MILLIMETER-WAVE SPECTRUM OF FeNO($X^2\Delta_i$) IN THE GROUND AND VIBRATIONALLY EXCITED STATES

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Rotational spectrum of the FeNO radical generated by the ultraviolet photolysis of $Fe(CO)_2(NO)_2$ was measured in the millimeter-wave region. The measurements were performed in the supersonic jet expansion with a millimeter-wave multi-reflection cell. Three rotational transitions ($J = 9.5 - 8.5 \sim 11.5 - 10.5$) in the $\Omega = 5/2$ spin substate of the $X^2\Delta_i$ ground vibronic state were measured in the frequency region of 87−106 GHz. The rotational lines were split into 2 components ($\Delta F = 0, +1$) due to the hyperfine interaction of the N($I = 1$) nucleus. In the upper spin substate $\Omega = 3/2$ ($A_{\rm SO} \approx -417$ cm^{-1}) of the electronic ground state, seven rotational transitions ($J = 28.5-27.5 \sim 34.5-33.5$) were measured with a conventional absorption cell (2.7 m in length) in the room temperature. Moreover, six rotational transitions ($J = 28.5 - 27.5 \sim 33.5 - 32.5$) in the ν_2 vibrationally excited state (for both P = 3/2 and 7/2 components) and the high-J lines of $\Omega = 5/2$ spin substate of the ground state were also observed with the conventional absorption cell. Rotational line intensity of the $\Omega = 3/2$ substate was about one tenth of that for the $\Omega = 5/2$ substate because of the large spin-orbit interaction constant $A_{\rm SO}$. Molecular constants, including the rotational constant B, centrifugal distortion constant D, hyperfine constant $a + b_F/4 + c/6$, and vibration rotation constant α_2, were determined by a least squares fitting of the observed spectrum. The electronic ground state of FeNO was confirmed to be $X^2\Delta_i$ as in the case of CoCO and the unpaired electron is localized almost in the 3*d* orbital of Fe. The hyperfine constant of FeNO, $a + b_F/4 + c/6 = -1.359(57)$ MHz, is much smaller than that of CoCO, 466.073(54) MHz. Rovibrational transitions were also observed by the infrared diode laser spectroscopy with the ultraviolet photolysis of $Fe(CO)_2(NO)_2$.[a]

[a]Radicals and Ions session in the present symposium.