Rare isotopologues

The collisional excitation of a rare isotopologue (*e.g.* HDO + H$_2$) takes place on the same full-dimensional Born-Oppenheimer potential energy surface (PES) as the main isotopologue (H$_2$O + H$_2$). Excitation differences between isotopologues therefore reflect the dynamical (nuclear) effects. Within the rigid-rotor approximation, these involve small changes in:

- the center of mass position

- the reduced mass of the total system

- the energy level spacing (rotational constants)

- the rotation of the principal axes of inertia (broken symmetry effects)

- the state-averaged geometry (zero-point vibrational effects)

All these effects were investigated by Wiesenfeld et al. (2011) in their study on the rotational excitation of the water deuterated isotopologues (HDO and D$_2$O) by H$_2$ below 100 K. In general, H$_2$O, HDO and D$_2$O rotational de-excitation rate coefficients were found to differ by a factor of $\sim 2 - 3$ for the dominant transitions. These differences were attributed to, first, the change in reduced mass and rotational constants and, second, the change in internal geometry and the shift of centre of mass. When the symmetry of the main isotopologue is broken, like in HDO, the main effect becomes the rotation of the principal axes of inertia. In this case, the collisional selection rules are also modified.

H/D isotopic effects were also investigated by Denis-Alpizar et al. (2015) in the case of the rotational excitation of HCN and DCN by He below 100 K. The substitution of H by D was found to modify the HCN de-excitation rate coefficients by typically 10-30% for the dominant transitions. As expected, H/D isotopic effects scale with the relative change in target mass and rotational constants and can be neglected for large and heavy molecules. Heavy atom isotopic effects were also studied by Dagdigian (2022) for the isotopologues of CO: ^{13}C^{16}O, ^{12}C^{17}O and ^{12}C^{18}O. The isotopologue-specific rate coefficients were found to differ by typically 10-20%. Except in the special case of hyperfine transitions (see below), heavy atom isotopic effects can thus be considered as negligible, as expected from the corresponding small change in mass and rotational constants. Finally, isotopic substitution can also modify the hyperfine structure of a given molecular target when the total nuclear spin I is changed. This is in particular the case when substituting ^{12}C ($I = 0$) with ^{13}C ($I = 1/2$) or ^{14}N ($I = 1$) with ^{15}N ($I = 1/2$), as considered by Flower and Lique (2015) in the case of CN.

EMAA provides de-excitation rate coefficients for a number of rare isotopologues including the isotopic elements D, ^{13}C, ^{15}N, ^{18}O, ^{34}S, ^{38}Ar, ^{40}Ar. When a set of collisional data for a rare isotopologue, *e.g.* H^{13}CO$^+$, is not available, the de-excitation rate coefficients of the main isotopologue (HCO$^+$) are provided and the actual data ('HCO$^+$ data') is specified with the reference. On the other hand, EMAA always provides the isotopologue-specific spectroscopic data.

References

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