

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

FILIPPO TAMASSIA, *Dipartimento di Chimica Fisica ed Inorganica, Facoltà di Chimica Industriale, Università di Bologna, Viale del Risorgimento 4, 40136, Bologna, Italy*; JOHN M. BROWN, *The Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford, OX1 3QZ, UK*; JAMES K. G. WATSON, *Steeacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6*.

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.

^aJ. M. Brown and J. K. G. Watson, *J. Mol. Spectrosc.* **65**, 65 (1977).

^bT. D. Varberg, F. Stroh, and K. M. Evenson, *J. Mol. Spectrosc.* **196**, 5 (1999).

^cF. Tamassia, J. M. Brown, and K. M. Evenson, *J. Chem. Phys.* **110**, 7273 (1999).