

FLUORESCENCE DETECTION OF ORGANIC MOLECULES IN THE JOVIAN ATMOSPHERE*

JOEL S. LEVINE and ROBERT S. ROGOWSKI

*Environmental and Space Sciences Division, NASA Langley Research Center,
Hampton, Va. 23665, U.S.A.*

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Abstract. A search for fluorescent emission due to the presence of possible organic molecules in the Jovian atmosphere is described. We first consider natural Jovian fluorescent emission excited by precipitating auroral particles. Due to our lack of knowledge of the Jovian precipitating particle energies and fluxes we next consider fluorescent emission excited by a laser system aboard a Jupiter spacecraft. Laser-induced fluorescence is routinely used to monitor trace constituents and pollutants in the terrestrial atmosphere. Several spacecraft laser systems are currently under development. Our calculations indicate that laser-induced fluorescent detection is approximately two orders of magnitude more sensitive than rocket ultraviolet measurements of possible Jovian absorption features at 2600 Å that have been attributed to the presence of adenine or benzene.

1. Organic Molecules in the Jovian Atmosphere

It is believed that the present composition of the Jovian atmosphere: molecular hydrogen, methane, ammonia and water (while water has not actually been detected, its presence in the Jovian atmosphere is assumed based on cosmic abundance and chemistry considerations) closely resembles the composition of the early terrestrial atmosphere which through chemical evolution gave rise to complex organic molecules, the precursors of life. It is further suggested that at this time the Jovian atmosphere is the seat of intense prebiological chemical evolution (Sagan, 1971; Rasool, 1972). Ponnampertuma and Woeller (1969) have shown that a simulated Jovian atmosphere irradiated by ultraviolet radiation produces complex organic molecules such as amino acids and nucleotides. Furthermore, the color of the synthesized organic molecules is very similar to the yellow-orange-reddish hue of the Jovian clouds and the Giant Red Spot. In other laboratory studies, adenine, a basic constituent of both DNA and RNA, was found to be the single largest non-volatile compound in the electron irradiation of methane, ammonia and water. Various experimental and computer studies suggest that complex organic molecules may exist in the atmosphere of Jupiter and may be responsible for the coloration of the Jovian clouds (Sagan, 1971).

2. Ultraviolet Spectra of Jupiter

The organic molecules such as adenine believed to be present in the Jovian atmosphere are expected to exhibit absorption features between 2000 and 3000 Å. Unfortunately,

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TABLE I
Ultraviolet spectra (2000–3000 Å) of Jupiter

	Date	Comment
Stecher (1965)	July 23, 1963 (1 scan) Nov. 14, 1964 (3 scans)	Absorption feature at 2600 Å
Evans (1967)	Aug. 22, 1964	Absorption feature at 2600 Å
Jenkins <i>et al.</i> (1969)	June 9, 1967	Possible 'broad continuous depression' at 2600 Å
Anderson <i>et al.</i> (1969) ^a	May 17, 1968	No absorption feature at 2600 Å
Kondo (1971) ^a	May 17, 1968	No absorption feature at 2600 Å
Wallace <i>et al.</i> (1972)	May 17, 1969 May 31, 1969 (OAO-2 measurements)	No absorption feature at 2600 Å

^a Measurements made on the same night.

radiation short of 3000 Å is strongly absorbed by molecular oxygen and ozone in the Earth's atmosphere. A number of rocket-borne instruments, as well as the Orbiting Astronomical Observatory have obtained ultraviolet spectra of Jupiter between 2000 and 3000 Å. The results of these investigations are summarized in Table I. It appears that the existence of a Jovian absorption feature at 2600 Å is somewhat questionable.

Greenspan and Owen (1967) have proposed that if the 2600 Å absorption feature is real it may be due to benzene, the simplest aromatic hydrocarbon. As an alternative, Sagan (1968) proposed that the absorption may be due to purines and pyrimidines, or their derivatives such as adenine. Sagan (1968) reported that only a small amount of adenine, $\sim 1 \mu\text{gr cm}^{-2}$ is required to match the Stecher (1965) absorption feature at 2600 Å. Any organic molecules that absorb at 2600 Å will most likely be structurally similar to adenine or benzene. Sagan (1968) has pointed out that such absorption features are likely to be caused by condensed phase molecules in the Jovian clouds, rather than by molecules in the gas phase.

How can we test the interesting hypothesis that the visible, colorful 'surface' of Jupiter may be the seat of intense pre-biological activity? Rasool (1971) has suggested several possibilities: ultraviolet spectroscopy, *in situ* exploration of the Jovian atmosphere and the return of samples to Earth. To date, ultraviolet spectroscopy has given questionable results. Both *in situ* exploration and sample return are very expensive and many years away. To the list of observational techniques we add fluorescence, which we believe to be a sensitive tool to detect organic molecules if they exist in the Jovian atmosphere.

3. Fluorescent Emission

Fluorescent emission is produced when molecules are excited from the ground electronic state (S_0) to higher energy states (S_1) by the absorption of energy. The excited molecules emit radiation of characteristic wavelengths upon returning to the ground

electronic state. The fluorescence wavelength is always longer than the absorption or excitation wavelength because transitions take place between the various vibrational states of the molecules. Not all of the excited molecules return to the ground state with the emission of a photon. Other relaxation processes compete with the emission process such as collisions between molecules depleting the population of the excited state. The fraction of molecules that emit radiation after excitation is represented by the fluorescent scattering quantum efficiency, ϵ_{FL} which can vary from 0–100% for organic molecules.

TABLE II
Fluorescence of biological molecules

Molecule	Fluorescence maximum
Benzene	3000 Å
DNA	3400–3600 Å
Tryptophan	3480 Å
RNA	3500–3600 Å
Adenine	3550 Å
Guanine	3700 Å
Cytosine	5000 Å

Table II lists several molecules of biological interest that are expected to fluoresce after excitation at 2650 Å. Note that adenine and benzene are easily distinguishable with proper filtering by the difference in their fluorescence spectra. Fluorescent emission is a powerful technique since it not only yields the presence of organic molecules (as does ultraviolet spectroscopy) but permits the identification of the particular species through the determination of the line shape which is easily obtainable via narrow-band filter photometry between 3000 and 5000 Å.

4. Natural Fluorescence

Fluorescent emission may be a regular feature of the nocturnal atmosphere in the Jovian auroral zone. Energetic particles precipitating out of the Jovian radiation belts may be a natural source of fluorescent excitation. Although the particle fluxes are not known, the nature of dekametric radio emission from Jupiter suggests that energetic electrons frequently impinge on the Jovian upper atmosphere. Several attempts have been made to detect Jovian auroral activity by performing ground-based measurements of H α (6563 Å) enhancement (Smith *et al.*, 1963; Schwitters, 1968; Hunter, 1969; Dulk *et al.*, 1970). A search for nightside fluorescence emission within the Jovian auroral zone could be performed by placing a narrowband filter photometer covering the spectral range 3000–5000 Å aboard a Jupiter fly-by or orbiter. Due to our lack of knowledge of particle fluxes and energies in the Jovian auroral zone we will next consider laser-induced fluorescence in the Jovian atmosphere.

5. Laser-induced Fluorescence

Fluorescence emission can also be induced with lasers. Laser-induced fluorescence is routinely used to detect trace constituents and pollutants in the Earth's atmosphere (Wang, 1974). Light-weight miniature laser systems are currently being planned and developed for Earth-orbit missions (for example, see Thomas, 1973 and Proctor *et al.*, 1974). A Nd-YAG laser capable of frequency doubling resulting in continuous emission of 2650 Å photons is presently being developed for Earth-orbit missions.

A possible experiment for a future Jupiter orbiter consists of a laser/detector system. The laser would be pulsed on the nightside of Jupiter to eliminate the effects of scattered solar radiation on the return signal. To satisfy power requirements the laser pulse could be performed during a period when the other orbiter experiments are not on.

We have computed the fluorescence signal due to the column of adenine reported by Sagan (1968) that matches the absorption feature found by Stecher (1965) and Evans (1967). The proposed orbiter laser emits a 2650 Å pulse. After fluorescent scattering by condensed-phase adenine, the 2650 Å incident photons result in 3550 Å photons. The intensity of the 3550 Å photons received by the detector aboard the orbiter can be calculated using the laser radar equation for fluorescent scattering given in Equations (1) and (2) (after Kim, 1973):

$$P_{f(3550 \text{ \AA})}^{\text{Det}} = \frac{P_{f(3550 \text{ \AA})} A e^{-kz}}{4\pi R^2}, \quad (1)$$

where $P_{f(3550 \text{ \AA})}^{\text{Det}}$ is the number of fluorescence scattered photons received per unit area at the detector aboard the orbiter; A is the area of the detector; k is the attenuation coefficient at 3550 Å due to absorption and scattering; z is the distance traversed through the Jovian atmosphere and R is the distance from the orbiter to the target. $P_{f(3550 \text{ \AA})}$ is the total number of fluorescence photons generated by the incident beam at the target and is given by:

$$P_{f(3550 \text{ \AA})} = \varepsilon_{\text{FL}} P_{(2650 \text{ \AA})} N \sigma, \quad (2)$$

where $P_{(2650 \text{ \AA})}$ is the number of photons at 2650 Å emitted by the laser per pulse; ε_{FL} is the efficiency for fluorescent scattering; N is the column density of the fluorescently scattering species, and σ is the absorption cross section.

For our calculations, we have used the following parameters:

- (1) The orbiter is 1000 km above the Jovian reflecting layer.
- (2) The detector area is 1 m².
- (3) We assume a laser with an energy ($P_{2650 \text{ \AA}}$) of one joule per pulse (1.33×10^{18} photons at 2650 Å per pulse).
- (4) We assume Sagan's (1968) adenine column density of 1 μgr cm⁻² corresponding to 4.4×10^{15} adenine molecules cm⁻². The fluorescent scattering efficiency, ε_{FL} for adenine is 0.01 (Konev, 1967) and the absorption cross section, σ is 4×10^{-17} cm⁻² at 2650 Å (Konev, 1967).

(5) We further assume that absorption of the return signal is negligible since no known constituent of the Jovian upper atmosphere absorbs at these wavelengths.

For the conditions specified in (1) to (5), we calculated a return signal of about 180 photons per one-joule pulse. We further estimate that with proper filtering and gating circuits an adenine column density of approximately 10^{13} molecules cm^{-2} could be detected by fluorescent techniques. This sensitivity is approximately two orders of magnitude better than that achieved with ultraviolet spectroscopy. Furthermore, with appropriate gating circuits and at some loss of the return signal, laser-induced fluorescence permits acquisition of data regarding the vertical distribution of the scattering species.

6. Conclusion

A fundamental question to planetary scientists, biologists and chemists concerns the presence and identification of organic molecules in the Jovian atmosphere. We believe that fluorescent detection is a sensitive technique to answer these questions. It can reasonably be expected that laser technology will progress to the point that laser-induced fluorescence will be a viable experiment for a future Jupiter mission.

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