ELECTRONIC SPECTRA OF RhH AND RhD

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Electronic transitions have been observed with LIF techniques in a supersonic molecular beam of He doped with H_2 or D_2 and laser-ablated Rh vapor. Bands of RhH have been found near 464.73 and 438.38 nm, which are assigned as (0,0) and (1,0) vibrational bands of a $^3\Delta_3$ - $X^3\Delta_3$ electronic transition. There is a sudden disapperance of the rotational structure in the (1,0) band of RhH above $J'=7$ and the spectra associated with higher vibrational levels in the excited states are missing. These observations are attributed to predissociation. Its onset agrees with an *ab intio* calculation of 22 664-23 955 cm^{-1}[a] and the estimate of 20 650 $\pm$ 1 750 $cm^{-1}$from thermochemistry.[b] The RhH(0,0) band also shows irregular Λ-doubling. The corresponding (0,0) and (1,0) transitions in RhD appear at 463.40 and 443.02 nm. Analyses of the spectra indicate that the ground state of RhH is an inverted $^3\Delta$ state, which is believed to derive from the electronic configuration ...$\delta^3\pi^4\sigma^1$, and provide the following RhH molecular constants(cm^{-1}): B_0''=6.546 [r_0''=0.1610 nm], B_0'=6.175, B_1'=5.823, ω_e''=1927, $\omega_e''x_e''$=35.7, ω_e'=1645, $\omega_e'x_e'$=174. The observed ground state symmetry and internuclear distance agree with *ab initio* predictions.[a] Six additional bands have been found for RhD: near 445.15 nm(Ω'=3 - Ω''=3), 428.05 nm(Ω'=3 - Ω''=3), 427.83 nm(Ω'=3 - Ω''=3), 424.40 nm(Ω'=2 - Ω''=3), 422.58 nm(Ω'=3 - Ω''=3), and 409.24 nm(Ω'=4 - Ω''=3).

[a] F. Illas, J. Rubio, J. Canellas and J. M. Ricart, J. Chem. Phys., 93, 2603(1990)
[b] P. B .Armentrout and J. L. Beauchamp, Acc. Chem. Res., 22, 315(1989)