3-lenses, G-plane grating, B-beam expander, D-dye cell, M-output mirror, F1 and F2-filters, T-two photon cell, P-photomultiplier.

Two photon absorption spectra have also been observed using a high-powered ruby laser (up to 10 MW) to provide one of the photons and a xenon arc lamp to provide the other (Eisenthal, Dowley and Peticolas 1968, Monson and McClain 1970, 1972). The spectra were plotted point by point and show only low resolution.

IV.B. High Resolution Spectra without Doppler Broadening

The 4d-3s transition in Na vapor has been studied by Hänsch, Harvey, Meisel and Schawlow (1974) using a single mode CW tunable dye laser with 30-50 mW power. The transition is forbidden for a single-photon electric dipole process but is allowed for double-photon absorption.

The apparatus is similar to the one in Fig. 4 except that the dye cell is pumped continuously by an argon ion laser. When the dye laser is tuned to half the transition frequency (λ=5787.32 Å), two-photon absorption occurs and is monitored by emission at 3302 Å corresponding to the second step in the 4d→4p→3s cascade process. The two-photon absorption is particularly strong in this system since a 3p intermediate state lies close in energy to the exciting radiation and the transitions 3p-3s and 4d-3p are both strongly allowed.

When a concave mirror is placed behind the absorption cell and is accurately aligned so that the return beam overlaps the incident beam in a narrow waist inside the absorption cell, there is a dramatic increase in the signal. If the frequency of the laser is scanned slowly, four sharp resonances are observed with widths ∿30 MHz. These resonances correspond to the hyperfine components of the 3s state; the hyperfine splittings in the 4d state are much smaller. Under these experimental conditions, the two photons are taken one from each beam and the effects of Doppler motion cancel. Furthermore all the molecules in the beam contribute towards the signal. If the two beams are misaligned then the two photons are taken from one of the beams only and a much weaker Doppler-broadened profile is observed.

It appears that this technique for overcoming the effects of Doppler broadening will have valuable application in high resolution molecular spectroscopy.

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