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PHOSPHORESCENCE-MICROWAVE DOUBLE-RESONANCE (PMDR) SPECTROSCOPY

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ABSTRACT

The effect of saturating the zero-field transitions with microwave radiation on the phosphorescence spectrum is demonstrated at low temperatures. The application of this type of double-resonance experiment in determining the most probable intersystem crossing routes, the mechanism of the phosphorescence radiation of the different vibronic bands, the determination of zero-field splittings, and the electronic distribution in the triplet state is indicated.

I. INTRODUCTION

The different vibronic bands in the phosphorescence spectra of most molecules are known to be highly polarized. This fact indicates that for each band the radiative transition probability from one of the three zero-field sublevels of the emitting triplet state is larger than that from the other two. Furthermore, it is generally possible to find in a phosphorescence spectrum different vibronic bands which originate from different zero-field levels of the lowest triplet state. At very low temperatures, the electron spin-lattice relaxation time may become longer than the phosphorescence radiative lifetime, and a non-Boltzmann population distribution among the zero-field levels might result.(1,2,3) As the temperature increases, the rates of

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+ Contribution No. 2411.

* Alfred P. Sloan Fellow.

the spin-lattice relaxation processes increase and the relative intensity of these vibronic bands will then change, reflecting the changes in the populations of the zero-field levels from which the emissions originate. Such changes have been recently observed,[4] and the most probable route for the entry to the lowest triplet state determined from the changes in relative vibronic intensity with temperature within the phosphorescence spectrum for 2,3-dichloroquinoxaline.

The population of the zero-field levels of the lowest triplet state can also be varied at a constant, very low temperature by pumping the zero-field transitions with microwave power at the resonance frequencies. Since the spin-lattice relaxation times are long, and since sufficiently high radiation densities are readily obtainable at the frequencies of the zero-field transitions, these transitions are easily saturated, i.e., the populations of the upper and lower levels of the transition are readily equalized. If a population difference existed prior to saturation, the population change induced by the microwaves can be detected optically by monitoring the relative intensities of vibronic bands originating mainly from either of the two zero-field sublevels being pumped. Thus, one can assign the zero-field sublevel which is responsible for most of the intensity in each of the different vibronic bands in the phosphorescence spectrum. This assignment is extremely valuable in elucidating the different phosphorescence mechanisms in polyatomic molecules.

Another equally important application of phosphorescence-microwave double-resonance spectroscopy (PMDR) is that the degree and direction of spin alignment in the lowest triplet state at low temperatures can be determined. This information is useful in determining the most probable route for the intersystem crossing process.[4]

A third application of PMDR is to determine the zero-field splittings in phosphorescent molecules. The prior discussion assumed these were known from ESR experiments, but they need not be. PMDR offers a more sensitive technique than the one recently described,[5] which is based on observing the changes in the total phosphorescence intensity by the application of microwave radiation. For systems having mixed polarizations in the phosphorescence, some vibronic bands would increase in intensity while others would decrease in intensity upon microwave saturation. The percentage change in the total phosphorescence intensity upon microwave saturation generally would be smaller than the percentage change in the intensity of certain individual vibronic bands originating from one of the two zero-field levels being saturated.

The method is demonstrated here using 2,3-dichloroquinoxaline, for which temperature studies have recently suggested[4] that the 0,0 band originates from the τ_z sublevel and that the (0,0-260 cm^{-1}) band originates from the τ_y sublevel of the $^3B_2^{(\pi,\pi^*)}$ state. Furthermore, it was concluded[4] that the population of the τ_y sublevel is ~ 7 times larger than that of the τ_z sublevel at 1.9°K. The PMDR results, reported below, show that the above interpretations are correct. Furthermore, a definite assignment of the emitting sublevels and the non-totally symmetric vibration (260 cm^{-1}) appearing in the phosphorescence spectrum can be made.

II. EXPERIMENTAL

A single crystal of 2,3-dichloroquinoxaline in durene (~ 10^{-3} mole/mole) is cut to fit inside a helical slow-wave structure of 0.3-cm inside diameter. The helix is matched to a rigid coaxial line which supports it vertically inside a helium dewar. A Hewlett-Packard signal generator is used as a microwave source, and the frequency and incident power are monitored through a 10 DB directional coupler.

The sample is excited through the open helical structure at 1.9°K with 3500Å radiation. The phosphorescence is recorded, at an angle of 45° from the exciting light direction, using a 2-meter Jarrell-Ash spectrometer. All experiments were performed under c.w. conditions for both the microwave and optical radiations.

The zero-field energies were determined by isolating the 0,0 band, the (0,0-260 cm^{-1}) band, or the (0,0-490 cm^{-1}) band using $\lesssim 5$ cm^{-1} slits on the 2-meter spectrometer, and scanning the microwave frequency. In order to assign the zero-field levels, a conventional magnetophotoselection experiment[6,7] was carried out in ethanol glass at ~ 100°K using a Varian E.S.R. spectrometer.

III. RESULTS

A. The microwave spectrum

The observed zero-field transition energies of 2,3-dichloroquinoxaline in durene at 1.95°K are:

$E_z - E_y = 1.055$ GHz, $E_z - E_x = 3.512$ GHz, and $E_y - E_x = 2.457$ GHz.

The order of the three zero-field levels as found by the magnetophotoselection experiment is $\tau_x < \tau_y < \tau_z$, from which $|D| = 0.09955$ cm^{-1}, $|E| = 0.01760$ cm^{-1} for the usual spin Hamiltonian parameters.*

The intensity of the 0,0 band increases when the transitions at 1.055 and 3.512 GHz are saturated, while that of the (0,0-260 cm^{-1}) band decreases when the transitions at 1.055 and 2.457 GHz are saturated. Each of the three zero-field transitions saturates at approximately 10 μ-watts of incident power. The largest intensity changes are observed when

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* In an ethanol glass at ~ 100°K the spin Hamiltonian parameters are $|D| = 0.0974$ cm^{-1} and $|E| = 0.0174$ cm^{-1}.

the 1.055 GHz ($\tau_z \longleftrightarrow \tau_y$) transition is saturated, and in this note we will concentrate on the results obtained at this frequency.

The zero-field transitions, as shown in Figure 1, exhibit considerable structure. The origin of this structure is not yet fully understood. At least two interactions have been mentioned previously in this context for quinoxaline,[5] viz., second-order nitrogen hyperfine and first-order nitrogen quadrupole interactions. Another cause for the observed structure might be the presence of more than one trapping site for the guest molecule in the host lattice. It is worth noting that the individual lines comprising the fine structure are extremely sharp, e.g., in the 1.055 GHz transition, where the highest resolution and signal-to-noise was obtained, the full line width at half intensity in the low frequency component is $\lesssim$ 0.6 MHz. The origin of the observed fine structure is now under examination.

B. The phosphorescence spectrum

Valuable information concerning the radiative and nonradiative properties of the triplet state can be obtained by saturating the zero-field transitions and observing the changes in the complete phosphorescence spectrum. This is demonstrated in Figure 2, which compares the phosphorescence spectrum at 1.95°K with that obtained when simultaneously saturating the 1.055 GHz transition at 1.95°K, as well as with that obtained at ~ 20°K in the absence of microwave power.

When saturating with 1.055 GHz, the intensity of the 0,0 band increased by a factor of ~ 4.3, whereas that of the (0,0-260 cm^{-1}) band decreased by a factor of ~ 0.7. These results are in good agreement with the previous conclusion[4] regarding the origin of the 0,0 band (the τ_z sublevel) and of the (0,0-260 cm^{-1}) band (the τ_y sublevel). Furthermore, the observed magnitude of the intensity changes is in reasonable agreement with the population of the τ_y level being seven times greater than that

of the τ_z level, as concluded from the earlier temperature studies.[4] Upon saturating the $\tau_z - \tau_y$ transition, the 0,0 band is predicted to increase by a factor of 4, while the (0,0-260 cm^{-1}) is predicted to decrease by a factor of ~ 0.6. Saturating transitions involving the τ_x sublevel gives results that are consistent in terms of the sign of the intensity changes, but the observed magnitudes are not quantitatively understood. They can be qualitatively explained if the emission of certain vibronic bands originates from more than one spin level with different radiative lifetimes. This possibility is now under further examination.

Figure 2 shows that the 0,0, the (0,0-138 cm^{-1}), and the (0,0-599 cm^{-1}) bands all increase in intensity to the same extent upon saturation. The (0,0-340 cm^{-1}), (0,0-491 cm^{-1}), and (0,0-1087 cm^{-1}) bands also increase in intensity, but to a lesser extent than the previous group. On the other hand, the (0,0-260 cm^{-1}) band and all other remaining bands shown in Fig. 2 decrease in intensity. The ~ 20°K spectrum in the absence of microwave power closely resembles the PMDR spectrum at 1.95°K.

These results indicate that the first and third groupings of bands each originate mostly from one of the two zero-field sublevels being saturated by the 1.055 GHz radiation, whereas the second group of bands originate from more than one zero-field level, one of these levels being τ_z. The polarization characteristics of the 0,0 band are similar to those of quinoxaline, whose origin has been shown to be the τ_z sublevel.[8] It is thus clear that the (0,0-260 cm^{-1}) band, which behaves in a manner opposite to the 0,0 band upon saturating the $\tau_z \longleftrightarrow \tau_y$ transition, originates from the τ_y sublevel. This is in agreement with its polarization characteristics[9] only if the 260 cm^{-1} vibration is assigned to an a_2 mode.

PMDR will also be very useful in differentiating between assignments involving different combination bands as well as between assignments involving combination bands and fundamentals originating from different zero-field levels. This is accomplished from the observed change in their intensity upon microwave saturation. False origins and their combination bands with totally symmetric vibrations originating from the same zero-field levels are expected to change their intensity to the same extent upon saturation with microwave radiation.

In summary, it is obvious that PMDR spectroscopy will open new fields of study of the triplet state. Using this method, the following information can be obtained:

1. The degree of spin polarization of molecules in the lowest triplet state at very low temperatures can be ascertained. This information is useful in elucidating the most probable mechanism(s) for the intersystem crossing (singlet $\rightsquigarrow$ triplet nonradiative) processes in polyatomic molecules.

2. The initial zero-field level involved in the radiation of an individual vibronic band in the phosphorescence spectrum can be assigned, along with the mechanism whereby the transition gains intensity.

3. The zero-field splittings can be measured directly.

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REFERENCES

1. M. S. de Groot, I. A. M. Hesselmann, and J. H. van der Waals, Mol. Phys., 12, 259 (1967).

2. L. Hall, A. Armstrong, W. R. Moomaw, and M. A. El-Sayed, J. Chem. Phys., 48, 1395 (1968).

3. M. Schwoerer and H. Sixl, Chem. Phys. Letters, 2, 14 (1968).

4. M. A. El-Sayed, D. S. Tinti, and D. V. Owens, Chem. Phys. Letters, in press.

5. J. Schmidt and J. H. van der Waals, Chem. Phys. Letters, 2, 460 (1968).

6. P. Kottis and R. Lefebvre, J. Chem. Phys., 41, 3660 (1964).

7. a. J. M. Lhotse, A. Haug, and M. Ptak, ibid., 44, 648, 654 (1966).

   b. M. A. El-Sayed and S. Siegel, ibid., 1416 (1966).

8. M. S. de Groot, I. A. M. Hesselmann, J. Schmidt, and J. H. van der Waals, Mol. Phys., 15, 17 (1968).

9. Y. Murakami, R. Shimada, and Y. Kanda, Molecular Luminescence, E. Lim, Editor; W. A. Benjamin (1969), p. 119.

FIGURE CAPTIONS

Figure 1. The microwave spectrum of the $\tau_z \leftarrow \tau_y$ (right) and $\tau_z \leftarrow \tau_x$ (left) zero-field transitions of 2,3-dichloroquinoxaline in durene, as monitored by detecting the changes of the 0,0 band intensity of the $^3B_{2u}^{\pi,\pi^*} \longrightarrow {}^1A_1$ phosphorescence at 1.95°K as the microwave frequency changes.

Figure 2. The effect of saturating the $\tau_z \leftarrow \tau_y$ zero-field microwave transition on the phosphorescence spectrum of 2,3-dichloroquinoxaline in durene at 1.95°K in a PMDR experiment. From experiments of this type, the mechanism of the phosphorescence emission of the individual bands in the spectrum can be elucidated. At temperatures for which the electron spin-lattice relaxation is slower than phosphorescence, the sign of the intensity change of the vibronic bands originating from a certain zero-field level should yield information concerning the most probable route for the $S_1 \rightsquigarrow T_1$ nonradiative processes.

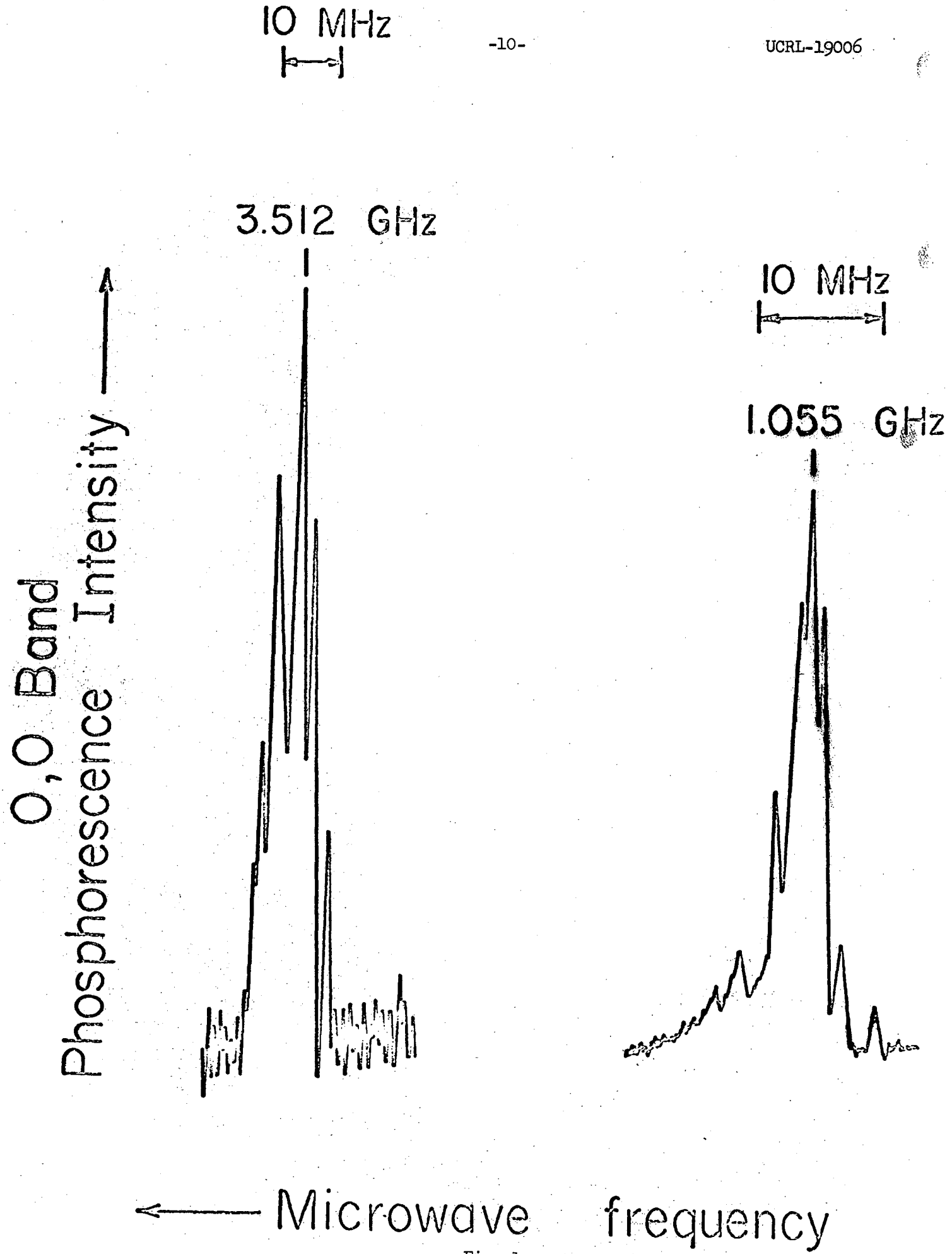
10 MHz
3.512 GHz
10 MHz
1.055 GHz
0,0 Band
Phosphorescence Intensity
Microwave frequency

Fig. 1

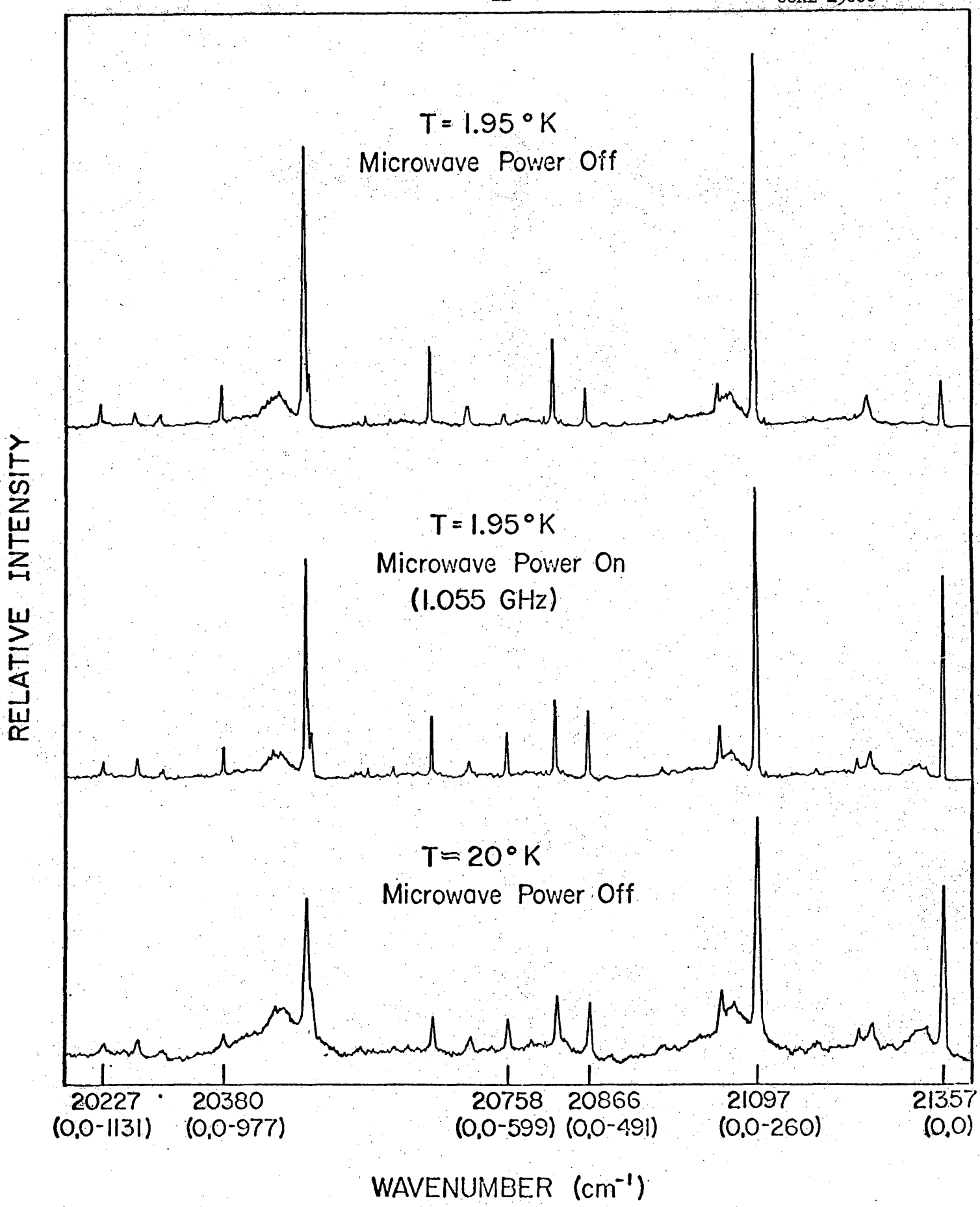
T = 1.95 °K
Microwave Power Off
T = 1.95 °K
Microwave Power On
(1.055 GHz)
T = 20 °K
Microwave Power Off
RELATIVE INTENSITY
20227
(0,0-1131)
20380
(0,0-977)
20758
(0,0-599)
20866
(0,0-491)
21097
(0,0-260)
21357
(0,0)
WAVENUMBER (cm⁻¹)

Fig. 2

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