

## Formation of Ions and Radicals From Icy Grains in Comets

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### ABSTRACT

Two theoretical models for the formation of radicals from ice grains are examined to determine if this can explain the jets in comets. It is shown that the production rates for these radicals by the photolysis of molecules in the icy grains are not high enough to explain the jets. A new mechanism is proposed involving the release of cations and anions in the gas phase as the icy mantle surrounding the grains is evaporated. Solar visible radiation can then form radicals by photodetachment of the electrons from these anions. The production rate of radicals formed in this manner is in accord with the production rates of the observed radicals.

### Introduction

Recent observations of jet-type CN and C<sub>2</sub> structures with diameters of 24,000 km in Halley's comet by A'Hearn et al. [1986] have prompted their group as well as others [Clairemidi et al., 1990a, 1990b] to suggest that radicals might be produced directly from the photodissociation of molecules in the grains. In this paper, this idea will be investigated along with the possibility of producing radicals via photodetachment of electrons from negative ions that might already be present in the grains.

### Photochemical Production of Radicals from Grains

Combi [1987] attempted to model the photochemical production of radicals from grains by assuming they were produced by photosputtering of radicals and atoms from the grains. In this model, the photodissociation rate was assumed to be the same as it was in the gas phase. The photodissociation rate in the grains will depend, however, on the photodissociation mechanisms of the individual molecules. Those molecules which dissociate in one molecular vibration, i. e., direct dissociation, after they are electronically excited will be less affected by the presence of the solid than those molecules that only dissociate after many molecular vibrations, i.e., predissociate. The former process will occur in times of the order of 0.01 to 0.1 ps while the latter process will take place in times of the order of 1 to 100 ps. Photodissociation in the grains will compete with quenching of the excited state energy into the phonon modes of the solid, which will occur on a time scale of 0.1 to a few ps. A further complication is the "cage effect", which is the enhanced recombination of the fragments because of the surrounding solid matrix [Schriever, et al., 1991]. Thus, bulky or slow fragments are not able to escape the surrounding cage before they collide with each other and recombine to form the original molecule. Hydrogen atoms and other first row atoms escape more effectively from the cage than heavier atoms or fragments because they are smaller and recoil with a higher velocity. These ideas are incorporated in the following equations describing the total yield, Y, for free radical production from one icy grain in a Halley type comet at 1 AU;

$$Y(r_g) = \left\{ \sum_{\lambda} \Phi(\lambda) I_{\lambda} 2\pi r_g^2 [1 - \exp(-\sigma_{\lambda} \rho 2r_g)] \right\} \tau \quad (1)$$

In Eq. 1, the radius of the grain is  $r_g$ , the intensity at a given wavelength ( $\lambda$ ) of the solar radiation at 1 AU is  $I_{\lambda}$ , the number density of the molecules in the grain is  $\rho$ , the absorption cross-section of the molecule,  $\sigma_{\lambda}$ , and  $\tau$  is the lifetime of the grain, which is taken to be  $10^5$  s. The quantum yield,  $\Phi(\lambda)$ , for dissociation is equal to  $[k_d / (k_d + k_q)]$ , where  $k_d$  and  $k_q$  are the rate constants for

dissociation and quenching, respectively. Both of these rate constants can vary with wavelength, and they are unknown quantities that can drastically reduce the yield of the free radicals. For simplicity, the quantum yield is assumed to be one. Equation 1 was used in Eq. 2 to compute the production rate of the radical R,  $Q(R)$ , by multiplying it by the flux at a particular  $r_g$ ,  $F(r_g)$ , and then summing over all  $r_g$ :

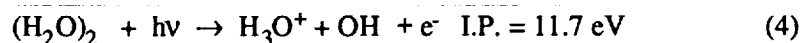
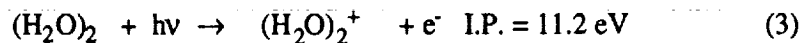
$$Q(R) = \sum_{r_g} Y(r_g)F(r_g) \quad (2)$$

The grain fluxes were taken from the in-situ measurements of Giotto [McDonnell, et al., 1987]. The  $Q(R)$  for OH is  $1.8 \times 10^{25} \text{ s}^{-1}$ , which is four orders of magnitude less than the observed rate [Feldman, 1991]. Clearly, this mechanism does not explain any OH jets in the comets because the contrast between the OH produced by gas phase photolysis will be too small. The calculated  $Q(R)$ 's for CN from HCN and  $C_2N_2$  are  $8.4 \times 10^{24}$  and  $3.2 \times 10^{25} \text{ s}^{-1}$ , respectively. This is closer calculated rates are based upon very optimistic assumptions. The calculated rates assume that the quantum yield is one and independent of wavelength. Both HCN and  $C_2N_2$  are known to predissociate, so the true rates will be much smaller than those that were calculated. The calculated rates also assume the radicals formed on the interior of the grain eventually arrive in the gas phase. This can only be true if the grains completely evaporate and if the radicals do not recombine before evaporation. Thus it can be concluded that the photochemical production of gas phase radicals from grains can not be used to explain the jets in comets.

### **Free Radicals from the Photodetachment of Negative Ions**

Blakely et al. [1980] have shown that ions can be generated in the gas phase without the use of an external ionizer, if ice particles containing anions and cations are evaporated. When this happens, the positive and negative ions that were trapped inside of the ice particle are released. This mechanism does not require charged ice particles because overall neutrality is maintained, since the charges on the anions and cations balance. If the icy grains in comets contain both cations and anions, then the radicals in the coma might be formed by photodetachment of electrons from the gas phase anions in the coma.

All of the models of comets suggest they were originally formed  $10^9$  to  $10^{10}$  years ago in the primordial solar nebula or in the nearby interstellar medium [Swamy, 1986]. It is thought that this occurred by agglomeration of ice particles and mineral grains. Ions in the grains could be formed by cosmic radiation, radioactive decay and photoionization before the ice particles agglomerate to form the comet nucleus. Photoionization is the most efficient mechanism for forming ions in a small ice particle. The photoionization threshold for a single  $H_2O$  molecule is at 12.6 eV [Lide, 1990], however, when the molecule dimerizes and forms clusters the following type of reactions will lower this threshold [Nishi et al., 1984]:



This will decrease the photoionization lifetime by a factor of five due to the increase in the photon flux [Huebner and Carpenter, 1979]. In Eqn. 2, a free radical and an ion are both produced by a single photon. This is a result of the added stability of the protonated ion, which not only lowers the ionization potential of the cluster relative to water, but also leads to a lower dissociation energy for the radical and the ion. Similar mechanisms should be possible for other hydrated molecules [Nishi et al., 1986, and Castleman et al. 1986].

The wavelength distribution of the UV radiation present during comet formation should be similar to the UV distribution in H II regions around young stars. Greenberg and Hage [1990] have shown that it only takes  $10^4$  years to completely process the mantle of a grain. This is a very short time compared to the  $10^8$  to  $10^9$  years available for this purpose, so it is likely that the

outer mantle has been processed many times before the grains agglomerate to form the cometary nucleus. The shortest wavelength of VUV radiation in the H II region is at 13.6 eV, which is low enough to ionize most of the possible cometary molecules except CO and CO<sub>2</sub> [Duley and Williams, 1984]. The electrons that are formed during the photoionization process can attach themselves to atoms and radicals with a high electron affinity, E.A. The E. A. of the most common cometary ions such as CH, OH, CN, C<sub>2</sub>, and C<sub>3</sub> are 1.24, 1.82, 3.82, 3.39, and 1.98 eV, respectively [Lide, 1990]. Thus, some of the most stable negative ions can be formed from cometary radicals. The charge on the negative ions formed from these radicals can be counterbalanced by the positive charges on stable species such as H<sub>3</sub>O<sup>+</sup>, and H<sub>2</sub>CO<sup>+</sup>. Both CO and CO<sub>2</sub> could be bound up in CO<sub>3</sub><sup>-</sup>, which could be formed by the reaction of O<sub>2</sub><sup>-</sup> and O<sup>-</sup> with them in the icy grains. If these grains are shielded from visible radiation inside the nucleus and are kept cold, then these cations and anions will be stable for long periods of time. When these negative ions are later released from the grain into the gas phase they will quickly form free radicals, since the photodetachment lifetimes are only of the order of a few seconds. These arguments suggest that it is not unreasonable to believe that the VUV radiation in a HII region could have formed cations and anions in the mantles of icy grains that later form the nucleus of a comet.

An estimate of the production rate of radicals that can be produced via the release of anions that are trapped in the icy grains can be made by calculating the number of molecules in the mantle,  $N(r_g)$ , as a function of the grain radius. The thickness of the mantle is independent of the grain size, and can be approximated from the optical depth of water ice in the VUV spectral region. This is 0.03 mm for ice grains with a density of 1 gm/cc and a mean absorption cross section of  $1 \times 10^{-17}$  cm<sup>2</sup>. The production rate,  $Q^-(R)$ , is then calculated using Eqn. 5 by multiplying  $N(r_g)$  by the flux of grains with a given radius, the fraction,  $\xi$ , of the mantle that contains the radical anion precursor, and then summing over all grain radii:

$$Q^-(R) = \sum_r N(r_g)F(r_g)\xi \quad (5)$$

The result of this calculation is that the  $Q^-(R)$  for all of the mantle molecules is  $2.4 \times 10^{29}$  s<sup>-1</sup>. The ratios of the production rate of OH to the production rates of C<sub>2</sub>, C<sub>3</sub>, and CN are 250, 6700, and 770, respectively [Fink, et al., 1991]. The production of OH in Halley at 1 AU was  $4 \times 10^{29}$  s<sup>-1</sup> [Feldman, 1991], thus only tenths to hundredths of a percent of the escaping molecules must be anions to explain the observation of jet structures in comets. There is no physical reason why this cannot be the case, since stable solids such as ionic crystals can be made with 100 % ions.

### Conclusions

Theoretical calculations have shown that even with the most optimistic assumptions, the yield of free radicals from the photochemical destruction of grains is much too low to explain the observed jets in comets. An alternate mechanism for the production of free radicals and ions in the gas phase from cometary ice grains has been proposed. This mechanism involves the direct evaporation of trapped anions and cations in the icy grain. Radicals are then produced by photodetachment of the electrons on the anions by solar radiation.

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