EMISSION SPECTRA OF NiH SHOWING EXTENSIVE ELECTRONIC ENERGY TRANSFER BETWEEN EXCITED STATES

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Fourier transform resolved laser induced fluorescence spectra have allowed us to investigate the low-lying electronic states of NiH arising from the Ni($3d^9$ $4s^1$) configuration. Although laser excitation with a single mode laser should promote the molecule (formed in a hollow cathode discharge running at 1 torr pressure, with 10% H_2 in argon) to a unique excited state that should be readily identifiable from the work of Kadavathu and co-workers,[a] the resolved fluorescence spectra are unexpectedly complex. Efficient energy transfer occurs between excited electronic states, retaining only isotopic selectivity. Analysis of the spectra locates energy levels up to 8000 cm^{-1} above v=0 in the electronic ground state (X $^2\Delta_{5/2}$), from all components of the $^2\Sigma$, $^2\Pi$ and $^2\Delta$ states forming the supermultiplet complex studied by Gray et al.[b] Measurements have been made so far for ^{58}NiH and ^{60}NiH. To observe heavier isotopes of nickel, an intracavity fluorescence experiment is required. Signals are increased by a factor 25, but the signal/noise ratio in Fourier spectra is disappointing when compared with intracavity excitation results.[cd] Nevertheless, this work has allowed us almost to double the range of known energy levels below 10000 cm^{-1} for NiH.

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[b] J. A. Gray, M. Li, T. Nelis, and R. W. Field, J. Chem. Phys., 1991, 95 7164 (1991)
[c] E. J. Hill and R. W. Field, J. Chem. Phys., 93 1 (1990)
[d] L. C. O'Brien and J. J. O'Brien, Astrophys. J., 621 554 (2005)