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This Week's Citation Classic

Schmeltekopf A L, Fehsenfeld F C, Gilman G I & Ferguson E E. Reaction of atomic oxygen ions with vibrationally excited nitrogen molecules.
Planet. Space Sci. **15**:401-6, 1967.
[Inst Telecom. Sci. and Aeron., Environmental Sci. Serv. Admin., Boulder, CO]

The authors measured the dependence of the reaction $O^+ + N_2$ NO+ — + N on the vibrational temperature of N_2 from 300 to 6000K. The rate constant increased by more than a factor of 30 over this range. This reaction controls electron loss in the earth's atmosphere, so that the measurement has had a major impact on aeronomy. [The *SCI*® indicates that this paper has been cited over 85 times since 1967.]

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"We are pleased to have our paper referred to as a *'Citation Classic'* As is often the case in science, our discovery of the very large vibrational effect on the $O^+ + N_2$ reaction was accidental. We had developed the flowing afterglow technique for ion-molecule reaction rate measurements in 1964 and were systematically determining rate constants for ionospheric reactions.[1,2] While measuring the reaction $O_2^+ + N–NO^+ + O$ by discharging N_2 added to the flow tube to produce N atoms, we noticed a greatly enhanced loss of O^+ ions. After some puzzlement we realized that this unexpected finding had to be due to enhanced vibrational excitation of N_2 by the discharge. The large N_2 vibrational excitation cross section via a negative ion resonance was an exciting new topic in atomic physics. The $O^+ + N_2 – NO^+ + N$ reaction is the most important one in the ionosphere, since it controls the electron loss at the electron density maximum. The implications of large changes in the rate constant were significant.

"While qualitative appreciation of the large vibrational effect was rather immediate, it took about a year's time to obtain quantitative measurements. We observed that the nitrogen vibrational levels were in a Boltzmann distribution, which we did not anticipate. We learned how to measure the vibrational temperature, which we did spectroscopically using helium metastable ionization-excitation of the nitrogen. This remains to date the only ionatom interchange reaction measured as a function of the vibrational temperature of the neutral reactant.

"This result has been applied to many ionospheric problems, such as electron loss during auroras, magnetic storms, and other disturbed atmospheric conditions. The large vibrational effect also explained a large spread in several earlier measurements of the rate constant. These had involved variable degrees of vibrational excitation, whose presence and role was not recognized. Because of the ionospheric importance of the reaction, we have subsequently measured it as a function of gas temperature up to 900K and as a function of kinetic temperature to ~23,000K, making this the most exhaustively studied ion-molecule reaction. Recently, analysis of simultaneously measured ion and neutral composition and solar flux from the AtmosphereExplorerC satellite has substantiated the laboratory measurements of this reaction."[3]

1. **Ferguson E E, Fehsenfeld F C, Dunkin D B, Schmeltekopf A L & Schiff H I.** Laboratory studies of helium ion loss processes of interest in the ionosphere. *Planet. Space Sci.* **12**:1169-71, 1964.
2. **Ferguson E E, Fehsenfeld F C & Schmeltekopf A L.** Flowing afterglow measurements of ionneutral reactions. *Adv. Atomic Molec. Phys.* **5**:1-56, 1969.
3. **St. Maurice J P & Torr D G.** Nonthermal rate coefficients in the ionosphere: the reactions of O with N_2, O_2 and NO. *J. Geophys. Res.* **83**:969-77, 1978.