must be independent of v asymptotically since we require $\eta \gg 1$, independent of v.)

It follows from our discussion that recent observations of cusp asymmetries[4] may represent the first experimental confirmation of the importance of the second Born contribution at high impact velocities. Other possibilities for detecting this contribution were recently suggested.[11]

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Doppler-Free Stimulated-Emission Spectroscopy and Secondary Frequency Standards Using an Optically Pumped Laser

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A new Doppler-free stimulated-emission technique using an optically pumped laser with applications in spectroscopy and optical frequency standards is reported. An argon-laser–pumped cw I_2 laser is used to demonstrate the technique as well as measure the complete hyperfine structure of the I_2 $B0_u^+$-$X^1\Sigma_g^+$ (43,83) $P(13)$ line. Hyperfine coupling strengths obtained for the $X^1\Sigma_g^+$ $v''=83$, $J''=13$ level are $eQq''=-1550.1\pm0.5$ MHz and $C''=59\pm5$ kHz. In addition, the I_2 laser has been actively stabilized to within 1 kHz of the observed line center of an I_2 hyperfine component.

We report a new Doppler-free stimulated-emission spectroscopic technique using a cw optically pumped laser (OPL). The molecule under study forms the gain medium of the OPL. The technique can also be used to generate a set of laser frequency standards covering a substantial spectral range. We have demonstrated this technique by observing narrow hyperfine-structure (hfs) features in an I_2 OPL with linewidths of less than 1 MHz which allowed us to perform high-resolution spectroscopic measurements. In addition, we have stabilized an I_2 OPL to one of the I_2 hyperfine-structure transitions.

This method of stimulated-emission spectroscopy may be compared with Doppler-free two-photon schemes[1,2] which require the use of two tunable lasers, a pump and a probe. The wavelength coverage in such schemes is limited by the tuning range of the probe laser. The OPL method described here involves only one tunable laser, since the OPL is effectively its own probe. Moreover, the wavelength coverage, in principle, extends over the entire spectrum accessible from the optically pumped level.

Related spontaneous-emission spectroscopic techniques using laser-induced fluorescence line narrowing have been previously demonstrated.[3-5] These techniques suffer from instrumental-resolution limits and also from low signal levels because of competing transitions. The stimulated-emission method reported here overcomes these disadvantages and in addition can provide convenient secondary laser-frequency standards.

In this Letter, we present measurements, using an argon-laser–pumped cw I_2 laser, of the complete structure of the $B0_u{}^+ - X^1\Sigma_g{}^+$ (43,83) $P(13)$ line in I_2, a transition that is inaccessible by Doppler-free absorption spectroscopy because the lower level, $v'' = 83$, in the $X^1\Sigma_g{}^+$ ground state is thermally unpopulated. Analysis of these hfs measurements has uncovered a nonzero nuclear spin-molecular rotation $(C\vec{I}\cdot\vec{J})$ interaction in the $v'' = 83$ level.

Figure 1 shows a schematic diagram of molecular energy levels involved in pump and laser transitions for a typical OPL. In the simplest case, the pump transition $(0\to1)$ consists of only one line. A single-frequency pump laser exciting the $0\to1$ transition will therefore prepare a class of molecules with velocity V_z in the upper laser level. This will give rise to laser oscillation at two frequencies ν_+ and ν_- for each allowed OPL transition given by

$$\nu_\pm = \nu_0\left(1 \pm \frac{V_z}{c}\right) = \nu_0 \mp \frac{\nu_0}{\nu_p}\Delta\nu_p, \qquad (1)$$

where ν_0 is the rest frequency of the lasting transition, V_z is the velocity of the molecules excited by the pump laser, ν_p is the rest frequency of the pump transition, and $\Delta\nu_p$ is $\nu_{\text{laser}} - \nu_p$. However, if the pump laser excites only the zero-velocity class, then each OPL rovibronic transition will appear as a single line. The width of individual gain lines is Doppler-free and determined only by the homogeneous linewidth. The situation is somewhat more complicated if the pump laser simultaneously excites several levels that lie within the Doppler width. In this case, the allowed OPL transitions consist of one ν_+, ν_- pair for each level excited by the pump and the individual pair separation will depend on the corresponding velocity group V_z selected by the pump. The entire spectrum of OPL transitions can be recorded by simply tuning the OPL cavity. A simple procedure permits measurement of the rest frequencies of the OPL transitions. This involves assignment of the ν_+ and ν_- pairs using Eq. (1) and recognition that the rest frequency is $\frac{1}{2}(\nu_+ + \nu_-)$.

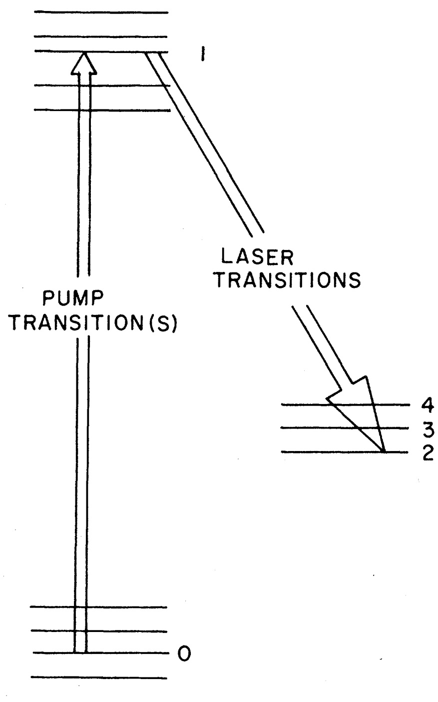

FIG. 1. Pump and laser transitions for a typical OPL.

In our experiments a single-frequency 5145-Å Ar^+ laser is isolated by an acousto-optic modulator and short-term stabilized to a high-finesse Fabry-Perot interferometer, which reduces the laser linewidth to 10 kHz.[6] The laser is long-term stabilized to an I_2 hyperfine transition in an external saturation cell by means of a third-derivative lock.[7] The stabilized Ar^+-laser output pumps the I_2 laser. Two 3-m–radius mirrors coated for maximum reflectivity at 1.2–1.4 μm and high transmission at 0.5145 μm are spaced 55 cm apart to define the I_2 laser resonator. The I_2 gain cell is 50 cm long. A 50-cm-focal-length lens focuses the Ar^+ pump within the TEM_{00} mode of the I_2 laser. One mirror of the I_2 laser is mounted on a piezoelectic translator.

The Ar^+ optical pump creates a population inversion between $v' = 43$, $J' = 12$ of the $B0_u{}^+$ state and thermally unpopulated levels the ground $X^1\Sigma_g{}^+$ state which results in laser oscillation for many B-X transitions.[8] A 0.75-m monochromator is used to select a single rovibronic line of the multiline I_2 laser output. Detection is with a Ge photodiode. In the experiments reported here, only the $(v',v'')=(43,83)$ $P(13)$ line at 1.34 μm is monitored.

The argon-laser pump power incident upon the I_2 cell is typically 50 mW. The I_2 pressure is about 100 mTorr, resulting in 1-mW average broad-band I_2 laser output power. Under these conditions, 50–100 nW is obtained for each lasing line in (43,83) $P(13)$, measured at the exit slit of the monochromator.[9] Threshold incident pump power for lasing in the (43,83) band is as low as 5 mW.

Spectra are generated by recording the I_2 laser output in the (43,83) $P(13)$ line as a function of a ramp voltage applied to the piezoelectric transducer. Figure 2 shows a typical I_2 laser spectrum. In this case the Ar^+ laser is locked to the $P(13)$, $I''=I'=5$, $F''=F'+1=8$ transition in the (43,0) band. Visible in this spectrum is the peak due to zero-velocity molecules (a_1) and two ν_+ and ν_- doublets due to the $I''=I'=1$, $F''=F'+1=13$ (a_2) and $I''=I'=5$, $F''=F'+1=18$ (a_3) lasing transitions. The other hyperfine components require larger $\Delta\nu_p$ and are therefore insufficiently populated to reach threshold and do not appear in Fig. 2. Spectra of the remaining hyperfine components are generated by tuning the argon-laser pump to the a_2-a_6, a_{12}, a_{15}, a_{17}, and a_{21} hfs components in the (43,0) $P(13)$ line (using notation of Ref. 10).

Since laser oscillation occurs only when the gain exceeds cavity loss, the linewidth of the observed transitions can be narrower than the homogeneous width. Moreover, because the peak gain in a direction copropagating with the pump is greater than that in the counterpropagating direction,[11] the intensities of the ν_+ and ν_- lines of each doublet are not equal, as shown in Fig. 2.

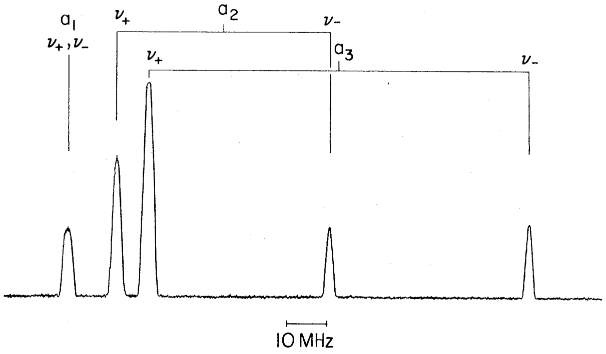

FIG. 2. Hyperfine spectrum of the (43,83) $P(13)$ line in the I_2 OPL when the Ar^+ laser is locked to the a_1 hfs component in the (43,0) $P(13)$ pump transition. Laser gain linewidths shown are 2–3 MHz; I_2 pressure is ~100 mTorr. The scan rate is 10 MHz/sec; time constant is 2 msec. The peak signal at the detector is ~75 nW.

The frequency scale in each recorded spectrum such as Fig. 2 can be calibrated either by conventional techniques or by exploiting the fact that the doublet separation is given by

$$\nu_+ - \nu_- = 2(\nu_0/c)V_z = 2(\nu_0/\nu_p)\Delta\nu_p. \tag{2}$$

Since the pump transition in this case has previously been well characterized,[10] the values of $\Delta\nu_p$ are known to better than 5 kHz. Moreover, ν_0 and ν_p corresponding to (43,83) $P(13)$ and (43,0) $P(13)$ are known from Fourier-transform-spectroscopy measurements[12,13] with an accuracy of 0.003 cm^{-1}. In this way, each doublet separation may be predicted to ± 5 kHz, far better than our present measurement accuracy.

Table I shows measured frequency separations of several hyperfine components in the (43,83) $P(13)$ line. Not all the experimental points are included in Table I as the same splittings are multiply determined when the Ar^+ laser is locked to different hfs components. In all cases, different determinations of the same hfs interval

TABLE I. Frequencies of the hyperfine structure of the (43,83) $P(13)$ line in I_2 and fits.

Lines[a]	Obs. separation (MHz)	Obs. − Calc. (MHz)[b]	Obs. − Calc. (MHz)[c]
a_1-a_3	72.87	7.73	−0.51
a_3-a_4	37.89	−7.10	0.16
a_4-a_5	67.93	3.19	−1.21
a_4-a_6	88.27	1.59	−1.28
a_8-a_9	6.81	5.01	0.16
a_9-a_{10}	10.62	−2.07	−0.62
a_{10}-a_{11}	12.82	1.32	0.36
a_{11}-a_{12}	20.11	−5.79	−1.14
a_{12}-a_{13}	35.83	2.11	−0.15
a_{13}-a_{14}	8.77	−1.15	0.55
a_{14}-a_{15}	37.25	0.31	−0.54
a_{15}-a_{17}	39.03	1.46	−0.10
a_{17}-a_{18}	41.16[d]	−0.80	0.44
a_{17}-a_{19}	41.16[d]	1.10	0.50
a_{20}-a_{21}	30.74	1.83	0.72
Standard deviation of fit		3.19 MHz	0.82 MHz

[a] We use the notation of Ref. 10.

[b] Includes only nuclear quadrupole effects.

[c] Includes nuclear quadrupole and spin-rotation $(\vec{I}\cdot\vec{J})$ effects.

[d] Components a_{18} and a_{19} overlap.

agree within the estimated measurement uncertainty which ranges from 0.3 to 1.0 MHz, depending upon the degree of line overlapping in the spectra. Also displayed are the results of two least-square fits to 49 measured hfs separations. Only the nuclear electric quadrupole coupling constant eQq'' is varied in one while both eQq'' and C'' (spin-rotation coupling constant) are fitted in the other. The upper-state constants are held fixed at their values from Ref. 10. By including only eQq'', the standard deviation of the fit is 3.19 MHz and by adding C'' the standard deviation is reduced to 0.82 MHz which is consistent with the uncertainty in our present measurements.

The values of $eQq'' = -1550.1 \pm 0.5$ MHz and $C'' = 59 \pm 5$ kHz show a large departure from the corresponding values for the $v''=0$ level,[10] namely, $eQq'' = -2448.025$ MHz and $C''=0$.[14] The nonzero value of C'' for $v''=83$ results from the interaction of the ground $X^1\Sigma_g{}^+$ state with an $O_g{}^+$ repulsive state which shares the same dissociation asymptote, namely, two $^2P_{3/2}$ iodine atoms.[15] A detailed study of the vibrational dependencies (in progress) of C'' and eQq'' will permit an approximate determination of the repulsive $O_g{}^+$ potential curve as well as a fuller characterization of the $X^1\Sigma_g{}^+$ ground state.

The precision of the present measurements can be increased by heterodyning two OPL's, which are frequency stabilized to different hfs transitions. The width of individual lines can be reduced by decreasing the pressure as well as the power in both pump and I_2 laser. The natural widths of Ar^+-laser–excited I_2 transitions range from 10 to 400 kHz.[16] Heterodyne experiments are underway in our laboratory for the study of hyperfine interactions in the $X^1\Sigma_g{}^+$ state of I_2 as a function of v'' and J''.

The use of an OPL to generate a set of standard laser frequencies is very promising. The 5145- and 5017-Å lines of the argon laser are known to excite at least 752 I_2 laser transitions spanning a spectral range from 0.55 to 1.34 μm.[17] Moreover, each lasing transition has a hyperfine-structure spread of about 1 GHz. If the pump frequency is long-term stabilized, then the stability of individual I_2 lasers (with the OPL cavity locked to the center of an I_2 hfs transition) is determined primarily by the absolute stability of the pump laser and pressure shifts in the I_2 cell. Intensity-dependent frequency shifts due to the ac Stark effect must also be considered. In addition, the short-term frequency instability of the I_2 laser is expected to be very small, less than 10 kHz, determined mainly by I_2-laser cavity-length fluctuations, since the I_2 gain medium is very "quiet."

In our present experiments, we have locked the OPL laser to the observed center of one of the I_2 gain lines with an uncertainty of 1 kHz ($\tau = 10$ msec). We plan to study the performance of stabilized OPL lasers using two independent pump-OPL systems. Long-term stability and reproducibility are expected to be comparable with those of I_2 stabilized He-Ne and argon lasers.

Optically pumped cw lasers have been demonstrated for other diatomic molecules such as Li_2,[18] Na_2,[19] Bi_2,[20] and Te_2.[20] The techniques described here are clearly applicable to these and other diatomic molecules.

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[15] The nonzero value of C'' and the significant change in eQq'' near dissociation illustrate a novel angular-momentum recoupling effect which cannot occur for the I_2 $B0_u^+$ state. The spin-orbit mixing effect occurs only when two states of identical Ω, g/u, and +/− symmetry dissociate to the same separated-atom fine-structure asymptote.

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