THE ACCURATE DETERMINATION OF MAGNETIC HYPERFINE AND ZEEMAN PARAMETERS FOR $^2\Pi$ DIATOMIC MOLECULES FROM EXPERIMENTAL DATA

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The Hamiltonian for a $^2\Pi$ state of a diatomic molecule has an indeterminacy between the parameters γ and A_D, which can be removed by a unitary transformation to give either an effective $\tilde{\gamma}$ with $\tilde{A}_D = 0$ or an effective $\tilde{A}_D$ with $\tilde{\gamma} = 0$.[a] The present work extends this transformation to the magnetic hyperfine and Zeeman terms in the Hamiltonian. Among the hyperfine contributions, the term $b\mathbf{I}\cdot\mathbf{S}$ is particularly affected by the transformation. Care is therefore required in relating the observed value $\tilde{b}$ to the electron spin density. Similar considerations apply to observed Zeeman parameters. Applications to the spectra of NO[b] and FO[c] will be presented.

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[b] T. D. Varberg, F. Stroh, and K. M. Evenson, *J. Mol. Spectrosc.* **196**, 5 (1999).
[c] F. Tamassia, J. M. Brown, and K. M. Evenson, *J. Chem. Phys.* **110**, 7273 (1999).