VI. ELECTRON MAGNETIC RESONANCE[*]

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RESEARCH OBJECTIVES

Various problems, all of which are related to the question of energy transfer, are being attacked by our group. Specifically, some of them are the following.

1. <u>Excited States</u>. We are studying excited triplet states of simple molecules by the combined technique of flash irradiation and electron spin resonance spectroscopy. We now have in our laboratory a spectrometer capable of scanning 350 Gauss, or more, in 25 msec, which with flash discharge (100-10,000 J into a Xenon-filled tube) of comparable duration provides the most powerful method extant for the study of excited electronic states.

2. <u>Collisional Effects</u>. Gas phase relaxation studies of hydrogen atoms with hydrogen molecules (ortho and para separately and together) and other species are being undertaken to learn more about intermolecular interactions. Other atoms in the gas phase are being studied similarly. We are also looking at collisional cross sections of excited alkali atoms (e. g., $^2P_{1/2}$ and/or $^2P_{3/2}$ states) with their ground states. Part of the instrumentation for data handling is described in Section VI-A.

3. <u>Charge Transfer</u>. We are studying, via ESR, fluorescence and phosphorescence, charge and energy transfer in semiconductorlike materials in solution and the solid state, to determine the nature of the donor-acceptor complex.

4. <u>Photoionization</u>. Work is being done on the mechanism of photoionization in large molecules in the vacuum ultraviolet.

5. <u>Radicals in the Gas Phase</u>. Work is proceeding in the study of the electronic, vibrational, and rotational structure of alkyl radicals (methyl, ethyl, and so forth) in the gas phase from work with gaseous discharges, flash photolysis, and thermal dissociation processes at high temperatures.

6. <u>Processes Related to Combustion.</u>

K. W. Bowers

A. DATA HANDLING FOR MAGNETIC RESONANCE EXPERIMENTS

The purpose of this report is to describe an appropriate technique for the conversion of electron magnetic resonance data to a convenient digital form that is consistent with the special requirements of the rest of the apparatus. The EPR spectrometer that is being used is a Varian V4502-13. Our initial purpose in designing this apparatus was to study light-induced phenomena, although the design is sufficiently general to have

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wide applicability. In our present arrangement we use a cylindrical cavity (TE_{011} mode) made of stacked rings, the space between rings being roughly equal to the ring thickness. Irradiation of samples is accomplished by focusing the emission of an electrodeless microwave resonance lamp or other source into the cavity.

The radiation seen by the sample is mechanically chopped at a frequency of 50 Hz. The chopper is driven by a hysteresis synchronous motor whose driving frequency is controlled by the reference signal of a Princeton Applied Research Type HR-8 lock-in amplifier. Since the reference output of the HR-8 is only 1 Volt, it must be amplified and transformed to drive the motor. Our sample in the spectrometer is now field-modulated at 100 kHz and 400 Hz, and light-modulated at 50 Hz, with a separate lock-in amplifier for each modulation frequency.

Signal-to-noise is now the main difficulty with the experiment. The first thought was simply to attach the output of the light modulation lock-in amplifier to a time-averaging computer (CAT); however, there are small temperature variations that make the resonant frequency of the cavity wander slightly, thereby causing signal degradation rather than enhancement as signals are accumulated. To overcome this drift problem, we decided that the unknown light-modulated signal should be taken simutaneously with the known first-derivative spectrum, in order to have a reference for the spectrum center. Both of these parameters are recorded on magnetic tape and then processed on an IBM 360 computer. Having a reference point for each spectrum enables one to correct for drift before summing. Putting these spectra onto tape presented a problem, however, as the output signals of the V4502-13 spectrometer were floating at 6 and 15 V above ground for the 400-Hz and 100-kHz modulation units, respectively. To solve this problem, the signals were fed into biased differential amplifiers. The 400-Hz signal was amplified by a factor of 200, and the 100-kHz by unity.

Since only one piece of information can be recorded at a time, it is necessary to insert an electronic switching circuit between the differential amplifiers and the buffer to the magnetic tape unit. To accomplish proper synchronization between the switching circuit and the stepping motor of the tape unit, the pulse that advances the tape unit is used to trigger a flip-flop, which in turn triggers the switching circuit.

With these units synchronized, the buffer (EAI digital voltmeter) samples the information of channel A until the tape is advanced. The advancement pulse triggers the switch, and until the next pulse the unit samples channel B. The next pulse again triggers the switch, and channel A is sampled.

To standardize the information blocksize, a pulse counter was built to control the advancement of the tape drive. When the pulse counter is initially activated, power is applied to the stepping motor of the tape unit, and information is recorded until a predetermined number of pulses have elapsed. At this time, a relay is activated, and the power to the stepping motor is stopped, thereby causing the end of data transfer. An

inter-record gap is put onto the tape, the magnetic field is reset, and pulse train is started again, which causes data again to be transferred onto the tape. In order that both signals can be monitored visually during the tape recording, the system is tapped between the differential amplifiers and the switching circuit and attached to a dual-channel recorder.

Once the data are on tape, the analysis is done on the IBM 360 computer. First, the data that have been put onto the tape alternately must be sorted out and inspected for large noise bursts. Next, the DC level drift is subtracted off, the center of the standard absorption curve is determined, and the curve is realigned such that its center is at the center channel of the field scan. Since the light-modulated signal was taken at the same time as the standard curve, the center channel for both curves should be the same, so if the center is known for one of the curves, it is really known for both. With the data realigned, the next data record is read in and it is also realigned. This process is continued until all of the data records have been read in and processed. Now all of the realigned data of each type are added together, point by point, and the resulting spectra are further analyzed according to the nature of the experiment. The result of the addition of the realigned data is the same as would have been obtained by using a CAT on a system with no field drift. To further increase the readability of the spectrum, it is subjected to modified least-squares fit to further smooth noise bursts. The increase in the signal-to-noise is proportional to the square root of the number of points used in the least-squares averaging interval. A paper on this research will be submitted to the Review of Scientific Instruments.

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B. GEOMETRICAL CONFORMATIONS IN THE LOWEST EXCITED TRIPLET STATES OF POLYPHENYLS

The zero-field splittings and phosphorescence spectra of a large number of ortho, meta and para polyphenyls have been measured for their lowest excited triplet states. Apparent anomalies in the EPR spectra have been interpreted and analyzed on the basis of twisted conformers. This is the first accurate determination of excited-state geometries. A report on this work will be presented at the Spring Meeting of the American Chemical Society, in San Francisco, and a paper will be submitted for publication to the Journal of the American Chemical Society.

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