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Extension of Microwave Absorption Spectroscopy to 0.37-mm Wavelength*

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High-resolution sweep spectroscopy has been extended to submillimeter wavelengths as short as 0.37 mm. The sensitivity of microwave spectroscopy in the submillimeter region (0.37 to 1 mm) has been improved by more than an order of magnitude. The highest-frequency spectral lines measured are the $J=6\rightarrow 7$ transition of $^{12}C^{16}O$ at 806 651.719 MHz and the $J=66\rightarrow 67$ transition of $^{16}O^{12}C^{32}S$ at 813 353.706 MHz. The rotational constant B_0 for DF is observed to be 325 584.96 MHz.

Although microwave spectral measurements were extended into the submillimeter wave region[1] in 1954 and measurements are commonly made now in the upper submillimeter wave region[2] from $\lambda=\frac{1}{2}$ to 1 mm, the region below $\frac{1}{2}$ mm is still essentially undeveloped. The only two absorption transitions previously observed at wavelengths below $\frac{1}{2}$ mm,[3] HCl at 625 GHz ($\lambda=0.48$ mm) and CO at 691 GHz ($\lambda=0.43$ mm), were measured with difficulty on signals not much above the noise level. Beat notes of microwave harmonic generators with submillimeter-wave gaseous discharge lasers have also been detected, including the well-known HCN laser line[4] at $\lambda=0.33$ mm. However, these lasers are fixed in frequency and operate only on exceptional transitions so that they are not suitable for general spectral measurements.

We have now advanced the operating range of the tunable microwave spectrometers to 813 GHz or to wavelengths of 0.37 mm and have increased the sensitivity of the submillimeter wave spectrometers in the 0.4- to 1-mm range by more than an order of magnitude. Microwave spectroscopy is now highly practical to 750 GHz ($\lambda=0.40$ mm). This advance was achieved by the replacement of the silicon-crystal diode detector in our earlier spectrometer[1-3,5] with a Mullard photoconducting indium antimonide detector[6]

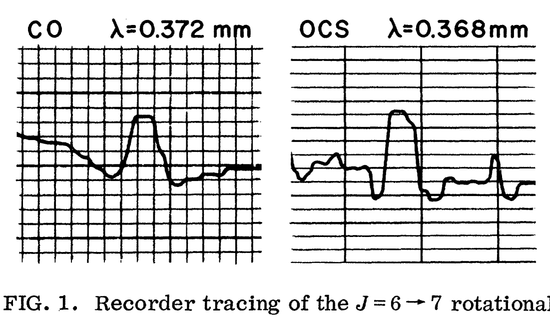

FIG. 1. Recorder tracing of the $J=6\rightarrow 7$ rotational transition of CO at 806 651.719 MHz, at left, and of the $J=66\rightarrow 67$ transition of OCS at 813 353.706 MHz, at right. Both were observed at the fourteenth harmonic of the klystron frequency.

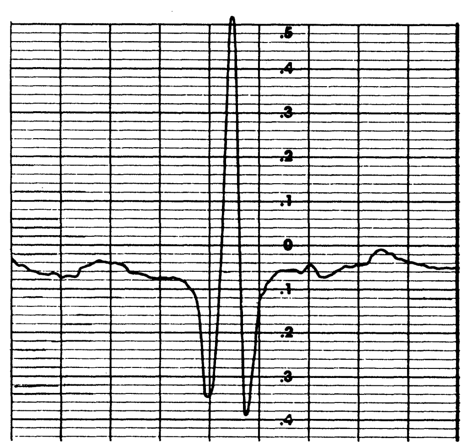

FIG. 2. Recorder tracing of the $J=0\rightarrow 1$ rotational transition of DF at 651 099.393 MHz ($\lambda=0.46$ mm).

Table I. Observed submillimeter wave frequencies and spectral constants of OCS.

Transition	Observed frequency (MHz)	Calculated frequency (MHz)	Difference (MHz)
	Present work		
$J=57\rightarrow58$	704 437.052	704 437.052	0.000
$J=58\rightarrow59$	716 546.559	716 546.568	−0.009
$J=65\rightarrow66$	801 259.782	801 259.824	−0.042
$J=66\rightarrow67$	813 353.706	813 353.716	−0.010
	Derived constants[a,b]		
	$B_0=6081.492\,55\pm0.000\,17$ MHz		
	$D_0=0.001\,301\,92\pm0.000\,000\,04$ MHz		

[a]Low-frequency measurements from Ref. 7.
[b]Errors listed are twice probable error.

operated at 1.6°K. As a source we have retained the klystron-driven crystal harmonic generator originally designed by King and Gordy[5] and used for many millimeter and submillimeter wave measurements. This coherent, tunable source, for which frequency is accurately determined by a comparison of the klystron frequency with harmonics of a 5-MHz oscillator referenced to WWVB, insures the high resolution of the spectrometer and provides a means of precision measurement of a line frequency. With this source the only requirement for the detector is that it be sensitive to the submillimeter wave radiation. We find the indium antimonide detector is both sensitive and remarkably broad-banded. Throughout the submillimeter wave region now covered, 0.37 to 1.0 mm, it appears to be appreciably more sensitive than the crystal point-contact detector.

Figure 1 shows lines of CO and OCS recorded at wavelengths below 0.40 mm, and Fig. 2 shows a recording of the $J=0\rightarrow1$ transition of DF in the region of 0.46 mm. Because of its small moment of inertia the spectrum of this molecule had not been previously detected with microwave spectroscopy.

Tables I and II list the OCS and CO lines observed in the present work; spectral constants determined from a combination of these measurements with earlier low-frequency work[7-9] are also given in the tables. The higher frequency data allow a more precise evaluation of the ef-

Table II. Observed submillimeter wave frequencies and spectral constants of CO.

Transition	Observed frequency (MHz)	Calculated frequency (MHz)	Difference (MHz)
	Present work		
$J=2\rightarrow3$	345 795.989	345 795.997	−0.008
$J=3\rightarrow4$	461 040.811	461 040.768	0.043
$J=4\rightarrow5$	576 267.934	576 267.915	0.019
$J=5\rightarrow6$	691 472.978	691 473.032	−0.054
$J=6\rightarrow7$	806 651.719	806 651.712	0.007
	Derived constants[a,b]		
	$B_0=57\,635.971\pm0.006$ MHz		
	$D_0=0.183\,59\pm0.000\,14$ MHz		

[a]The $J=0\rightarrow1$ measured frequency is taken from Ref. 8 and the $J=1\rightarrow2$ measured frequency from Ref. 9.
[b]Errors listed are twice probably error.

Table III. Measured frequency of the $J=0\rightarrow 1$ transition of DF.

Klystron harmonic	Observed frequency (MHz)
11	651 099.402
12	651 099.384
$\nu_0 = 651\,099.393$ MHz	
$D_0 = 17.63$ MHz	
$B_0 = 325\,584.96$ MHz	

[a]Infrared value of R. N. Spanbauer, K. N. Rao, and L. H. Jones, J. Mol. Spectrosc. 16, 100 (1965).

fects of centrifugal distortion. To insure positive identification, the $J=0\rightarrow 1$ transition of DF was measured with both the eleventh and twelfth harmonics of the fundamental klystron frequency. The results are shown in Table III. All lines shown in Tables I-III were obtained with harmonics of an OKI 55V11 klystron. We have measured the $J=1\rightarrow 2$ transitions of both $^{14}ND_3$ and $^{15}ND_3$ as well as the spectra of hydrogen and deuterium halides in the region of 0.37 to 0.50 mm, the results of which will be reported elsewhere.

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Collisional Effects on Induced Emmission and Absorption Transition Probabilities in Atomic Systems*

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The transition probabilities for induced emission and absorption of electromagnetic radiation by an excited atom interacting, in addition to the radiation field, with a system of "perturbers" (in single, binary, and completed encounters) are evaluated. It is found that Dirac's result $W_{\rm ind}/W_{\rm abs} = (\bar{n}_{l\sigma}+1)/\bar{n}_{l\sigma}$ must be modified by a factor $(1-\alpha n)^2/(1+\alpha n)^2$, where α is related to the interaction potential of the emitter-perturber system as well as to the level structure of the "colliding" atoms, and n is the perturber number density.

The problem of radiation interacting with an excited atom was investigated by Dirac,[1] who found that the ratio of the transition probability per unit time for induced emission $W_{\rm ind}$ and that for absorption $W_{\rm abs}$ is

$$W_{\rm ind}/W_{\rm abs} = (\bar{n}_{l\sigma}+1)/\bar{n}_{l\sigma}, \tag{1}$$

where $\bar{n}_{l\sigma}$ is the mean number of photons of polarization σ in the frequency range around ν_l. Dirac's result is obtained by assuming that the emitting atom is fixed in space, and no other external field exists except the radiation field. The dipole approximation is also assumed to be valid. In this work, we have investigated the related problem of an excited atom interacting, in addition to the radiation field, with the field due to the surrounding atoms (perturbers) in their ground state. We find that $W_{\rm ind}$ decreases, whereas $W_{\rm abs}$ increases, with increasing density of perturbers.

Consider a system consisting of a fixed emitter, a perturber, and the radiation field. The total Hamiltonian (Coulomb gauge[2]) may be written as

$$\mathcal{H} = \frac{1}{2M}(\vec{P}+e\vec{A})^2 + \frac{1}{2m}(\vec{p}_1 - e\vec{A})^2 + \frac{1}{2m}(\vec{p}_2{}' - e\vec{A})^2 - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R} - \frac{e^2}{|\vec{R}+\vec{r}_2|} - \frac{e^2}{|\vec{R}-\vec{r}_1|} + \frac{e^2}{|\vec{R}+\vec{r}_2-\vec{r}_1|} + \mathcal{H}_r \tag{2}$$

where $\vec{P}$, $\vec{p}_1$, and $\vec{p}_2{}'$ are the total momenta of the perturber nucleus, optical electrons of emitter and