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# Calculation of the Refractive Index Change in Dissociating Shocked Benzene

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A calculation is made of the refractive index (n) of a shocked solution of hydrocarbon species and spheroidal carbon particles that would be the dissociation products of benzene. The result is evaluated for benzene shocked to 15 GPa for particles of different morphologies. In the case of diamond particles, the refractive index is predicted to decrease through the dissociation from 1.96 to 1.75. For particles of graphite in platelet form (10:1 aspect ratio) the refractive index increases from 1.96 to 2.2. Thus the measurement of n(t) could indicate the morphology of the carbon particulates and the time scale for this reaction, as well as the instantaneous amount of carbon particulate. The latter information is valuable in conjunction with recent Mie scattering experiments for example.

### 1. Introduction

Recent experiments<sup>1</sup> have been performed measuring the optical transmission spectra of shocked benzene. The goal of these experiments was to detect, through the scattering of light, the formation of carbon particulates predicted to occur in the decomposition of hydrocarbons under shock. Information that is presently unknown, for example, is the number density, size, growth rate and solid phase of the carbon particulates. According to the Mie theory of the scattering of light, the extinction of the transmitted light due to scattering will depend on both the size and number density of scattering particles. Thus, using this transmission data alone it is not possible to uniquely determine the particle size without an independent determination of the total volume of carbon that is in particulate form. The refractive index (n)can supply this information because n is dependant on the total particulate volume, but independent of particle size (for particles smaller than the wavelength of light).

In this way, we propose using the refractive index as a measure of completion of a chemical reaction, by comparing its instantaneous value to its initial and final values. This may provide valuable information on the reaction rates of chemical reactions uniformly initiated at a well-defined time by shock. In addition, in the case of dissociating benzene and other hydrocarbons, the polarity and magnitude of the refractive index change is calculated to be dependent on the morphology of the carbon particles produced. Thus for example, this measurement may indicate whether particles are precipitating as diamond spherules or as graphitic platelets.

#### 2. Species Distribution

Benzene shocked<sup>2</sup> to pressures exceeding the neighborhood of 15 GPa decomposes into carbon and hydrocarbons. It is useful to express the time evolution of the distribution of molecular species so-produced by  $m_x$ , the number of moles of carbon in the form of species x. Then 1 mole of reactant benzene upon shock becomes:

$${m_{\rm B}(t=0) = 6} \xrightarrow{\text{upon shock}} m_{\rm B}(t) + m_{\rm P}(t) + m_{\rm A}(t) + m_{\rm E}(t)$$
 (1)

where B = benzene, P = particulate, A = alkanes and E = alkenes. The particulate is considered to be either graphite or diamond. The alkanes are molecules of the form  $C_iH_{2i+2}$  (including *i*=0) and alkenes are  $C_iH_{2i}$  where *i* is the number of carbon atoms.

For alkanes, the contribution to the refractive index on a per atom basis is virtually independent of the number of carbon atoms in the molecule. This allows us to represent a distribution of alkanes by a single alkane species of mean carbon number  $\alpha$ . A similar simplification for alkenes is made. (The approximation in this case is not as good, but it is still reasonable for the three alkene species considered.)

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### 3. Reaction Map

For 1 mole reactant benzene, the equations for conserving carbon and hydrogen imply:

$$6 = m_B + m_P + m_A + m_E \tag{2}$$

$$6 = m_B + \frac{2\alpha + 2}{\alpha} m_A + 2 m_E$$

If  $m_E$  is ignored, Eq. (2) describes a plane, which for nonnegative  $m_x$  is bounded by a triangle as shown in Fig. 1. This is a map of the species distribution following the form of carbon. Equation (3) constrains the locus to the half of the triangle adjacent to the PB line as shown. When  $m_E$  is considered, the map becomes a tetrahedron. A reaction path would begin at the benzene vertex and end on the PA line. A statistical mechanical calculation<sup>3</sup> suggests the equilibrium endpoint would be in the neighborhood of the dot (referred to below as the Nellis endpoint) on the PA line shown in the Figure, and that the alkenes are unstable. Hence  $m_E$  is only temporarily non-zero and not expected to be large; the reaction path will remain mostly in the PAB plane.



Figure 1. Species distribution map following the form of carbon, for 1 mole reactant benzene. The parameters  $m_x$  are the number of moles of cabon in the form of species x and attain their maximum value (6) at the respective vertices and are zero at the opposite sides.  $\alpha$  is the mean alkane carbon number. Lines of constant  $\alpha$  are drawn as dashes. The region above the  $\alpha = \infty$  line is unattainable. The endpoint distribution of Nellis is indicated by the dot. A hypothetical reaction trajectory is shown as curved path.

We have calculated the refractive index of the species distribution for every point on the map for the cases of diamond or graphitic particles. Diamond particles are assumed to be spherical (as observed recently in detonation soot<sup>4</sup>). Graphite particles are modeled as oblate spheroids with the oblateness a free parameter. The calculated refractive index for the diamond and graphitic cases is shown in Fig. 2. Note that in the graphitic case the lines of constant refractive index are nearly parallel to lines of constant mp, so that mp derived from a given measured index is insensitive to the reaction path.

# 4. Method of Calculation

The refractive index of a solution was calculated through the Lorentz-Lorenz formula

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{V_0} \sum_i m_i A_i$$

(4)

where  $V_0$  is the volume occupied by the entire solution,  $m_i$ and  $A_i$  are the number of moles and molar refractivity of constituent *i*. The molar refractivity contains the polarizability (and in the case of a particles, also the geometry) information. For the hydrocarbon liquids and diamond, the 0 GPa molar refractivity was computed from published values of the refractive index, density and molecular weight through Eq. (4).

**Table I**. Per atom molar refractivity (A) contributed by carbon and hydrogen versus the host species, used to calculate the refractive index plotted in Figure 2.

	carbon		hydrogen	
Host species	0 GPa	15 GPa	0 GPa	15 GPa
benzene alkanes alkenes	3.329 2.558	2.87 2.33	1.038 1.038 1.038	0.945 0.895 0.895
ethene propene butene average	3.27 3.09 2.95 <i>3.10</i>	2.98 2.81 2.68 2.82		
diamond spheres graphite spheres graphite platelets	2.11 3.4 - i 0.6 7.6 - i 5	2.11 2.3 - i 0.3 4.4 - i 1.7	- - ned under	- it perform
(10:1 oblate)				10411000.1





### 4.1. Hydrocarbon Refractivity

For alkanes of size up to at least 9 carbon atoms, it is found that the molar refractivity of the entire molecule follows a linear relation to the number of carbon atoms to a high degree. Thus, the molar refractivity of carbon and hydrogen for alkanes is constant on a per atom basis. Since we are not constrained, for convenience we arbitrarily assign the same per atom value to hydrogen in all the species and let the associated carbon contribution accommodate. The values of the per atom molar refractivity so produced are listed in Table I under the 0 GPa headings.

From published measurements<sup>5</sup> of the shock loaded refractive index, the normalized molar refractivity versus compression was computed (Fig. 3) for several liquids. (We assume dissociation was not important for these liquids in this compression range.) The data was fit to lines of slope  $\beta$ . Benzene is shock compressed<sup>2</sup> to  $\rho/\rho_0=1.92$  at 15 GPa. For benzene  $\beta=0.15$  and A<sub>15</sub> GPa = 0.86 A<sub>0</sub> GPa. For all other hydrocarbon species, we estimated  $\beta=0.1$ , (A<sub>15</sub> GPa = 0.91 A<sub>0</sub> GPa), since more specific data was not available. Table I shows the resulting 15 GPa values of A on a per atom basis.



Figure 3. Molar refractivity versus compression of shocked liquids. A is normalized to its unshocked value, thus the first datum of all liquids coincide. The data fits to lines of slope  $\beta_{1}$ 

### 4.2 Particulate Refractivity

The molar refractivity of randomly oriented spheroids of graphite was computed using formulae in the literature<sup>6</sup> accounting for anisotropic dielectric properties and averaging over all angles. The dielectric constant of 0 GPa graphite in the basal plane was measured by ellipsometry to be  $\varepsilon$ =6.5±1.5 - i10.5±1. The equator of the spheroid was

taken to be in the basal plane. Using a simple model for the compression of a hexagonal lattice, comparison with the dielectric constant of diamond and with absorption measurements<sup>7</sup> of 45 GPa graphite, we estimate that at 15 GPa  $\varepsilon$ =6.5 - i3.5 in the basal plane and  $\varepsilon$ =1.6 normal to the plane. The molar refractivity so-calculated increases with increasing oblateness. The molar refractivity of diamond was taken to be the same at 15 GPa as at 0 GPa, since its lattice is comparatively rigid.



Figure 4. Calculated final refractive index of 15 GPa shocked benzene for different particulate morphologies and at the Nellis endpoint distribution. The oblateness is the ratio (a/c) between the equatorial and polar semiradii.



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### 5. Conclusions

Figure 4 plots the calculated refractive index at the Nellis endpoint at 15 GPa versus oblateness of the graphitic particle, and also indicates the diamond spherule and unshocked values. If the refractive index is observed to decrease, the particulates are probably diamond spherules, since graphite is believed to more likely form platelets. A increase in n would indicate oblate platelets.

The fundemental reason for the change in refractive index through chemical dissociation is that the molar refractivity of carbon is greater when in a structure of unsaturated bonds, such as benzene or graphite, as opposed to the saturated bonds of an alkane or diamond.

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computation was compared (Fig. 3) for several liquids. We assume discontation was not important for these liquids at fills compression range.) The data was fit to lines of large  $\beta$ . Bennene is shock compressed? to  $\rho(\rho_0=1.92)$  at 13 GFa. For bonzene  $\beta=0.15$  and  $A_{15}$  GFa = 0.86 Aq GFa. For all other hydrocarbon species, we estimated  $\beta=0.1$ . A 13 GFa = 0.91 Aq GFa), since more specific data was not wallable. Table 1 shows the resulting 15 GFa values of A