ANOMALOUS ISOTOPE EFFECT IN VUV PHOTODISSOCIATION OF HYDROGEN SULFIDE: IMPLICATIONS FOR CHONDRITE and CHONDRULE ISOTOPIC DATA.

Subrata Chakraborty[1*], Ryan Davis[1], Teresa L. Jackson[1], Musahid Ahmed[2], and M. H. Thiemens[1], [1]Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093-0356 (subrata@ucsd.edu), [2]Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720.

Introduction: Mass independent sulfur isotopic compositions have been observed in chondritic chondrules and organics [1, 2] and bulk achondritic meteorites [3, 4]. A significant excess of $\Delta^{33}S$ (= $\delta^{33}S$ – 0.515 $\delta^{34}S$) was observed in the Dhajala chondrite. Sulfonic acid extracts from the carbonaceous chondrite, Murchison also displayed a significant ^{33}S anomaly and may be associated with deuterium enrichment and it was suggested that methanesulfonic acid could have resulted from gas-phase ultraviolet irradiation of a precursor, carbon disulfide [2]. It was shown through a step wise chemical extraction protocol that the mass independent sulfur component was mostly carried by chondrule rims [1]. Large ^{33}S excesses in sulfides from achondrite meteoritic groups have been found [4]. The ^{33}S excess present in oldhamite from the Norton County aubrite ($\Delta^{33}S$ = 0.161 ‰) suggests that refractory sulfide minerals condensed from a nebular gas with an enhanced carbon to oxygen ratio [3]. Stellar nucleosynthesis and cosmic ray spallation have been ruled out as the cause of the observed $\Delta^{33}S$ anomaly [3]. Photochemical reactions in the early solar nebula was inferred to be a leading process to generate mass independent sulfur composition.

Several photolysis experiments have been carried out in the laboratory to understand the isotope effect in photolysis of sulfur bearing molecules relevant to presumed solar nebular conditions [5-7]. SO_2, H_2S and CS_2 photolysis was carried out using different kinds of UV lamps with λ 180 nm. All these experiments showed that significant mass independent sulfur ($\Delta^{33}S$ and $\Delta^{36}S$) have been produced through photolysis of sulfur bearing molecules. However, there is no experiment at short (vacuum) UV (VUV) wavelengths. Photodissociation by VUV photons are more relevant to the early solar environment. We have carried out photolysis experiments using VUV photons from the Chemical Dynamics Beamline at the synchrotron facility at the ALS on H_2S, one of the relevant sulfur carrying molecules in solar nebula. Here we report these new experiments, present the isotope results and discuss the implications.

Experimental: We performed H_2S photolysis experiment using a differential pumping system as described in [8] with a slight modification. A 60 cm long reaction chamber was used with three outlets. Two of them were used for gas in and out and the third one was used for a Baratron pressure gauge to sensitively monitor the pressure. An appropriate sized high purity (99.99%) Aluminum foil was rolled and inserted inside the reaction chamber (as an inner jacket). Small holes (¼ inch) were made on the ends of the jacket to match the chamber outlets. VUV photolysis of H_2S will produce elemental sulfur (as described later) and the purpose of this jacket is to collect the product elemental sulfur. The entire jacket is treated as a sample and collected after each photolysis experiment and a fresh jacket for each experiment was utilized. After photolysis, elemental sulfur was extracted from the Al-jacket by CCl_4 treatment. Elemental sulfur was converted to SF_6 through a series of chemical procedures including fluorination of silver sulfide as described in [1]. We performed pressure dependent photolysis of H_2S at Lyman-α line wavelength (121.6 nm, $D\ ^1A_1$ surface) as well as at 90 ($D\ ^1A_2$) and 157 ($A\ ^1B_1$) nm.
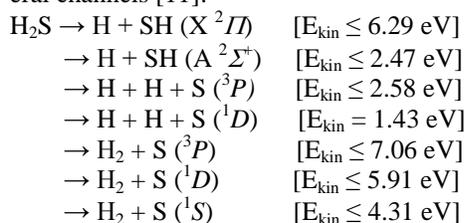
Results: Here we present the isotope data of pressure dependent H_2S photolysis at 121.6 nm VUV photons from the synchrotron. Elemental sulfur produced in all experiments show mass independent fractionation. $\Delta^{33}S$ depicted negative anomaly (maximum up to -0.7 ‰), where as $\Delta^{36}S$ trend show positive anomaly (maximum up to 1.8 ‰). Interestingly, both ^{33}S depletion and ^{36}S excess show a pressure dependent trend as shown in Figure 1.
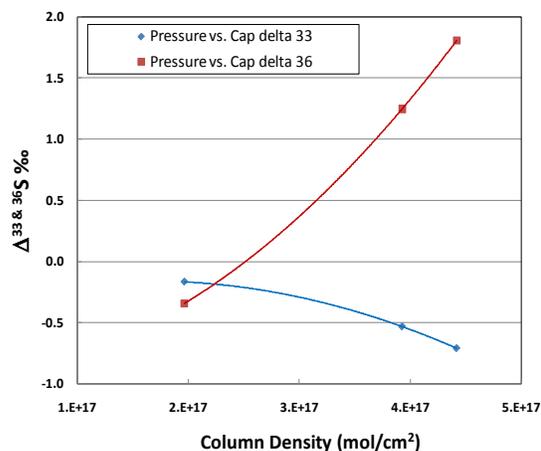
Figure 1. Column density (pressure) dependent sulfur isotopic fractionation measured in H_2S photolysis at 121.6 nm photons.

H_2S Photochemistry: H_2S absorption spectra show non-continuum features below 160 nm [9]. There are numerous bands in the VUV region of H_2S that are

linked to various Rydberg series [10]. There is a strong absorption band present at 121.6 nm and absorption in this band is followed by photo fragmentation via several channels [11]:

$$H_2S \rightarrow H + SH\ (X\ ^2\Pi) \quad [E_{kin} \leq 6.29\ eV]$$
$$\rightarrow H + SH\ (A\ ^2\Sigma^+) \quad [E_{kin} \leq 2.47\ eV]$$
$$\rightarrow H + H + S\ (^3P) \quad [E_{kin} \leq 2.58\ eV]$$
$$\rightarrow H + H + S\ (^1D) \quad [E_{kin} = 1.43\ eV]$$
$$\rightarrow H_2 + S\ (^3P) \quad [E_{kin} \leq 7.06\ eV]$$
$$\rightarrow H_2 + S\ (^1D) \quad [E_{kin} \leq 5.91\ eV]$$
$$\rightarrow H_2 + S\ (^1S) \quad [E_{kin} \leq 4.31\ eV]$$

The $D\ ^1A_1$ Rydberg state is known to be homogeneously predissociated by the dissociative $B\ ^1A_1$ state. A molecule predissociates with a certain probability when a bound electronic state couples to a continuous state. Coupling of a bound state to another intermediate bound state, which itself is predissociative may lead to electronic predissociation. Accidental near resonances may occur between vibronic levels of different electronic states. There is a striking correlation between those $^1B_1$ vibronic levels which undergo the most efficient heterogeneous predissociation and those which are accidentally resonant with a level of the $D\ ^1A_1$ state. This may be understood in terms of a-axis coriolis coupling between the B_1 and A_1 states giving rise to "mixed" states which, because of their partial A_1 character, are more susceptible to predissociation by the dissociative $B\ ^1A_1$ surface.

Accidental near resonances between vibronic levels of different electronic states can significantly enhance radiationless transfer into the final dissociative state; such resonances are responsible for the markedly vibronic level dependent heterogeneous predissociation rates and an unusual isotope effect in the predissociation of one particular electronic state of H_2S may occur [12] as observed. Moreover, SH fragments formed in two of the H_2S dissociation channels further dissociate to form S + H. Among two SH states, SH (A $^2\Sigma^+$) possesses predissociative character and forms S and H fragments through predissociation.

As discussed above, most dissociations are normal (or "homogenous"), however, some vibronic levels of the Rydberg states of H_2S and SH are *accidental predissociation*, as occurs in CO [11, 12]. It is different for CO because there is no homogeneous component. In CO photodissociation experiments we have observed a huge anomalous isotope effect due to *accidental predissociation* [8] at the 105.1 and 107.6 nm bands. The anomalous fractionation observed in the present H_2S photolysis experiment may be explained though the accidental predissociative channel similar to CO. However, the majority of the channels in this wavelength dissociate in a normal way and there is only a few channels contributing in an anomalous way that dilutes the overall isotope effect. Therefore, the

observed anomalous effect is much less compared to that observed for CO [8]. Predissociation from the excited states of H_2S is demonstrated to be a sensitive function of parent rotational level [12] and the rotational levels are greatly affected by pressure, favoring greater coupling at higher pressures that could lead to the pressure dependency in the isotope effect. Other absorption bands e.g. 90 and 157.6 nm are also accessed in these experiments and both of these bands also follow predissociative pathway and the results from those bands will be discussed in the conference.

Discussion: H_2S is one of the major sulfur-bearing species in the gas phase of the solar nebula and was a chemically active environment with VUV photochemistry and ion-molecule chemistry [13]. It was argued that the sulfur abundance in Jupiter reflects a depletion in H_2S that is the result of inner nebula sulfur chemistry under varying oxygen concentration [14]. VUV photodissociation of H_2S could change the isotopic composition of this major sulfur reservoir as shown through these experiments. The observed meteoritic sulfur isotopic anomaly may be due to the isotope shift of this precursor sulfur reservoir from which other sulfur bearing minerals have formed at different environmental settings within the solar nebula.

References: [1] Rai V. K. and Thiemens M. H. (2007) *Geochimica Et Cosmochimica Acta, 71,* 1341-1354. [2] Cooper G. W. et al. (1997) *Science, 277,* 1072-1074. [3] Rai V. K. et al. (2005) *Science, 309,* 1062-1065. [4] Farquhar J. et al. (2000) *Geochimica Et Cosmochimica Acta, 64,* 1819-1825. [5] Farquhar J. et al. (2001) *Journal of Geophysical Research-Planets, 106,* 32829-32839. [6] Farquhar J. et al. (2000) *Nature, 404,* 50-52. [7] Colman J. J. et al. (1996) *Science, 273,* 774-776. [8] Chakraborty S. et al. (2008) *Science, 321,* 1328-1331. [9] Ibuki T. et al. (1985) *Chemical Physics Letters, 119,* 327-330. [10] Price W. C. (1936) *The Journal of Chemical Physics, 4,* 147-153. [11] Schnieder L. et al. (1990) *The Journal of Chemical Physics, 92,* 7027-7037. [12] Ashfold M. N. R. et al. (1985) *Berichte der Bunsengesellschaft für physikalische Chemie, 89,* 254-261. [13] Fegley B. (1999) *Space Science Reviews, 90,* 239-252. [14] Pasek M. A. et al. (2005) *Icarus, 175,* 1-14.