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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) concluded that an anomalously enriched atomic oxygen reservoir can be generated through carbon monoxide photodissociation without self-shielding. We show that this conclusion is based on the incorrect assumption that the spectral shifts of the 97.03-nanometers and 107.61-nanometers vibrational bands for $C^{16}O$, $C^{17}O$, and $C^{18}O$ are negligible and point out shortcomings of the low-resolution light source used in their experiments.

Inner solar system materials have distinct oxygen isotopic compositions, suggesting large-scale mixing between ^{16}O-rich and ^{16}O-poor reservoirs. Exactly how these reservoirs originated in the solar nebula has remained elusive since the discovery of the oxygen isotope anomalies in 1973 (*1*). Recently, building on earlier suggestions (*2*, *3*) and well-known astronomical observations [e.g., (*4*)], an intriguing model known as CO "self-shielding" has been invoked (*5*–*7*) to explain the observed oxygen isotope anomalies in the early solar system materials. The model is important in that the proposed mechanism and reaction pathways involve all major oxides in the early solar nebula (CO ~50%, H_2O ~33%, and the rest in oxides of other elements ~17%) (*8*). According to the model, oxygen isotope anomalies were produced with CO, stored in H_2O and reacted with dust, and discovered in meteorites today. Some of the predictions of the model have recently garnered observational support (*9*–*11*).

Chakraborty *et al*. (*12*) investigated whether CO self-shielding could produce the expected mass-independent oxygen isotope fractionation. They concluded that an anomalously enriched atomic oxygen reservoir can be generated through CO photodissociation without self-shielding. In the presence of optical self-shielding of vacuum ultraviolet (VUV) light, the fractionation associated with CO dissociation dominates over self-shielding. We disagree that Chakraborty *et al*.'s experimental results prove that self-shielding is not required and raise a number of issues for further discussion.

Self-shielding arises from the difference in the photoabsorption of $C^{16}O$, $C^{17}O$, and $C^{18}O$, that is, the photoabsorption spectra in the VUV range (90 to 110 nm) of interest are shifted for each of these isotopologs. After photoabsorption at VUV (below the ionization threshold of CO), excited CO can decay by fluorescence and photodissociation. Fluorescence is insignificant compared with photodissociation [see the difference between columns 5 and 6 of table S1 in (*12*) and section 4.1. in (*13*)]. Because decay of excited CO formed by photoabsorption of CO in this VUV region is mostly dominated by photodissociation compared to fluorescence (*13*), self-shielding should be predominately manifested in CO photodissociation.

Chakraborty *et al*. (*12*) build the case against self-shielding with their experiments on four different $C^{16}O$ vibrational bands centered at 94.12, 97.03, 105.17, and 107.61 nm. They showed mass-independent isotopic effects on all four bands, thus questioning the validity of the self-shielding model. We argue that the case for no self-shielding expected to occur on 97.03 nm and 107.61 nm in their experimental condition is weak. The absorption spectra of these bands recorded in a previous study were found to exhibit clearly resolved rotational structures. The vibrational bands for $C^{18}O$ are known to shift by 54, 0.18, 47, and 0.18 cm^{-1}, respectively, with respect to the corresponding bands for $C^{16}O$ (*14*–*16*). For the room temperature flow cell used in (*12*), the full-width at half-maximum (FWHM) originated from Doppler broadening is estimated to be $\Delta\nu_D \approx 0.12$ cm^{-1}. Combining this with the FWHM, $\Delta\nu_P \approx 0.03$ to 0.13 cm^{-1}, due to pressure broadening for the gas cell pressure of 100 to 400 mTorr gives the effective FWHM, $\Delta\nu_{eff} \approx$ 0.12 to 0.17 cm^{-1}, for the rotational transitions. Because these values are smaller than the spectral shift of 0.18 cm^{-1} found between the $C^{16}O$ and $C^{18}O$ isotopologs for the 97.03 and 107.61 nm vibrational bands, we can conclude that the rotational lines of the two isotopologs still have >50% separation, thus allowing self-shielding to be operative. Lowering the gas cell temperature to –66°C would lower the $\Delta\nu_D$ and raise the $\Delta\nu_P$ by 20% and is not expected to change the latter conclusion. Furthermore, the absorption, and thus the dissociation cross sections for the 107.61-nm band, are larger than that for the 105.17-nm band by a factor of 15, according to Letzelter *et al*. (*13*) [see also table S1 in (*12*)]. Therefore, the net effect for self-shielding on the 107.61-nm band can be more significant than on the 105.17-nm band, contrary to the key argument in (*12*).

The reaction products in (*12*) are unanimously enriched in ^{17}O and ^{18}O over ^{16}O relative to the starting composition, suggesting that the first-order abundance dependency (as opposed to the conventional mass dependency) of the oxygen isotope fractionation advocated by the CO self-shielding theory is proved by their experiment. However, Chakraborty *et al*. (*12*) developed an arbitrary criterion that the expected slope in the three-oxygen isotope plot must be strictly 1 for self-shielding to be operative. We find this argument problematic and such an expectation unwarranted. The criterion of a slope of unity [figure S2 in (*12*)] was based on an incorrect assumption that the absorption cross sections of $C^{16}O$, $C^{17}O$, and $C^{18}O$ are all the same. Due to the lack of experimental data, Chakraborty *et al*. (*12*) used the absorption cross section of $^{12}C^{16}O$ for all isotopologs of CO and applied a Beer-Lambert light absorption law to calculate the "expected" slope of unity. Such calculation is not appropriate to the self-shielding model. Instead, the results of Chakraborty *et al*. demonstrate that the cross sections of $C^{16}O$, $C^{17}O$, and $C^{18}O$ cannot be the same.

In reporting their experimental data, Chakraborty *et al*. (*12*) should have summed up yields at different bands normalized by time-integrated VUV photon fluence at different wavelengths, and weighted by the solar or interstellar VUV radiation field to get one oxygen isotopic composition. By varying the degree of "shielding" through changing gas cell pressure, a series of data points on the three-oxygen isotope plot needs to be obtained to test the self-shielding hypothesis.

Finally, Chakraborty *et al*. set their monochromator at a wavelength bandwidth of 2.2 nm or ≈2000 cm^{-1} (FWHM) at 105 to 107 nm. The VUV beam profile centered at 105.17 nm and 107.61 nm would overlap. This could explain why the slopes derived from the two wavelengths are identical [1.38 in figure 1 in (*12*)]. A modern VUV laser has an optical resolution in the range of 0.1 to 0.008 cm^{-1} (FWHM), which is several orders of magnitude higher than that of the VUV synchrotron light source used by Chakraborty *et al*. The brightness (intensity times resolving power) for an ultra-high-resolution VUV laser is more than six orders of magnitude greater than that of the broadband synchrotron light source. This will result in higher signal-to-noise ratios when studying weak transitions or transitions of less abundant isotopomers, such as $^{13}C^{17}O$. Because the high resolution

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offered by the VUV laser is needed to resolve the rotational absorption lines of CO in the VUV range of interest, the use of VUV laser should allow proper determination of the isotopic fractionation of oxygen atoms from CO self-shielding.

To test the hypothesized astrophysical sites of CO self-shielding at more relevant conditions, CO molecules should be controlled to a temperature range of 10 to 150 K, H_2 coincident shielding should be included, and isotopic exchange reactions must be avoided. None of these were achieved in (*12*). The fact that the slope regression lines in figure 1 in (*12*) do not regress through a 0 intercept (initial starting composition) suggests that the reaction (O + CO) at high temperature may alter the experimental results and complicate the interpretation of the data. Pandey and Bhattacharya (*17*) showed that anomalous oxygen isotope enrichments in CO_2 can result from the O + CO reaction alone, and the enrichment does not depend on the isotopic composition of O atom or the sources from which it is produced. Self-shielding may or may not ultimately explain the oxygen isotope anomalies for the early solar system, but we contend that Chakraborty *et al*. (*12*) have not adequately disproved the case for self-shielding for the reasons outlined above. Much work remains to be done with the potential of the molecular beam technique combined with high-resolution VUV laser in a windowless environment (*18*). Such experiments will shed new light on the oxygen isotope anomalies in the solar system that have been known for more than three decades but still lack a consensus explanation.

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