Infrared Microwave Double-Resonance Investigations on Trifluoromethyljodide (CF_3I)

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An additional set of infrared microwave double-resonance signals was observed using the 9 R 12 line of the CO_2 laser. The vibrational transition involved is assigned to the ${}^QQ_5(8)$ transition of the ν_1-fundamental. $\Delta J = 1$, $K = 5$ rotational transitions were found for $J = 5$, 6, 7, and 8 in both vibrational states. A detailed description of the apparatus and methods is given.

I. Introduction

The band centred at 1073 cm^{-1} of Trifluoromethyljodide (CF_3I) was assigned to the ν_1-fundamental by Edgell and May [1]. This band is superimposed by a number of combination bands which are normally very weak. Infrared microwave double-resonance (IR-MW-DR) studies [2, 3] have shown that several of these bands are "borrowing" intensity from the ν_1-fundamental which gives rise to several double-resonance signals. IR-MW-DR investigations using molecular fixed frequency lasers as infrared source give detailed informations but only on very isolated points of the spectrum. A complete analysis of all observed double-resonance signals which considers all signals simultaneously will give further informations about interactions in rovibronic spectra.

In this paper we report an additional set of IR-MW-DR signals using the 9R12 line of the CO_2 laser. Both possibilities of performing IR-MW-DR studies — using the laser radiation as signal source and the microwave radiation as pump source and vice versa — are used. The first method — using the laser radiation as the signal source — allows the very sensitive detection of IR-MW-DR signals. The gain of sensitivity is due to the "transfer" of a microwave quantum to an infrared quantum. As we will discuss later this method allows only in very favourable cases the determination of the related infrared transition.

In most cases the rotational quantum numbers of the infrared transition may be determined by using the microwave radiation as the signal source. The application of a strong infrared pump radiation results in a significant change in population of the related levels in both vibrational states. This gives rise to a characteristic change in the absorption behavior of the rotational transitions if a pumped level is involved.

II. Using the Laser Radiation as Signal Source

a) *Experimental*

The block diagram of the apparatus used in this type of experiments is shown in Figure 1. The laser has a 3 m cavity length and a 1.8 m semisealed-off gain tube. The resonator consists of a plane grating at one end and a semitransparent concave Ge-mirror (80% reflectivity) at the other end. A frequency

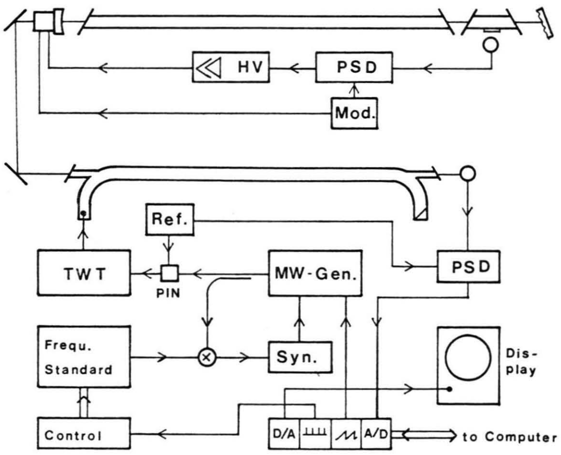

Fig. 1. Block diagram of the apparatus for IR-MW-DR experiments using the laser radiation as signal source.

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stabilisation via the 4.3 μ fluorescence radiation [4, 5] is used throughout all experiments.

The double-resonance cell outside the laser cavity consists of a 2.5 m long X-band waveguide provided with a centre electrode. This electrode is used for Stark-modulated observations in the other type of experiments. The centre electrode has a special shaped transition to the coaxial connectors [6, 7] on both ends. This and a similar type [7] of double-resonance cell is used by us for IR-MW-DR experiments with microwave frequencies up to at least 40 GHz. For microwave frequencies up to 10 GHz the microwave power together with an optional DC voltage up to 2 kV is fed to the cell via the coaxial connectors while for higher frequencies the waveguide port is used.

The nearly parallel beam of laser radiation enters the double-resonance cell via a 8 mm bore in a E-plane waveguide bend sealed with NaCl Brewster windows. By careful adjustment a minimum of 35 to 40% loss of laser power in the double-resonance cell may be obtained. This loss is mainly due to the absorption by the teflon strips supporting the centre electrode which are hit by the slightly divergent laser beam.

The microwave power is provided by YIG-oscillators or BWO-oscillators and on/off modulated by a PIN-switch. Before feeding to the double-resonance cell the microwave radiation may be optionally amplified by a TWT-amplifier. In the course of our experiments we experienced that microwave power higher than ca. 20 mW produces appreciable double-resonance signals with an optimum pump power in the order of 500—1000 mW. Hence for nearly all measurements we used the microwave sources with output power in the range of 20 to 100 mW without further amplification. The laser power entering the double-resonance cell was in the order of 50 mW.

The laser power used as signal source is detected by a liquid-nitrogen cooled PbSnTe detector. After impedance matching the signal is fed to a lock-in amplifier and averaged by means of a minicomputer system (TEXAS TI 990/10). To preserve the resolution over the averaging periode it is necessary not only to stabilize the laser but to stabilize the microwave source too. Consequently the averaging system provides not only a ramp by which the source is swept but also a pulse train to step the frequency standard to which the microwave oscillator is locked. After each averaging cycle the contents of the memory is displayed on an oscilloscope for inspection.

A program is available to perform manipulation on the recorded data like displaying of the trace on the oscilloscope, recording the spectrum on a XY-recorder, smoothing or frequency determination. The sample of Trifluoromethyljodide (CF_3I) was supplied by Fluorochem Ldt England and was used without further purification.

b) *Observations*

The observed double-resonance signals together with the assignments are listed in Table 1. Since the rotational constants are well known from microwave spectroscopy [8—12] the assignment of the rotational quantum numbers is straightforward. For symmetric rotor molecules like CF_3I the $\Delta J = 1$ rotational transitions are spaced by 2B (ca. 3 GHz for CF_3I), hence the determination of the J quantum number is obvious. The assignments of the K

Table 1. Observed IR-MW Double-Resonance Signals of CF_3I. Infrared Transition: ${}^{Q}Q_5(8)$; Microwave Transitions: $\Delta K = 0$, $K = 5$; Frequencies in MHz.

J	J'	$2F$	$2F'$	Ground State	Mes. —Cal.	Excited State	Mes. —Cal.
5	6	7	9			18317.85	0.38
5	6	9	11	18214.42	0.01		
6	7	7	9			21405.25	− 0.26
6	7	9	11	21367.95	− 0.04		
6	7	11	13	21270.29	− 0.01		
7	8	9	11	24469.56	− 0.03	24382.07	− 0.16
7	8	11	11	24382.86	− 0.05	24295.42	0.29
7	8	11	13	24389.77	− 0.03	24302.23	0.21
7	8	13	13	24321.98	0.01	24234.59	0.77
7	8	13	15	24328.36	0.07	24240.90	0.74
7	8	15	15	24296.37	0.03	24208.00	0.00
7	8	15	17	24301.44	0.07	24213.94	0.86
7	8	17	17	24330.37	− 0.13	24242.84	0.50
7	8	17	19	24329.17	0.04	24241.68	0.70
7	8	19	19	24460.92	0.02	24373.36	− 0.23
7	8	19	21	24438.29	0.07	24350.76	0.05
8	9	11	13	27483.25	0.01	27384.85	− 0.42
8	9	13	13	27476.28	− 0.07	27378.06	− 0.32
8	9	13	15	27425.25	− 0.02	27326.90	− 0.06
8	9	15	15	27418.92	− 0.02	27320.67	0.05
8	9	15	17	27384.17	0.02	27285.80	0.18
8	9	17	17	27379.11	− 0.01	27280.90	0.35
8	9	17	19	27369.04	− 0.01	27270.76	0.33
8	9	19	19	27370.28	− 0.15	27271.93	0.14
8	9	19	21	27391.40	0.05	27293.07	0.22
8	9	21	21	27414.15	0.13	27315.70	− 0.03
8	9	21	23	27466.69	0.05	27368.38	− 0.20

and F quantum numbers are obtained by the characteristic hyperfine pattern. Due to the large nuclear quadrupole coupling constant of the jodine nucleus of $eqQ = -2144$ MHz the hyperfine components are well separated and the assignment is clear. The assignments for the upper vibrational state were based on the assumption that there will be no important changes of the rotational constants.

The rotational spectra for both vibrational states were fitted separately using perturbation theory up to the second order as given in [13]. Since we observed only signals originating from one K-subsystem it was not possible to fit the D_{JK} centrifugal distortion constant. Hence this parameter was fixed to its ground state value. The rotational parameters for the lower vibrational state are in excellent agreement with the ground state constants [12]. Hence the assignment of the lower vibrational state is doubtless. A possible assignment of the upper vibrational state is discussed later.

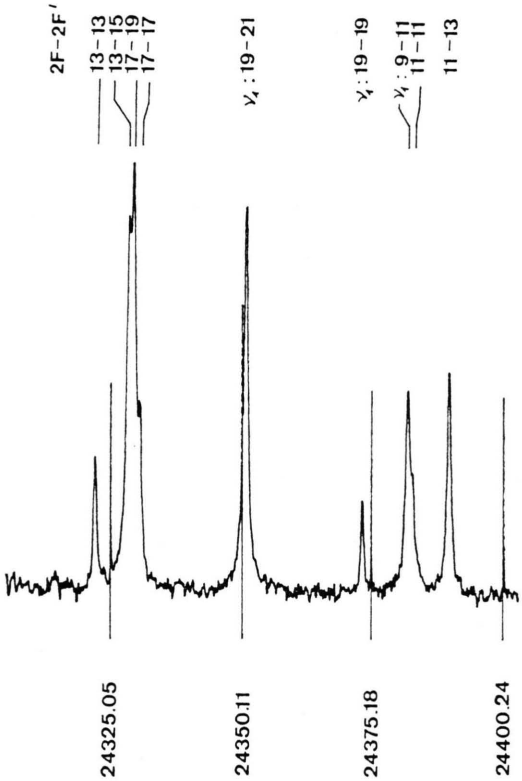

Fig. 2. Part of the IR-MW-DR spectrum of CF_3I. IR-transition: $^QQ_5(8)$; MW-transition: $J - J' = 7 - 8$; sample pressure: 10 mT; No of data points: 1000; No of average cycles: 50; sample interval: 0.2 msec. MW-pump power: 20 mW; IR-signal power: 50 mW. Frequencies in MHz.

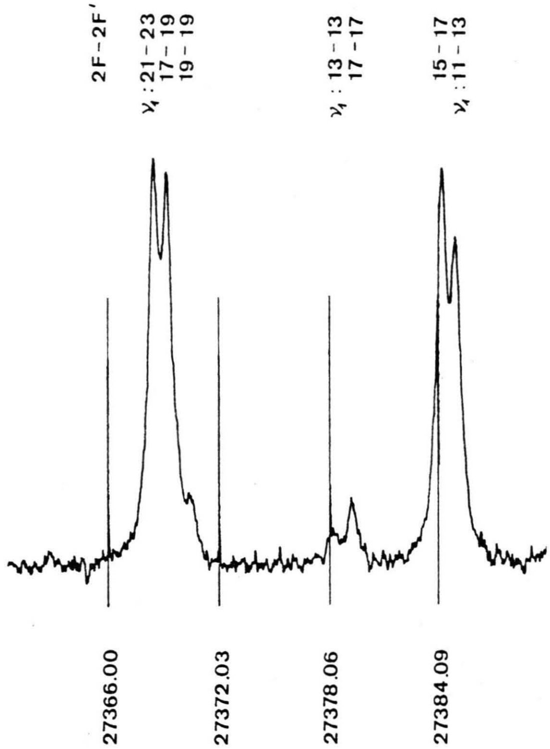

Fig. 3. Part of the IR-MW-DR spectrum of CF_3I. IR-transition: $^QQ_5(8)$; MW-transition: $J - J' = 8 - 9$; sample pressure: 9 mT; No of data points: 1000; No of average cycles: 200; sample interval: 0.2 msec. MW-pump power: 20 mW; IR-signal power: 50 mW. Frequencies in MHz.

Figure 2 and Fig. 3 give examples of the observed double-resonance signals. The experimental data are given in the captures. As one may see from the recordings this type of spectroscopy is quite sensitive with good resolution. The observed line width of 200—300 kHz (HWHM) is mostly due to pressure broadening. As it is indicated in Table 1 we observed for both $J - J' = 7 - 8$ and $J - J' = 8 - 9$ transitions not only all $\Delta F = 1$ components but also all the ten times weaker $\Delta F = 0$ components. This is true for both vibrational states. Therefore we had strong indication that the vibrational transition should be a $^QQ_5(8)$ transition.

III. Using the Microwave Radiation as Signal Source

a) *Experimental*

A block diagram of the apparatus used in this type of experiments is given in Figure 4. The heart

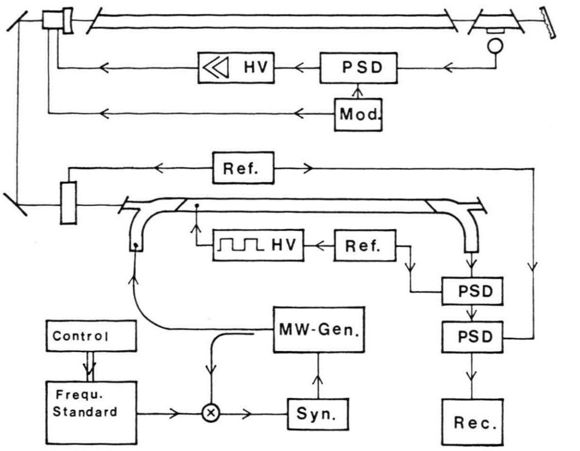

Fig. 4. Block diagram of the apparatus for IR-MW-DR experiments using the MW-radiation as signal source.

of the setup is a conventional microwave spectrometer consisting of a stabilized microwave source, the double-resonance cell used as Stark-cell and the first lock-in amplifier. A squarewave modulated Stark-field of about 200 V/cm is applied to the centre electrode. The first phase sensitive detector (PSD) is locked to this modulation frequency of about 16 kHz. Since we are interested in the change of absorption behavior we used double modulation. The laser radiation used as pump source is chopped with a frequency of about 5—7 Hz. Thus the absorption signal detected by the first PSD is modulated with this frequency. Using a second PSD locked to the chopper frequency we observe only the change in absorption behavior. A decrease or increase of the absorption signal is discriminated by the opposite phases of the two signals. To check whether there is a decrease of absorption or an emission we have to record the absorption signal itself once with and without pump radiation since the double modulation method does not discriminate between these two cases.

b) Observations

The only purpose of performing this type of experiments was to confirm the tentative assignment of the rotational quantum number of the vibrational transition given before.

The application of a strong infrared pump radiation results in a significant depopulation of the lower vibrational level and an appropriate overpopulation of the upper level as indicated schematically in Figure 5. For rotational transitions of the type "a" (Fig. 5) the application of the pump radiation leads to a depopulation of the upper rotational level and hence to an increase of absorption intensity. Vice versa for the rotational transition of the type "b" (Fig. 5) the application of the pump radiation results in decrease of population of the lower level and hence to a decrease of absorption intensity or even in an emission.

Without pump radiation the upper vibrational state carries only about the 190th part of the population of the ground state. Therefore no rotational spectra of this state will be observed in conventional microwave spectroscopy. Using the same argumentation as above the application of the infrared pump radiation results at the upper vibrational state in an emission for the type "c" (Fig. 5) and in an absorption for the type "d" (Fig. 5) rotational transitions. Hence from these experiments a clear determination of the rotational quantum numbers of both vibrational levels may be obtained.

For each observed $\Delta J = 1$ transition in both vibrational states we checked the signals for the

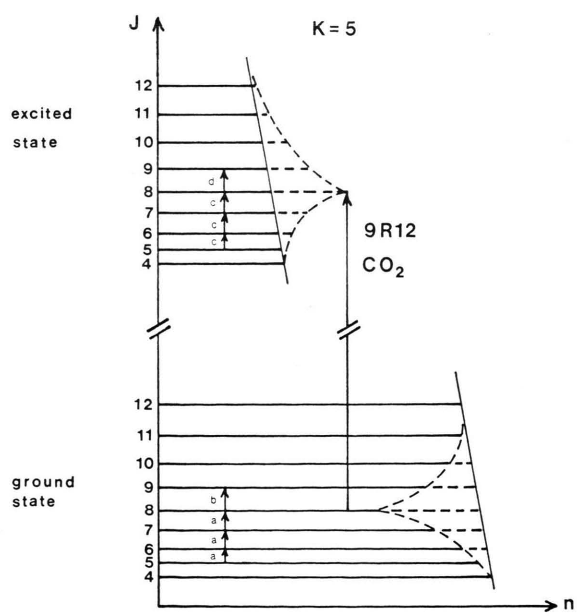

Fig. 5. Schematical energy level diagram for IR-MW-DR observations using the MW-radiatior as signal source. The Boltzmann distribution (straight curve) is disturbed (dashed curve) by a strong IR-pump. As a result the rotational transitions marked "a" and "d" show an increase in absorption while the transitions marked "b" and "c" show a decrease in absorption or an emission.

discussed behavior. By this we confirmed definitely the assignment of the vibrational transition given before, i.e.

$$J - J' = 8 - 8\,, \quad K - K' = 5 - 5\,({}^{Q}Q_5(8))\,.$$

IV. Conclusion

The J and K quantum numbers are well determined by the described experiments. Since we observe three level double-resonance signals for all hyperfine sublevels in both vibrational states the infrared transition affects all F-sublevels. This is only possible if we assume $\Delta F = 0$ vibrational transitions since these are located within a range of 190 kHz which agrees very well with the line width of the stabilized laser of about 150 kHz. The $\Delta F = \pm 1$ vibrational transitions are spread over a range of 30 MHz but one of those ($F - F' = 13/2 - 15/2$) is located in the range of the $\Delta F = 0$ transitions.

Unfortunately we found no further double-resonance signals with an additional transition of the same parallel band. To estimate the band centre we have to assume a value for the ΔA-parameter. If we compare $\Delta A = 16.2$ MHz for CF_3Cl [14] and $\Delta A = 11.2$ MHz for CF_3Br [15] this parameter should be in the order of 10 MHz. Assuming $\Delta A = 10.0$ MHz for CF_3I and using the standard energy expression for a parallel band of a symmetric rotor we calculated the band centre to be 1073.2785 cm^{-1} (Table 2). This value agrees quite well with the band centre of 1073 cm^{-1} [1] determined by conventional infrared spectroscopy.

Jones and Kohler had observed a set of IR-MW-DR signals with the 9R16 CO_2 laser line [2]. From intensity arguments they assumed the involved ${}^{Q}R_2(7)$ transition to belong to the ν_1-fundamental band. They explained their resulting $\Delta A =$ 25 MHz and the band centre of 1075.1915 cm^{-1} by a local anomality. Since the double-resonance signals observed by us have nearly the same intensity it is not possible up to now to give a unique set of parameters for the ν_1-fundamental.

Table 2. Molecular Constants of CF_3I. a — assumed; b — from microwave data [12]; c — fixed to ground state value.

	Ground State	Excited State	
ν		1073.2785 (3)	cm^{-1}
ΔA		10.0 a	MHz
B	1523.2901 (50)	1517.6839 (277)	MHz
D_J	0.0002 (3)	− 0.0007 (1)	MHz
D_{JK}	0.0010 b	0.0010 c	MHz
eqQ	− 2144.66 (52)	− 2156.81 (180)	MHz

As Table 1 shows we observed not only three level double-resonance signals but also four level or collision induced double-resonance signals. Although all hyperfine levels are affected by the infrared transition we observed for the $J - J' = 6 - 7$ only two respectively one ($F - F' = 9/2 - 11/2$, $11/2 - 13/2$; ν_1: $7/2 - 9/2$) and for the $J - J' = 5 - 6$ only one ($F - F' = 9/2 - 11/2$; ν_1: $7/2 - 9/2$) hyperfine transitions. So this system allows further investigations on collision induced transitions.

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