

---

## Optical Double Resonance with Laser-Induced Fluorescence Detection [and Discussion]

R. N. Dixon, G. W. Series and G. Duxbury

*Phil. Trans. R. Soc. Lond. A* 1982 **307**, 603-615  
doi: 10.1098/rsta.1982.0133

---

### Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

---

To subscribe to *Phil. Trans. R. Soc. Lond. A* go to: <http://rsta.royalsocietypublishing.org/subscriptions>

---

## Optical double resonance with laser-induced fluorescence detection

BY R. N. DIXON

*Department of Theoretical Chemistry, School of Chemistry, The University,  
Bristol BS8 1TS, U.K.*

The saturation of level populations induced in a molecule by an intense laser beam may be probed by a second beam at the same or a different frequency. A number of schemes have been based on this principle for simplifying complex spectra or for achieving sub-Doppler resolution. Fluorescence detection provides the sensitivity for studies on free radicals and other transient molecular species. The two beams may be provided by two separate lasers, or by sideband modulation of a single laser. These techniques are reviewed. Emphasis is placed on recent studies of hyperfine structure, of Stark splittings, and of Zeeman splittings.

## INTRODUCTION

Spectroscopic experiments invariably involve the four main steps of sample preparation, selection of the photon frequency to be studied, signal detection, and spectral line assignment. Unfortunately, in classical linear spectroscopy with spectrometers the optimization of one part of the experiment often degrades the performance of another part. For example, in emission spectroscopy high spectral resolution conflicts with high sensitivity. Furthermore many molecular spectra have such a crowded line density that the lines overlap within their Doppler width. Even where this is not so, complex molecular spectra may defy all attempts at unambiguous assignment. The development of the laser has not only lessened many of the conflicting requirements of classical spectroscopy, but has also made possible the development of new experiments that assist the spectroscopist in his theoretical analysis.

This paper surveys some of the applications of visible lasers to the simplification of complex spectra, to the resolution of hyperfine structure, to the determination of Stark or Zeeman splittings, and to the analysis of perturbations. Particular attention is given to optical–optical double-resonance experiments.

## DISPERSED LASER-INDUCED FLUORESCENCE

A molecule excited to fluorescence by absorption of photons from a narrow-band laser will in general emit photons in a number of subsequent transitions (figure 1*a*). With total fluorescence detection the laser-induced fluorescence (l.i.f.) excitation spectrum will take the form of the absorption spectrum multiplied by the excited state quantum yield. Thus, if this latter quantity is more or less constant from level to level the l.i.f. excitation spectrum obtained with a tunable laser will be very similar to the absorption spectrum, but with enhanced sensitivity. However, the power of l.i.f. for spectral simplification becomes fully apparent if the fluorescence is dispersed by a monochromator, thus providing a crude form of optical–optical double resonance.

For example, if a single R-branch line  $R(J)$  is excited in one vibrational band of a  ${}^1\Sigma^- \rightarrow {}^1\Sigma$  band system of a diatomic molecule, then the fluorescence spectrum consists of the two lines

[ 137 ]

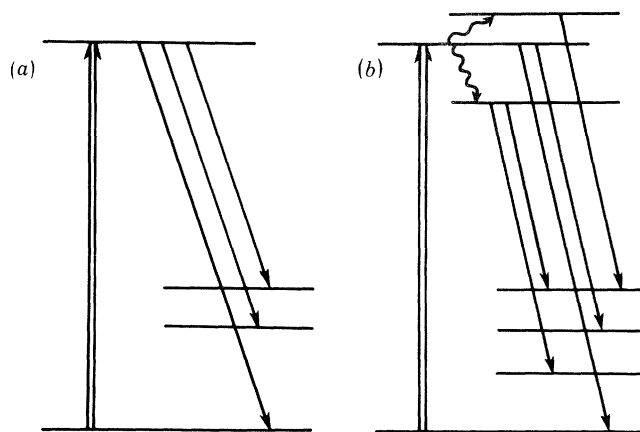


FIGURE 1. (a) Dispersed laser-induced fluorescence under collision-free conditions. The only observed transitions originate from the initially excited level. (b) Satellite transitions appear when collisional energy transfer occurs during the excited state lifetime.

$R(J)$  and  $P(J+2)$  for each  $v''$  in the  $v'-v''$  progression. A simplified spectrum can be obtained either by scanning the monochromator while holding the laser frequency constant (l.i.f. spectrum) or by scanning the laser frequency for a fixed monochromator frequency (photo-excitation spectrum). There is, of course, a long history of similar studies with the use of fixed frequency atomic lamps.

This technique has been used to simplify the spectrum of the  $\text{BO}_2$  radical, which is complicated by overlapping vibronic bands, as well as overlapping branches (Johns 1961). The resolution of l.i.f. spectra recorded by Russell *et al.* (1977) and Dixon *et al.* (1977) was limited by the pass-band of the monochromator, and did not fully resolve the rotational structure. More recently Beaudet *et al.* (1979) have used a single-mode dye laser with both methods of scanning to deconvolute fully lines that overlap within their Doppler widths in the undispersed excitation spectrum. These new data have permitted a more extensive analysis than hitherto (Weyer *et al.* 1980).

Dispersed l.i.f. also makes possible studies of energy transfer within the emitting excited states (figure 1*b*). Absolute rates can be measured with time-resolved l.i.f. excited by pulsed lasers, as in recent studies on  $\text{Li}_2$  (Ennen *et al.* 1974),  $\text{Na}_2$  (Brunner *et al.* 1979) and  $\text{NH}_2$  (Dearden *et al.* 1982).

Despite its successes, dispersed l.i.f. has a number of serious limitations, of which the more important are that it only probes final levels below the fluorescing levels, its theoretical resolution on the l.i.f. is restricted to that of the monochromator, and frequently low signal strengths prevent achievements of that theoretical resolution.

#### TWO-LASER OPTICAL-OPTICAL DOUBLE RESONANCE

The use of a second laser to probe the population redistribution produced by the pump laser offers advantages in signal strength, resolution and flexibility of possible level schemes, which removes many of the limitations of dispersed l.i.f.

Figure 2 illustrates two possible level schemes for such two-colour optical-optical double resonance (o.o.d.r.). In figure 2*a* the pump laser excites molecules from the state X to level A, which may or may not be fluorescent. The probe laser then further excites these to a higher

state B, from which the undispersed fluorescence is monitored. If both lasers are dye lasers operating in the visible, the resultant B state fluorescence may be in the ultraviolet, and can then be discriminated from intermediate A state fluorescence by means of a blocking filter. Alternatively with a beam splitter and two filter-photomultiplier combinations the A and B state fluorescence may be detected simultaneously. This two-colour sequential absorption technique with a real intermediate state should not be confused with two-photon nonlinear absorption, which is discussed by Professor Cagnac in another paper at this meeting.

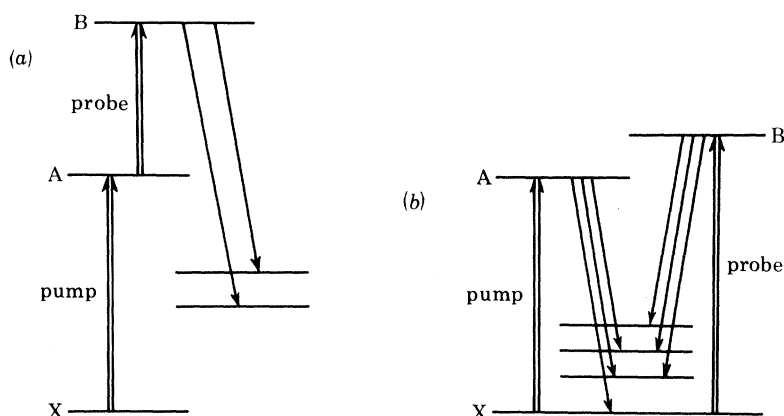


FIGURE 2. (a) Two-colour sequential o.o.d.r. with a real intermediate state. Either the pump laser or the probe laser may be scanned with the frequency of the other held fixed. (b) The pump and probe lasers compete in depopulating the lower state X.

King and coworkers have used two tunable dye lasers pumped by a single pulsed  $N_2$  laser to implement sequential o.o.d.r. in studies of  $I_2$  (Danyluk & King 1977; King *et al.* 1981a),  $ICl$  (King *et al.* 1979) and  $Na_2$  (King *et al.* 1981b). Bernheim *et al.* (1979, 1980) have made similar studies of  $Li_2$ . The probe laser pulse could be optically delayed by up to 24 ns to permit relaxation in the intermediate state if so desired, and the beams counterpropagated and focused in the centre of the cell. In centrosymmetric molecules the overall selection rules are  $g \rightarrow u \rightarrow g$  or  $u \rightarrow g \rightarrow u$ , so that the final states are not directly accessible from the initial states by one-photon transitions. Indeed a number of new electronic states have been discovered in these studies. The narrow bandwidth of  $0.07 \text{ cm}^{-1}$  for the pump laser was usually sufficient to select only one intermediate level, the resolution of the o.o.d.r. spectrum being limited by the  $1 \text{ cm}^{-1}$  bandwidth of the probe laser.

Field and coworkers have implemented the same scheme with two single-mode continuous wave (c.w.) dye lasers (Field 1981). In this case the pump laser excites a velocity-selected population, so that the second excitation by the probe laser is sub-Doppler. In studies on  $BaO$  the  $C^2\Sigma^+ \rightarrow A^1\Sigma^+ \rightarrow X^1\Sigma^+$  sequential o.o.d.r. excitation has been found to have 10% of the sensitivity of fluorescence excitation spectroscopy, but 100-fold higher resolution (Gottscho *et al.* 1980a, b).

In a variant on this experiment, Amano *et al.* (1980) have used a single-mode dye laser to excite  $NH_2$  to the  $A(0,9,0)2_{20}$  rovibronic state, followed by excitation to the  $(0,10,0)2_{11}$  level with the P(28) line of an  $N_2O$  laser. Because the infrared laser was fixed in frequency the resonance condition was satisfied by placing the cell intracavity and in the pole gap of a magnet. The spectrum was then detected by scanning the field.  $^{14}N$  hyperfine splitting was clearly

resolved in this experiment. The advantage of an intracavity cell was strong saturation of the second excitation step at resonance, giving an excellent signal:noise ratio. However, it complicates the observed hyperfine structure. The dye laser frequency,  $\nu_d$ , will in general not be tuned to the centre of the first molecular transition at  $\nu_1$ , so that a velocity group with parallel velocity  $v_{\parallel}$  is selected according to

$$\nu_1 = \nu_d(1 - v_{\parallel}/c). \quad (1)$$

The copropagating and counterpropagating components of the standing wave infrared field of frequency  $\nu_{i.r.}$  then come into resonance with the second transition  $\nu_2$  under the conditions

$$\nu_2 = \nu_{i.r.} \{1 \mp (\nu_d - \nu_1)/\nu_d\}. \quad (2)$$

In consequence the hyperfine pattern of  $\nu_2$  is doubled with a splitting proportional to the mismatch of  $\nu_d$  to  $\nu_1$ .

The scheme in figure 2*a* has the advantage that the sequentially stimulated fluorescence is observed without any background. However, its power to simplify either the B—A or A—X spectrum rests on the existence of stable high excited states. The scheme in figure 2*b* provides an alternative method of simplifying spectra without the need for such high states. In this case the probe laser interrogates the population depletion of the lower level X induced by the pump laser. This form of o.o.d.r. may be regarded as the inverse of dispersed l.i.f., in that different excited levels are coupled through a common lower level (cf. figure 1*a*). This technique was used by Klein (1977) on Na<sub>2</sub>. An argon ion pump laser ( $\lambda = 476.5$  nm) excited a single line of the B—X band system, while a tunable c.w. dye laser probed the A—X band system near 610 nm. Detection of o.o.d.r. was achieved by chopping the pump beam and using phase-sensitive detection of the fluorescence excited by the unchopped probe beam.

Johnson *et al.* (1981) have also used this technique of population labelling to simplify the crowded spectrum of the BaI C—X system, where many of the lines overlap within their Doppler widths. The pump and probe lasers were tuned to the two spin components of this  $^2\Pi(a)$ — $^2\Sigma^+$  transition near 561 nm and 538 nm. Both beams were chopped at different frequencies, and a beam splitter used with two different filter–photomultiplier combinations to detect each spin-orbit component separately. In this case o.o.d.r. signals of one phase were detected via the depleted common levels, with signals of the opposite phase resulting from overpopulation of other lower levels after optical pumping plus fluorescence decay. These oppositely phased signals for related lines in different branches were a great aid to assignment.

In all the experiments described above, the pump and probe beams excited transitions well separated in frequency. It is equally possible for both lasers to excite the same close group of levels. For example Demtroder *et al.* (1980) have used two slightly tunable argon ion lasers operating on  $\lambda = 488$  nm to pump and probe the hyperfine structure of NO<sub>2</sub> in a molecular beam. By this means hyperfine components with a common lower level were labelled through the o.o.d.r. signal.

The use of two-laser o.o.d.r. for sub-Doppler studies requires high stability in the frequency of both lasers. Furthermore it is difficult enough to maintain one single-mode laser operating reliably for long periods, let alone two. The remaining part of this paper will be devoted to the applications of o.o.d.r. with a single laser to the resolution of close groups of levels.

## ONE-LASER OPTICAL-OPTICAL DOUBLE RESONANCE

Provided that the frequencies of two copropagating laser beams are tuned to within the Doppler profile of a line with fine structure, then the condition for three-level double resonances has been defined by Brewer (1970) as

$$\Omega_1 - \Omega_2 = \nu_1 - \nu_2, \quad (3)$$

where  $\Omega_1$  and  $\Omega_2$  are the two optical frequencies, and  $\nu_1$  and  $\nu_2$  are two allowed transition frequencies with a common level. The amplitude modulation of a laser beam at radio frequencies provides a suitable stable frequency difference  $\Omega_1 - \Omega_2$  between sidebands. Gouedard *et al.* (1976) used an acousto-optic modulator in a study of Zeeman splittings in  $I_2$ . Orr & Oka (1977) used an electro-optic modulator for similar studies with a  $CO_2$  laser.

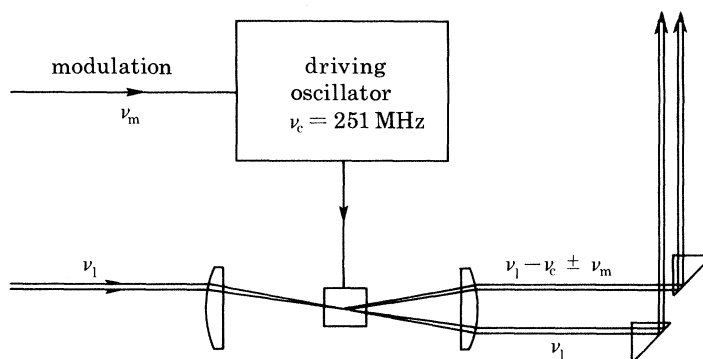


FIGURE 3. The generation of laser sidebands with an acousto-optic modulator. In one mode of operation, (a), the Bragg zero diffraction order is blocked, giving  $\Omega_1 - \Omega_2 = 2\nu_m$ . In an alternative mode, (b), the oscillator is not modulated, giving  $\Omega_1 - \Omega_2 = \nu_c$ .

We have used an acousto-optic modulator (SORO IM50) with one of two c.w. dye lasers for o.o.d.r. studies. When r.f. power at a resonant carrier frequency of  $\nu_c = 251$  MHz is applied to the modulator, the travelling acoustic wave gives Bragg diffraction, the  $n$ th diffraction order being Doppler shifted by  $n\nu_c$  from the laser frequency. In one mode of operation we have oriented the modulating crystal to concentrate the power into the zero and first orders of diffraction, and crossed the two beams at a narrow angle in the sample, thus giving a fixed  $\Omega_1 - \Omega_2$  of 251 MHz. Alternatively the driving oscillator is itself modulated with tunable r.f. at frequencies  $\nu_m$  up to 45 MHz, and the laser power concentrated into the first diffraction order with the zero order blocked. In this case the transmitted beam is the superposition of two frequencies with

$$\Omega_1 - \Omega_2 = 2\nu_m \quad (4)$$

(figure 3). In either mode the stable difference frequency between the two active optical frequencies can give sub-Doppler o.o.d.r. signals in either the upper or lower levels of a rovibronic transition. It is not necessary to stabilize the dye laser frequency provided that it remains within the Doppler-broadened molecular line profile, and indeed it need not be single-mode.

#### Hyperfine structure in $NH_2 \tilde{A}, {}^2A_1$

The hyperfine structure of levels of the  $\tilde{A}$  state of  $NH_2$  has been observed by a number of workers (Hills *et al.* 1976; Dixon & Field 1977; Dixon *et al.* 1979; Hills *et al.* 1982). The analysis

of the splittings in terms of a hyperfine Hamiltonian is greatly complicated by the almost random nature of perturbations involving high levels of the  $\tilde{X}$ ,  ${}^2B_1$  state. The  $N = 0$  rotational levels in the  $\tilde{A}$  state are unique in that they have the opposite parity from that of the  $N = 0$  levels of the  $\tilde{X}$  state. Furthermore the hyperfine splitting depends solely on the  ${}^{14}\text{N}$  Fermi contact interaction.

O.o.d.r. signals within the components of the  $0_{00}$  rotational level of the  $\tilde{A}(090)$  vibronic state have been observed by tuning the transitions into resonance with a weak magnetic field.

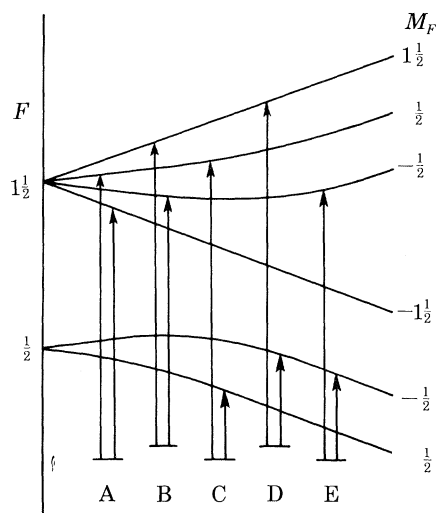


FIGURE 4. Schematic diagram of the magnetic field tuning of the  ${}^{14}\text{N}$  hyperfine structure of the  $\tilde{A}(090)0_{00}$  rotational level of  $\text{NH}_2$ . A, B, C, D and E are the upper-state three-level resonances observed when pumping the  $0_{00}-1_{10}$  transition at  $16705\text{ cm}^{-1}$ .

Figure 4 indicates schematically all the possible upper-state three-level resonances. Resonances A and B have been observed with  $\nu_m$  ranging from 8 to 32 MHz by using perpendicular polarization ( $\Delta M_F = \pm 1$  for each transition), and detected by using audio-frequency field modulation (figure 5). Resonances A, C, D and E have been detected by using the 251 MHz fixed-frequency mode, C and D remaining closely degenerate. The use of both parallel and perpendicular polarization confirmed the assignments (figure 6). Least-squares analysis of these data (table 1) leads to:

$$\left. \begin{aligned} a_N/\text{MHz} &= 153.6 \pm 0.4; \\ g_J/g_s &= 0.986 \pm 0.005 \end{aligned} \right\} \quad (5)$$

(one standard deviation).

The near-equality of  $g_J$  for this rotationless level and the free spin  $g_s$  confirms the absence of any perturbation. The Fermi contact term may be compared with the value of  $154.6 \pm 2.6$  MHz determined by Hills *et al.* (1982) from a careful assessment of microwave-optical double-resonance measurements on higher rotational levels in this state, many of which are perturbed.

The rapidly increasing number of  $M_F$  components for higher rotational levels leads to very complex magnetically tuned o.o.d.r. spectra, which are not readily analysed. We are now extending our measurements on  $0_{00}$  levels to other vibronic states.

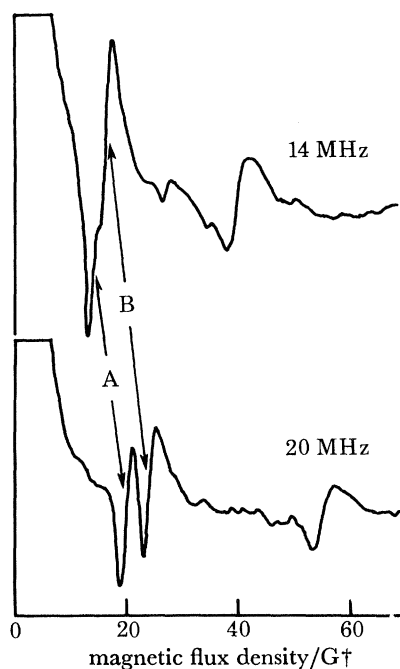


FIGURE 5. The three-level resonances A and B of the  $\tilde{A}(090)0_{00}-\tilde{X}(000)1_{10}$  transition of  $\text{NH}_2$  (figure 4), observed in mode (a) with perpendicular polarization, and with  $\nu_m = 14$  and 20 MHz. The strong zero-field resonance arises from the Hanle effect.

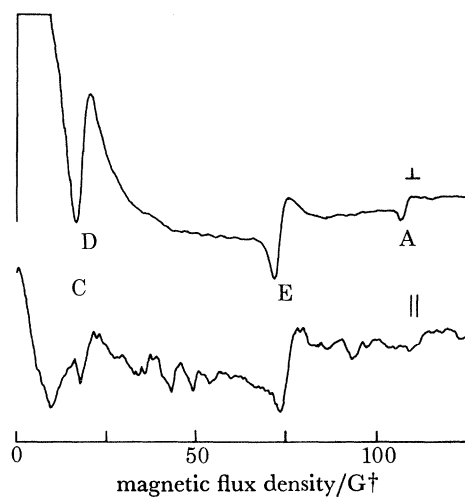


FIGURE 6. The three-level resonances A, C, D and E of the  $\tilde{A}(090)0_{00}-\tilde{X}(000)1_{10}$  transition of  $\text{NH}_2$  (figure 4), observed in mode (b) with  $\nu_c = 251$  MHz (see table 1).

TABLE 1. O.O.D.R. TRANSITIONS IN  $\text{NH}_2$   $\tilde{A}(090)0_{00}$  FOR  $\Delta\nu = 251$  MHz

$F_1$	$M_1$	$F_2$	$M_2$	$ \Delta M $	polarization	$B/\text{G}^\dagger$	
						obs.	calc.
$1\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	$\parallel, \perp$	18.5	$\left\{ \begin{array}{l} 17.7 \\ 19.2 \end{array} \right.$
$1\frac{1}{2}$	$1\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	2	$\perp$		
$1\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	0	$\parallel, \perp$	73.4	73.3
$1\frac{1}{2}$	$\frac{1}{2}$	$1\frac{1}{2}$	$-1\frac{1}{2}$	2	$\perp$	108.1	108.1

$^\dagger$  1 G =  $10^{-4}$  T.

[ 143 ]



*Stark splittings in HNO  $\tilde{A}^1A''$* 

O.o.d.r. methods should be particularly useful for determining the field splittings of levels with high angular momentum in which there is a first-order Zeeman or Stark effect. In such cases, with perpendicular polarization, all the  $\Delta M = 2$  three-level resonances in each state will superimpose to give a single strong resonance signal. The  $I_2$  Zeeman study of Gouedard *et al.* (1976) was of this type.

HNO is an asymmetric top, but it was expected from the known rotational constants that the asymmetry splittings should be negligible in many of the rotational levels. The  $M$  components of such levels should therefore exhibit a first-order Stark effect leading to the o.o.d.r. resonance condition

$$h\Delta\nu = \mu_a \mathcal{E} K_a \Delta M / J(J+1), \quad (6)$$

where  $\Delta M$  relates to the two close levels coupled through the three-level interaction.

A study was made of o.o.d.r. spectra for a number of levels of the 100—000 and 020—000 bands in the HNO  $\tilde{A}$ — $\tilde{X}$  band system near 619 nm (Dixon & Noble 1980), again with the use of field modulation for detection. In the event, few of these spectra conformed to this simple pattern because of finite asymmetry splittings in one or both levels. Not only does such a splitting lead to a departure from (6), thereby splitting the degeneracy of the symmetric top resonances, but  $K_a$  is no longer a signed quantum number, so that new transitions become possible. For a transition between a level of negligible asymmetry (symmetric top level) and a level of significant asymmetry, many of these additional resonances conform to (6) but with apparent values of  $\Delta M$  up to  $2J$ . A number of the observed spectra were of this type.

The analysis of o.o.d.r. for five ground-state levels gave a value of  $\mu_a'' = 0.996$  D, in close agreement with a value derived by Johns & McKellar (1977) from an infrared laser-Stark study. For the excited state, four levels with small or negligible asymmetry splittings yielded

$$\left. \begin{aligned} \mu_a'(100) &= 1.081 \pm 0.007 \text{ D;} \\ \mu_a'(020) &= 1.052 \pm 0.010 \text{ D.} \end{aligned} \right\} \quad (7)$$

As in  $\text{NH}_2$  many of the levels of HNO  $\tilde{A}^1A''$  are perturbed. For two levels,  $J', K' = 5, 4$  and  $6, 4$  of the 100 vibronic state, the Doppler-broadened line profiles have an f.w.h.m. of 1.7 GHz, compared with 1.05 GHz for the sharpest lines. Only ground-state o.o.d.r. transitions were observed with the acousto-optic modulator, suggesting a large but unresolved excited-state asymmetry splitting. For these two levels sharp resonances were observed at much higher electric fields, with or without the modulator.

The dye laser used (CRL 490 with a single 0.5 mm etalon) oscillates on three frequencies. From scans recorded on two different interferometers each interval was shown to be four cavity modes: a consequence of interference between standing-wave hole-burning patterns in the dye jet. These high-field resonances (figure 7) are mainly upper-state o.o.d.r. transitions, in which the measured 1192 MHz mode separation exceeds the asymmetry splitting. It is a feature of such field-scanned spectra that, even for a finite asymmetry splitting, the resonances with  $\Delta M = 0$  are given exactly, and those with  $\Delta M = 1$  or 2 (for appropriate polarization) are approximated, by

$$V = V_0 / \Delta M, \quad (8)$$

but  $V_0$  is a function both of  $\mu_a$  and the zero-field asymmetry splitting  $\Delta_0$ .  $\Delta_0$  and  $\mu_a$  can only be accurately determined independently where  $M = 0$  for one level. It was not possible to obtain

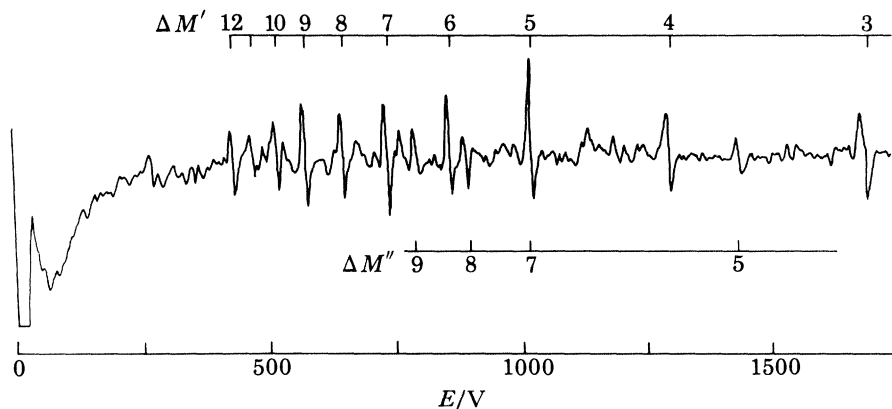


FIGURE 7. An o.o.d.r. spectrum recorded in mixed polarization within the  ${}^R R_3(5)$  line of the  $\tilde{A} \ 1A''(100) - \tilde{X} \ 1A'(000)$  band of HNO at  $16175.6 \text{ cm}^{-1}$ . The three-level resonances are generated by the 1192 MHz mode separation of the dye laser. The voltages are across a 3 mm spacing between the Stark electrodes. These resonances fit (8) to within 1% for the indicated upper state and lower state ' $\Delta M$ ' values with  $V'_0 = 5207 \text{ V}$  and  $V''_0 = 7205 \text{ V}$ .

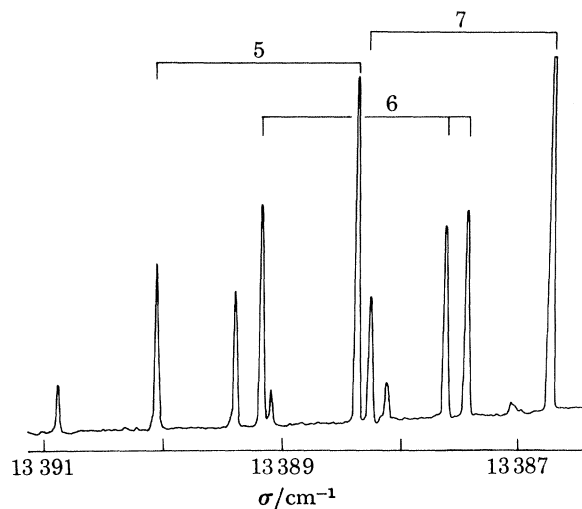


FIGURE 8. The first members of the  ${}^R Q_4$  branch of the  $\tilde{A} \ 1A''(000) - \tilde{X} \ 1A'(000)$  band of HNO recorded in the l.i.f. excitation spectrum, indicating 'extra' lines arising from perturbations. The unassigned lines are members of other branches.

high enough fields to record such resonances in these spectra. The lower-state resonances agreed to within 1% with the values calculated from the known  $\mu''_a$  ( $\Delta''_0 = 0$  for these levels). The upper-state resonances were analysed by assuming that  $\mu'_a$  could be assumed from  $J'K' = 4,4$ , despite the perturbed value of  $\Delta'_0$ , giving

$$\left. \begin{aligned} 100, J'K' = 5,4, \quad \Delta_0 = 750 \pm 10 \text{ MHz}; \\ 100, J'K' = 6,4, \quad \Delta_0 = 782 \pm 10 \text{ MHz}. \end{aligned} \right\} \quad (9)$$

These examples illustrate a limitation of field-swept o.o.d.r. spectra. It is essential that the optical difference frequency  $\Omega_1 - \Omega_2$  should be tunable if the levels have other than a first-order splitting in the field.

*g-Values for perturbed levels in HNO  $\tilde{A}^1A''$* 

The  $\tilde{A}$  state of HNO is subject to very many minor perturbations (Dalby 1958; Bancroft *et al.* 1962). We have recently found in an l.i.f. study that some but not all of the perturbed levels are magnetically active. We have therefore postulated that the perturbations arise through interaction with high levels of both the  $\tilde{X}^1A'$  and  $\tilde{a}^3A''$  states (Dixon *et al.* 1981). One of the clearest regions of perturbation was observed by Dalby near 746 nm in the 5—4 sub-band of the 0—0 transition. We have recorded the whole of this sub-band in l.i.f. at Doppler-limited

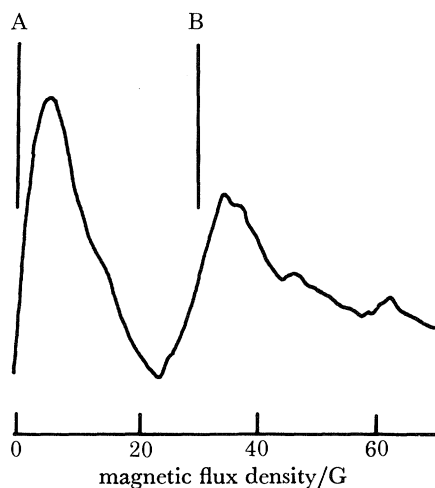


FIGURE 9. An o.o.d.r. spectrum recorded in mode (a) with perpendicular polarization within the perturbed  ${}^3R_4(5)$  line of the  $\tilde{A}^1A''(000)$ — $\tilde{X}^1A'(000)$  band of HNO at  $13404.716\text{ cm}^{-1}$ , and with  $\nu_m = 5\text{ MHz}$ . A arises from the Hanle effect, and B is the superposition of all  $\Delta M' = 2$  three-level resonances. This resonance has been recorded with  $\nu_m$  ranging from 4 to 10 MHz and tunes linearly over this range.

resolution, both field free and in magnetic fields up to 10 kG. Very many 'extra lines' have been observed in all three of the  ${}^3R_4$ ,  ${}^3Q_4$  and  ${}^3P_4$  branches. Most of the levels with  $J' = 6, 7, 8$  and  $9$  are magnetically active, as are a few weak unassigned transitions, but the activity is extremely varied: lines broaden, split, shift asymmetrically, disappear, or in one case appear to suffer a Paschen–Back effect. It is clear that an analysis of the perturbations requires knowledge of the low-field  $g$ -values, and hence the parentage of the zero-field levels.

For the lowest  $J'$  value of 5 there are two levels, neither of which has any detectable magnetic activity. For  $J' = 6$  there are three levels (figure 8) all magnetic, the close pair collapsing to one observed level in a high field. Figure 9 shows an o.o.d.r. Zeeman spectrum of the lowest-frequency component, showing one  $\Delta M = 2$  resonance. The measured  $g$ -values are:

$$\left. \begin{aligned} \tilde{A}^1A''(000). \quad J', K' = 6, 5. \quad T = 13718.219\text{ cm}^{-1}, \quad g_J = 0.16_4\text{ MHz G}^{-1}; \\ T = 13718.402\text{ cm}^{-1}, \quad g_J = 0.21_5\text{ MHz G}^{-1}; \\ T = 13719.967\text{ cm}^{-1}, \quad g_J \approx 0.01\text{ MHz G}^{-1}. \end{aligned} \right\} \quad (10)$$

The sum of these values of  $g_J$  is  $0.39\text{ MHz G}^{-1}$ . The theoretical value for an  $F_3(J = 6, N = 7)$  level of a case (b) triplet state is  $0.40\text{ MHz G}^{-1}$ . In conclusion, the  $J' = 5$  level is perturbed only by another singlet level, whereas  $J' = 6$  is perturbed by a triplet level in addition.

By using the relative line strengths as indicating  ${}^1A''$  parentage, and  $g_J$  values for  ${}^3A''$

parentage, it is possible to de-perturb these interactions uniquely (figure 10). This analysis shows that the triplet activity arises indirectly by interaction between the  $\tilde{a}^3A''$  state and the  $\tilde{X}^1A'$  state, which then interacts with the  $\tilde{A}^1A''$  state. If this is generally true, it would explain the great complexity of the magnetic interactions. It may also have important consequences for excited-state dynamics. A more extensive analysis of this region of perturbation is in progress.

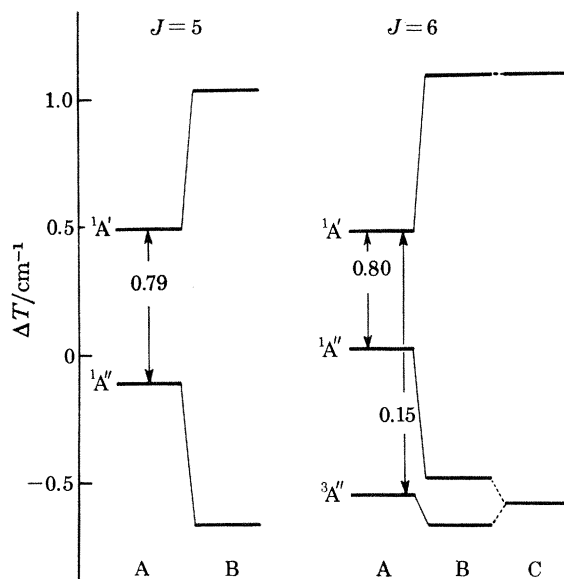


FIGURE 10. The de-perturbation of the levels with  $K' = 5$ ,  $J' = 5$  and  $6$  in the  $\tilde{A}^1A''(000)$  state of HNO. A, deduced de-perturbed level positions and coupling matrix elements; B, observed levels; C, observed partial de-perturbation for  $J' = 6$  in a magnetic field of 10 kG. The ordinate is the difference between the term values and those predicted by Dalby (1958) from unperturbed levels. For  $J' = 6$  the  $^1A'':^3A'$  coupling matrix element is zero to within the experimental error.

## DISCUSSION

From the examples given above it is seen that o.o.d.r. with two stable independently tunable lasers is more versatile than the sideband technique. In particular the two-colour form of o.o.d.r. can of itself give sufficient information to permit detailed spectral assignments and analyses.

We have attempted to sweep the modulation frequency of the acousto-optic modulator for the sub-Doppler resolution of zero-field splittings, but have found that this produces artefacts due to electronic resonances. This form of o.o.d.r. is therefore likely to remain one of a number of saturation techniques in the armoury of the molecular spectroscopist. In common with other double-resonance techniques it has the advantage that it can give information directly about one state at a time.

I am grateful to my colleagues David Field, Bob Jennings, Marcus Noble, and Caroline and Keith Rosser who have contributed to work described in this paper. I also thank the S.E.R.C. for equipment grants.

## REFERENCES

- Amano, T., Kawaguchi, K., Kakimoto, M., Saito, S. & Hirota, E. 1980 *A. Rev. Inst. molec. Sci., Okazaki*, p. 45.
- Bancroft, J. L., Hollas, J. M. & Ramsay, D. A. 1962 *Can. J. Phys.* **40**, 322.
- Beaudet, R. A., Weyer, K. G. & Walther, H. 1979 *Chem. Phys. Lett.* **60**, 486.
- Bernheim, R. A., Gold, L. P., Kelly, P. B., Kittrell, C. & Veirs, D. K. 1979 *Phys. Rev. Lett.* **43**, 123.
- Bernheim, R. A., Gold, L. P., Kelly, P. B., Kittrell, C. & Veirs, D. K. 1980 *Chem. Phys. Lett.* **70**, 104.
- Brewer, R. G. 1970 *Phys. Rev. Lett.* **25**, 1639.
- Brunner, T. A., Driver, R. D., Smith, N. & Pritchard, D. L. 1979 *J. chem. Phys.* **70**, 4155.
- Dalby, F. W. 1958 *Can. J. Phys.* **36**, 1336.
- Danyluk, M. D. & King, G. W. 1977 *Chem. Phys.* **22**, 59.
- Dearden, S. J., Dixon, R. N. & Field, D. 1982 *J. chem. Soc. Faraday Trans. II*. (In the press.)
- Demtröder, W., Eisel, D., Foth, H. J., Höning, G., Raab, M., Vedder, H. J. & Zevgolits, D. 1980 *J. molec. Struct.* **59**, 291.
- Dixon, R. N. & Field, D. 1977 *Molec. Phys.* **34**, 1563.
- Dixon, R. N., Field, D. & Noble, M. 1977 *Chem. Phys. Lett.* **50**, 1.
- Dixon, R. N., Field, D. & Noble, M. 1979 In *Proc. 14th Int. Symp. on Free Radicals*, p. 239. Yamada Science Foundation.
- Dixon, R. N. & Noble, M. 1980 *Chem. Phys.* **50**, 331.
- Dixon, R. N., Noble, M., Taylor, C. A. & Delhoume, M. 1981 *Faraday Discuss. chem. Soc.* **71**, 125.
- Ennen, G. & Ottinger, C. 1974 *Chem. Phys.* **3**, 404.
- Field, R. W. 1981 *Faraday Discuss. chem. Soc.* **71**, 111.
- Gottscho, R. A., Field, R. W., Bacis, R. & Silvers, S. J. 1980a *J. chem. Phys.* **73**, 599.
- Gottscho, R. A., Weiss, P. S., Field, R. W. & Pruett, J. G. 1980b *J. molec. Spectrosc.* **82**, 283.
- Gouedard, G., Broyer, M., Vigne, J. & Lehmann, J. C. 1976 *Chem. Phys. Lett.* **43**, 118.
- Hills, G. W., Brazier, C. R., Brown, J. M., Cook, J. M. & Curl, R. F. 1982 *J. chem. Phys.* **76**, 240.
- Hills, G. W., Philen, D. L., Curl, R. F. & Tittel, F. K. 1976 *Chem. Phys.* **12**, 107.
- Johns, J. W. C. 1961 *Can. J. Phys.* **39**, 1738.
- Johns, J. W. C. & McKellar, A. R. W. 1977 *J. chem. Phys.* **66**, 1217.
- Johnson, M. A., Webster, C. R. & Zare, R. N. 1981 *J. chem. Phys.* **75**, 5575.
- King, G. W., Littlewood, I. M. & Littlewood, N. T. 1981b *Chem. Phys. Lett.* **80**, 215.
- King, G. W., Littlewood, I. M. & Robins, J. R. 1981a *Chem. Phys.* **56**, 145.
- Klein, F. K. 1977 Diplom thesis, Physics Department, University of Kaiserslautern.
- Orr, B. J. & Oka, T. 1977 *Appl. Phys. Lett.* **30**, 468.
- Russell, D. K., Kroll, M. & Beaudet, R. A. 1977 *J. chem. Phys.* **66**, 1999.
- Weyer, K. G., Beaudet, R. A., Straubinger, R. & Walther, H. 1980 *Chem. Phys.* **47**, 171.

## Discussion

G. W. SERIES, F.R.S. (*University of Reading, U.K.*) Professor Dixon mentioned that the use of two separate lasers could be avoided by using sidebands of the light from one laser generated by an acousto-optic modulator. Indeed, that is true, but the partial coherence between the beams from two separate lasers is to be distinguished from the full coherence between the fundamental and sideband radiation from one laser. The coherence in the latter case could give rise to interference effects not present in the former.

R. N. DIXON. I fully agree that double resonance involving fundamental and sideband radiation from one laser could give rise to coherent interference effects that would not occur with two separate lasers.

One possible manifestation of this interference could be a change in the angular distribution and polarization of the laser-induced fluorescence when the three-level system satisfies the Brewer resonance condition, as is familiar with the zero-field Hanle effect. However, our experiments have been confined to polyatomic molecules with undispersed fluorescence. Under these conditions the summation over all branches of the fluorescence spectrum tends to cancel any polarization anisotropy, so that our o.o.d.r. signals are mainly due to changes at resonance

in the extent of population saturation. Our use of audio-frequency detection techniques (*ca.* 1 kHz) would also average out any high-frequency beat signals resulting from temporal coherence.

In our analysis of Stark o.o.d.r. spectra of HNO (Dixon & Noble 1980) we calculated intensities ignoring any coherent effects, and obtained a qualitative fit to the observations. It is possible that coherence might have contributed to the lack of a quantitative fit.

G. DUXBURY (*Department of Natural Philosophy, University of Strathclyde, Glasgow, U.K.*). The o.o.d.r. method described in this paper is equally applicable to infrared sub-Doppler spectroscopy. Both Orr & Oka (1980) and Bedwell & Duxbury (1979) have shown the power of the method for achieving very high-resolution spectra within the Doppler width of an absorption line in near coincidence with CO<sub>2</sub> lasers. As in the dye laser experiments the infrared acousto-optic modulator (a.o.m.) can be modulated by using a second r.f. oscillator to give an amplitude-modulated sideband (Duxbury & Kato 1982). The reliance on near-coincidences can be improved by the replacement of low-pressure CO<sub>2</sub> lasers by more tunable higher-pressure waveguide lasers.

$M_J$ -resolved double-resonance signals can be seen in low  $J$  transitions of molecules such as ammonia, even when the energy levels connected by the Stark perturbation are separated by a frequency far greater than that of the a.o.m. Examples of this type of signal have been seen in transitions in <sup>15</sup>NH<sub>3</sub> when the Stark perturbation involved inversion doublets (Duxbury *et al.* 1982) and when it involved levels differing in  $J$  by 1, with  $K = 0$  (Orr & Oka 1977).

Recently Mlynek *et al.* (1981) have shown that o.o.d.r. signals can be detected by the method of polarization spectroscopy, where the observation of the signals depends on the generation of Hertzian coherence. We have observed similar effects in the Stark spectra of several molecules by using a technique involving combinations of polarizers (Bedwell & Duxbury 1979; Duxbury *et al.* 1982). In the infrared region the line widths of the signals due to population saturation and Hertzian coherence are indistinguishable at our resolution, which is limited by the residual electric field inhomogeneity and by the transit time of the molecules in the radiation field in the narrow gap between the plates in the cell, between 1 and 3 mm.

In the signals observed by using amplitude modulated sidebands we have seen no effects due to the interference between coherences induced by the two r.f. drive oscillators. This may be due to the fact that our signals are a mixture of those due to coherence effects and to population saturation, and also to the low frequency of the Stark modulation, *ca.* 5 kHz, so that the effect of rapid fluctuation in the high-frequency coherence effects is averaged out.

### References

- Bedwell, D. J. & Duxbury, G. 1979 *Chem. Phys.* **37**, 445.  
 Duxbury, G. & Kato, H. 1982 *Chem. Phys.* **66**, 161.  
 Duxbury, G., Kato, H., Le Lerre, M. L., McCombie, J. & Petersen, J. C. 1982 In *Proceedings, 5th National Quantum Electronics Conference*. Wiley. (In the press.)  
 Mlynek, J., Drake, K. H., Kersten, G., Frölich, D. & Lange, W. 1981 *Optics Lett.* **6**, 87.  
 Orr, B. J. & Oka, T. 1977 *J. molec. Spectrosc.* **66**, 302.  
 Orr, B. J. & Oka, T. 1980 *Appl. Phys.* **21**, 293.