SYMMETRIC ROTOR LINE STRENGTH FACTORS IN ZEKE-PFI SPECTRA

SERGEY I. PANOV, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139*; and TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, OH 43210*.

In the two color ZEKE-PFI study[a] of the $\mathrm{CdCH_3}$ radical well-resolved K rotational structure has been observed in some vibronic states. We have extended the previous theoretical formulation of the selection rules[b] to cover the observed transitions. An important result is that the selection rules are determined by the vibronic structure of the intermediate state of the neutral from which the ionizing ZEKE transition occurs. For example, the Hönl-London-type line strength factor S for the ionizing $e-e$ vibronic transition can be written as

$$S\left(N^+K^+p^+;NKp\right) \;=\; \delta_{p^+,-p}\,(2N^+ + 1)(2N+1) \sum_{l_A\,,\,\lambda_A=1,-2,4,-5,\ldots} a^2_{l_A\lambda_A}\; A_{l_A NN^+} \begin{pmatrix} N^+ & l_A & N \\ -K^+ & -\lambda_A & -K \end{pmatrix}^2 ,$$

where p denotes the state's parity and the $A_{l_A NN^+}$ are determined by the wavepacket composition of the Rydberg state that is subsequently field ionized. The $a_{l_A\lambda_A}$ are coefficients in an expansion of the neutral state's vibronic wavefunction $|\phi\rangle$ in terms of a core wavefunction $|\phi_{cor}\rangle$, its vibrational wavefunctions $|\phi_{vib}\rangle$, and its single electron atomic wavefunctions $|l_A\,,\lambda_A\rangle$:

$$|\phi\rangle = |\phi_{cor}\rangle \sum_{l_A\,,\lambda_A} a_{l_A\lambda_A}\,|\phi_{vib}\rangle\,|l_A\,,\lambda_A\rangle$$

[a] S. I. Panov, David E. Powers and T. A. Miller *J. Chem. Phys.* **108** 1335 (1998).
[b] Klaus Müller-Dethlefs *J. Chem. Phys.* **95** 4821 (1991).