

C-H Hot Bands in the Near-IR Emission Spectra of Leonids

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Abstract

The reported infrared (IR) emission spectra from 1999 Leonid fireballs show a $3.4\mu\text{m}$ C-H emission band and unidentified bands at longer wavelengths. Upon atmospheric entry, the Leonid meteorites were flash-heated to temperatures around 2400K , which would destroy any organics on the surface of the meteorite grains. We propose that the ν_{CH} emission band in the Leonid emission spectra arises from matrix-embedded $\text{C}_n\text{-H-O}$ entities that are protected from instant pyrolysis. Our model is based on IR absorption ν_{CH} bands, which we observed in laboratory-grown MgO and natural olivine single crystals, where they arise from $\text{C}_n\text{-H-O}$ units imbedded in the mineral matrix, indicative of aliphatic $-\text{CH}_2-$ and $-\text{CH}_3$ organics. Instead of being pyrolyzed, the $\text{C}_n\text{-H-O}$ entities in the Leonid trails become vibrationally excited to higher levels $n = 1, 2, 3$ etc. During de-excitation they emit at $3.4\mu\text{m}$, due to the $(0 \Rightarrow 1)$ transition, and at longer wavelengths, due to hot bands. As a first step toward verifying this hypothesis we measured the C-H vibrational manifold of hexane (C_6H_{14}). The calculated positions of the $(2 \Rightarrow 1)$, $(3 \Rightarrow 2)$, and possibly $(4 \Rightarrow 3)$ hot bands agree with the Leonid emission bands at 3.5 , 3.8 and $4.1\mu\text{m}$.

1. Introduction

The 1999 Leonid emission spectra in the C-H stretching region (Russell *et al.* 2000) offer an opportunity to test the hypothesis whether the “organics” in the dust grains in such cometary trail material consist of surface organics, or if they are structurally imbedded within the mineral grains. Furthermore, we can compare these Leonid spectra to “hot” C-H laboratory emission spectra.

Russell *et al.* (2000) recorded the infrared (IR) emission spectrum of persistent 1999 Leonid trains (see Fig. 1), which cooled from $\approx 2400\text{K}$ to $\approx 1200\text{K}$ in less than 2 minutes. As shown in Fig. 1, there is an emission band around $3.4\mu\text{m}$ ($2850 - 2900\text{cm}^{-1}$), indicative of ν_{CH} emission due to the C-H stretching band of “organic” matter. There are further emission bands at $3.55\text{-}3.6\mu\text{m}$, $3.8\mu\text{m}$, and $4.05\text{-}4.1\mu\text{m}$, which could not be assigned. Whereas the $3.4\mu\text{m}$ band is too broad to resolve any splitting into subcomponents at 3.42 and $3.5\mu\text{m}$ (indicative of symmetrical and antisymmetrical C-H stretching modes, respectively) it is similar to the $3.4\mu\text{m}$ bands absorption bands from dust in the interstellar medium, ISM (see Pendleton and

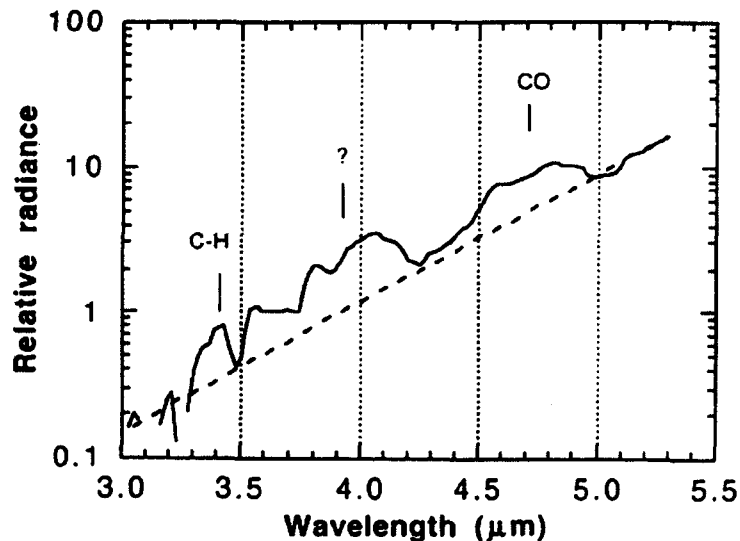


Fig. 1.— Leonid near-IR spectra after Russell *et al.* (2000); note the different emission features.

Allamandola (2002)). These observations support the idea that the dust component in the Leonid parent comet derives from the dust in the pre-solar molecular cloud that formed the solar system. Thus, the “organics” that led to the $3.4\mu\text{m}$ emission spectrum of the Leonid fireballs should be similar to the “organic” component in the dust in the ISM.

At the estimated temperature of the Leonid train, any surface organics would normally degrade irreversibly through pyrolysis of their C-H bonds during flash heating. When MgO and olivine crystals containing imbedded $\text{C}_n\text{-H-O}$ entities are heated in the laboratory to temperatures between 550-1000K, the C-H bonds pyrolyze, but recover during annealing (Freund *et al.* 2001). Therefore, even though the C-H bonds break during heating, the H atoms remain close-by in the mineral structure, diffuse back and bond again to the C_n entities. Furthermore, when imbedded $\text{C}_n\text{-H-O}$ entities are rapidly heated, they will not immediately pyrolyze. They first pass through a series of vibrationally excited states of the C-H oscillator, because these C-H oscillators are confined by the matrix and coupled to the surrounding atoms and ions of the mineral structure. The $\text{C}_n\text{-H-O}$ are able to transfer a fraction of their vibrational energy to the matrix, which delays C-H bond breakage. Therefore, when the matrix is flash-heated, imbedded $\text{C}_n\text{-H-O}$ entities will emit hot bands arising from transitions between higher vibrationally excited states of the C-H oscillator.

2. Results

To obtain the vibrational manifold of the C-H oscillator we measured the ν_{CH} absorption spectrum of hexane, C_6H_{14} with a CH_3/CH_2 ratio of 2:4, from the allowed ($0 \Rightarrow 1$) transition at $3.4\mu\text{m}$ to the forbidden higher transitions ($0 \Rightarrow n$) extending well into the VIS region, with n up to 7 as shown in Fig. 2a. From these values we derive the wavelengths of the hot bands as shown in Fig. 2b. From the measured transition energies we obtain $\alpha = 1.29 \times 10^8$, and for $-\text{CH}_2-$: $D_e = 3.62\text{eV}$ and CH_3 : $D_e = 3.69\text{eV}$.

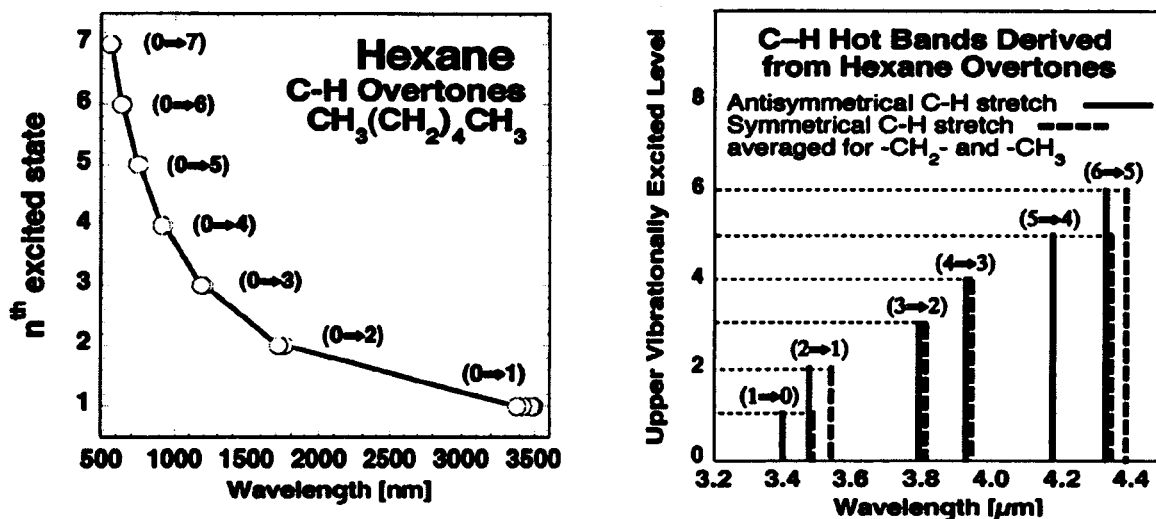


Fig. 2.— (a: left) Series of C-H stretching modes from the fundamental, allowed ($0 \Rightarrow 1$) transition through the overtones ($0 \Rightarrow n$) to the 7th excited state. (b: right): Hot bands ($n \Rightarrow n - 1$) calculated from the measured overtone series.

To a good approximation, the C-H vibrational stretching manifold can be described by a Morse potential, wherein D_e is the dissociation energy, α a constant, and r_0 the equilibrium bond distance:

$$V(r) = D_e \left(1 - \exp \frac{-\alpha(r-r_0)}{r_0} \right)^2$$

Using this Morse potential, wherein n is the quantum number for the energy Levels, we solve the Schrödinger equation to obtain the eigenvalues:

$$E_n = \frac{D_e}{y^2} \left[2\alpha n + \alpha y - \alpha^2 \left(n^2 + n + \frac{1}{4} \right) \right]$$

The transition energies are $E_{0n} = E_n - E_0$, where E_0 is the ground state energy.

Noting that, $E_0 = \frac{D_e \alpha}{y} - \frac{D_e \alpha^2}{4y^2}$, we have $E_n = \frac{D_e}{y^2} [2\alpha n - \alpha^2(n^2 + n)] + E_0$

Subtracting the ground state energy E_0 and rearranging the terms gives

$$\tilde{E}_n = \left(\frac{2D_e \alpha}{y} - \frac{D_e \alpha^2}{y^2} \right) n - \frac{D_e \alpha^2}{y^2} n^2$$

Equating these coefficients to the coefficients of the quadratic fits, we arrive at:

$$\text{for } -\text{CH}_2\text{-: } \frac{2\alpha D_e^{3/2} h(2\mu)^{1/2}}{r_0} - \frac{2\alpha^2 h^2 D_e^2 \mu}{r_0^2} = 2929.81 \quad \text{and} \quad \frac{2\alpha^2 h^2 D_e^2 \mu}{r_0^2} = 61.81$$

$$\text{for } -\text{CH}_3\text{: } \frac{2\alpha D_e^{3/2} h(2\mu)^{1/2}}{r_0} - \frac{2\alpha^2 h^2 D_e^2 \mu}{r_0^2} = 3006.8 \quad \text{and} \quad \frac{2\alpha^2 h^2 D_e^2 \mu}{r_0^2} = 63.83.$$

We can compare the IR emission spectrum of the 1999 Leonids in Fig. 1 with the expected hot band positions given in Fig. 2b. From this comparison we conclude that the observed Leonid emission bands have a one-to-one correspondence with de-excitation of C-H, with (3.6 μm , (2 \Rightarrow 1)), (3.8 μm , (3 \Rightarrow 2)), and (4.0 μm , (4 \Rightarrow 3)).

3. Discussions and Conclusions

As we have shown, the dust component in the Leonid parent comet probably derives from dust in the pre-solar molecular cloud that formed the solar system, and the 3.4 μm emission spectrum of the Leonid fireballs should be similar to the "organic" component in the dust in the ISM. At the high temperatures during atmospheric entry, any surface "organics" will be destroyed, and they can only survive irreversible pyrolysis if they are well protected. We have shown that imbedded C_n-H-O entities in synthetic MgO and natural olivine will not be irreversibly destroyed. Instead they are able to transfer their thermal energy to the matrix, and they emit in a series of near-IR emission bands. Furthermore, we have seen that there is a one-to-one correspondence between the observed Leonid emission bands and the de-excitation of C-H.

The Leonid spectra as recorded by Russell *et al.* (2000) don't have enough resolution to resolve the different near-IR emission lines. The flash heating of the Leonids could be also simulated in the laboratory using dust grains, which contain structurally imbedded C_n-H-O entities. Furthermore, one should be able to observe the ν_{CH} de-excitation emission hot bands in astrophysical environments, where interstellar dust is subjected to flash-heating, for instance in the front of supernova shockwaves.

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