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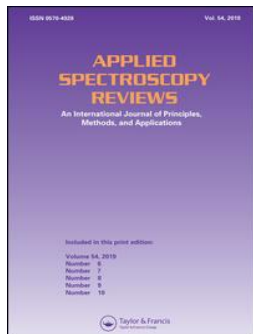
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Remote molecular composition analysis of laser-ablated material

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ABSTRACT

A novel method is described for remotely interrogating bulk molecular composition of rocky materials. Laser energy heats a local area on the substrate; flux is optimized to melt and evaporate target constituents with low rates of molecular dissociation. Substrate temperature rises until an equilibrium is established between incident flux and latent phase-change energies, reaching ~2500 K in vacuum. A blackbody signal is emitted by the heated spot, traveling outward through the evaporated material; reflective optics direct the signal into a spectrometer. Ro-vibrational absorption in the plume provides a diagnostic for identifying bulk molecular composition of the substrate. Absorption spectra are modeled for compounds with available a priori molecular cross-sections, based on laser and receiver characteristics, and target material properties. Mass ejection flux drives the plume density profile. Qualitative, species-specific spectral profiles are derived by integrating molecular cross section along a path through the plume. Simulations indicate robust absorption profiles.

KEYWORDS

Infrared spectroscopy; laser ablation; molecular spectroscopy; CubeSats

1. Introduction

Remotely interrogating the composition of rocky materials is relevant to space exploration. For example, resource assays of solar system objects such as asteroids could inform future *in situ* resource utilization missions. Remote composition analysis also supports scientific inquiries for space expeditions, and systems utilizing directed energy have been deployed in recent years. One such method is Laser Induced Breakdown Spectroscopy (LIBS), an established technique for analysis of atomic composition of geological samples in space environments [1]. Theoretically, plasma are generated by using a high power, pulsed laser, while the optical signal emitted by the ablated mass is detected with an optimized spectrometer [2].

Due to straight-forward physical principles, as well as flexibility of experimental instrumentation, LIBS and similar techniques have been found suitable in many fields, such as environmental science, anthropology, and, most relevant to the context of this

paper, for space exploration. In particular, LIBS has been applied to the analysis of planetary soils and identification of the composition of asteroids and meteorites [3]. Analysis of optical spectra allows determination of the atomic composition of the target, *via* methods similar to those developed for reflectance spectra of minerals [4].

In contrast, the method described here relies on detecting spectral characteristics of energy absorbed by the target material, after the material has been evaporated into a molecular gas. The method proposes to exploit “back-lit absorption” to characterize compound molecular structures. Emitted radiation is then absorbed by the ablated material, producing a characteristic spectrum determined by materials in the evaporated plume. By measuring absorption spectra using an infrared spectrometer, it is possible to probe, from a distance, the molecular composition of mineral species present in cold objects. Compared to existing technologies, the ability to directly analyze molecular composition has potential to contribute complementary information to efforts aimed at understanding target composition. One of the most obvious and immediate benefits is that the presence of hydrogen and oxygen *may* indicate water, whereas the proposed method provides a direct test of whether molecular water is present in a material. The proposed method is also naturally suited to remote interrogation, using modest laser and optical technology [5–7].

The proposed method of remote molecular composition analysis relies on the ability to heat a distant target to the point of vaporization, but without inducing molecular dissociation of mineral species. Black body (thermal) photons emitted from the laser-heated spot on the target surface pass through the evaporated gas, wherein some energy bands are absorbed *via* rotational and vibrational modes specific to molecules in the gas. Re-emission of the absorbed energy occurs at the same wavelengths that were absorbed, but in random directions. As the heated spot is viewed from a distance through the gas, selective dimming of the background blackbody signal is observed in a pattern consistent with the ro-vibrational energy spectrum of materials in the gas. Initially, the evaporated material is in thermal equilibrium with melted material within the heated spot; thermal emission from gas at the target surface is indistinguishable from the background signal. As the expelled gas expands and cools, thermal emission from the gas rapidly becomes dim and diffuse, and any transient contribution to the background signal quickly becomes insignificant.

If the absorption properties (i.e. cross sections) of the ablated material are known, then an expected spectrum can be calculated for any material. The theory underlying this novel technique is presented. A model to calculate the particle ejection flux of evaporated materials as function of laser irradiance has been developed, considering a circular spot geometry, with cases of radial and uniform power distribution. The integrated absorption along the line of sight is described as a relation of the particle ejection flux. Making some assumptions on the collector optical system, examples of spectra for selected compounds have been computed, establishing that the radiation from the heated spot and absorption in the plume is sufficient to assess the molecular composition of the plume material by comparison with reference spectra.

2. Theory

In the following sections, a theoretical model is developed for characterizing the evaporation of a target material, and the subsequent density of the ablated material plume at

Table 1. Given above are values for ξ (cf. Equation (2)), the Antoine coefficients A , B , and C (dimensionless) for selected atoms, and T_{min} and T_{max} , which define a range of validity for the coefficients.

Comp.	ξ	A	B	C	T_{min} (K)	T_{max} (K)
MgO	133.32	6.92276	13862.2	-170.464	3105	5950
TiO	1.01325×10^5	8.3793	16213.5	88.5202	1708.15	3133.35
H ₂ O	133.32	8.72209	18107.6	273.093	100	300

any distance from the target. In Section 2.1, the particle number ejection flux is characterized *via* a relationship with the temperature and pressure at the laser spot, which are in turn dependent on laser irradiance, as presented in Section 2.2. The particle density at a distance z from the laser spot along the line of sight is then calculated in the case of a radial spot, considering both a radial and isothermal distribution.

2.1. Evaporation of target material

The Langmuir equation is a well-known kinetic model for the description of a coherent theory of absorption onto a flat surface [8,9]. At equilibrium, a continual process of bombardment of molecules onto the surface corresponds to the evaporation (desorption) of molecules from the surface itself, in order to maintain a null rate of accumulation at the surface. Equivalently, the rate of absorption, multiplied by an accommodation coefficient, gives the rate of desorption. The model applied to homogeneous flat surfaces, in which the process can be assumed to be localized. The Langmuir equation can be written as:

$$\Gamma = \alpha \sqrt{\frac{M}{2\pi RT}} (P - P_e), \quad (1)$$

where Γ is the mass ejection flux ($\text{kg/m}^2 \text{ s}$), T is the temperature, M is the molar mass (kg/mol), α is the evaporation coefficient, P is the vapor pressure, and $P_e = 0$ in vacuum is the ambient vapor pressure.

For elements and molecules, the vapor pressure can be related to temperature – over a suitable temperature range – by using the Antoine equation:

$$P = \xi \cdot 10^{A - \frac{B}{T_C + C}}, \quad (2)$$

where A , B , and C are the empirically determined, Antoine coefficients, T_C is temperature in degrees Celsius, ξ is a constant, and P is the vapor pressure [10]. Note that the Antoine coefficients' validity depends on a given temperature range for each compound or element. Some sample temperature ranges and ξ values are shown in Table 1. Given the pressure, it is possible to determine the particle number ejection flux, which is the number of particles ejected per unit of surface area per unit of time, Σ ($/ \text{m}^2 \text{ s}$). This flux is given by

$$\Sigma = N_A \frac{\Gamma}{M}, \quad (3)$$

where N_A is Avogadro's number.

2.2. Laser power required for evaporation

The energy necessary to vaporize materials on the surface of an asteroid is determined by the combination of the heat of fusion and the required amount of energy to bring the surface material temperature to the melting point from an (assumed) initial, low temperature starting point. Laser-induced desorption is a widely used technique to vaporize nonvolatile organic molecules for gas-phase studies [11]. In this case, the fluence release is such that a soft ionization of the molecules is obtained, avoiding fragmentation and/or molecular dissociation of the samples. The system obtained is then analyzed using mass spectrometry, thus requiring *in situ* instrumentation. In the new method, the backlight source combined with a vaporization regime that prevents atomization and fragmentation provides the capability to interrogate the system with remote instrumentation. In the present section, the relationship between the laser flux used and the temperature to which the sample rises is determined, so that using Equations (1) and (2), the mass ejection flux can be calculated. Laser fluxes of greater than 10^{15} W/m^2 are necessary to ionize materials with relatively low ionization energies; the cases considered are far below this regime [12]. This will be presented along with example spectra in Section 3.2.

As the laser beam impinges on the target, energy is converted between several forms. The basic equations are based on energy conservation, which relates laser-in power to laser-out power and asteroid internal energy,

$$\tilde{P}_l = \tilde{P}_{rad} + \tilde{P}_{ref} + \tilde{P}_{eject} + \tilde{P}_{int}, \quad (4)$$

where $\tilde{P}_l$ is the laser-in power, $\tilde{P}_{rad}$ is laser-out power, $\tilde{P}_{eject}$ is the ejected power, and $\tilde{P}_{int} = \frac{dU}{dt}$ is the internal power, which is equal to zero at equilibrium. Here, laser-in refers to the incident laser power on the target and laser-out refers to the power that returns from the target. Assuming

$$\tilde{P}_l = \tilde{P}_{rad} + \tilde{P}_{ref} + \tilde{P}_{eject} + \tilde{P}_c, \quad (5)$$

where $\tilde{P}_{rad}$ is the radiative power, $\tilde{P}_e$ the power of ejecta, and $\tilde{P}_c$ the power of conduction, it follows that:

$$\oint (\bar{F}_l - \bar{F}_{rad} - \bar{F}_{ref} - \bar{F}_{eject} - \bar{F}_c) \cdot \hat{n} dA = 0. \quad (6)$$

Under specific conditions of thermal conductivity, the ejecta flux $\bar{F}_e$ (W/m^2) can be calculated using the particle number ejection flux Γ as determined in the previous section:

$$\bar{F}_e = \Gamma H \hat{n}, \quad (7)$$

where H (J/Kg) is the heat of fusion plus vaporization (since it sublimates in vacuum). Combining Equations (1) and (2), the following relationship is obtained:

$$|F_e| = \alpha \sqrt{\frac{M}{2\pi RT}} P H_v = \alpha \sqrt{\frac{M}{2\pi RT}} 10^{A - \frac{B}{T_C + C}} H_v. \quad (8)$$

Since

$$|F_l| = |F_{rad}| + |F_e|, \quad (9)$$

it follows that

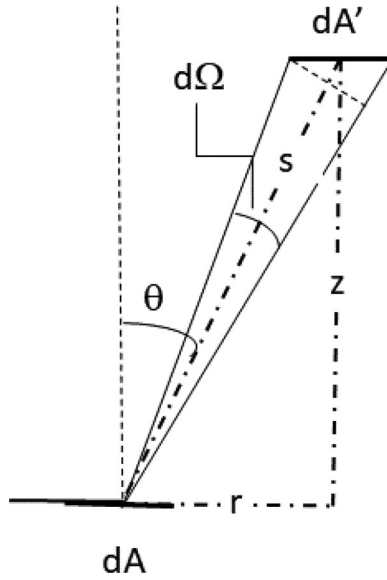


Figure 1. Layout.

$$|F_l| = \sigma T^4 + \alpha \sqrt{\frac{M}{2\pi RT}} 10^{A - \frac{B}{T_C + C}} H_\nu. \quad (10)$$

Given Equation (10), it is possible to calculate the laser flux F_l necessary to reach a temperature T for various compounds by numerically solving the inverse problem to retrieve T as a function of the flux. Then, $P_\nu(|F_l|)$, $\Gamma(|F_l|)$, and $\Sigma(|F_l|)$ can be determined using Equations (2), (1), and (3), respectively. Since radiation goes as T^4 , while mass ejection from evaporation goes roughly exponentially in T , at low laser flux levels the outward flow is completely dominated by radiation (the asteroid is heated slightly and radiates).

In this discussion, it is assumed that F_l is constant over the spot area, so that T is constant over the laser spot. This is the case of an isothermal spot. In reality, F_l has a profile distribution which depends on the characteristics of the laser. In the case of a single-mode laser, a Gaussian beam profile can be assumed, which is given by

$$|F_l| = \frac{\tilde{P}_l}{2\pi\sigma^2} e^{-r^2/2\sigma^2}. \quad (11)$$

The profile temperature at the spot $T(F_l(r))$ can then be retrieved, and $P_\nu(F_l(r))$, $\Gamma(F_l(r))$ and $\Sigma(F_l(r))$ can be derived.

2.3. Plume density calculation for a surface spot without boring

Assume the laser spot has a circular surface of area A and radius R characterized by an ejection flux $\Sigma(r, \nu)$, which is the number of particles having velocity ν emitted per unit surface area and unit time (Figure 1). Assuming that $\Sigma(r, \nu)$ depends on r , the radial distance from the center of the spot, and thus has circular symmetry as, for

example, in the case of a Gaussian beam. The particles are assumed to be emitted isotropically in all directions. The number of particles emitted per second by the elemental area dA is thus $dA \cdot \Sigma(r, v)$. The number of particles having velocity v and hitting dA' per second is given by $\Sigma'(v)$, where dA' is an elemental area viewed under the solid angle $d\Omega$ and at a distance s from dA , can be derived by combining the following equations:

$$d\Omega = \frac{dA' \cos \theta}{s^2}, \quad (12)$$

$$\int_A \frac{\Sigma(r, v) d\Omega dA}{2\pi} = \Sigma'(v) dA'. \quad (13)$$

As a result, $\Sigma'(v)$ can be expressed as:

$$\Sigma'(v) = \int_A \frac{\Sigma(r, v) \cos \theta}{2\pi s^2} dA. \quad (14)$$

Given

$$\cos \theta = \frac{z}{\sqrt{r^2 + z^2}} = \frac{z}{s}, \quad (15)$$

$\Sigma'(v)$ can be re-written as

$$\Sigma'(v) = \frac{1}{2\pi} \int_0^R \frac{\Sigma(r, v)}{s^2} \cdot \frac{r}{s^2} 2\pi r dr = \int_0^R \Sigma(r, v) \frac{zr}{(r^2 + z^2)^{\frac{3}{2}}} dr. \quad (16)$$

Equation (16) gives the general solution for isotropic emission assuming a circular, symmetric spot. It shows the dependence of $\Sigma'(v)$ on z , so that here for clarity the notation $\Sigma'(v) = \Sigma'(v, z)$ is used.

The velocity distributions of the ablated particles are commonly described in terms of a Maxwell–Boltzmann distribution function on a stream velocity, $f(v)$, even though a modified distribution function which provides a consistent description of the axial and radial velocity distributions has been proposed [13]. Although the current model uses a Maxwell–Boltzmann distribution, improvements can certainly be made, which will involve no more than a straight-forward calculation of integrating the new distribution into the necessary equations. It will be shown that the Maxwell–Boltzmann distribution is a valid approximation for the actual particle speeds by an examination of the mean-free-paths of the emitted particles for several example cases that will be considered. See Section 3.2 and Figure 2 in that section.

Therefore,

$$\Sigma(v, r) = \Sigma_r f(v), \quad (17)$$

where Σ_r is the total number of particles emitted per unit surface area per unit time.

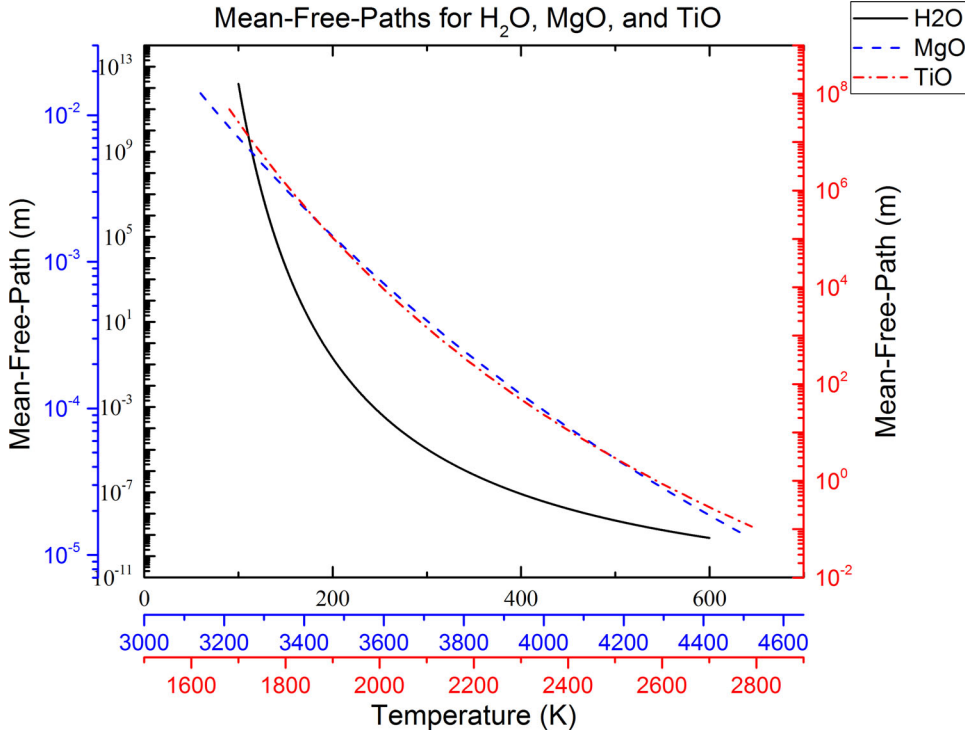


Figure 2 Mean-free-paths for water, MgO, and TiO *at the heated spot*. Note that for nominal molecular diameters of order Å, the mean-free-paths are orders of magnitude below this even at the maximal temperatures considered. Thus, a Maxwell-Boltzmann distribution is valid for each of the compounds at the laser fluxes chosen (see Figure 4).

According to Equation (16), $\Sigma'(v, z)$ is given by

$$\Sigma'(v, z) = \int_0^R \Sigma_r f(v) \frac{zr}{(r^2 + z^2)^{\frac{3}{2}}} dr. \quad (18)$$

The density $n'(v, z)$ (#/m³) of particles having velocity v at distance z can be calculated (assuming no collisions) using

$$n'(v, z) = \frac{4\Sigma'(v, z)}{v}. \quad (19)$$

Then, integrating the previous equation over v gives

$$n'_z = \int_0^\infty n'(v, z) dv. \quad (20)$$

It is also possible to obtain n_z , which represent the total number of particles at distance z .

2.3.1. Isothermal spot

Consider now the case in which the particle number emission flux is constant with respect to r , which corresponds to a uniform irradiation over the area A . It follows that

$\Sigma(r, \nu) = \Sigma(\nu) = \Sigma^* f(\nu)$ where Σ^* is a constant. Thus, the integral in Equation (18) can be solved by substitution:

$$\begin{aligned} u^2 &= z^2 + r^2, \\ du &= 2z dz, \\ \Sigma'(\nu, z) &= \frac{1}{2} \Sigma(\nu) z \int_{\frac{z^2}{z^2+R^2}}^{\frac{z^2+R^2}{z^2}} u^{-\frac{3}{2}} ds = -\Sigma(\nu) u^{-\frac{1}{2}} \Big|_{\frac{z^2}{z^2+R^2}}^{\frac{z^2+R^2}{z^2}}, \\ \Sigma'(\nu, z) &= \Sigma(\nu) z \left[\frac{1}{z} - \frac{1}{\sqrt{z^2 + R^2}} \right] = \Sigma(\nu) \left[1 - \frac{1}{\sqrt{1 + \frac{R^2}{z^2}}} \right]. \end{aligned}$$

Finally, $\Sigma'(\nu, z)$ can be re-written as

$$\Sigma'(\nu, z) = \Sigma^* f(\nu) \left[1 - \frac{1}{\sqrt{1 + \frac{R^2}{z^2}}} \right]. \quad (21)$$

Note that, as expected,

$$\Sigma'(\nu, z) \rightarrow \Sigma(\nu) \text{ as } R \rightarrow \infty,$$

$$\Sigma'(\nu, z) \rightarrow 0 \text{ as } R \rightarrow 0,$$

$$\Sigma'(\nu, z) \rightarrow \Sigma(\nu) \text{ as } z \rightarrow 0.$$

The expression for $n'(z, \nu)$ can be written as:

$$n'(z, \nu) = \frac{4\Sigma'(\nu, z)}{\nu} = \frac{4\Sigma^* f(\nu)}{\nu} \left[1 - \frac{1}{\sqrt{1 + \frac{R^2}{z^2}}} \right], \quad (22)$$

$$\begin{aligned} n'(z) &= \int_0^\infty 4\Sigma^* \left[1 - \frac{1}{\sqrt{1 + \frac{R^2}{z^2}}} \right] \left(\frac{m}{2\pi k_B T} \right)^{3/2} \nu e^{-m\nu^2/2k_B T} d\nu \\ &= 4\Sigma^* \left[1 - \frac{1}{\sqrt{1 + \frac{R^2}{z^2}}} \right] \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty \nu e^{-m\nu^2/2k_B T} d\nu \\ &= 8\Sigma^* \sqrt{\frac{m}{2\pi k_B T}} \left[1 - \frac{1}{\sqrt{1 + \frac{R^2}{z^2}}} \right]. \end{aligned} \quad (23)$$

2.3.2. Isothermal spot at $z \gg R$

In the case that z becomes large with respect to the spot size – $z \gg R$, then Equation (18) can be re-written as:

$$\Sigma'(\nu, z) \sim \Sigma(\nu) \left[1 - \left(1 - \frac{R^2}{2z^2} \right) \right] = \Sigma(\nu) \frac{R^2}{2z^2}. \quad (24)$$

By letting $\Sigma^* f(\nu) \pi R^2$ the number of total particles having velocity ν emitted by area A per second we can write

$$\Sigma'(\nu, z) = \frac{\Sigma^* f(\nu)}{2\pi z^2} \quad (25)$$

and

$$n'(z, \nu) = \frac{4\Sigma^* f(\nu)}{2\pi \nu z^2}. \quad (26)$$

Noting that $f(\nu) \equiv \left(\frac{m}{2\pi k_B T}\right)^{3/2} 2\pi \nu^2 e^{-m\nu^2/2k_B T}$, Equation (26) is integrated over all ν to obtain

$$\begin{aligned} n'_z &= \int_0^\infty \frac{4\Sigma^*}{z^2} \left(\frac{m}{2\pi k_B T}\right)^{3/2} \nu e^{-m\nu^2/2k_B T} d\nu \\ &= \frac{4\Sigma^*}{z^2} \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty \nu e^{-m\nu^2/2k_B T} d\nu \\ &= \frac{\Sigma^*}{\pi z^2} \sqrt{\frac{8m}{\pi k_B T}}. \end{aligned} \quad (27)$$

2.4. Mean-free-path

It has so far been assumed that a Maxwell–Boltzmann distribution of the particle speeds is valid. It is well known that in the laser-induced evaporation process the interface between the material and the vapor and a liquid/solid is characterized by a region in which the gas is in non-equilibrium, named the Knudsen layer [14]. Within this region, which is of the order of the mean-free-path from the solid surface, the molecules collide each others less frequently than with the surface itself, so that distribution of molecular velocities deviates significantly from the Maxwellian state. Along the Knudsen layer, the velocity distribution function changes from non-Maxwellian at the surface, to a local Maxwellian distribution with an average forward speed at some distance from the surface.

In the assumption of an ideal gas but with a non-zero collision cross section, the mean-free-path is given by

$$\lambda = \frac{k_B T}{P\sigma\sqrt{2}}, \quad (28)$$

where P is the pressure of the gas and σ is the collisional cross section. For the typical regimes considered, the mean-free-path is of order 10 – 100 μm , see Figure 2

Considering that the distances from the spot are orders of magnitude above the mean-free-path, the method to calculate n which itself uses a Maxwell–Boltzmann distribution for the speeds of the particles is valid. Moreover, so that such. Equation (26)

can be used to further evaluate the mean-free-path as a function of distance from the heated spot at constant temperature. This is plotted in [Figure 2](#).

3. Spectra

Following the above discussion, the theory developed has been used to calculate spectra of some compounds. In [Section 3.1](#), we calculate the number of photons impinging on the optical system per second and unit of bandwidth assuming to collect light by an optical system having an aperture A_s and an étendue Ω_s for the case in which there is an isothermal spot. In order to simulate the spectra, the absorption cross section of the given compound must be known as a function of incident photon frequency, which is available for very few molecules and even fewer interesting for the present case [15,16]. In [Section 3.2](#), the simulated spectra obtained for some selected molecules are given.

3.1. Spectra modeling

The integrated absorption line coefficient along column length L as a function of wavelength can be found by

$$\tau(\lambda) \equiv \sigma(\lambda) \int_0^L n'(v, z) dz = \sigma(\lambda) \int_0^L \frac{4\Sigma'(v, z)}{v} dz, \quad (29)$$

where $\sigma(\lambda)$ is the absorption cross section. For $z \gg R$ and an isothermal spot,

$$\begin{aligned} \tau(\lambda) &= \sigma(\lambda) \int_0^L n'(v, z) dz \\ &= \sigma(\lambda) \int_0^L \frac{4\Sigma'(v, z)}{v} dz \\ &= 8\Sigma^* \sigma(\lambda) \sqrt{\frac{m}{2\pi k_B T}} (L + R - \sqrt{L^2 + R^2}). \end{aligned} \quad (30)$$

At temperature T , the spot radiative flux F_{rad} can be written as

$$F_{rad} = \int_0^\infty F(\lambda) d\lambda, \quad (31)$$

where, according to black body physics,

$$F(\lambda) = \frac{2hc^2}{\lambda^5} (e^{\frac{hc}{\lambda kT}} - 1)^{-1}. \quad (32)$$

The number of photons emitted at the spot per unit of area, per second, per steradian, per unit of bandwidth $N(\lambda)$ is then

$$N(\lambda) = \frac{F(\lambda)}{h\nu} \Rightarrow N(\lambda) = \frac{2c}{\lambda^4} (e^{\frac{hc}{\lambda kT}} - 1)^{-1}. \quad (33)$$

Assuming that the area of the spot is $A = \pi R^2$, and that radiation is collected by an optical system of aperture A_s , where Ω_s the solid angle of optical system as viewed from the asteroid spot, the number of photons impinging on the optical system per second and unit of bandwidth is given by:

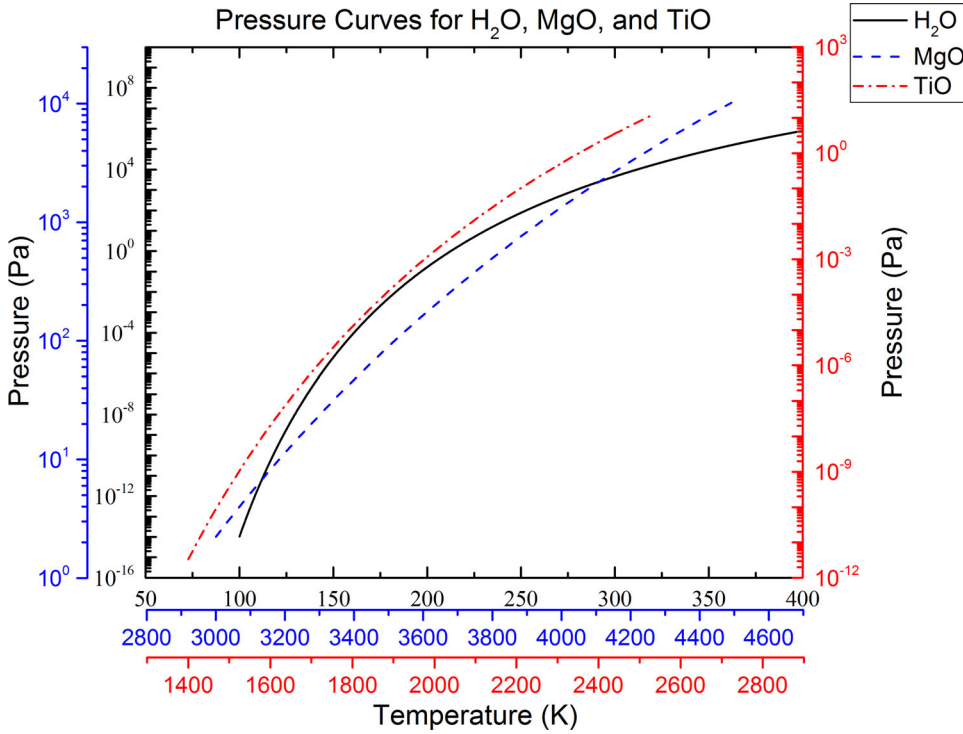


Figure 3. Vapor pressure derived from the Antoine coefficients for the compounds analyzed. Notice the different temperature ranges corresponding to similar pressures.

$$G(\lambda) = AN(\lambda)\Omega_s \cdot \exp \left[-\sigma(\lambda) \int_0^L n'(v, z) dz \right]. \quad (34)$$

Since

$$\Omega_s = \frac{A_s}{4\pi L^2}, \quad (35)$$

$G(\lambda)$ can be re-written as

$$G(\lambda) = \frac{AA_s}{4\pi L^2} N(\lambda) \cdot \exp \left[-\sigma(\lambda) \int_0^L n'(v, z) dz \right] = \frac{AA_s}{4\pi L^2} N(\lambda) e^{-\tau(\lambda)}. \quad (36)$$

Using these equations to obtain $G(\lambda)$ in units of $\text{m}^2 \mu \text{m}^{-1} \text{s}^{-1}$, the following spectra for H_2O , MgO , and TiO are obtained.

3.2. Simulations

This section will provide example cases for the theory developed above. The relevant parameters of the compounds considered are detailed in Table 1. The compounds chosen are thought to be common in asteroids [17].

Figure 3 shows the relationship between vapor pressure in pascals versus temperature for the considered compounds. According to the literature, the typical energy per m^3 to

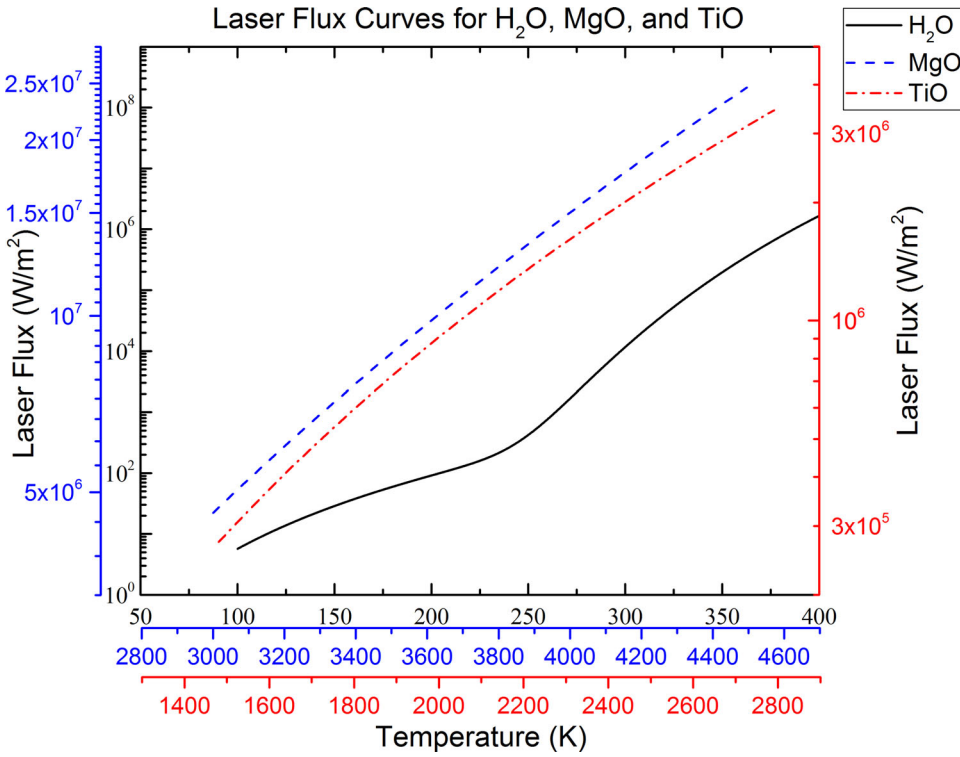


Figure 4. F_L given for the various compounds analyzed. Due to the vastly different temperature ranges for the Antoine coefficients for water compared with the other two compounds, the associated fluxes are accordingly disparate.

vaporize most materials is on the order of 10^{10} J. At temperatures exceeding ~ 2250 K, which occur at fluxes greater than $\sim 10 \text{ MW/m}^2$, the vapor pressures of all compounds are very high. That is, none of these materials remain solid, and mass ejection rates will be high. Even vapor pressures in the range of 10^3 Pa correspond to large mass ejection rates. However, ionization and dissociation are not attained for the regimes considered. In order to achieve a relative ionization of 1%, laser fluxes of order 10^{15} W/m^2 are required [12]. As is evident from Figure 4, the regimes considered are many orders of magnitude below this. Likewise, the application of the Maxwell–Boltzmann distribution to the particle speeds must be validated. Using Equation (28), mean-free-paths were obtained for the example compounds as functions of temperature, see Figure 2. Since particle density decreases (so mean-free-path increases) as distance from the heated spot increases, a Maxwell–Boltzmann distribution remains valid as a description of the particle speeds.

As an example, in Figure 5, Γ is plotted as function of temperature in the case $\alpha = 1$ for some selected compounds, whose parameters are given in Table 1.

As shown by the derivations above, as the laser flux level increases (spot size shrinks, power increases, or both), evaporation becomes increasingly dominant and, eventually, at about $T \sim 2000\text{--}3000$ K, which correspond to fluxes of $10^6\text{--}10^7 \text{ W/m}^2$, as shown in Figure 4, mass ejection by evaporation becomes the dominant outward power flow. At the same time, the temperature stabilizes, so that increasing flux increases the rate of mass ejection with only minute increases in temperature.

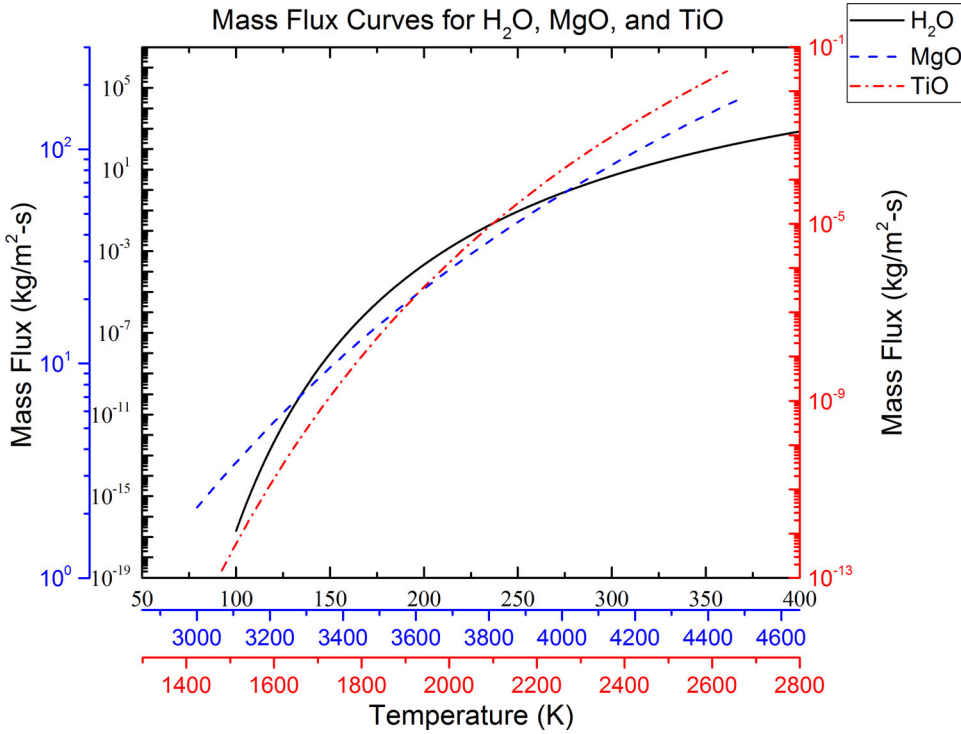


Figure 5. Γ as a function of T for various compounds, given in the range of temperatures where the Antoine coefficients are valid.

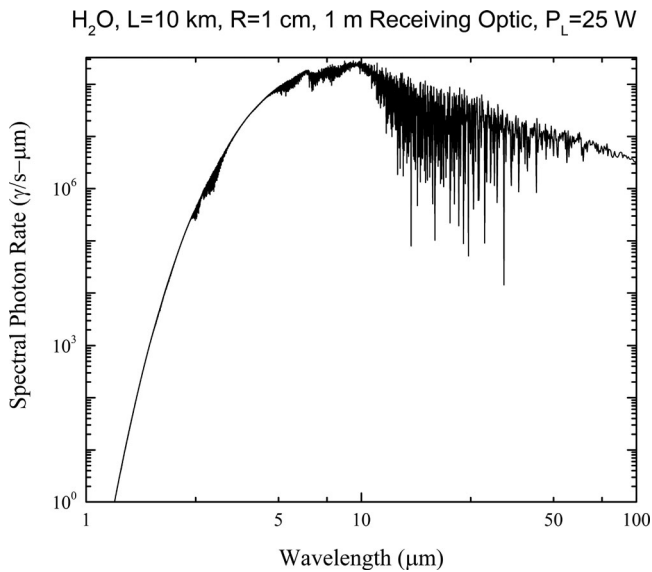


Figure 6. A theoretical spectrum derived for H_2O . Here, L is the distance from the laser aperture to the spot, R is the diameter of the spot, and P_L is the power of the laser. The contrast ratio for these parameters is high, so it allows one to easily discern H_2O if some of the spectrum's features are visible above noise and other compounds/elements spectra. The parameters were chosen to be reasonable for a practical cubesat mission.

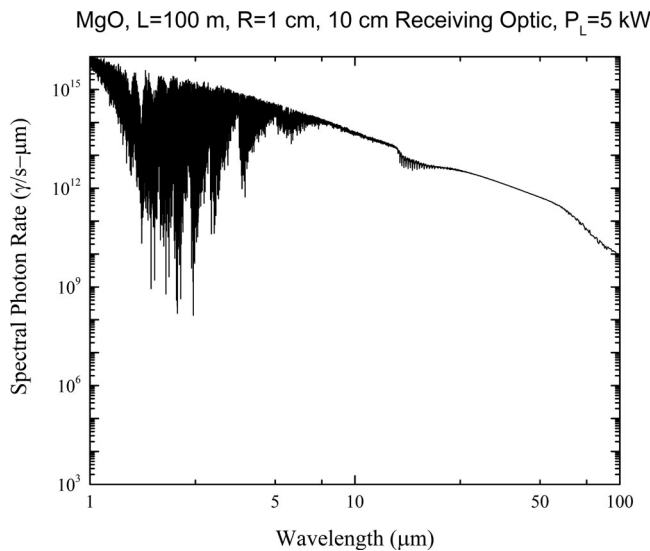


Figure 7. Theoretical spectrum derived for MgO. Again, the input parameters have been chosen as to increase the contrast ratio and allow a clear definition of the spectrum while still remaining realistic mission parameters.

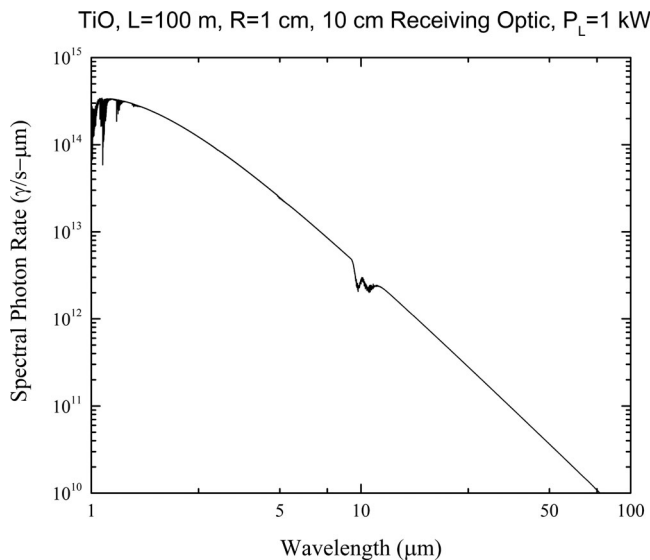


Figure 8. Theoretical spectrum for TiO tuned to have high contrast ratio. Comparison with [Figures 6](#) and [7](#) will show that this material has much less contrast at the realistic laser fluxes, spot sizes, and distances considered.

Parameters were selected to allow the comparison of three spectra under similar conditions, shown in [Figures 6–8](#), to simulate the possibility of viewing all three spectra simultaneously with a Fourier transform infrared spectrometer (FTIR). The parameters were chosen as to simulate the possibility of this measurement being performed on an asteroid from a nearby cubesat at a distance of 100 m. The laser power was chosen to

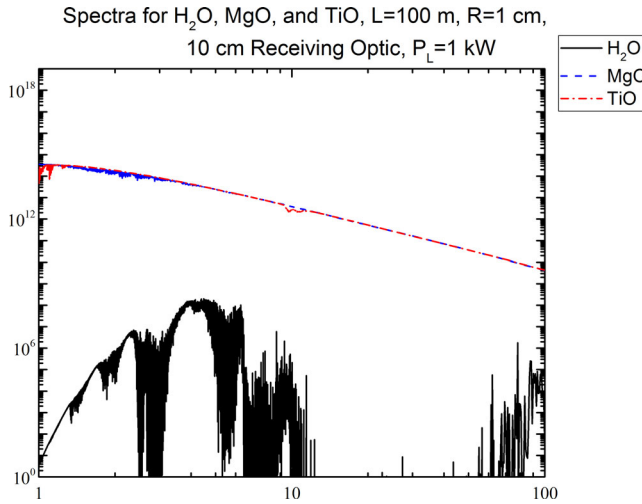


Figure 9. Spectra for H_2O , TiO , and MgO for a possible realistic test case of observing all three spectra simultaneously. Although the water spectrum may be indiscernible, the variations between the TiO and MgO spectra may allow molecular identification.

be 1 kW, which – although high – is achievable on cubesat size scales, These are shown in Figure 9.

The simulations performed above allow one to attempt to determine the *molecular* composition of materials in the laboratory as well as in other (e.g. extraterrestrial) environments. Potentially, this can revolutionize laser ablation spectroscopy, as this technique is currently based on the dissociation of materials, which provides elemental identification only. As has been shown, the absorption cross sections for various materials are necessary in order to generate spectra. However, few cross sections are available, severely limiting the number of materials whose spectra can be generated. This limits the extent of applications of the theory here derived, as compound spectra (i.e. those containing the spectra several materials simultaneously) cannot be generated for many materials. Because of this, many materials containing several compounds mixed together cannot be readily identified with this method, until more cross sections are derived. Nonetheless, deriving these cross sections is a process whose theory has already been developed – only the required time needs to be invested [16].

4. Conclusion

A novel method to derive bulk molecular composition of rocky materials by using absorption spectroscopy has been presented. A continuous laser beam heats a local area on a rocky materials, in a regime in which melting occurs, but molecules are not dissociated. The heated materials emits blackbody radiation, which is absorbed by the molecules, providing an infrared spectrum. The required laser fluxes are of the order 10^6 – 10^7 W/m², so that mass ejection by evaporation becomes the dominant outward power flow, while ionization and dissociation are negligible. A model to evaluate the ejection flux has been implemented. The results are then used to calculate the absorption line coefficient along a column of length L , the distance at which a collecting

system is placed. Defining the detecting instrument by its aperture and étendue, it is then possible to compute the collected spectrum, provided the absorption cross section of the compounds in the material are known. Fine-tuning of different parameters, such as laser flux, spot size, and distance to the laser to the receiving spectrometer is necessary to achieve the contrast and emission required for proper identification of a compound. At present, however, few cross sections are known due to the intensive calculations and time that must be invested into deriving them from first principles quantum theory. Therefore, more work in this area must be done to enable the use of this technique in near-future spectroscopic analyses, which can potentially revolutionize laser ablation spectroscopy by allowing molecules identification.

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