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PHOTOLYSIS OF SPACECRAFT CONTAMINANTS

By Gary L. Workman
PBR Electronics, Inc.
P. O. Box 752
Athens, Alabama 35611

March 29, 1974

Final Report

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NASA-GEORGE C. MARSHALL SPACE FLIGHT CENTER
Marshall Space Flight Center, Alabama 35812

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Gary L. Workman

PBR Electronics, Inc.

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Athens, Alabama 35611

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A molecular beam facility, which has been designed to measure photochemical cross-sections, has been constructed at the Athens College science facility. The integration of this vacuum system into an operational photochemical instrument has been performed with signal processing consisting of both dc and ac techniques. Of the experiments performed to date on the vacuum ultraviolet photolysis of water vapor, it is apparent that a larger pumping capacity (preferably with differential pumping) is required to improve upon the background signal. Both phase-sensitive detection and ion-counting techniques are recommended for future studies.

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I. INTRODUCTION

The determination of the photochemical cross-sections of simple molecular gases and vapors is an important step in understanding the complex processes in solar induced reactions, whether the reaction occurs on Earth, Venus, a comet, or in an interstellar medium. The primary processes are important, if we are to determine what secondary reactions may occur and consequently predict overall what chemical products are formed as well as how rapidly the reactions proceed. Hence knowledge about the initial photodissociative step is required if quantitative predictions are to be made concerning the nature of such clouds (spacecraft, planetary, or interstellar) and their formation.

The emphasis of this study has been directed toward resolving a
1-4
problem originally occurring around spacecraft. The water vapor outgassing from most manned spaceflights has been very heavy and usually surrounds the spacecraft with the water vapor and some ice crystals forming a cloud. Spaceflight experiments which require no "atmosphere" then have been deprived of their original intent as a space experiment with no atmospheric effects. As cloud formation progresses it was felt that spectroscopic measurements might be used to determine the column density of such a cloud and also to monitor the possibility of interferences to certain low light level experiments. The nature of such measurements and their utility as a monitoring tool will be presented later.

The experimental approach used in this study has been to simulate a spacecraft atmosphere (infrequent collisions, solar radiation, and moderate molecular densities) composed chiefly of water vapor and irradiate the molecules with vacuum ultraviolet radiation. The photodissociated molecules can be formed in either vibrationally or electronically excited species. The ability to observe radiation from these excited species would be very useful as a column density monitor. Also the molecular emissions observed from other planets and from other inter-galactic bodies may arise from similar processes. More research is needed in order to understand the nature of these radiative processes, and their relationship to photochemical processes.

II. TECHNICAL DISCUSSION

In general, for any photochemical reaction the primary chemical process may be defined as the first chemical step following the act of absorption of radiation. The excited molecule may lose this excess energy in several different ways, however, the primary process of interest to us is the photodissociative step. We can label the cross-section which leads to photodissociation as the photochemical cross-section, defined by the relation

$$dn_a = I_\lambda \sigma_\lambda \phi_\lambda n_a dx$$

where

n_a = number density of species a

I_λ = light intensity

σ_λ = absorption cross-section

ϕ_λ = quantum yield of dissociation

dx = interaction element

the competing processes, i. e., fluorescence, phosphorescence, and even direct chemical reactions, do affect the value of ϕ . At low pressures or in molecular beam experiments where the collision rate is low, direct chemical reactions or energy transfer processes should not significantly affect ϕ .

The quantum yield should be a varying quantity depending upon the nature of the excited state which is populated by absorption of light at

wavelength λ . The usual definition is given by

$$\phi_{\lambda} = \frac{\text{number of molecules dissociated}}{\text{number of molecules absorbing at } \lambda}$$

and is thus labelled as the quantum yield for dissociation. Several workers in the field make measurements at only one wavelength and assume that the quantum yield remains the same throughout the electronic transition. This is not always true since different vibronic states can lead to different dissociative channels and also one cannot always be sure of the existence of more than one electronic transition in the same spectral region. The nature of the excited states in water vapor which lead to spectral absorption from 183.0 - 123.6 nm is not very well known and more information is needed for this spectral region. Figure 1 illustrates the spectral cross-section for water vapor.

The radiative spectra of the dissociated species is important in determining how the initial photon energy is distributed among the photolysis products. Thus our efforts here were aimed also at the nature of the spectral emissions from the hydroxyl radical. It has been documented that OH emission near 310.0 nm occurs if the electronic state near 130.0 nm is populated, where the crossover point to this photodissociation channel occurs is not known. It is fairly evident that one has to be able to continuously scan the excitation energy to observe where this crossover energy occurs. It is also near this spectral region (123.6 nm) that H₂ has been observed as a photolysis product. Measurements of this

nature are required if photodissociated products (say of water vapor) are to be used as column density monitors of clouds, etc. .

III. EXPERIMENTAL DETAILS

The experiments performed for this study were carried out on a vacuum system specifically constructed for this project at Athens College. The experimental apparatus consisted of a vacuum chamber approximately 52 cm long and 34 cm in diameter. An Extranuclear quadrupole mass spectrometer was located inside the chamber parallel to the long dimension. A copper tubing with a one inch 0.5 mm diameter orifice for directing the water flux into the chamber was located at the other end of the chamber. The water flux has been directed toward the quadrupole (parallel) as well as perpendicular to the line extending out from the ionizer. The two positions are labelled parallel and perpendicular in Table I. The main chamber has been pumped through a liquid nitrogen baffle with an oil diffusion pump rated at approximately 700 liters/second, giving an overall pumping speed of about 500 liters/second.

A one-meter vacuum spectrograph has been used as a monochromator in order to isolate particular wavelengths for the photolysis experiments. A hydrogen discharge lamp has been used as the vacuum ultraviolet light source. Its emission spectrum is given in Figure II. The line structure around 165.0 nm is the most intense region and is a very good photochemical light source. The 121.6 nm is also a useful region. These two spectral regions were used in our preliminary studies since more positive results are to be expected for these regions.

The light beam and the water flux cross in an interaction region approximately 4 centimeters from the quadrupole ionizer. The usual experimental parameters consisted of a photon flux of approximately 10^{12} photons/sec. The water flux was calculated using the relationship 9

$$\text{molecular flux} = \frac{1}{K} 1.26 \times 10^{11} \frac{A_s P_s}{\sqrt{MT_s}} \quad \text{molecules/sec.}$$

where

K = geometry of source

A_s = area of source

P_s = pressure of source

M = molecular weight of vapor

T_s = temperature within source

Hence for water vapor at 298°K, $K=1$, pressure = 0.21 newtons/m²

(10^{-2} mm Hg) and a 0.2 mm orifice we have been obtaining approximately 2.8×10^{15} molecules/sec. A one centimeter reaction volume then gives approximately 2×10^{13} molecules/cm³.

Since water vapor has an absorption cross-section of approximately 5×10^{-18} cm², at least 10^{12} water molecules absorb radiation. Assuming a quantum efficiency ~ 0.5 (which we have not proven yet) and isotropic scattering then at least 4×10^9 fragments should scatter toward the mass spectrometer to be detected. Thus we do not expect to see a very large fragment current. From the above conditions, the ionizer efficiency will dictate the overall signal.

A number of techniques have been applied in this work. The main variations for the light source have been either to use a pulsed light source or to use a cw discharge. The pulsed light source is richer in vacuum ultraviolet radiation but gives a very low dc signal, so we tried a cw light source using dc electronics and simple phase-sensitive detection. No perceptible photolyzed species were detected using either approach. One major difficulty is that OH fragments can be formed either by bombarding water molecules with electrons (as the mass spectrometer does) as well as with photons of certain energies. In order to decrease the fragmentation of H₂O by electron impact, we had to use very low energy electrons (~ 16 ev) and consequently a low electron flux. Hence we typically ran at 15 ev and 2 ma electron filament current which gives an electron flux approximately 10⁻⁶ amperes.

The typical background pressure with a water flux of 10¹³ molecules/sec was 2.13 x 10⁻⁵ newtons/m² (1 x 10⁻⁶ mm Hg), which was really too high since the background OH (amu = 17) was then approximately 3 x 10⁻¹⁰ amps. The cw discharge also has been tried, but also with no success. The effect of the light source was substantiated by the opening and closing of the spectrograph shutter. In all the experiments reported here, there was no perceptible change in the measured hydroxyl current which correlated with vacuum ultraviolet radiation. The installation of a light chopper between the incoming cw beam and the interaction region plus

phase-sensitive detection did not seem to help. The measured hydroxyl current dropped to nothing although the sensitivity of the experiments should be enough. Another approach which would have been tried if time had not run out was to use the photon counter and a pulsed light source. The signal-to-noise ratio may still not be enough if the background signal was too high. A review of experimental arrangements and remarks about their results is given in Table I. A number of runs were made in which a gas chromatograph integrator was used to increase the signal-to-noise ratio. Under the prevailing conditions above, there was no perceptible increase in the signal-to-noise ratio.

LIGHT EXCITATION MODE BEAM DETECTOR GEOMETRY SIGNAL PROCESSING REMARKS

1. Pulsed	Parallel	Electrometer - DC Mode	DC current too low compared to background.
2. Pulsed	Parallel	Electrometer + Integrator	Same, DC drift too high, gave random results.
3. Pulsed	Parallel	Phase sensitive detection	S/N ratio still too low to extract OH (photolyzed) signal from electron impact signal.
4. Pulsed	Parallel	Phase sensitive detection + integrator	S/N ratio low plus DC drift which created false signals.
5. DC Discharge	Perpendicular	Electrometer	DC signal too small to measure relative to background, which was very large.
6. DC Discharge	Perpendicular	Phase sensitive detection	S/N ratio still too low, although background reduced.
7. DC Discharge	Parallel	Phase sensitive detection	Background high, as also signal, but could not measure the difference between them.

TABLE I. EXPERIMENTAL ARRANGEMENTS FOR PHOTOLYSIS STUDIES

IV. RECOMMENDATIONS FOR FUTURE EXPERIMENTS

It is recommended that experiments of this nature be continued with the same emphasis on the photochemical cross-section. A few modifications to the present photolysis system, which is located at Athens College, is recommended. The addition of a vacuum chamber section, which contains the interaction region and beam source, and is differentially pumped would alleviate the background problem. It is suggested that a faster pumping speed be used (i. e., 1400 liters per second). Bringing the background pressure to 2.31×10^{-8} newtons/m² (10^{-9} mm Hg) will result in negligible background so that either phase sensitive detection or ion counting techniques are possible. The use of ion counting should eliminate some of the signal-to-noise problems, provided the background is reduced. It is also recommended that some kind of chopping mechanism be retained since the phase sensitive detection is required for the signal handling of the hydroxyl (photolyzed) to OH (electron impact) ratio.

A further consideration is to the nature of the excited electronic state involved in the photodissociated step. If polarized light were used then one can interpret by the scattering angles what symmetries are involved in the excited state. There should be some consideration for extending this approach to the vacuum ultraviolet.

V. SUMMARY

A molecular beam system has been constructed at Athens College for observing the photodissociation of molecular compounds and for determining their photochemical cross-sections. The research to date has indicated the types of modifications necessary to improve experimental determinations. Our results with dc signal processing indicates that the high background level is deleterious to measuring photolyzed fragment currents. The ac techniques have more potential for observing only the photolysis events, assuming that the background signal does not swamp the detector.

It is recommended that future experiments incorporate higher pumping speeds and that the quadrupole chamber and the photolysis chamber be pumped differentially. Both ac and ion counting techniques should be investigated as both techniques maintain a high signal-to-noise ratio. With a substantial decrease in the background signal then we should also consider the possibility of using polarized light so that the nature of the fragmenting states can be better defined.

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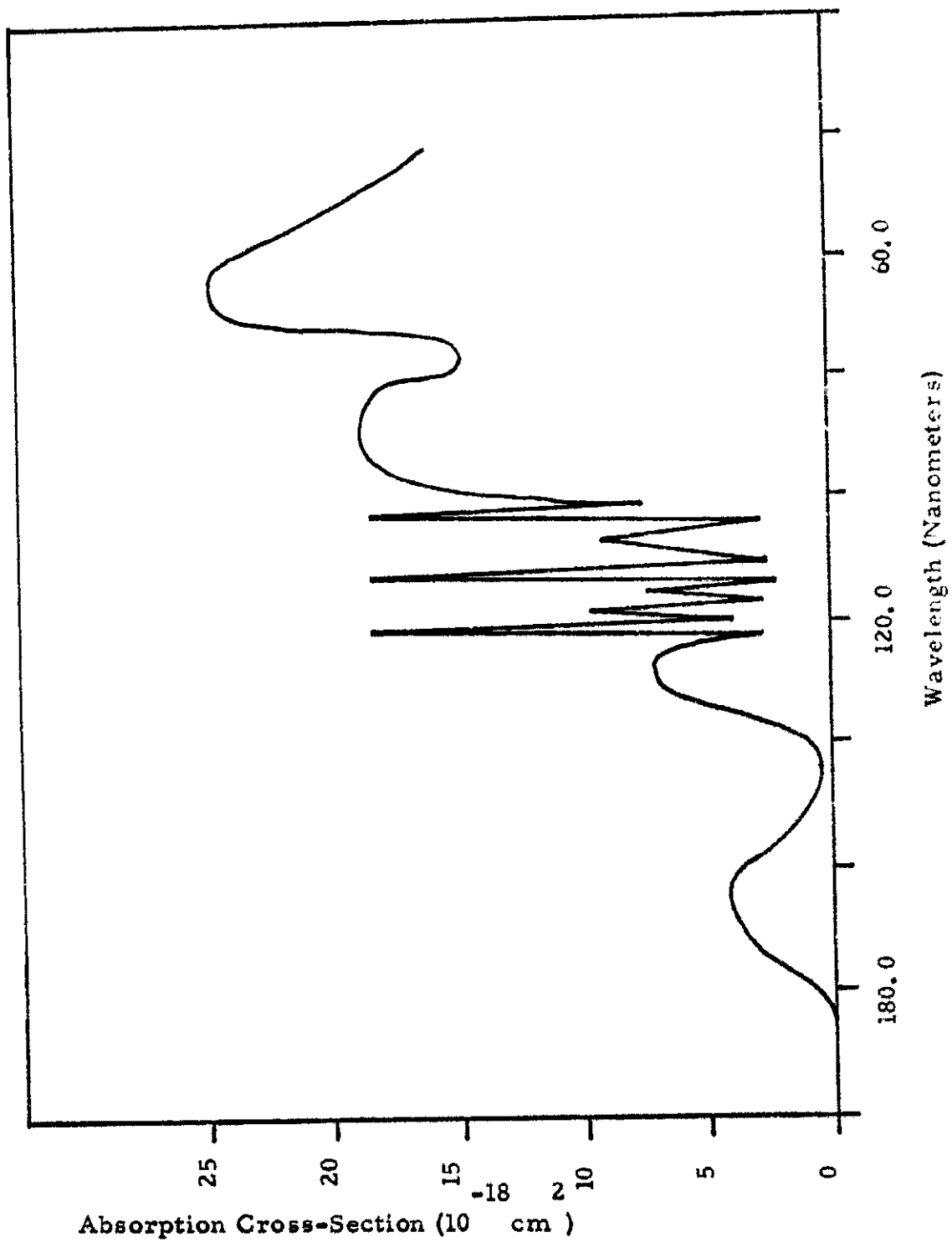
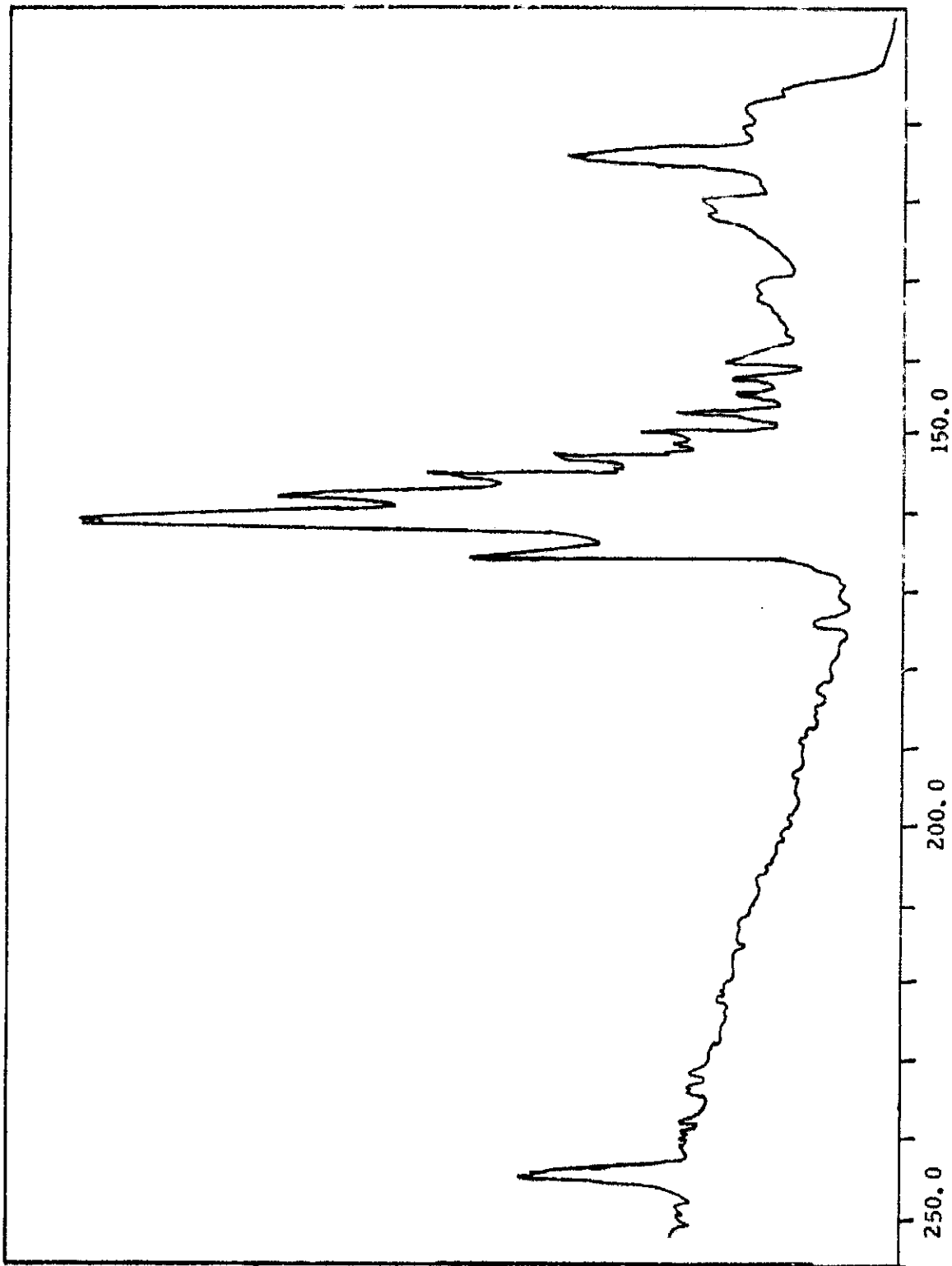


FIGURE 1. WATER ABSORPTION SPECTRUM



Wavelength (Nanometers)
FIGURE II. HYDROGEN EMISSION SPECTRUM

Intensity (Arbitrary Units)