Insertion and abstraction mechanisms in collisions of O^- with H_2^+ and CH^+

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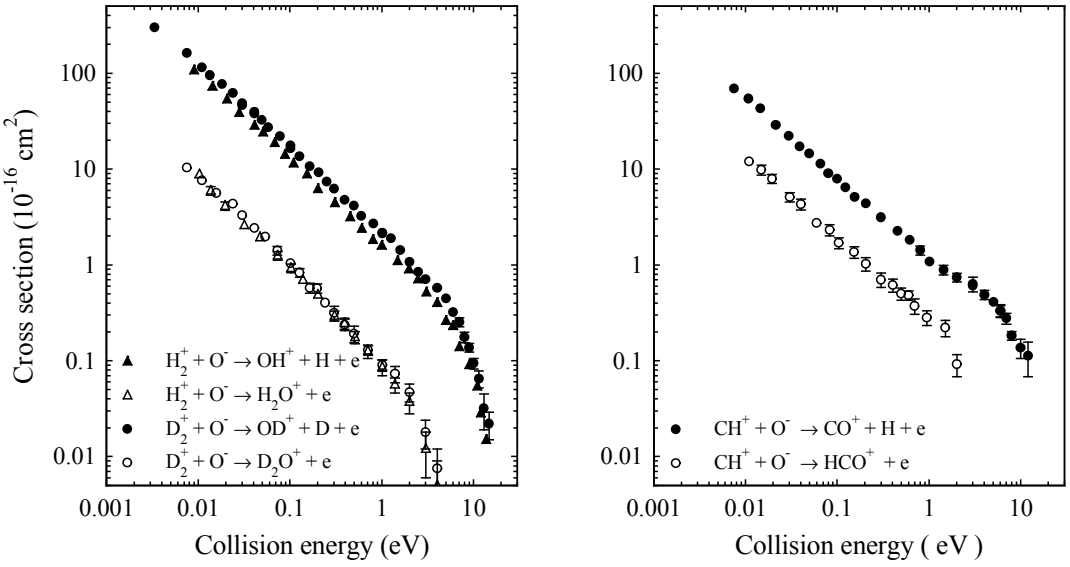
Our merged ion beams set-up [1] has been used to measure the total cross section of the following reactions:

$$H_2^+ + O^- \rightarrow H_2O^+ + e \,/\, OH^+ + H + e \qquad (1)/(2)$$
$$D_2^+ + O^- \rightarrow D_2O^+ + e \,/\, OD^+ + D + e \qquad (3)/(4)$$
$$CH^+ + O^- \rightarrow HCO^+ + e \,/\, CO^+ + H + e \qquad (5)/(6)$$

This study completes our previous investigation of associative ionisation (AI) in the CNO sequence [2,3] (reactions of O^- and C^- with C^+, N^+ and O^+). Reactive cross sections (2),(4),(6) are found to be rather large at thermal energy (>10^{-15} cm^2), and exceed the AI cross sections by an order of magnitude for reactions (1) and (3), and about a factor of 4 for reaction (5). They all behave as 1/E as a result of Coulomb attraction between reactants, and AI cross sections are more rapidly falling above the detachment threshold of O^-.

Furthermore, a clear isotope effect was found, when comparing reactions (2) and (4), the latter having a larger cross section by a factor of 1.4, suggesting an influence of the velocity of the reactants at a given collision energy. Deuterated species may have more time to rearrange and/or to undergo autoionisation in the reactive domain of the potential energy surface. AI cross sections on the other hand do not differ significantly.

The strong predominance of the reactive channel may stem from the fact that the collinear approach corresponds to the asymmetric stretch of the complex and does not lead to water cation formation, which is only possible via an insertion mechanism [4]. On the other hand, all geometries are likely to contribute to the formation of HCO^+ and its isomer, HOC^+, undistinguishable in the present experiment.



References

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