Comment on "Experimental Test of Self-Shielding in Vacuum Ultraviolet Photodissociation of CO"
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Comment on "Experimental Test of Self-Shielding in Vacuum Ultraviolet Photodissociation of CO"

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Chakraborty *et al*. (Reports, 5 September 2008, p. 1328) suggested that experimental results provide support for CO photodissociation having caused the oxygen isotope ratio associated with the early solar nebula. We point out that further analysis is required before other mechanisms, such as self-shielding, are shown to be of little importance.

Chakraborty *et al*. (*1*) described experimental results pertaining to CO photochemistry in the early solar nebula. They suggested that CO photodissociation without self-shielding dominates. Here, we raise several points that indicate a need for further analysis before their interpretation can be accepted.

Observational (*2*, *3*) and theoretical (*4*, *5*) studies of interstellar diffuse clouds and the solar nebula reveal that self-shielding becomes important when an isotopolog reaches a column density of about 10^{14} to 10^{15} mol/cm^2. The experiments presented in (*1*) have column densities of 3.93 to 11.9 × 10^{17} mol/cm^2. Such values are large enough that even the rarer isotopologs [$^{12}C^{18}O$ and $^{12}C^{17}O$, with relative abundances of 0.2005 and 0.0373% compared with $^{12}C^{16}O$ (*6*)] are self-shielded to a large extent. Thus, the experimental conditions in (*1*) correspond to column densities where self-shielding is expected to dominate.

The remaining points center on the FWHM (full width at half maximum) of the beam giving a spread of about 2 nm. The CO spectrum contains numerous bands [some of which are noted in the supporting online material of Chakraborty *et al*. (*1*)], and at the wavelengths used in (*1*), several bands are probed at once. For instance, the 97.03 nm setting includes not only the $K - X$ (0-0) band but also the $L - X$ (0-0), $L' - X$ (1-0), and possibly $W - X$ (0-0) bands, all of which have substantial absorption cross sections or oscillator strengths (f values) (*7*, *8*). Furthermore, the photodissociation yield, which arises from a combination of band oscillator strength and predissociation rate, is a sensitive function of the bands being observed. The purely electronic part of the photodissociation phenomenon (the f value) will not depend on isotope substitution in its entirety, but in detail, individual bands have isotope specific f values. Therefore, while the sum of the f values for the $K - X$, $L - X$, and $L' - X$ complex of bands is the same for different isotopologs, the individual band f values vary for $^{12}C^{16}O$, $^{13}C^{16}O$, and $^{13}C^{18}O$ (*7*). Because the energies of rovibrational levels depend on isotopolog, predissociation rates for the same band, but different isotopologs, can be quite different (*8*, *9*). As noted in these references, there is an extensive body of results on these facets of the dissociation process.

All these factors need to be considered in the interpretation of the experimental results described by Chakraborty *et al*. (*1*). Only then can the consequences for the solar nebula be described with more confidence.

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