Negative Ion Loss. Loss mechanisms for negative ions include photodetachment (cf. Table B.12), recombination with positive ions (cf. Table B.17) and associative detachment with neutrals (cf. Table B.19).

For the photodetachment calculations, we adopt a cross-section σ (cm^2) that depends on the photon energy ϵ (eV), according to the empirical formula:

$$\text{for } \epsilon \geq \text{EA}, \sigma = \sigma_\infty (1 - EA/\epsilon)^{0.5}, \tag{E24}$$

where σ_∞ denotes the asymptotic cross-section (cm^2) for large photon energies and EA the electron affinity (eV) of the corresponding neutral (Millar et al., 2007). Ion traps have recently been successfully employed to study absolute photodetachement cross-sections for O^- and OH^- (Hlavenka et al., 2009), C_2H^-, C_4H^- and C_6H^- (Best et al., 2011), and CN^- and C_3N^- (Kumar et al., 2013).

For these ions, σ_∞ is derived from fits to the measured cross-sections using Equation (E24) and literature electron affinities. For the other ions for which no experimental data are available, we assume σ_∞ to be equal to 10^{-17} cm^2. The electron affinities and asymptotic cross-section values are given in Table (B.12).

The parameterization of Hickman (1979) for the recombination of negative with positive ions has been revised by Miller et al. (2012), following a new set of measurements. We therefore use the updated expression,

$$k = 2.8 \times 10^{-7} EA^{-0.13} \mu^{-0.5} (T/300)^{-0.9} \text{ cm}^3\text{s}^{-1}, \tag{E25}$$

where EA is the electron affinity of the corresponding neutral, μ is the reduced mass of the collision partners and T is the temperature of the gas. For the ions of interest here, we obtain rate coefficients varying from 5×10^{-8} to 3×10^{-7} cm^3 s^{-1} at 300 K.

We now consider reaction products and, in the absence of data, we use the

Table B.12 | Mass-to-charge (m/z), electron affinities (EA) and asymptotic cross-sections σ_0 used in the calculation of the photodetachment cross-sections.

Ion species	m/z (u)	EA (eV)	σ_0 (cm^2)	Ref.
H^-	1	0.75	1.0×10^{-17}	[1, 2]
CH_2^-	14	0.65	1.0×10^{-17}	[3, 2]
CH_3^-	15	0.08	1.0×10^{-17}	[4, 2]
C_2H^-	25	3.0	8.8×10^{-18}	[5]
C_4H^-	49	3.6	7.7×10^{-18}	[6, 5]
C_6H^-	73	3.8	4.8×10^{-18}	[6, 5]
CN^-	26	3.9	2.8×10^{-17}	[7, 8]
C_3N^-	50	4.3	5.2×10^{-17}	[9, 8]
C_5N^-	74	4.5	1.0×10^{-17}	[9, 2]
O^-	16	1.5	1.2×10^{-17}	[1, 10]
OH^-	17	1.8	3.3×10^{-17}	[11, 10]

Notes. The asymptotic cross-sections for O^- and OH^- are derived from fits to Eq. (E.15) using the literature electron affinities shown in column 2, and measured cross-sections at 1.87 and 2.33 eV for O^- and 1.87 and 1.96 eV for OH^- (cf. [10]).

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