

**Comment on “Resonant dissociative electron transfer of the presolvated electron to CCl<sub>4</sub> in liquid: Direct observation and lifetime of the CCl<sub>4</sub><sup>\*-</sup> transition state” [J. Chem. Phys. 128, 041102 (2008)]**

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Citation: [The Journal of Chemical Physics](#) **129**, 027101 (2008); doi: 10.1063/1.2953723

View online: <https://doi.org/10.1063/1.2953723>

View Table of Contents: <http://aip.scitation.org/toc/jcp/129/2>

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# Comment on “Resonant dissociative electron transfer of the presolvated electron to $\text{CCl}_4$ in liquid: Direct observation and lifetime of the $\text{CCl}_4^{*-}$ transition state” [J. Chem. Phys. 128, 041102 (2008)]

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(Received 27 March 2008; accepted 10 June 2008; published online 11 July 2008)

[DOI: 10.1063/1.2953723]

In a recent paper, Wang *et al.*<sup>1</sup> report resonant dissociative electron transfer (RDET) to  $\text{CCl}_4$  in liquid ethanol. RDET involves resonant electron transfer, followed by dissociative electron attachment (DEA). Wang *et al.*<sup>1</sup> state that part of the motivation for their study was the importance of RDET processes for stratospheric ozone chemistry. Indeed,  $\text{CCl}_4$  is an important (anthropogenic) source gas for stratospheric chlorine under present atmospheric conditions.<sup>2</sup> Further, RDET/DEA processes have also been reported in molecular beam experiments, in submonolayers and nanoscale thin films for other chlorofluorocarbons (CFCs) of significance for stratospheric chlorine (in particular,  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$ ).<sup>3–5</sup>

However, the statement by Wang *et al.*<sup>1</sup> that “RDET plays a crucial role in [...] ozone-depleting reactions in the stratosphere” is misleading in two ways. First, there is no publication that argues for the importance of the DEA-induced loss of CFCs in the stratosphere outside the polar regions. Solely for the polar winter stratosphere, Lu and Sanche<sup>6</sup> suggested that the DEA-induced loss of CFCs might be a relevant process for stratospheric chemistry. Their proposed mechanism requires the presence of polar stratospheric clouds (PSCs) that only occur in the polar stratosphere in winter. Indeed, Lu and Sanche<sup>6</sup> state that “DEA processes are not believed to be significant in the general atmosphere.” Moreover, the observed patterns in the extrapolar stratosphere of CFCs,<sup>7–9</sup> of HCl,<sup>2,10</sup> and of ClO (Refs. 2 and 11) are incompatible with a significant loss of CFCs in the extrapolar lower stratosphere.

Second, the statements by Wang *et al.*<sup>1</sup> convey the impression that the importance of DEA for stratospheric ozone chemistry is an established scientific fact. This is clearly not the case. The importance of DEA for stratospheric polar ozone loss is indeed put forward in several papers,<sup>4–6</sup> but this view was criticized on the basis of the argument that no significant correlation exists between polar column ozone levels and cosmic ray intensity,<sup>12,13</sup> and that both observed CFC distributions and observed CFC– $\text{N}_2\text{O}$  correlations in the polar stratosphere are inconsistent with a destruction of CFC on PSC surfaces by DEA.<sup>12–14</sup> Furthermore, model calculations of polar ozone chemistry implementing<sup>13</sup> the mechanism of CFC destruction of Lu and Sanche<sup>6</sup> demonstrated that this mechanism can only have a limited impact on polar chemical ozone loss. However, DEA-induced destruction of HCl on PSC surfaces potentially has some influ-

ence on stratospheric polar chlorine chemistry.<sup>13</sup>

The argument that no significant correlation exists between polar ozone and cosmic ray intensity has been based so far on rather simple measures of polar chemical ozone loss such as data from a single station or total ozone averages over the polar cap for Spring (March and October).<sup>12,13</sup> Recently, it has been proposed that the minimum of daily average total ozone poleward of a given equivalent latitude would be a more useful measure of polar ozone loss.<sup>15</sup> Figure 1 shows a comparison of cosmic ray intensity with this measure of polar ozone loss over the time period of 1979–2005. This comparison corroborates the findings of earlier studies<sup>12,13</sup> indicating that there is no significant correlation between cosmic ray intensity and polar ozone.

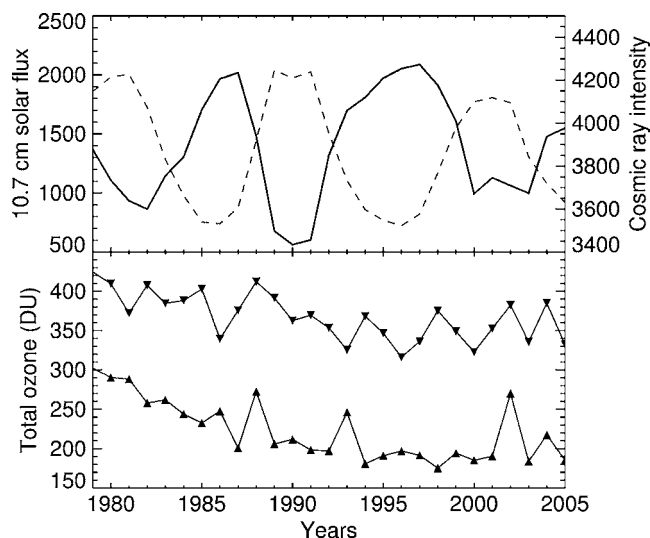


FIG. 1. The variation over the time period 1979–2005 of cosmic ray intensity (solid line, top panel), solar intensity (dashed line, top panel), and minimum of daily average column ozone in the polar region (bottom panel). Column ozone is commonly measured in Dobson units (DU), where one DU is defined as  $2.69 \times 10^{16}$  ozone molecules/ $\text{cm}^2$ . The pressure-corrected neutron count (counts/min) at Climax, Colorado is shown as a measure of cosmic ray intensity and the 10.7 (2800 MHz) solar flux adjusted to 1 A.U. in units of  $10^{-21} \text{ W m}^{-2} \text{ Hz}^{-1}$  as a measure of solar intensity. The minimum values of daily average column ozone poleward of  $60^\circ$  equivalent latitude for March in the Arctic and October in the Antarctic were taken from Müller *et al.* (Ref. 15). Winters in which the vortex broke up before March (1987, 1999, and 2001) are not shown for the Arctic ozone time series.

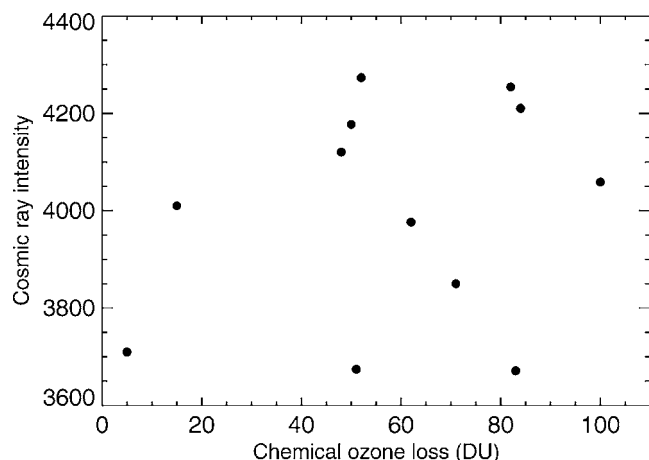


FIG. 2. Scatter plot of chemical ozone loss in the core of the Arctic vortex in the lower stratosphere for the time period 1992 to 2005 (no data are available for 2001 and 2004) deduced from ozone-tracer relations (Refs. 16–18) against the cosmic ray activity. As in Fig. 1, the neutron count (counts/min) at Climax is taken as a measure of the cosmic ray intensity.

When sufficient information is available, it is always preferable to employ sophisticated measures of chemical polar ozone loss that allow the signal of *chemical* ozone change to be isolated from ozone changes caused by transport.<sup>15,19,20</sup> Such measures of chemical ozone loss show a close correlation with the potential for heterogeneous chlorine activation on PSC.<sup>18–21</sup> In Fig. 2, for the time period of 1992–2005, chemical ozone loss values are plotted against cosmic ray activity; clearly, there is no correlation (the correlation coefficient is 0.21).

In summary, I argue that the relevance of the DEA-induced destruction of CFCs on PSC surfaces as a pathway to the formation of the ozone hole should not currently be a motivation for studies of DEA on CFC molecules. In any event, the relevance of this process as a key mechanism for the formation of the ozone hole should be presented as an issue debated in the scientific literature rather than as an established scientific fact.

The cosmic ray intensities were obtained from the space physics data system of the University of New Hampshire supported by the National Science Foundation under Grant No. ATM-0339527 ([http://ulysses.sr.unh.edu/NeutronMonitor/neutron\\_mon.html](http://ulysses.sr.unh.edu/NeutronMonitor/neutron_mon.html)). The 10.7 cm solar flux was obtained from the UK Solar System Data Centre ([http://www.ukssdc.ac.uk/wdccc1/wdc\\_menu.html](http://www.ukssdc.ac.uk/wdccc1/wdc_menu.html)).

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