

# Intracavity Infrared-Microwave Double-Resonance Spectroscopy [and Discussion]

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## Intracavity infrared–microwave double-resonance spectroscopy

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The paper discusses the development of the intracavity infrared–microwave (or radio-frequency) double-resonance method in which a microwave resonance of low-pressure gas placed inside a laser cavity is detected as a variation of laser power. Emphasis is laid on the very high sensitivity of this method and on the three phenomena observed by this method, i.e. (1) the transfer of saturation holes and spikes to other levels that are not directly pumped by the laser through weak intermolecular interactions without a change in velocity, (2) velocity-tuned multiphoton processes, which complicate the structure of saturation holes, and (3) the off-resonant ‘double’ resonance in which microwave pumping is detected through the dispersive response of the laser rather than absorption.

## 1. INTRODUCTION

For those of us using microwave double resonance to study the dynamics and spectroscopy of simple molecules in the 1960s the advent of the infrared laser opened up the possibility of infrared–microwave double resonance. Until then we had been attempting this using ordinary radiation sources (Shimoda & Oka 1958; Oka & Ramsay 1966). The high power, the excellent spectral purity, and the stable continuous wave (c.w.) operation of the CO<sub>2</sub> laser looked ideal as the pump radiation sources for double resonance and a few attempts were made in the late 1960s (Ron & Lide 1967, Lemaire *et al.* 1969; Fourier *et al.* 1970). In 1970 clear double-resonance signals were observed (Shimizu & Oka 1970*a, b*) in three-level and four-level systems of NH<sub>3</sub> by using the coincidence between the aQ(8, 7) vibration–rotation transition in the  $\nu_2$ -fundamental band and the P(13) line of the N<sub>2</sub>O laser (Shimizu 1970). We soon went on to develop microwave–infrared two-photon spectroscopy (Oka & Shimizu 1971) and two-photon and multiple-photon Lamb-dip spectroscopy (Freund & Oka 1972, 1976; Freund *et al.* 1975).

As we did more experiments, our apparatus gradually developed into the intracavity arrangement shown schematically in figure 1 (Freund & Oka 1972; Curl & Oka 1973; Curl *et al.* 1973; Curl 1973; Kreiner & Oka 1975). A similar arrangement was reached independently by Takami & Shimoda (1972, 1973, 1976) and subsequently used also by others (Jones 1977, 1978*a, b*; Kreiner *et al.* 1977*a, b*; Dale *et al.* 1977; Arimondo *et al.* 1978, 1980; Allegrini *et al.* 1980; Herman *et al.* 1979). The very successful application of this method to many heavy molecules by Jones and his collaborators (Botskor & Jones 1980; Jones 1980; Jones & Brown 1981; Jones & Morillon-Chapey 1982) and the use of frequency-tunable colour-centre lasers (DeLeon *et al.* 1981) are particularly noteworthy. Although the details of the design varies, the basic principle of operation is as follows. A sample cell containing low-pressure gas (*ca.* 10 mTorr; *ca.* 1.33 Pa) is placed inside a laser cavity and strong microwave (or radiofrequency) radiation is applied. The microwave frequency is swept and a resonance is detected as a sharp variation of the laser power. Thus the laser not only provides the radiation for double resonance but also acts as part of the detection system.

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The purpose of this paper is to describe briefly the operation of this method with the emphasis on its sensitivity and to discuss qualitatively the three phenomena that we stumbled on during our experiment, i.e. extra resonances caused by the transfer of saturation holes and spikes (§3), velocity-tuned multiphoton processes (§4), and off-resonant ‘double’ resonance (§5). The interesting applications of this method for observing extremely weak forbidden rotational transitions (Oka 1976) and multiple-photon Lamb-dip spectroscopy (Oka 1977) have been reviewed. Several reviews have appeared for microwave–infrared double resonance in general (Shimoda & Shimizu 1972; Shimoda 1976; Jones 1979).

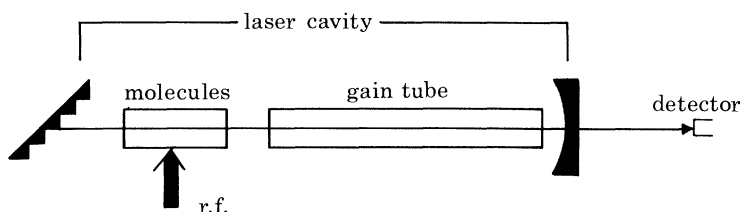


FIGURE 1. Basic experimental set-up for infrared–microwave (or radiofrequency) double resonance inside the laser cavity. A microwave resonance is detected as a variation of the laser power.

## 2. HIGH SENSITIVITY OF THE METHOD

If the intracavity gas sample has a vibrational–rotational transition whose frequency  $\nu_0$  is coincident with the laser frequency  $\nu_L$  within its Doppler profile, a steady state of pumped molecular flow among many vibrational–rotational states is established. This situation is shown schematically in figure 2. The laser ‘pumps’ molecules with a certain velocity  $v$  that satisfies  $\nu_{\pm} \equiv \nu_L(1 \pm v/c) = \nu_0$  up and down between level 1 in the lower vibrational state and level 2 in the upper vibrational state with the Rabi frequency  $\mu_{12}E_L/h$ . For a typical case of the vibrational transition moment  $\mu_{12} = 0.05 D$  (*ca.* 0.17 mC m) and the laser electric field of  $30 \text{ V cm}^{-1}$  (power density *ca.*  $1 \text{ W cm}^{-2}$ ), the Rabi frequency is 500 kHz. This equalizes the populations in levels 1 and 2 for molecules with the resonant velocity and creates a pair of holes and spikes in the levels 1 and 2, respectively, with an effective rate of  $(\mu_{12}E_L/h)^2/2\Gamma_{12}$ . The damping constant  $\Gamma_{12}$  can be expressed by using the rate constants  $k_{im}$  for collision-induced transitions between levels  $i$  and  $m$  as  $\Gamma_{12} = \frac{1}{2}\sum_m (k_{1m} + k_{2m})$  and is proportional to the pressure of the sample. If the Rabi frequency is much larger than  $\Gamma_{12}$ , which is typically *ca.* 200 kHz for 10 mTorr, the depths of holes and the heights of spikes are nearly 50 % of the molecular population with the resonant velocity.

The anomalous population distribution thus created in levels 1 and 2 by laser pumping is then transferred to other levels in the same vibrational states through collision-induced rotational transitions, which occur with rates  $k_{1i}$  and  $k_{2j}$ . Because of the selection rules operating for such transitions (Oka 1973) the transfer occurs efficiently to relatively few levels by one step but to other levels by cascading. Thus the effect of laser pumping is spread to nearly all rotational levels in the two vibrational states. The vibrational relaxation between levels 1 and 2 occurs more slowly through collisions and also through thermal exchange with the wall of the sample vessel. Thus a steady state of energy flow is established. The analytical treatment of this steady state is rather complicated because not only the change of quantum states of molecules have to be considered but also the variation of velocity due to collision. Such an attempt has been made by Arimondo *et al.* (1978).

When the resonant microwave (or r.f.) radiation is applied to the gas, this steady state is

disturbed and the laser responds to it. For the simplest case of three-level double resonance in which the microwave transition occurs between one of the pumped levels (level 1 or 2) and some other rotational level, the effect is the largest. The laser power decreases regardless of whether the microwave transition occurs in the lower or the upper vibrational state, in the former for the added charge of molecules and in the latter for the added drain of molecules. It is expected that the effect of microwave pumping is maximum when the Rabi frequency for microwave pumping  $\mu_{13}E_m/h$  is much greater than the collision-induced rate  $\gamma_{13}$  to fill the holes (or  $\gamma_{24}$  to dissipate the spikes), namely when  $\gamma_{13}$  is small or accompanies large velocity changes. Thus forbidden rotational transitions (Oka 1973) or pure quadrupole transitions (Arimondo *et al.* 1978, 1980; Scappini & Oka 1981) are particularly favourable. Such transitions have small radiative transition dipole moments but this can be compensated for by applying a large microwave electric field. For this reason microwave (or r.f.) radiation with high power (*ca.* 10 W) is used. The reasons for the high sensitivity of this method are summarized as follows.

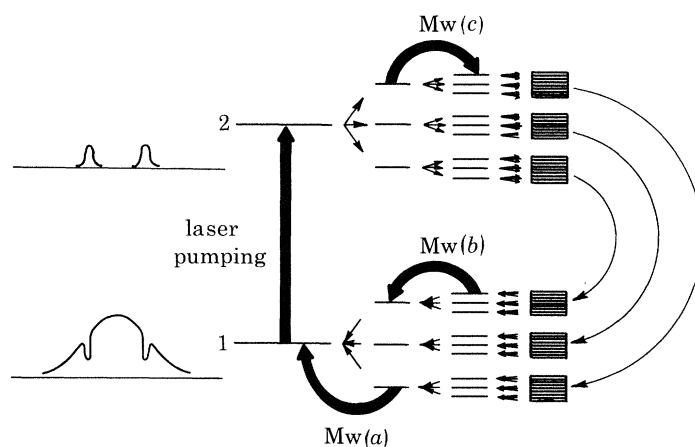


FIGURE 2. The steady state of energy flow in the intracavity gas sample due to laser pumping. A pair of holes are bleached in the Maxwellian velocity profile of the lower level 1 and a corresponding pair of spikes are created in the upper level 2. These anomalous population distributions are transferred to other levels by collision. An application of resonant microwave radiation perturbs this steady state and thus changes the performance of the laser. A microwave transition directly connecting to the pumped level (such as Mw(a)) affects the laser most but other transitions (such as Mw(b) and Mw(c)) may affect the laser sufficiently for its effect to be observable on the laser.

1. The molecules convert a microwave (or r.f.) signal to an infrared signal on a one-to-one basis in terms of numbers of photons and thus gains in energy of  $(\nu_L/\nu_m) \approx 10^3\text{--}10^6$ .
2. The infrared saturation creates anomalous population distribution and thus creates an effective population difference larger than the thermal value by  $(kT/2h\nu_m) \approx 10^2\text{--}10^5$ .
3. The nonlinearity of laser action further amplifies these gains. In particular, if the microwave radiation is frequency or amplitude modulated at the resonance frequency of the laser, a larger gain in sensitivity (*ca.* 30-fold) is obtained (Arimondo & Glorieux 1978).

The first two points apply to any saturated infrared–microwave double resonance, whereas the third point is special for intracavity double resonance. We considered only the effect of absorption, but the laser also reacts to intracavity molecules through dispersion. This effect is small when the laser is near the centre of the Doppler profile of the molecular absorption but is otherwise quite large and complicates the line shape of the double resonance (Kreiner & Oka 1975; Jones 1979). In particular, for the off-resonant case discussed in §5, the signal is produced only through dispersion.

## 3. COLLISION-INDUCED TRANSFER OF SATURATION HOLES AND SPIKES

When we operate a double-resonance spectrometer at its maximum sensitivity, we often observe many extra microwave resonances that are not directly connected to the infrared levels 1 and 2 pumped by the laser. An example is shown in figure 3. These extra resonances are caused by collision-induced transfer of molecules between the pumped levels and levels  $a$  or  $b$ , or both, of the microwave transition. From the consideration of the steady state given in §2, it is expected that the effect of laser pumping is transferred to all levels of molecules through collision and that the effect of microwave pumping of any levels in turn affects the laser operation. Thus, in principle, any microwave resonance can be detected through any laser line if the apparatus has sufficient sensitivity. In practice, of course, this does not happen because of limited sensitivity. Many collision-induced resonances have been observed for pure quadrupole resonances in  $\text{CH}_3\text{I}$  (Arimondo *et al.* 1978) and  $\text{CH}_3\text{Br}$  (Arimondo *et al.* 1980), but no extra resonance was observed for  $\text{AsH}_3$  (Scappini & Oka 1981) and  $\text{PH}_3$  (Shimizu *et al.*, unpublished) in spite of the fact that they were searched for to help assignments.

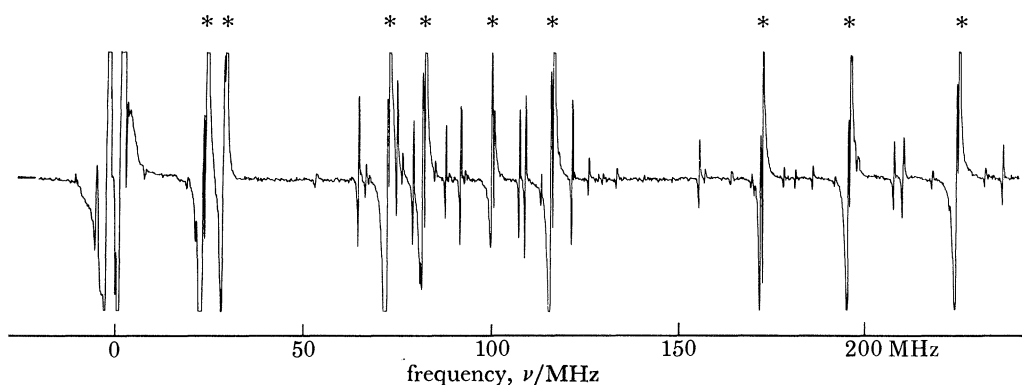


FIGURE 3. Quadrupole resonance spectrum of gaseous  $\text{CH}_3\text{I}$  with high sensitivity. The  $\text{CO}_2$  P(32)  $10.72 \mu\text{m}$  laser line is used. The nine features marked with an asterisk are three-level double-resonance signals directly connecting to the  $J = 16, K = 6, l = 1 \leftrightarrow J = 15, K = 5$  transition in the  $\nu_6$  band. Other lines are collision-induced resonances with  $J$  around 15 and 16. Sample pressure *ca.* 10 mTorr, time constant 100 ms.

The necessary condition for observing the collision-induced resonances is that the collisional transfer of the holes (or spikes) from the pumped level 1 (or 2) to the probed levels  $a$  and  $b$  (or  $c$  and  $d$ ) occurs in an asymmetric way, as shown in figure 4. The following two conditions are necessary for this to occur; (1) the collision-induced transfer occurs with selection rules, i.e. in figure 4 the rate of the collision-induced process  $1 \leftrightarrow a$  (or  $2 \leftrightarrow c$ ) or the multiple process  $1 \leftrightarrow \dots \leftrightarrow a$  (or  $2 \leftrightarrow \dots \leftrightarrow c$ ) is much larger than the corresponding rate between 1 and  $b$  (or 2 and  $d$ ); (2) the transfer of molecular populations occurs through very weak collisions so that the velocities of molecules do not vary appreciably by collision. Otherwise the holes (or spikes) are smeared out. The existence of selection rules for collision-induced rotational transitions is well established from microwave double-resonance experiments (Oka 1973). The evidence for velocity-conserving inelastic collisions and thus the transfer of saturation holes and spikes has been previously given from the direct four-level infrared-infrared double resonance (Freund *et al.* 1973) and laser Stark-centre dips (Ouhayoun & Borde 1972; Brewer *et al.* 1974; Shoemaker *et al.* 1974; Johns *et al.* 1975). Although rotational transitions studied in those papers are between very closely spaced inversion or Stark-component levels, the experiment by Meyer & Rhodes

(1974) and Bischel & Rhodes (1976) showed that such transfer with velocity memory also occurs between levels of  $\text{CO}_2$  differing by  $\Delta J = 2$  that are *ca.*  $30 \text{ cm}^{-1}$  apart.

In the pure quadrupole double-resonance spectrum of  $\text{CH}_3\text{I}$ , the collision-induced satellites up to  $\Delta J = 8$  have been observed from  $J = 15$ , as shown in figure 5 (Glorieux *et al.*, unpublished). An analysis of the relative intensities of these satellites shown that these extra resonances with  $\Delta J > 1$  are caused by cascading processes rather than by a single step. Although such cascading processes following selection rules are known in microwave double resonance (Oka 1967) for the *l*-doubling spectrum of HCN and the *K*-doubling spectrum of  $\text{H}_2\text{CO}$ , the result shown in figure 5 demonstrates the remarkable fact that not only are the selection rules followed

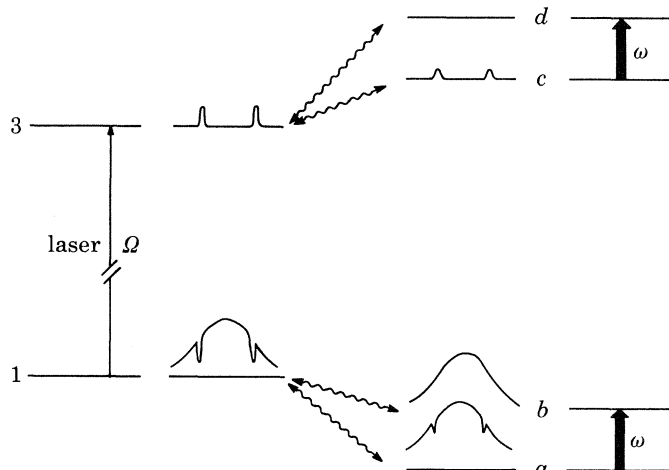


FIGURE 4. Operation of double resonance on levels where the non-thermal population distribution due to laser pumping is transferred by collisions. The two conditions for observation of this type of transitions are discussed in the text.

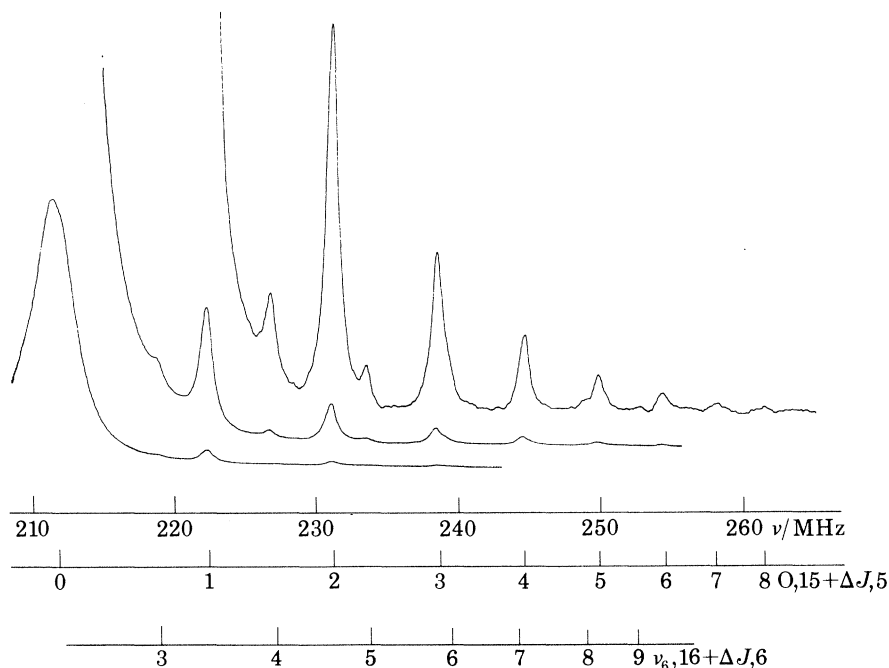


FIGURE 5. Collision-induced satellites of the double-resonance spectrum.  $\Delta J$  up to 8 and 9 are observed for the ground state and for the excited state respectively.

but the velocity memory is kept during this cascading process. This indicates that most intermolecular collision between  $\text{CH}_3\text{I}$  molecules causing the  $\Delta J = \pm 1$  (and  $\Delta F = \pm 1$ ) transitions are very weak and do not accompany a large change in total energy before and after the collision. Because the rotational energy levels of  $\text{CH}_3\text{I}$  ( $B = 0.25 \text{ cm}^{-1}$ ) are spaced by 8–12  $\text{cm}^{-1}$  for  $J = 15$  to  $J = 23$  (overall spacing *ca.* 312  $\text{cm}^{-1}$ ), which is smaller than  $kT$  (*ca.* 200  $\text{cm}^{-1}$ ) but not negligible, the rotational resonance (Anderson 1949; Oka 1967) must be contributing. In such a process one molecule increases its  $J$  value by one while its collision partner decreases its  $J$  value, keeping the total energy and total angular momentum nearly conserved. The  $J$  value for maximum molecular population is  $J \approx \sqrt{(kT/2Bh)} \approx 20$  and thus molecules with  $J = 15$  to  $J = 23$  find many resonant collision partners.

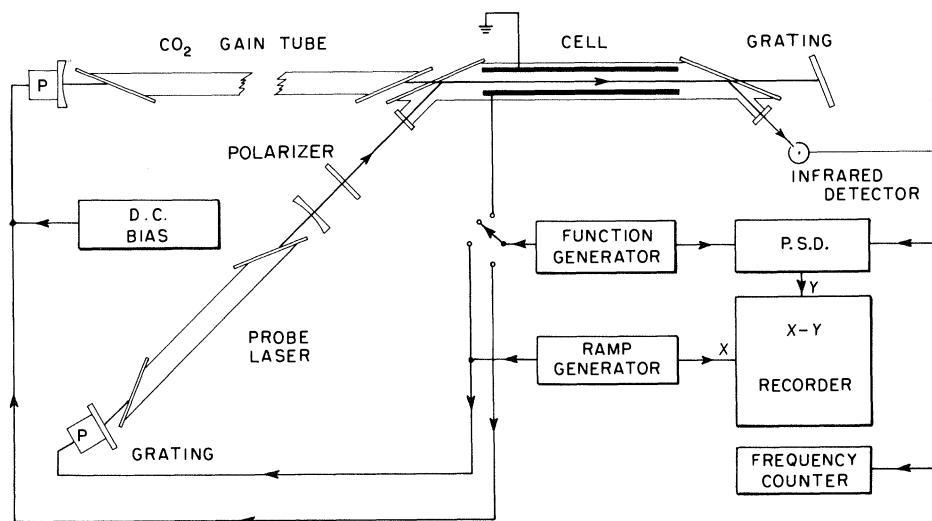


FIGURE 6. Experimental apparatus for the direct observation of the velocity-tuned multiphoton processes.

When the steady state discussed in the last section is treated analytically (Arimondo *et al.* 1978), we find that the relative intensity of the collision-induced  $\Delta J = 1$  resonance compared with that of the original resonance is smaller by a factor of

$$\eta = \left( \frac{k_{1a} - k_{1b}}{\Gamma_{ab} + k_{ab}} \zeta_{1a} \right)^2, \quad (1)$$

where  $k_{ij}$  denote rates of collision-induced transitions  $i \leftrightarrow j$ ,  $\Gamma_{ab} = \frac{1}{2} \sum_m (k_{am} + k_{bm})$  and  $\zeta_{1a} < 1$  is the fraction of velocity-conserving  $1 \leftrightarrow a$  transitions. The strong collision-induced resonances in  $\text{CH}_3\text{I}$  are due to the selection rule  $k_{1a} \gg k_{1b}$ , velocity conservation  $\zeta_{1a} \approx 1$  and the small value of  $k_{ab}$ , which occurs twice in the denominator of (1). The collision-induced pure quadrupole transition  $a \leftrightarrow b$  requires a nuclear spin reorientation with respect to the molecular frame. The transition probability for such a process is proportional to  $F^{-2}$ , where  $F$  is the total angular momentum ( $F = J + I$ ) and is very small for high  $J$ . The selection rule  $k_{1a} \gg k_{1b}$  is also understood from such a consideration (Cohen & Wilson 1973). The transition  $1 \leftrightarrow a$  ( $\Delta J = \Delta F = \pm 1$ ) is much faster than the transition  $1 \leftrightarrow b$  ( $\Delta J = \Delta F$ ) because the nuclear reorientation is minimal in the former but significant in the latter.

It will be an interesting problem in the future to monitor the transfer of saturation holes and spikes by using a frequency-tunable infrared laser.

## 4. VELOCITY-TUNED MULTIPHOTON PROCESSES

During an intra-cavity infrared-r.f. two-photon Lamb-dip experiment (Freund *et al.* 1975), we discovered that the shape of saturation dips and holes bleached in the Maxwellian velocity distribution of molecules is not as simple as that given schematically in figure 2. In addition to the two holes symmetrically bleached at the resonant velocity  $v_1$ , which satisfies the condition  $v_L(1 + v_0/c) = v_0$ , evidence of extra holes at  $\frac{1}{3}v_0$  has been observed. An elegant analysis of our result by Shimizu (1974) indicated that a three-photon process, which was earlier predicted by Haroche & Hartman (1972) in their detailed theory of Lamb dips, causes these extra holes.

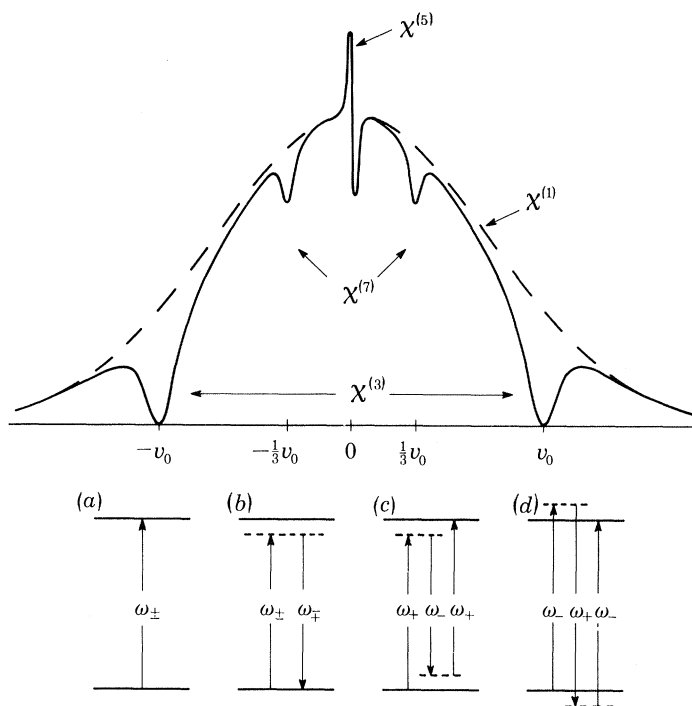


FIGURE 7. Absorption of probe laser radiation for the experimental set-up of figure 6 by the gas under laser pumping. The broken curve  $\chi^{(1)}$  shows the overall Doppler absorption profile. The features  $\chi^{(3)}$  are the normal saturation holes due to the single-photon process shown in (a). The feature  $\chi^{(5)}$  is due to the stimulated Rayleigh process shown in (b). The features  $\chi^{(7)}$  represent the effect of velocity-tuned three-photon processes shown in (c) and (d).

Thus we attempted to observe the velocity profile of molecules placed in the  $\text{CO}_2$  laser cavity by using a second  $\text{CO}_2$  laser (Reid & Oka 1977). The apparatus is shown in figure 6. The monitor-laser radiation with a plane of polarization perpendicular to that of the laser was coupled in and out of the  $\text{CO}_2$  laser cavity by reflexion on the Brewster windows.

The observation clearly demonstrated the existence of extra features, shown schematically in figure 7. Note that this picture is the direct result of observation, namely the absorption of the probe laser beam; it gives the susceptibility of the intracavity gas under laser pumping rather than the actual velocity profile of the population. We see that in addition to the ordinary saturation holes at the resonant velocities  $\pm v_0$  caused by the single-photon process of figure 7a, there are two extra holes at velocities  $\pm \frac{1}{3}v_0$  caused by the three-photon processes shown in figure 7c (for which  $v_L < v_0$ ) and figure 7d (for which  $v_L > v_0$ ). The former process pumps



molecules by using two up-shifted frequencies in absorption and one down-shifted frequency in emission; and the resonance condition is

$$\nu_L(1+v/c) - \nu_L(1-v/c) + \nu_L(1+v/c) = \nu_L(1+3v/c) = \nu_0.$$

Since the position of the virtual states shown in figure 7*c, d* are dictated by the velocity, we named them velocity-tuned three-photon process. Although the probability of such a process is proportional to the square of the effective Rabi frequency

$$\Omega = \frac{9|\langle 1|\mu E_{\pm}|2\rangle|^2|\langle 1|\mu E_{-}|2\rangle|}{16\hbar^3(\nu_L - \nu_0)^2}, \quad (2)$$

and thus is much smaller than that of the single-photon process for a large  $\nu_L \nu - \nu_0$ , the effect is certainly significant in the laser cavity, where the value of the Rabi frequency  $\mu E/h$  is not negligible compared with the laser mismatch  $\nu_L - \nu_0$ . In particular, when the laser frequency  $\nu_L$  is tuned close to  $\nu_0$  the effect of the three-photon process is greatly magnified. In such a condition higher  $2l+1$  velocity-tuned multiphoton processes occur efficiently and the monitor spectrum is greatly complicated at the centre of the profile (Reid & Oka 1977). A detailed theoretical treatment for such cases has been reported by Kyrola & Stenholm (1977, 1979).

It is interesting to note that during the velocity-tuned three-photon processes, three units of photon momentum  $h/\lambda$  are transferred to the molecule interacting with them because two up-shifted photons (in the  $+z$  direction, say) are used for absorption and one down-shifted photon (in the  $-z$  direction) are used for emission. All three photons are pushing the molecule in one direction. In general for a velocity-tuned  $2l+1$  photon process, all  $2l+1$  photons push the molecule in one direction; thus multiphoton processes are much more efficient in deflecting the molecular path than the normal single-photon process. Thus it is expected that the deflexion of an atomic or molecular beam is more effectively done by using a standing-wave radiation field than by a travelling-wave field. An experiment to demonstrate this point was carried out by using a Na beam and its D line (Arimondo *et al.* 1979). A large symmetrical deflexion of the beam, due to the resonant standing-wave field, was observed, although the coherence of the radiation pressure was not demonstrated.

An intriguing result of the experiment of Reid & Oka was the very strong feature at the centre of the velocity profile given in figure 7 with dispersive shape. This feature is produced by the stimulated Rayleigh process shown in figure 7*b*. The asymmetry of this feature with respect to the sign of velocity is due to the asymmetry of probe radiation shown in figure 6 with respect to the  $+$  and  $-z$  axis.

The intricate features in the velocity profile of intra-cavity gases discussed in this section not only affect the double-resonance and two-photon experiments but also play a role for the laser action by the gain medium itself. Such an effect has not so far been considered.

## 5. OFF-RESONANT DOUBLE RESONANCE

During the experiments of intra-cavity double resonance and two-photon Lamb dip, we found that often a laser line that is not coincident with any molecular absorption still gives fairly strong 'double' resonance signals (Freund & Oka 1976). Because the absorption falls off as  $(\nu_L - \nu_0)^2$  but the dispersion as  $(\nu_L - \nu_0)$  for off-resonant cases, the effect of dispersion is dominant. The microwave resonance changes the population by a fraction of  $h\nu/2kT$  and this is 'felt' by the laser through a small variation of dispersion. Because the variation of dispersion

changes the effective length rather than the quality factor of the laser cavity, the laser frequency has to be set to one side of the gain profile to allow observation of the power variation of the laser due to a microwave resonance. For a gas sample with a pressure of 30 mTorr and a frequency mismatch of *ca.*  $0.3 \text{ cm}^{-1}$ , the effective variation of cavity length is typically *ca.*  $0.1 \text{ \AA}$  ( $0.01 \text{ nm}$ ), the frequency shift *ca.*  $100 \text{ Hz}$  and the power variation *ca.*  $10^{-6}$ . Microwave resonances have been observed for off-resonant cases with infrared frequency mismatch up to  $3 \text{ cm}^{-1}$  (Arimondo & Oka 1982).

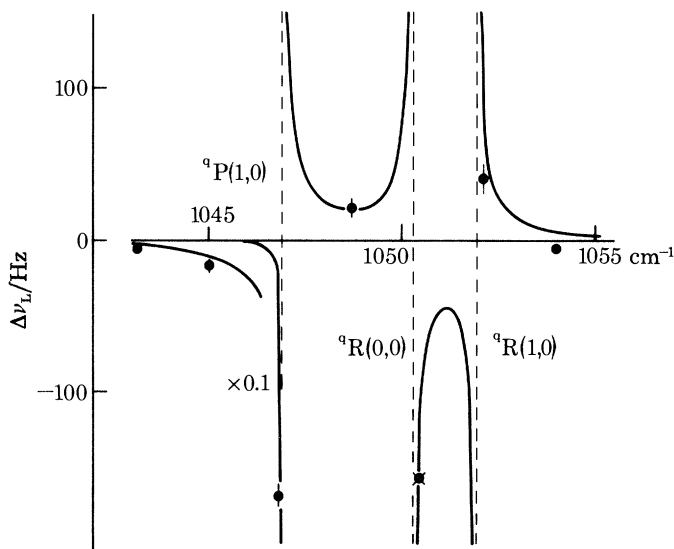


FIGURE 8. Observed intensities and signs of off-resonant double resonance signals in terms of frequency shift  $\Delta\nu_L$  of the laser, for  $1_0 \leftarrow 0_0$  in  $^{12}\text{CH}_3\text{F}$  at 25 mTorr, the microwave frequency being 51.072 GHz. The observed points represent results with  $\text{CO}_2$  laser lines (from the left) P(22), P(20), P(18), P(16), P(14) and P(12). The solid lines are the results of theoretical calculations (Arimondo & Oka 1982).

A theoretical analysis has been given, and it explains the experimental results as shown in figure 8. When the laser frequency is systematically tuned to one side of the gain profile, it is possible to determine the sign of the double-resonance effect.

The sensitivity of this method is not as high as the resonant case discussed in §2 because the second of the three reasons that make the resonant case so sensitive does not apply. The laser cannot create the large population difference for the microwave transition. For this reason the levels have to have a sizeable population difference at thermal equilibrium, and thus radio frequency transition cannot be observed effectively by this method. However, the great advantage of the off-resonant method is that we can apply this method in general to molecules that have an infrared absorption in the region of laser oscillation but may not have many coincidences.

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### Discussion

R. N. ZARE (*Physical Chemistry Laboratory, Oxford, U.K.*). What are the prospects for ‘triple resonance’ in which microwave double resonance is monitored through detection of a change in an optical carrier? Might this be used to unravel the complex CF<sub>3</sub>I double resonance spectrum that was presented to us?

T. OKA. The method of triple resonance in which one extra microwave radiation is used to reach out further to other levels has been in fact done by Takami & Suzuki (*J. molec. Spectrosc.* B 7, 144 (1978)). Using this technique they made most of the relatively few coincidences between absorption of propynal and the He–Xe laser line. As suggested, such a method may also be used to aid the assignment of very complicated spectra.