Anomalous Saturated-Absorption Pressure Shifts in CO_2

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Pressure shifts of the standing-wave saturated resonance have been measured in the 9- and 10-μm *P* and *R* lasing transitions of CO_2 with a heterodyne spectroscopic technique. At low pressures (≤ 100 mTorr) the measured shifts for four different isotopes were all blue, instead of red as predicted by semiclassical theory. Measurements at higher (> 1 Torr) pressures revealed red shifts. Perturber-gas data showed blue shifts for heavier perturber atoms or molecules, red shifts for He and H_2.

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We have performed pressure-shift measurements on CO_2 9- and 10-μm lasing transitions for a wide range of *J* values for different vibrational levels in four CO_2 isotopes. The pressure shifts were determined from the changes of the saturated-absorption resonance frequency with use of a heterodyne technique. In using the nonlinear spectroscopic technique, we found that the measured pressure shift was blue at low absorption-cell pressures (< 130 mTorr) instead of red as predicted from semiclassical theory.[1,2] Subsequent measurements at higher pressures (> 1.0 Torr) revealed red shifts. Pressure shifts were also measured with different perturber gases; in these measurements, Xe, Ar, N_2, and CH_3F gave blue shifts while He and H_2 gave red shifts with the relative magnitudes roughly corresponding to their respective polarizabilities.

Similar anomalous results have been obtained by Bagaev and Chebotayev,[3,4] for a CH_4-stabilized HeNe system in which extremely small blue shifts were measured for CH_4 perturbed by Xe, He, or Kr at pressures less than 10 mTorr while red shifts were measured for noble-gas perturbers (Xe,Kr, Ar,Ne,He) at pressures greater than 10 Torr.[5] Again, the blue shift at low pressures was measured by use of saturated-absorption techniques on a rovibrational molecular transition while linear techniques were used in the high-pressure regime.

A two-channel line-center–stabilized CO_2 heterodyne laser system, shown in Fig. 1, was used in our experiment and has been described elsewhere.[6,7] Each laser uses a grating for line selection, and is individually stabilized by means of the 4.3-μm standing-wave saturation resonance created in a low-pressure CO_2 absorption cell external to the laser cavity. The clear apertures of the cells at the beam entrance windows were 2 cm in diameter and the laser power directed into them generally ranged between 0.5 and 2.0 W. By varying the pressure in one of the stabilizing cells while keeping the pressure fixed in the other cell as a reference, the pressure shift was measured by heterodyning the two lasers and recording the changes in the beat frequency as the pressure was varied. The total frequency change ranged from 4 to 10 kHz as the pressure was varied from 20 to 120 mTorr. Special precautions were taken to minimize errors and offsets that could affect the measurements. In our estimate the residual shifts due to the combined geometric or wave-front and transit-time effects were less than 200 Hz blue shift superimposed upon a less than 200 Hz random shift due to changes caused by temperature variations.[6] The potentially most important source of error was caused by the nonzero slope of the power-versus-frequency characteristic of the laser over the frequency range of the nonlinear resonance dip. This "power slope" caused an "instrumental" shift of the laser

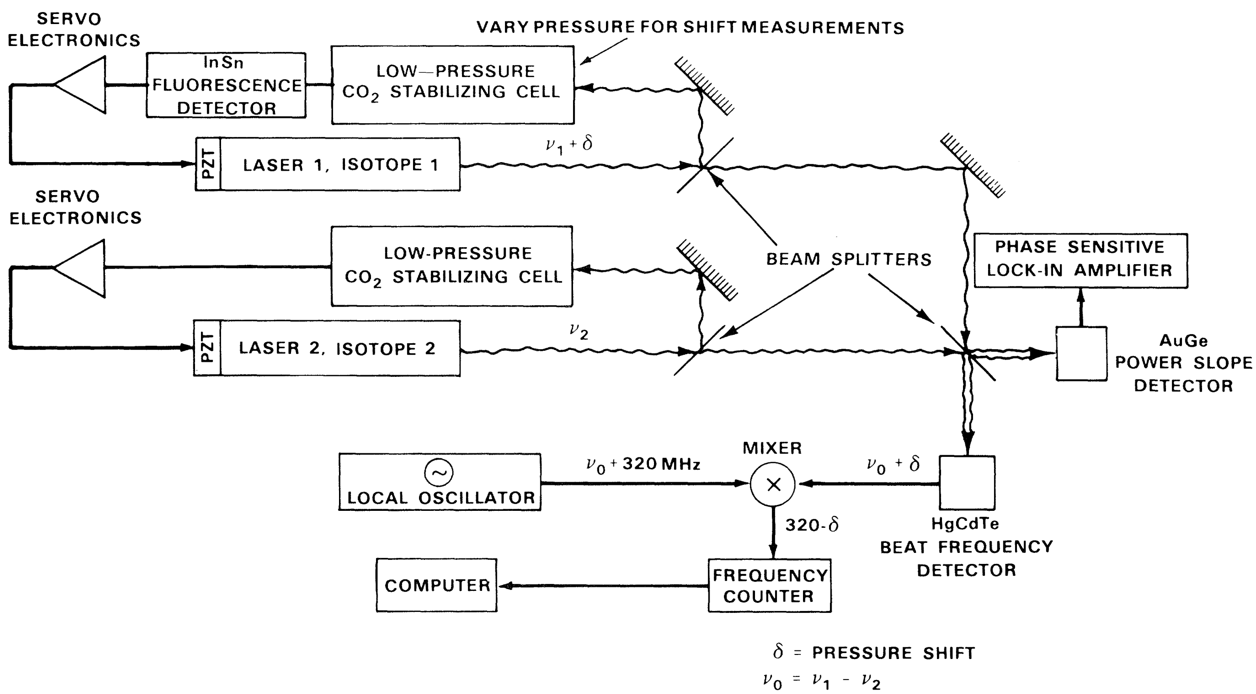

FIG. 1. Block diagram of the two-channel line-center–stabilized CO_2 laser heterodyne system used for measuring pressure shift.

frequency, resulting in a frequency error that increased with the pressure squared. This error would give rise to erroneous red or blue shifts depending on the sign of the power slope. Since the laser was frequency modulated, the power slope could be synchronously detected by means of a separate power detector. The power slope was then successfully eliminated by adjustment of the grating angle which in turn changed the gain profile resulting in zero power slope at the resonance dip. All measurements were performed after such adjustments were made.

Figure 2 is an example of a typical pressure shift. Three trial runs were taken at each pressure with each trial consisting of a 30-sec time average of the beat frequency. The pressure shift is toward increasing frequency, a blue shift.

Several hundred pressure-shift measurement sequences, similar to Fig. 2, were recorded for various J values in the 9- and 10-μm bands for four CO_2 isotopic species. Additional pressure-shift data were generated at fixed CO_2 pressure (20–25 mTorr) as a function of the pressures of various perturber-gas additives in the absorption cell. The pressure shifts for CO_2 and the perturber gases are summarized in Tables I and II.

Several CO_2 pressure-shift experiments have been reported previously. These measurements[7–10] gave shifts ranging from -300 to $+200$ kHz/Torr but were not very extensive nor did they correct for the power slope as in this experiment.

Measurements were also performed to determine the shift at elevated pressures up to 10 Torr. Here, the frequency-modulated laser radiation was split and directed into two external standing-wave absorption cells, one used as a reference cell at low pressure (30 mTorr), and the other cell at variable pressure. By simultaneously plotting both derivative fluorescence signals as the laser was tuned

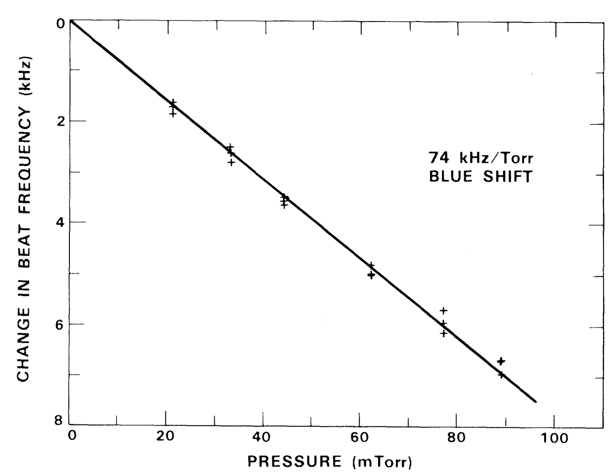

FIG. 2. Pressure shift measured for the $^{12}C^{16}O_2$ I-$P(28)$ transition.

TABLE I. Pressure shift for CO_2 in four isotopic species.

Isotope (O-C-O)	I Band Shift (σ) (kHz/Torr)	II Band Shift (σ) (kHz/Torr)
16-12-16	62.1 (18.1)	63.2 (18.1)
16-13-16	50.3 (16.8)	87.2 (37.8)
18-12-18	81.1 (28.6)	72.3 (29.8)
18-13-18	51.9 (21.2)	43.8 (22.3)

through the saturated resonance, it was determined that the shift turned red (-80 ± 50 kHz/Torr) at pressures greater than 1 Torr. The derivative signal's zero crossing was smeared out (as the resonance dip disappeared) in the intermediate pressure (300–500 mTorr to 1 Torr) regime so that the shift "inflection" pressure point could not be determined. A red shift has also been observed previously[11] in a linear absorption experiment done at high pressures (>10 Torr) on the $3\nu_3$ transition in CO_2.

Pressure shifts, δ, in terms of the Anderson-Tsao-Curnutte theory modified by Bonamy[2] and Leavitt[1] can be represented as

$$\delta = n v \int 2\pi b\, db \exp(-\mathrm{Re} S_2) \sin(S_1 - \mathrm{Im} S_2), \quad (1)$$

where n is the perturber density, v is the relative velocity, and b is the impact parameter. S_2 represents the J-dependent predominantly quadrupole-quadrupole interactions and S_1 represents the isotropic van der Waals dispersive (C_6) interaction. An average over perturber quantum numbers is implied in Eq. (1). The main contribution to the shift in CO_2 comes from the S_1 term which contains a first-order contribution from the expansion of the scalar potential in terms of the symmetric normal coordinate q_1. This is nonzero only if there is vibrational anharmonicity in the initial and final states such that the difference of the diagonal matrix elements of q_1 for the states is nonzero; this effect is dependent on the different Fermi resonances present in the various CO_2 isotopes. Hence S_1 is given by

$$S_1 = -\tfrac{3}{8}(C_6/h v b^5)(\alpha'/\alpha)\Delta M. \quad (2)$$

Here α' is the derivative of the polarizability α with respect to q_1 and ΔM represents the difference of the final- and initial-state matrix elements of q_1. For normally encountered values of J, S_2 is negligible and this theory predicts very little J dependence. None was seen in the P or R branches. However, for the 9- and 10-μm bands ΔM is positive, and this

TABLE II. Pressure shift as a function of the pressures of various perturber-gas additives; CO_2 pressure is held constant at 22.5 ± 2.5 mTorr. Values for C_6 (in atomic units) were obtained from Ref. 15.

Gas	C_6 ($e^2 a_0^5$)	18-12-18 I-P(22) (kHz/Torr)	16-12-16 I-P(24) (kHz/Torr)	16-12-16 I-R(34) (kHz/Torr)
Xe	282	+52	+53	+51
Ar	114.5	+37	+22	+20
He	16.7	−20	−33	−20
H_2	46	−36	−29	−39
N_2	118	+21	+23	+32
CH_3F		+99	+70	+41
CO_2	192			

theory predicts red shifts of about 80–120 kHz/Torr. Further, except for the light perturbers, the measured perturber-gas data were blue shifted in contradiction to semiclassical theory. This behavior is opposite to that normally encountered where light perturbers with low polarizability yield small red or slightly blue shifts and red shifts are observed for the heavier perturbers.

The nonlinear spectroscopic techniques employed in the experiments differ from linear spectroscopic techniques in that they are velocity selective, i.e., the $v_z \simeq 0$ molecules are studied. In this case, collision-induced velocity changes, Δv_z, of the molecular radiators can be important as a particle removal mechanism, whenever the corresponding Doppler shifts $\Delta\nu = \Delta v_z/\lambda$ (for $\lambda \simeq 10$ μm) are larger than the homogeneous linewidth.[13,14] This results in a nonlinear variation of the width and shift with pressure which may affect our measurements. For CO_2-CO_2 scattering, long-range diffractive velocity changes are ~ 340 cm/s (with $C_6 \sim 192$ a.u.)[15] and $\Delta\nu \sim 340$ kHz. For full width at half maximum (FWHM) linewidths < 680 kHz, the broadening rate is given by the real part of the radiator total scattering rate,[14] ~ 30 MHz/Torr FWHM, comparable to that observed by Kelly and Thomas[16] at low pressure. In this limit, the shift is given by the imaginary part of the radiator total scattering rate; this is $\sim \delta/3$ and $\delta/7$ for CO_2 and rare-gas perturbers, respectively (including the variation of both the elastic and the inelastic radius with vibrational state), but is also red. Since our linewidths are ~ 1 MHz, diffractive velocity changes probably have little effect. However, for the C_6 potential, classical small-angle velocity changes for trajectories grazing the inelastic radius (~ 7 Å)[17] are estimated to be ~ 24 m/s, comparable to the 28 m/s measured[18] for $\Delta J = \pm 1$ collisions, and correspond to $\Delta\nu \sim 2.4$ MHz. Hence classical velocity changes can alter our measured shifts. In this case, calculation of the line shape by means of scattering amplitudes in the stationary phase approximation shows that the expected shift of the zero-frequency derivative is reduced from δ of Eq. (1) by an arrival-frequency term which contributes a blue shift comparable to but always smaller than δ. Effects of repulsive potentials are not likely to be important since the range is substantially smaller than the inelastic radius.

In conclusion, we have measured anomalous blue pressure shifts for CO_2 with a saturated-absorption technique. A number of possible explanations have been discussed to account for this discrepancy; however, at present, no completely satisfactory explanation has been found. Perhaps further experiments measuring the pressure shifts by use of another Doppler-free technique, such as two-photon experiments, should be performed in order to provide additional information.

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