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Identification of Absorption Lines by Modulated Lower-Level Population: Spectrum of Na_2†

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Molecular absorption lines from a common lower level are intensity modulated by chopped-laser saturation of another line from that level. Populations of some other levels are also modulated by subsequent fluorescence. Both types of modulated lines are free of Doppler broadening. Also, collisional depopulation modulates absorption from rotational levels near the laser-depleted level. In Na_2, we have identified 113 lines. Analysis of the A state by Kusch and Hessel is confirmed and extended.

We present here a new technique for Doppler-free analysis of complicated molecular spectra, which identifies all absorption lines originating in a chosen level. We demonstrate its advantages in studying the $A^1\Sigma_u^+$ state of Na_2. A laser is used to deplete the population of the chosen ground-state level, by exciting a substantial number of the molecules out of that state.[1] The absorption of all lines originating in this same lower level is then decreased. Consequently, if the saturating laser beam is chopped, just these lines are intensity modulated and so distinguished from the many others in the same wavelength region. If the laser is monochromatic and tuned to the center of an absorption line's Doppler profile, the only molecules affected are those with zero component of velocity along the beam direction. Then all the modulated-population spectroscopy (MPS) absorption lines should also be very narrow and essentially without either Doppler broadening or Doppler shift.

In addition to this modulation by lower-level depopulation, which we will call type-1 MPS, there are several secondary ways in which other lines can be modulated (see Fig. 1). The saturating laser excites some molecules to the upper level of the transition which absorbs it. Absorption lines from this level to still higher levels could then be observed. This effect, which we shall call type-2 MPS, is simply stepwise excitation.[2] After the excitation, the molecules fluoresce in some nanoseconds to other vibrational levels of the ground electronic state, and absorption lines from these levels are strengthened when the laser is on. This kind, which we call type-3 MPS, is the probing of the effects of optical pumping. Finally, at higher pressures, collisions transfer molecules from nearby rotational levels to the depopulated one and thereby decrease the population of these neighboring rotational levels when the saturating laser is on. This effect we call type-4 MPS. Modulated-population spectra of types 1, 2, and 3 are Doppler free, while those of type 4 are not. The transmitted probe intensity in types-1 and -4 MPS will be in phase with the chopped saturating laser, while the transmitted intensity in types-2 and -3 MPS will be 180° out of phase. In these experiments, we have observed clear examples of types-1, -3, and -4, and perhaps type-2 MPS.

Sodium vapor was contained in a stainless steel oven with an active region up to 43 cm long, typically operated near 345°C, corresponding to

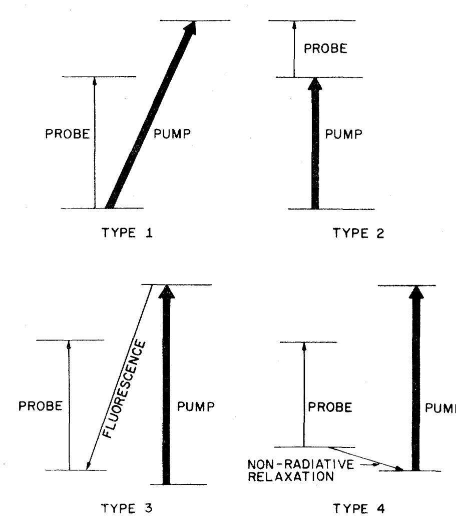

FIG. 1. The four types of modulated-population signals, produced by laser saturation of an absorption line.

a sodium pressure[3] of 7×10^{-2} Torr or a density of 10^{15} Na atoms and 1.6×10^{13} molecules per cubic centimeter, with an argon buffer-gas pressure of 0.2 Torr. A single-mode argon laser (Coherent Radiation 52G with a temperature-controlled intracavity etalon) was used unfocused to saturate individual rotational-vibrational transitions in the $B^1\Pi_u \leftarrow X^1\Sigma_g^+$ bands of Na_2.[4-6] At 4765 Å, 60 mW of laser power was available to saturate either $(v'=6,\ J'=27) \leftarrow (v''=0,\ J''=28)$ or $(10, 12) \leftarrow (3, 13)$, and at 4880 Å, a 160-mW beam saturated $(6, 43) \leftarrow (3, 43)$.[7,8] The saturating beam was chopped at 2000 Hz. In each case, the laser was tuned to the center of the absorption line's Doppler profile by the Hänsch-Bordé method,[4,5] with a weak blue probe beam propagating in the direction opposite to the saturating beam. This procedure ensured that transitions are saturated only in those molecules having zero velocity component along the beam direction. The tunable probe laser is a rhodamine 6G jet-stream dye laser, operable from 6175 to 5600 Å. This orange probe is split into two equal beams, the real probe and the dummy probe, both propagating in the same direction as the blue probe, but only one (the real probe) overlapping and interacting with the saturating beam. As the saturating beam and the real probe are propagating in opposite directions, modulated-population spectra are observed without Doppler shift or broadening. Absorption lines in the $A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ bands[9] were studied, as their wavelengths are in the region covered by the rhodamine 6G laser emission. For this $^1\Sigma \leftarrow {}^1\Sigma$ transition, we have the selection rule $\Delta J = \pm 1$, so we expect only a P branch $(J-1 \leftarrow J)$ and an R branch $(J+1 \leftarrow J)$.[10]

We observed a total of 113 identified MPS lines, as shown in Table I, and six unidentified MPS lines. Typical spectra of types 1, 3, and 4 are shown in Fig. 2. No type-2 MPS lines were definitely identified, although one candidate is a strong 5-GHz-wide negative signal observed with the argon laser at 4765 Å and the dye laser at 5948.1 Å, corresponding to a possible excitation to the continuum. The other five unidentified lines are probably type-4 MPS lines whose upper levels are slightly perturbed.

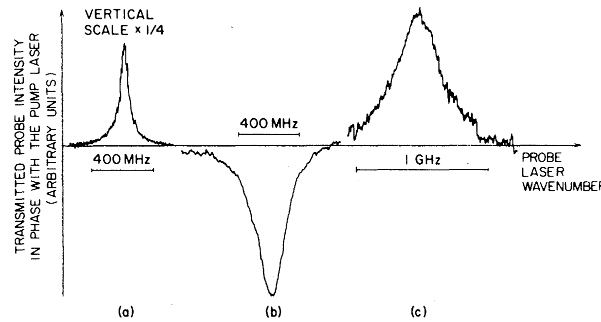

FIG. 2. Examples of the three observed types of modulated-population signals. (a) Type-1 MPS: $(24,44) \leftarrow (3,43)$ at 5985.87 Å. The signal is positive, narrow, and large, despite reduced pump intensity to avoid broadening. (b) Type-3 MPS: $(20,44) \leftarrow (1,43)$ at 6019.83 Å. The signal is negative, but somewhat wider and not as large. (c) Type-4 MPS: $(24,40) \leftarrow (3,41)$ at 5988.49 Å. The signal is positive, small, and about one third of the Doppler width.

Our observations confirm the A-state spectroscopic constants of Kusch and Hessel[9] to within our experimental accuracy, and within their experimental range ($v' \leq 20$). The modulation method shows lines with Franck-Condon factors at least twenty times smaller than those observed photographically by Kusch and Hessel. Using type-3 MPS, we can observe absorption from quite high ground-state vibrational levels, which enables us to see even higher A-state vibrational levels. At higher vibrational levels, a systematic deviation (see Fig. 3) is observed in all sequences. To our accuracy, the X-state results of Demtröder and Stock[8] are quite acceptable. This is to be expected, as all the X-state levels we observed are among the levels they used to derive their constants.

There is strong evidence for a perturbation at

TABLE I. Lines observed in modulated-population spectroscopy.

Pumping transition $B^1\Pi_u \leftarrow X^1\Sigma_g^+$	No. of lines identified Type 1	Type 3	Type 4	$A^1\Sigma_u^+$ v_{min}'	v_{max}'
$(6,43) \leftarrow (3,43)$	33	15	6	17	44
$(10,12) \leftarrow (3,13)$	30	0	4	19	33
$(6,27) \leftarrow (0,28)$	15	0	0	14	21

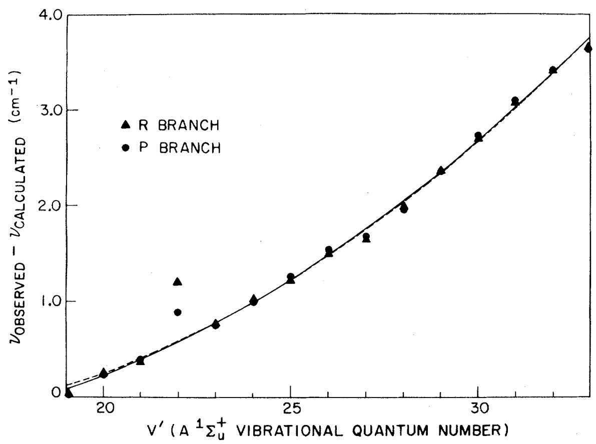

FIG. 3. Least-squares quadratic fit to type-1 MPS signals, showing perturbation at $v'=22$. P branch is $(v', 12) \leftarrow (3, 13)$. R branch is $(v', 14) \leftarrow (3, 13)$. Calculated frequency uses Kusch-Hessel (Ref. 9) constants for the A state and Demtröder-Stock (Ref. 8) constants for the X state.

$A^1\Sigma_u^+$ $v'=22$, $J'=14$. The observed linewidth for $(22, 14) \leftarrow (3, 13)$ is 500 MHz, while linewidths for other type-1 lines are typically 60–150 MHz (the variation is primarily due to intensity and pressure broadening). Also, $(22, 14) \leftarrow (3, 13)$ is 0.6 cm^{-1} from the quadratic least-squares fit to the other lines observed (see Fig. 3). $(22, 12) \leftarrow (3,13)$ is 0.3 cm^{-1} from this fit, while its linewidth is 150 MHz. Linewidths for type-3 MPS are under 250 MHz, showing some further broadening but still well under the Doppler width.

Type-4 MPS signals have linewidths about 400 MHz, only $\frac{1}{3}$ the Doppler width. This is experimental confirmation that collisions which transfer rotational energy are not strong enough to cause a complete randomization of the translational velocity distribution. These results show that the method can provide a new kind of information about molecular collisions. Sodium is a homonuclear diatomic molecule, and hence exists in ortho and para forms (odd and even J, respectively, in the X state, and even and odd J, respectively, in the A state) which are not mixed by collisions. Thus, we see only even ΔJ in type-4 MPS in Na_2. We searched for $\Delta J = \pm 1$, but found nothing, at least to $\frac{1}{10}$ the strength of $\Delta J = \pm 2$ lines.

Wavelength determinations to the accuracy that the narrow Doppler-free lines permit would result in a large increase in precision for the spectroscopic constants for both the A and X states in sodium. For a more thorough study, a tunable blue saturating laser capable of being locked to a sodium absorption line would be useful. However, a sizable number of lines may be found with our apparatus, as each $B \leftarrow X$ transition in coincidence with an argon laser line gives us one ground state for type-1 MPS signals, 5–20 ground states for type-3 signals, and four or more ground states for type-4 signals.

Doppler-free modulated-population spectroscopy, indentifying absorption lines with a chosen lower-level by modulating the population of that level, could be extremely useful in analyzing spectra of more complex molecules. For that purpose, laser saturation of an infrared vibrational transition could be used to modulate the population of the designated level.

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