

## Polarization effects in double resonance spectroscopy

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$R_1 = 1$ , then  $R_2 = 1$  gives values of  $\omega_0(\Gamma)$  which differ from experiment by only 1%. Hence, the only detectable consequence of the relation  $R_1 = R_2 = 1$  is a systematic lowering of the LA branch near  $L$  in Si, Ge, and  $\alpha$ -Sn. This effect was noted by Tubino *et al.*,<sup>6</sup> who suggested that some significant interaction had been neglected, and by Solbrig,<sup>7</sup> who attempted to eliminate this and other defects in the calculation by introducing new terms in the VFP.

Unless interactions beyond sixth neighbors are introduced, the only way to lift the restrictions  $R_1 = R_2 = 1$  is to introduce third-neighbor interactions. Solbrig considered 12 new terms involving interactions of first through sixth and eighth neighbors, and his best fit was obtained by adding to the original VFP three new terms, each of which involves third-neighbor interactions. Since no forces beyond sixth neighbors were introduced, the dramatic improvement in the fit to the LA branch near  $L$  obtained in Solbrig's nine-parameter model indicates that, at least in the case of Si, the inclusion of third-neighbor terms in the VFP is sufficient to remedy the defect described here.

Some success in lowering the TA branches has been obtained with the inclusion of anharmonicity,<sup>15</sup> but we have shown elsewhere<sup>16</sup> that the presently available calculations are inherently unable to reconcile the observed anharmonic behavior of the zone-boundary modes with that of the elastic constants. In the absence of an adequate model for the higher-order interactions, it is difficult to assess their importance in determining the shape of the TA branches, but the results of Solbrig's

nine-parameter model as well as those obtained recently with a bond-charge model<sup>17</sup> suggest that anharmonicity does not play a major role.

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## Polarization effects in double resonance spectroscopy\*

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(Received 4 December 1974)

Double resonance spectroscopy, using radiation of two different frequencies simultaneously to excite and to probe a set of molecular energy levels, is becoming an important technique for the study of molecular energy transfer.<sup>1</sup> Relatively little attention has been paid, however, to the influence of the relative polarizations of the radiation fields used in the experiment. Following the observation of a striking difference in signal intensity between parallel and perpendicular pump/probe polarizations,<sup>2</sup> we decided to investigate this phenomenon.

The double resonance apparatus is essentially the same as that used in earlier  $\text{BCl}_3$  experiments.<sup>3</sup> A grating-tuned Q-switched  $\text{CO}_2$  laser is used to vibrationally excite the molecules; and a grating-tuned, piezoelectrically stabilized cw  $\text{CO}_2$  laser is used for the probe. The transient absorption signals are averaged, processed, and displayed by a combination of PAR-160 boxcar integrator, PDP-8/L computer, and ARDS graphic-display

terminal. For this experiment, we insert a  $\frac{3}{2}$ -wave retardation plate<sup>4</sup> in the path of the Q-switched laser beam before it enters the double resonance cell. The effect of this plate is to rotate the plane of polarization of the Q-switched beam by twice the angle through which the optic axes of the plate itself are rotated. When the axes are parallel (or perpendicular) to the plane of polarization of the incoming light, no rotation occurs. If the axes of the crystal make a  $45^\circ$  angle with the plane of the radiation field, the beam which exits will have been rotated by  $90^\circ$ . Q-switched laser power transmitted by the plate was measured with a power meter (Coherent Radiation, Inc., model 201), and did not vary with the angle of rotation.

A mixture of 0.43 Torr  $\text{BCl}_3$  and 6.8 Torr Xe was pumped with the  $P(12)$  laser line. Absorption was monitored at the  $P(12)$  line itself, where a large absorption decrease appears due to "hole-burning" in the absorption

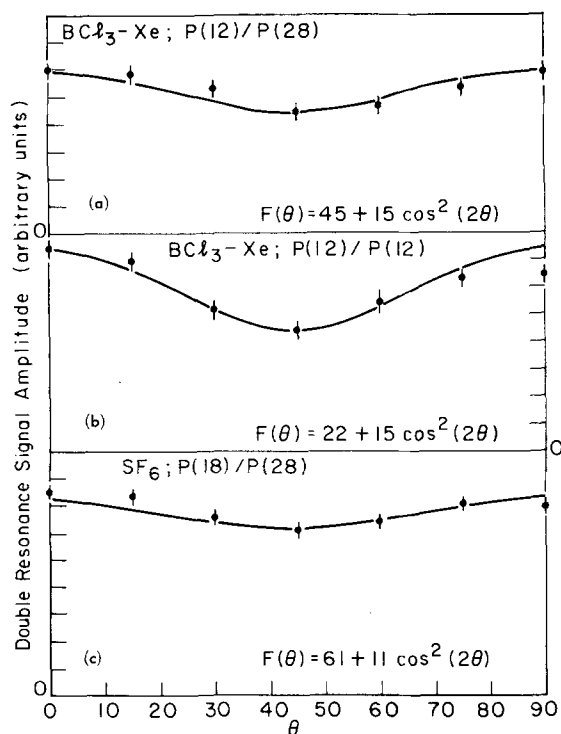


FIG. 1. Variation of double-resonance signal amplitude with relative polarization of the two laser beams ( $\theta$  is the waveplate setting). (a) and (b); 0.43 Torr  $\text{BCl}_3$ +6.8 Torr Xe; (c) 1.0 Torr  $\text{SF}_6$ . The notation  $P(J)/P(K)$  denotes that the  $P(J)$  line of the  $10.6\text{ }\mu\text{m}$  band of the  $\text{CO}_2$  laser was used for pumping, and the  $P(K)$  line for probing, the molecular absorption.

spectrum, and also at the  $P(28)$  line, where one sees an absorption increase due to vibrationally excited  $\text{BCl}_3$  molecules. An experiment was also carried out on 1.0 Torr of pure  $\text{SF}_6$ , using the  $P(18)$  line to pump and the  $P(28)$  to probe. In all cases, the maximum amplitude of the double-resonance signal was measured. This occurs about  $2\text{ }\mu\text{sec}$  after the beginning of the pump laser pulse, which is enough time for  $V \rightarrow V$  equilibration to occur, but before appreciable  $V \rightarrow T$  relaxation can take place. The pump pulse itself is about  $0.5\text{ }\mu\text{sec}$  wide.

The results are shown in Fig. 1. In each system studied, the signal amplitude shows a minimum at a waveplate setting of  $45^\circ$ , at which the polarizations of the two laser beams are mutually perpendicular. The data can be represented reasonably well by a simple function  $F(\theta) = A + B \cos^2(2\theta)$ , corresponding to a simple  $(P_0 + P_2)$  distribution of absorbing dipoles. The intensity variation is largest for the directly saturated "hole" in the absorption spectrum, with a nearly 40% modulation [Fig. 1(b)]. What is remarkable is that the four-level double-resonance signals are also modulated, although not as strongly. These signals involve a  $V \rightarrow V$  equilibration step, which requires about 5–10 collisions in  $\text{BCl}_3$ <sup>3</sup> and a like number in  $\text{SF}_6$ .<sup>5</sup> We can thus conclude that the molecular alignment survives, at least in part, through vibrationally inelastic collisions. A similar type of behavior was observed in the polarized fluorescence of  $I_2^*$  vapor,<sup>6</sup> in which even vibrationally and rotationally relaxed fluorescence features show residual 5%–10% polarization. In a recent R-matrix analysis of molecular relaxation phenomena, Pickett<sup>7</sup> has concluded that collisions which leave the orientation quantum number  $M$  unchanged will be preferred over  $M$ -changing collisions, even when energy transfer is occurring. Thus, there is theoretical justification for this persistence of induced polarization. Further investigations of this effect are planned, using a tunable laser probe source.

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## Polymorphism in solid $\text{CCl}_4$ \*

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In this investigation, optical birefringence has been used to study the sequences of phase changes that occur in solid  $\text{CCl}_4$  in the region below the melting point. Solid  $\text{CCl}_4$  is one of the so-called plastic crystals that are characterized by a low entropy of melting and the occurrence of solid-solid phase transitions. Two of the phases, a face-centered cubic one (now called Ia) and a

monoclinic one (phase II) have been known for some time<sup>1–3</sup>; the temperature of the transition is quoted<sup>3</sup> as  $225.5^\circ\text{K}$ . Since the discovery<sup>3</sup> of a third phase (now called Ib), identified as rhombohedral and existing over a temperature range similar to that for Ia, there has been an unresolved question concerning the relative stabilities of phases Ia and Ib.