Detailed study of pyridine at the C 1*s* and N 1*s* ionization thresholds: The influence of the vibrational fine structure

C. Kolczewski
Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

R. Püttner
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

O. Plashkevych and H. Ågren
Theoretical Chemistry, Royal Institute of Technology, S-10044 Stockholm, Sweden

V. Staemmler
Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

M. Martins
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

G. Snell
Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720 and Department of Physics, Western Michigan University, Kalamazoo, Michigan 49008-5151

A. S. Schlachter and M. Sant'Anna
Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720

G. Kaindl
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

L. G. M. Pettersson
Department of Physics, Stockholm Center for Physics, Astronomy and Biotechnology (SCFAB), Stockholm University, 10691 Stockholm, Sweden

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High resolution, vibrationally resolved, near-edge x-ray absorption fine structure (NEXAFS) spectra at the C 1*s* and N 1*s* ionization thresholds of pyridine and deuterated d_5-pyridine in the gas phase have been recorded. The high resolution of 65 meV (150 meV) at the C *s* (N 1*s*) ionization thresholds reveals vibrational structures in the spectra. Detailed *ab initio* and density functional theory (DFT) calculations were performed to interpret the experimental spectra and to assign the observed peaks. In particular we focused on the previously unexplained intensity ratio for the two components of the C $1s \rightarrow 1\pi^*$ transition. For this transition the vibrational structure is included through a linear coupling model in the DFT calculations and leads to the experimentally observed ~2:3 intensity ratio between the two π^* components in the C 1*s* spectrum rather than the ~3:2 ratio obtained without vibrational effects. After inclusion of relaxation effects in the excited states, in addition to the vibrational effects, both theoretical methods yield almost perfect agreement with experiment. [DOI: 10.1063/1.1397797]