MULTIPOLE-MOMENT EFFECTS IN COLD ION CHEMISTRY: THE REACTIONS OF He^+ WITH CO_2 AND OCS

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Exothermic, barrier-free ion-molecule reactions proceed with high rate coefficients even at very low temperatures. These reactions are typically described using the Langevin model, which predicts the rate coefficient to be independent of the temperature or the collision energy (E_{coll}). At near-zero collision energies, however, a strong E_{coll} dependence of the capture rate coefficients can arise because of the interaction between the charge of the ion and the electric dipole and quadrupole moments of the neutral molecule. To reach collision energies ($E_{\mathrm{coll}}/k_{\mathrm{B}}$) from 15 K down to $\sim$ 200 mK, we use a merged-beam approach and study ion-molecule reactions within the orbit of a highly excited Rydberg electron, which prevents the heating up of the ions by stray electric fields without influencing the reaction.

In this contribution, we present the results of the reactions between He^+ and two linear triatomic molecules that differ by a single atom: CO_2 and OCS. The rate of the $He^+ + CO_2$ reaction decreases by $\sim 35\%$ at low collision energies, whereas the rate of $He^+ +$ OCS displays a marked $\sim 60\%$ increase. We interpret our results in the realm of an adiabatic-channel capture model, inspired by earlier theoretical work[1,2], as arising from interactions between the ion charge and the quadrupole and dipole moments of CO_2 and OCS. These observations are in agreement with our previous studies of reactions involving He^+ and different small molecules, in which we found that for polar reactants, such as NH_3, a pronounced increase in the rate coefficient is observed with decreasing E_{coll}[3], while for molecules with a negative quadrupole moment, such as N_2 and CO, the reaction yield decreases with decreasing E_{coll}[4,5].

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