Collision-Induced Optical Double Resonance*

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The double-resonance concept is extended to the situation of two coherently driven optical transitions that do not share a common level but are coupled by molecular collisions that tip the angular momentum vector while preserving the molecular velocity and the rotational energy. This collision-induced double resonance is observed as sharp resonances, free of Doppler broadening, and can be explained in the same order of perturbation theory as the ordinary double-resonance experiment. They appear as satellite lines accompanying the usual double resonance or Lamb-dip spectra.

In the double-resonance effect, which is well known at both radio and optical frequencies,[1-3] a molecule interacts simultaneously with two radiation fields, causing a transition from an initial to a final state through an intermediate level [Fig. 1(a)]. This Letter reports observations and theory for a double-resonance phenomenon that involves a single molecular velocity group undergoing two optical transitions that do not share a common level [Fig. 1(b)]. The two transitions, excited by monochromatic laser radiation of frequencies Ω_1 and Ω_2, are coupled by molecular collisions that change the magnetic quantum state but tend to preserve molecular velocity. Recent quantitative measurements[4] have revealed this persistence in velocity for a molecular gas such as CH_3F where the average velocity jump for a binary collision is only 200 cm/sec. It has not been realized until now, however, that even if the velocity remains essentially unchanged by a collision, the molecular angular momentum vector for a symmetric top may be readily tipped, causing a transition from an initial M state to a neighboring one. This circumstance causes an unusual double-resonance effect, characterized by a sharp resonant tuning behavior, free of Doppler broadening, and with an intensity comparable to the traditional double-resonance signal. Indeed, the new and the older double-resonance effects appear, as we shall show, in the same order of perturbation theory. The effect thus provides a new and simple way of studying molecular collisions that reorient the angular momentum vector.

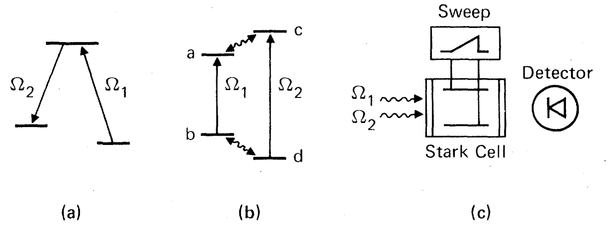

FIG. 1. (a) Traditional double-resonance level configuration. (b) Collision-induced double-resonance level configuration; wavy lines indicate collision-induced transition. (c) Experimental arrangement for monitoring optical double-resonance signals.

Collision-induced double resonance clearly is not restricted to angular momentum tipping alone but can involve other degrees of freedom as well. Velocity preserving collisions involving molecular inversion[5] or angular momentum transfer[6] have been reported also in other double-resonance experiments.[7]

Collision-induced double resonance can be understood easily in terms of the level structure of Fig. 1(b) and the optical geometry of Fig. 1(c). Consider first the coherent optical field $E_1\exp[i\times(\Omega_1 t - k_1 z)]$ (z is the direction of the optical beam) which is in resonance with the transition a-b for a narrow velocity group v_z, where saturation takes place. The second transition c-d involving the resonant field $E_2\exp[i(\Omega_2 t - k_2 z)]$ will communicate effectively with the first transition only (1) if it is tuned to the same velocity group and (2) if velocity-preserving collisions cause transitions of the type $c \rightarrow a$ and $b \rightarrow d$, which in the present case represent $\Delta M \neq 0$ transitions. In this way, population changes induced by the first field can be monitored by the second. The two laser fields select resonant velocity groups according to $\Omega_1 = \omega_{ab} - kv$ and $\Omega_2 = \omega_{cd} - kv'$, and the two transitions communicate when the velocities coincide giving the double-resonance condition

$$\Omega_2 - \Omega_1 = \omega_{cd} - \omega_{ab}, \tag{1}$$

where ω_{ij} is the transition frequency.

This tuning behavior, as well as other features, is contained in a more rigorous calculation,[8] derived from the coupled Maxwell-Scrödinger equations. The change in intensity of both optical fields arising from collision-induced double resonance is thus of the form (after time and Doppler averaging)

$$\frac{c}{8\pi}(\Delta E^2)=16\sqrt{\pi}(\hbar\Omega)\frac{NL\alpha_1{}^2\alpha_2{}^2(\Delta\rho_{dc}{}^0+\Delta\rho_{ba}{}^0(\gamma'/\gamma)\exp[-\Delta_1{}^2/(ku)^2]}{[(\Delta_2-\Delta_1)^2+4\gamma^2]ku}, \tag{2}$$

where we do not distinguish between Ω_1 and Ω_2 in the prefactor $\hbar\Omega$. Equation (1) is now evident in the resonance denominator where $\Delta_2=\Omega_2-\omega_{cd}$ and $\Delta_1=\Omega_1-\omega_{ab}$ and the linewidth of 2γ is just twice the width predicted for the ordinary double resonance. Like the ordinary double resonance,[9] this new effect is proportional to the product of the two intensities $\alpha_1{}^2\alpha_2{}^2$ where $\alpha_1\equiv\mu_{ab}E_1/2\hbar$ and $\alpha_2\equiv\mu_{cd}E_2/2\hbar$. Here, ku is the Doppler width, L is the optical path length, and $\Delta\rho_{ij}$ is the zeroth-order difference in occupation probability of levels i and j. It will be noticed that Eq. (2) is virtually the same as that for the usual double-resonance effect except that it is reduced by the factor (γ'/γ), where γ' is the linewidth contribution for the specific collision channel which couples the two transitions and γ represents the total linewidth arising from all sources. Since γ is composed of a pressure-independent contribution (molecular time of flight across the laser beam) and a pressure-dependent part, the new double-resonance signal will vary as the molecular density N at elevated pressure and as N^2 at low pressure.

Other mechanisms, based on purely optical interactions, could also give double-resonance behavior for Fig. 1(b). However, calculations show these effects to be too weak and with a line shape contradicting the experiments.[8]

Collision-induced double resonance has been observed in our laboratory in two different types of experiments. Consider again the experimental arrangement of Fig. 1(c). The two radiation fields are derived from two fixed frequency, continuous-wave CO_2 lasers and propagate together through a $^{13}CH_3F$ gas sample that can be tuned by sweeping a dc Stark field.[10] In Fig. 2, a double-resonance spectrum is shown for the $^{13}CH_3F$ ν_3-band line $(J, K)=(4,3)\rightarrow(5,3)$ at 1035.474 cm^{-1}. One laser is frequency locked to the other with $\Omega_1-\Omega_2=30.008$ MHz by a servo loop that compares their beat frequency with an rf reference. After being expanded to 1 cm diam, the two beams have power densities of ~1.2 and 0.4 W/cm^2; they are polarized perpendicularly to the Stark field, imposing $\Delta M=\pm1$ selection rules.

All of the lines of Fig. 2 satisfy the relation $\Omega_1-\Omega_2=(m\Delta_l-n\Delta_u)\epsilon$, where ϵ is the Stark field, m and n are integers, and Δ_u and Δ_l are the first-order Stark tuning rates of the upper and lower vibration-rotation states.[11] Thus, in Fig. 2 we find that $(\Omega_1-\Omega_2)/\epsilon$ equals $4\Delta_l-2\Delta_u$ (line a), $3\Delta_l-\Delta_u$ (b), $2\Delta_l$ (c), $\Delta_l+\Delta_u$ (d), $2\Delta_u$ (e), and $3\Delta_u-\Delta_l$ (f) to an accuracy of one part in 1000 or better. The strong lines c and e are the ordinary double resonances [Fig. 1(a)] and correspond to $\Delta M=2$ intervals in the lower and upper vibrational states. The other lines are the collision-induced reso-

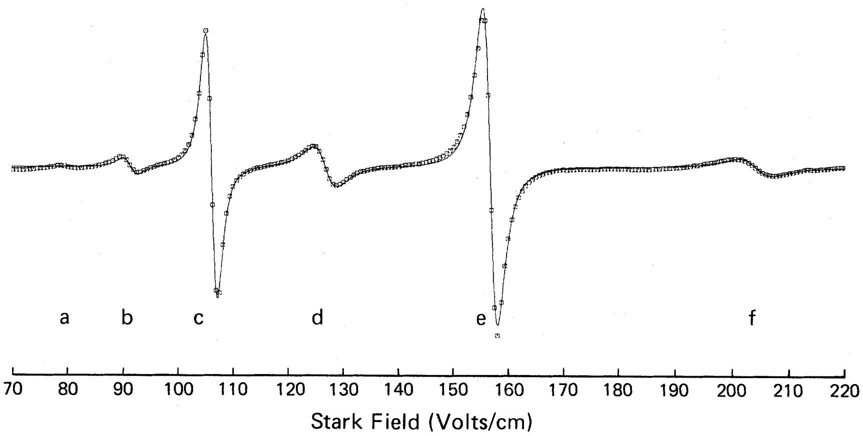

FIG. 2. Optical double-resonance spectrum for $^{13}CH_3F$ at ~3 mTorr pressure and $\Omega_1-\Omega_2=30.008$ MHz. Lines c and e correspond to the level configuration of Fig. 1(a) and the others to Fig. 1(b). The Stark sweep is computer driven in steps and the output signal is digitized (squares) and least-squares fitted to Lorentzian line shapes (solid line). The Stark gap spacing is 0.602 56 cm and the sample path length is 10 cm.

nances; they all have the level configuration of Fig. 1(b) where the two transitions do not share a common level; they display linewidths (~800 kHz) about twice as large as that of c and e, in agreement with Eq. (2), but considerably narrower than a 60 MHz Doppler width. If the plane of polarization of one or both beams is rotated by $\frac{1}{2}\pi$, to allow $\Delta M=0$ transitions, the spectrum is drastically altered but the fundamental behavior remains unchanged. From Fig. 2, both types of double-resonance signals are seen to be of the same order of magnitude and, furthermore, depend on the product of the two field intensities, as predicted by Eq. (2). As expected, the collision-induced signals vary linearly with pressure at high pressure and appear to approach a quadratic dependence at very low pressure.

We have also observed analogous collision-induced resonances in Lamb-dip spectra for the same transition of $^{13}CH_3F$. For example, when the selection rule is $\Delta M=0$, Lamp dips are monitored for the $M=3\rightarrow 3$ and $4\rightarrow 4$ transitions, but an additional line occurs midway between them due to the collision-induced resonance. Clearly it cannot be an ordinary double resonance ("crossover" resonance) since there is no level common to both transitions. In this case, a double resonance occurs when the resonance conditions $\Omega_1 - k_1 v_z = \omega_{ab}$ and $\Omega_1 + k_1 v_z' = \omega_{cd}$ are simultaneously satisfied for the same velocity group, $v_z = v_z'$. Consequently, the double-resonance condition becomes $\Omega_1 = (\omega_{ab}+\omega_{cd})/2$. Here, the two oppositely propagating waves play the same role as the two unidirectional waves of different frequency in the above discussion, and the two transitions are similarly coupled by collisions.

The mechanism which tips the angular momentum vectors of two colliding CH_3F molecules is the long-range anisotropic interaction of their permanent electric dipoles. For this process, collision partners will retain their initial rotational energy but will exchange a small orientational or Stark energy for translational energy, which is not detected in the linewidth. The collisional transition $(J,K,M)\rightarrow(J,K,M\pm 1)$ occurs for this interaction because symmetric tops like CH_3F have a nonvanishing dipole matrix element.[12] To first order, the corresponding transition rate for one of the collision partners will be proportional to the matrix element squared $K^2(J\pm M\pm 1)(J\mp M)/[J^2(J+1)^2]$. Hence, molecules with high rotational quantum number J or small K are not tipped easily in agreement with the classical gyroscope description. It is for this reason that collision-induced double resonance has been seen here in the $^{13}CH_3F$ transition $(J,K)=(4,3)\rightarrow(5,3)$ but not in our earlier studies[10] of the $^{12}CH_3F$ $(J,K)=(12,2)\rightarrow(12,2)$ transition. From the intensity ratio of lines d to c or d to e, we obtain $(\gamma'/\gamma)=0.15$, and a cross section of ~100 Å^2 for $\Delta M=\pm 1$ reorienting collisions of the $(J,K)=(4,3)$ or $(5,3)$ state. Hence, for this case about 15% of the collisions change the M state while J remains fixed and the remaining 85% presumably involve changes in J and M. Microwave experiments[13] in OCS, on the other hand, failed to show any evidence for $\Delta M=\pm 1$ collisions, because the symmetry of a linear molecule prevents electric dipole transitions between magnetic sublevels of a given J.

In future experiments, the collisional selection rules might be tested. Multiple quantum jumps in M could occur either in a single step or sequentially and might depend critically on the choice of a foreign buffer gas and its specific interaction with CH_3F.

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