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Sensitive detection of metastable NO and N_2 by reactive collisions with laser-excited Li

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Atoms and molecules in electronically excited states are referred to as metastable, if their decay to lower-lying states is forbidden by electric-dipole selection rules. Owing to their high electronic energy, metastable species can induce the ionization of other atoms or molecules upon collision, a process often referred to as autoionization. Autoionization processes are of great importance in the Earth's upper atmosphere, where metastable atoms and molecules are generated by UV photolysis and electric discharges. To date, the properties of many metastable species are still poorly understood.

In a proof-of-principle experiment, we demonstrate that metastable nitric oxide molecules, NO(a), and metastable N_2 molecules, generated inside a pulsed, supersonic beam, can be sensitively detected by reactive gas-phase collisions with ground- and excited-state Li atoms. Since the internal energy of NO(a) in the rovibrational ground state is lower than the ionization potential of Li in the 2^2S_{1/2} electronic ground state, autoionization is strongly suppressed for NO(a)-Li(2^2S_{1/2}) collisions. Using this detection method, we infer densities of only 300 NO(a) molecules/cm^3 and 3x10^4 metastable N_2 molecules/cm^3 in the interaction region. Our results also allow for an estimate of the vibrational-state population of NO(a) prior to the collision process.

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