

Infrared-Radio-Frequency Two-Photon Investigations on Deutero-Fluoroform (CDF₃)

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Some rotation-vibration transitions of the ν_5 -band of Deutero-Fluoroform using the infrared-radio-frequency two-photon technique are reported. An absorption cell for infrared-radio-frequency or infrared-microwave two-photon and double-resonance measurements inside a CO₂ laser cavity is described. This type of cell may be used in a wide frequency range.

Introduction

The method of infrared (IR)-radio-frequency (RF) or infrared-microwave (MW) two-photon spectroscopy has been applied to several molecules in the gas phase [1–6]. In this technique a tunable radio frequency is added to or subtracted from a fixed laser frequency using the nonlinearity of molecular transition processes. By this mechanism, in effect, an

infrared source is produced which is tunable about the fixed laser frequency with the linewidth and the stability of the molecular gas laser. The IR-RF or IR-MW two-photon spectroscopy enables us to measure the frequency of a rotation-vibration transition with the accuracy of microwave spectroscopy.

We report observations of infrared-radio-frequency two-photon transitions. The transition moment of those two-photon processes is

$$M_{12} = \frac{\langle 1 | \mu_p \cdot E_r | 1 \rangle \langle 1 | \mu_v \cdot E_1 | 2 \rangle - \langle 1 | \mu_v \cdot E_1 | 2 \rangle \langle 2 | \mu_p \cdot E_r | 2 \rangle}{2 \hbar^2 \omega_r},$$

where E_r and E_1 are the electric field amplitudes of the RF and the infrared radiation, respectively, μ_p and μ_v are the permanent dipole moment and the vibrational transition moment, respectively, and $\omega_r = 2\pi\nu_r$ is the applied radio frequency [3, 7]. To saturate a two-photon transition high electric fields of the two radiations are necessary. The RF fields will be provided by high power amplifiers, while the strong infrared fields will be obtained by placing the absorption cell inside the laser cavity. Using this arrangement saturation dips may be observed.

Experimental Details and Measurements

A block diagram of the IR-RF double-resonance or two-photon spectrometer is given in Figure 1. The CO₂ laser used as the infrared source is described in detail elsewhere [8]. The laser is frequency stabilized via the 4.3 μ fluorescence radiation [8, 9]. The RF radiation is supplied by a

sweep generator (Hewlett-Packard 8620 with RF plug-in 86222 A), on/off modulated by a PIN-switch, amplified and fed to the absorption cell. For amplifying the RF radiation a transistor amplifier (Hughes 46141 H 50–500 MHz, 10 W) is used. The frequency of the RF radiation is determined by a microwave counter (EIP 548). The frequency

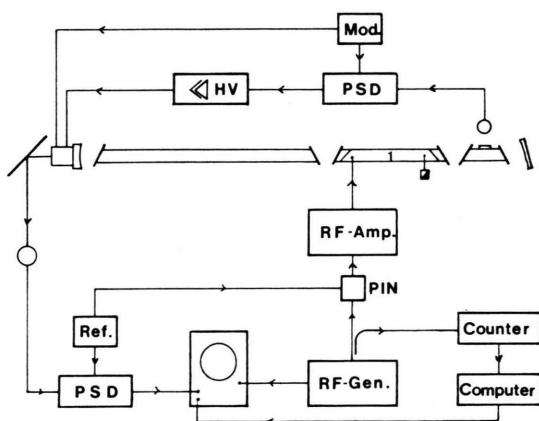


Fig. 1. Block diagram of the spectrometer. 1 Double-resonance or two-photon absorption cell with termination.

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value may be read out to a microcomputer to generate frequency markers. The laser radiation is detected by a liquid-nitrogen cooled PbSnTe detector. The output is impedance matched and fed directly to a phase sensitive detector (PAR 128 A). The obtained signal is displayed on an oscilloscope or an XY-recorder.

The absorption cell is made of a 0.5 m section of an X-Band waveguide sealed with NaCl windows at Brewster angle. A brass conductor of 11 mm × 1 mm cross section is arranged in the centre plane of the cell fixed by small teflon blocks as shown in Figure 2. The RF radiation is fed to the centre conductor by vacuum tight SMA-type connectors. This construction of the centre conductor generates a nearly homogeneous field in the interaction volume of the cell and concentrates a larger part of the RF power in this area than in a corresponding coaxial cell. For microwave frequencies up to 10 GHz a nearly constant transmission of about 80% was obtained. To higher frequencies the transmission of the cell rapidly decreases and strongly varies over small frequency ranges.

For the two-photon studies the cell was mainly used in the radio frequency range from 30 to 2000 MHz. By a 90°-rotation of the cell around the cavity axis both orientations, parallel and perpendicular, of the electric fields of laser and RF radiation are possible. With an additional DC voltage

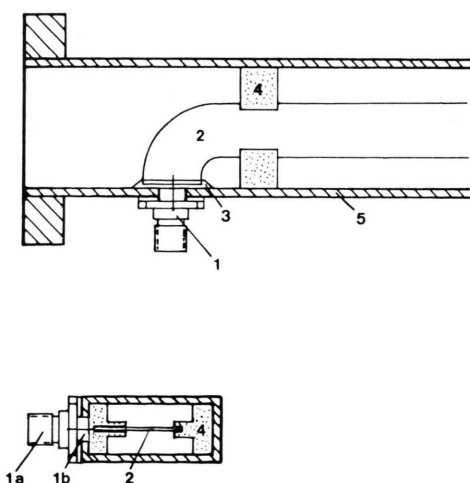


Fig. 2. Construction of the absorption cell. The other end of the cell is of the same form. 1, 1a, 1b SMA connector, Fa. ECM part no. 64HS-80-0 and 6520; 2 Centre conductor 11 mm × 1 mm; 3 Teflon strip 10 mm × 1.5 mm, groove 1 mm × 0.75 mm; 4 Teflon block; 5 X-band waveguide.

applied to the centre conductor, M-resolved measurements of the molecular transition are possible. With this absorption cell IR-RF double-resonance observations on German (GeH₄) have been carried out [10]. A similar type, as described in [11] in detail, has been used for IR-MW double-resonance experiments on Trifluoromethyljodide (CF₃I) outside the laser cavity [12].

The arrangement of an X-band waveguide with a centre conductor inside the laser cavity limits the free aperture of the cavity to 4.5 mm and therefore the frequency range of the laser. With the intracavity cell the CO₂ laser oscillates from P 42-P 8 and R 8-R 40 in both the 9.4 μ and 10.4 μ bands.

To distinguish between double-resonance and two-photon signals the laser frequency is slightly changed by varying the resonator length while the stabilisation is switched off. Double-resonance signals are observed at unchanged radio frequencies, whereas the two-photon signals are found at different radio frequencies, since the sum of radio and infrared frequencies has to be constant. The direction of the observed frequency shift indicates the position of the rotation-vibration transition with respect to the corresponding laser line.

With the described spectrometer arrangement saturation dips of IR-RF two-photon transitions were detected with an offset to the stabilized laser frequency up to 200 MHz. For observations of the weaker transitions with greater offsets to the laser frequency the absorption signal was periodically recorded and averaged in a minicomputer system (TI 990/10). A detailed description of the computer controlled signal averager will be given elsewhere [12]. In the case of signal averaging the radio frequency is stabilized and the frequency of the rotation-vibration transition may be determined with an accuracy of about 150 kHz of the corresponding laser frequency [8].

Figure 3 gives an example of a two-photon saturation dip of a rotation-vibration transition observed at Deutero-Fluoroform. All measurements on CDF₃ were carried out with a sample pressure of 10–20 mTorr, with an infrared power of about 25 W inside the laser cavity and an RF power of about 5–10 W.

In Table 1 the observed two-photon rotation-vibration transitions of the ν_5 -vibration of CDF₃ are listed. Additional to the measured radio frequencies of the observed saturation dips the differences be-

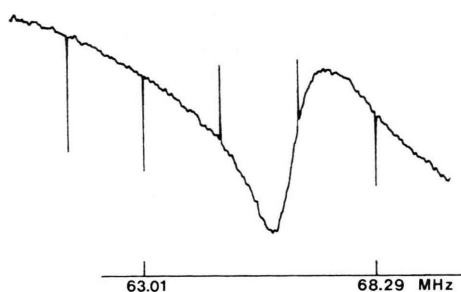


Fig. 3. Observed IR-RF two-photon saturation dip. The dip corresponds to the ${}^RQ_3(12)$ transition of the ν_5 -fundamental of CDF_3 at the 10R16 laser line. The sample pressure was 20 mTorr and the time constant for detection was 10 msec.

tween the rotation-vibration transition frequency and the laser frequency obtained from our Laser-Stark studies [8] are given. The frequencies of the corresponding laser lines are those reported by Petersen *et al.* [13]. In Laser-Stark spectroscopy the Stark-shifted transition frequencies are observed and the zero-field transition frequencies have to be calculated, whereas two-photon spectroscopy enables us to measure the infrared transitions directly. The frequencies obtained from Laser-Stark spectroscopy agree well with those now determined by the two-photon technique. The differences are in the order of the experimental error given in the Laser-Stark studies. The observed transition frequencies, used in a modified least-squares fit [14], do not significantly improve the molecular constants resulting from Laser-Stark experiments [8].

Table 1. Comparison of Two-Photon and Laser-Stark Observations.

Molecular transition	Two-photon $\nu_m - \nu_l$ [MHz]	Laser-Stark	Laser line	Laser frequency ν_l [MHz]
$\Delta K \Delta J_K(J)$				
${}^R P_0(11)$	— 85.42	— 64.5	10R 8	29011133.0
${}^R P_1(8)$	96.48	77.9	10R10	29054072.7
${}^R P_{11}(16)$	— 73.43		10R12	29096274.4
${}^R Q_3(13)$	—303.53	—311.1	10R16	29178455.7
${}^R Q_3(12)$	— 66.37	— 71.3		
${}^R Q_3(11)$	153.49	149.7		
${}^R Q_3(10)$	354.19	352.0		
${}^R Q_3(9)$	533.94	535.5		
${}^P Q_4(13)$	—399.29	—407.7	10R22	29296136.4
${}^P P_4(6)$	—294.49			
${}^P Q_4(12)$	—147.55	—158.3		
${}^P Q_4(11)$	85.86	71.7		
${}^P Q_4(10)$	298.37	282.1		
${}^P Q_4(9)$	498.65	473.2		

The frequencies ν_m of the observed molecular transitions are in the order of the laser frequencies ν_l .

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