

## OBSERVATION OF INVERTED INFRARED LAMB DIPS IN SEPARATED OPTICAL ISOMERS

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A comparison of ro-vibrational transitions in the separated optical isomers of camphor is presented. An ir-rf double resonance experiment inside the laser cavity confirms that some ro-vibrational transitions of camphor are efficiently saturated by 9.4  $\mu\text{m}$  CO<sub>2</sub> laser lines. Inverted Lamb-dips of d- and l-camphor have been measured for such transitions with a high accuracy by taking beats between the laser used to monitor the dip and a reference laser stabilized by 4  $\mu\text{m}$  fluorescence Lamb-dip. The transition frequencies of d- and l-camphor have been found to agree to within an accuracy of  $1 \times 10^{-8}$ .

Molecular compounds that do not possess plane symmetry are found in two isomeric forms, mirror images of each other. The two isomers known by the designations dextro (d-) and levo (l-) are in most cases optically active and produce a rotation of the plane of polarization of a plane polarized light beam propagating through the compound in the vapour phase or dissolved in a liquid. The rotary dispersion and the circular dichroism of compounds have been investigated for a long time in the visible and near ultraviolet and recently also in the infrared. The optical rotation of the two isomers has been compared and is utilized as a test of the purity of an isomer. In those studies the energy levels of optical isomers have been assumed to be exactly the same. However there has not been an accurate experimental check by high resolution spectroscopy of separated optical isomers. The best accuracy in this check appears to have been realized in the microwave spectroscopy investigations where many unseparated optical isomers have been studied and the absence of splitting of rotational transitions puts an upper limit on the rotational energy difference with an accuracy of about  $10^{-5}$ . The technique of inverted Lamb-dips using infrared lasers and the use of separated optical

isomers enables us to perform with a higher accuracy the comparison of ro-vibrational energy levels of optical isomers.

This kind of experiment has significance in relation to the problem of spectroscopic display of parity non-conserving interaction in atomic and molecular physics [1]. Letokhov [2] has pointed out that because of the parity-violating electron-nucleon interaction, the energy levels of dextro and levo molecules should differ by a very small amount. Preliminary results have been published for a non-linear laser spectroscopy experiment aimed to detect a splitting in the infrared ro-vibrational transitions of a simple optically active molecule using unseparated optical isomers [3].

We have used for our study the well known compound camphor which occurs in nature as d-camphor and can be prepared synthetically in the laboratory as l-camphor. The structures for the two forms are illustrated in fig. 1. Camphor has an absorption in the 9.5  $\mu\text{m}$  region corresponding to the bending of the  $-\text{C}-\text{C}^*-\text{CO}$  group ( $\text{C}^*$  denoting the optically active carbon atom) [4]. The rotation-vibration spectrum of this compound has many coincidences with CO<sub>2</sub> laser lines in the 9.4  $\mu\text{m}$  region. However, in order to select transitions which are well saturated by the laser and thus suitable for the Lamb-dip study, we first attempted an infrared-radiofrequency double resonance experiment [5] which is very simple to carry out. An rf power to 5 watt was amplitude modulated at 30 kHz

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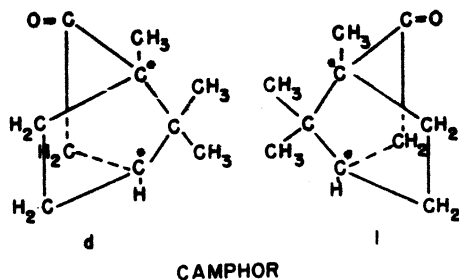


Fig. 1. Structure of d- and l-camphor. C\* denotes optically active carbon atoms.

and phase-sensitive detection was applied to the observed laser output. The signal obtained by irradiation with the  $9.22\ \mu\text{m}$  R(28)  $\text{CO}_2$  laser line is shown in fig. 2. The modulation of the infrared absorption by the applied rf electric field produces the rf absorption around zero frequency. The signals observed around 9.7 MHz and 14.7 MHz were interpreted as direct transitions between K-type doublets. These intense lines occur between the levels that are degenerate in a symmetric top but are slightly split in an asymmetric top molecule. In a heavy molecule such as camphor where levels with high  $J$  and  $K$  numbers are thermally populated, many  $K$ -doubling resonances can be observed in the low-frequency region. Zero-frequency signals and a few  $K$ -doubling resonances have also been observed on several R-branch laser lines of  $\text{CO}_2$  in the  $9.2\ \mu\text{m}$  region. We do not know the assignment of the ro-vibrational transitions involved in the double-resonance signals, but this is not necessary for the compari-

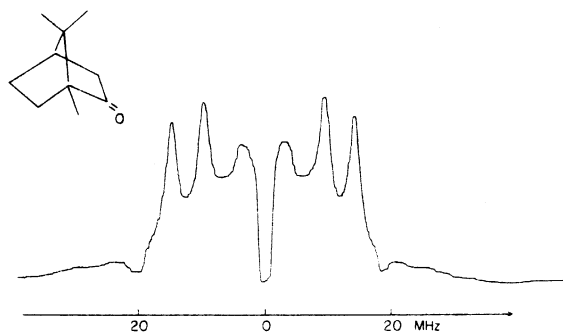


Fig. 2. An example of the observed IR-RF double resonance signal of d-camphor. Pressure of the gas was 80 mtorr and the time constant of detection 0.3 s. The  $9.22\ \mu\text{m}$  R(28)  $^{12}\text{CO}_2$  laser line was used.

son of the energy levels in the dextro and levo forms. The important thing is that the observation of the double-resonance signals confirmed that vibration-rotation transitions of camphor do have coincidences with the laser lines and are efficiently saturated by the laser radiation [5].

After these preliminary double resonance experiments were carried out, high resolution Doppler-free non-linear laser spectroscopy was performed by the technique of inverted Lamb-dips. An absorption cell containing a camphor sample was placed inside the laser cavity. The laser output power was monitored while its frequency was scanned over the cavity profile by applying a sawtooth voltage to the piezoelectric transducer on which the output concave mirror was mounted (fig. 3). In order to increase the sensitivity of detection, 80 kHz Stark modulation of the camphor absorption and phase sensitive detection were used. Inverted Lamb-dips were observed on several lines of the  $9.2\ \mu\text{m}$   $\text{CO}_2$  R-branch. In the upper trace of fig. 4 the inverted Lamb-dip observed on a d-camphor sample using the R(24) laser line is shown. The pressure of the sample was 40 mtorr, the time constant of detection 10 ms and the applied modulated electric field 40 V/cm. The observed lineshape originates from a modification of the Lamb-dip by the Stark modulation. The half-maximum-half-width of the Lamb-dip was  $\sim 400$  kHz due to Stark modulation and pressure broadening. The high sample pressure was needed because the camphor absorption is weak due to the thermal distribution of the population over a large number of rotational levels.

For all the investigated Lamb-dips, we observed that different laser oscillation conditions are required to obtain the best signal-to-noise ratio for the signal in each isomer. Qualitatively we have interpreted this behaviour as due to the optical activity of our sample. The measurement of optical activity in the infrared region has recently been reported by Keiderling and Stephens [6]. Each observed absorption line should have an optical activity with a dispersion-like dependence on the frequency, and also a non-linear optical activity associated with the Lamb-dip saturated absorption. The laser electric field is plane polarized by the Brewster windows on the sample cell and by the grating at one end. If some elements of this optical system have a small asymmetry, the opposite optical activity of the sample makes a difference in laser con-

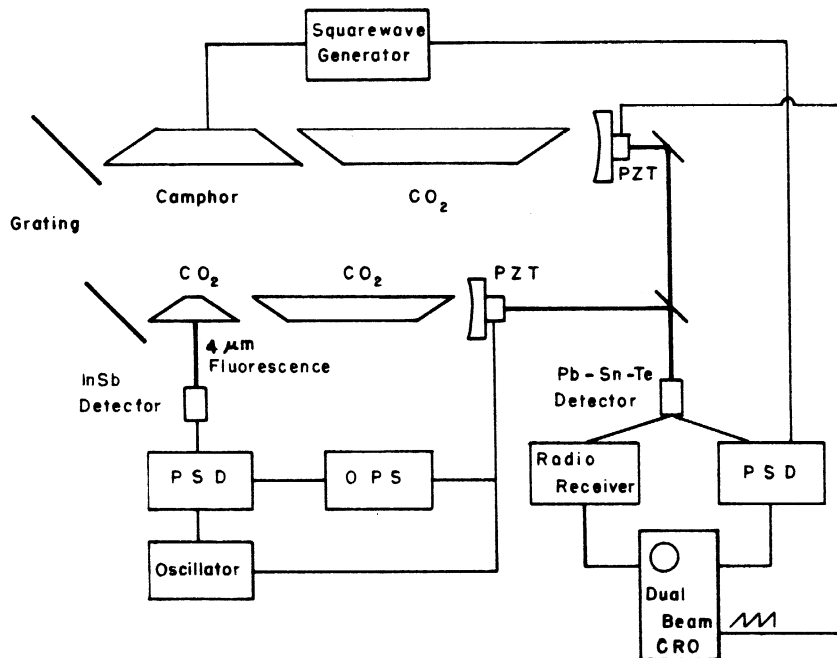
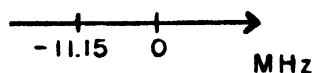
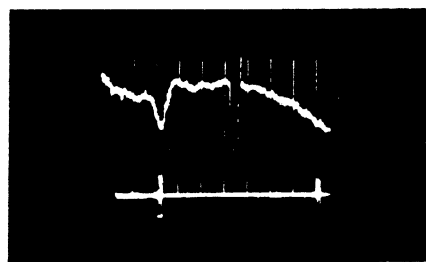


Fig. 3. A block diagram of the apparatus for Lamb-dip observation and beat-signal detection.

dition and thus in Lamb-dips which are very sensitive to the balancing between the active medium gain and the sample absorption.

The Lamb-dip positions of d-camphor and l-camphor were compared by evacuating carefully and filling suc-



$$\nu_{\text{Laser}} - \nu_{\text{Ref}}$$

Fig. 4. An example of oscilloscope traces of the d-camphor inverted-Lamb-dip and of the beat signal monitored through a tuned radio-receiver. The pressure of the sample was 40 mtorr and the time constant of detection was 10 ms.

cessively the sample cell with the same pressure of each optical isomer, while keeping constant the optical and electronic conditions of the laser and the detection apparatus. An accurate determination of the Lamb-dip position was obtained by measuring the frequency difference between the center of the camphor Lamb-dip and that of the CO<sub>2</sub> laser. To do this measurement we used two CO<sub>2</sub> lasers, one swept around the center of the camphor Lamb-dip and the other one servo-controlled to the CO<sub>2</sub> Lamb-dip resonance observed in the 4.3 μm fluorescence radiation [7]. The beat note between the two lasers was monitored by means of the Pb-Sn-Te infrared detector and a tuned radio receiver (fig. 3). The lower trace of fig. 4 shows the beat marker, measured at the center of the camphor Lamb-dip, at 11.5 MHz below the center of the R(24) CO<sub>2</sub> laser line. The jump at the center of the upper trace arises when the beat note between the two lasers passes through zero frequency.

The accuracy in the comparison of transition frequencies in d- and l-camphor was limited by the laser stability and the linewidth of the observed signal when conditions for best contrast in both isomer Lamb dips were realized. For the measurement so far conducted the transition frequencies of d- and l-camphor agreed

to within an uncertainty of  $\sim 300$  kHz which corresponds to the accuracy of  $1 \times 10^{-8}$ .

As far as the test of parity-non-conserving interaction is concerned, the present error limit is well above the magnitude of the theoretically predicted effect of  $10^{-16}$  [2]. The precision of the measurement can be improved by some orders of magnitude by performing the Lamb-dip experiment outside the laser cavity with an expanded laser beam. Moreover the choice of a light molecule, if available in the two separated optical isomers, would improve the signal-to-noise ratio. From the theoretical point of view as a consequence of recent atomic physics experiments [8], the parity-violating potential should be smaller than was expected, and thus the difference in energy levels of optical isomers may also be smaller than the predicted value. Nevertheless we publish these results because they improve the accuracy of equivalence between optical isomers by a factor of  $10^3$  over the previous microwave experiments.

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