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THEORETICAL SIMULATION OF THE ZEKE SPECTRA OF NAPHTHALENE FROM SINGLE VIBRONIC LEVELS OF S_1

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We present the simulations and analysis of the two-color ZEKE spectra of naphthalene, performed with the help of quantum chemical calculations of molecular parameters followed by the modelling of vibronic intensities. *Ab initio* and semi-empirical calculations were carried out to obtain molecular structures of neutral and ionic naphthalene, and vibronic perturbations that couple the electronic states. It is shown that the intensities, simulated with a model based on the perturbative expansion of vibronic states, nicely reproduce the observed spectra and contribute to reassign some of the ground state frequencies of naphthalene cation.

Keywords: ZEKE spectra; simulations; semi-empirical calculations; *ab initio* calculations; vibronic interactions

The measurement of zero kinetic energy (ZEKE) photoelectron spectra depends on the long life-time of the highly excited Rydberg states of molecules [1] which lie just below the threshold for photoionization. Since Rydberg electrons interact only marginally with the core of the molecule, the vibronic structure of the ZEKE spectra generally reflects the geometry change between the neutral species and the ion. In this sense, the Franck–Condon (FC) mechanism usually suffices to explain the observed vibronic intensities.

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The two-color ZEKE spectra of naphthalene recently measured by Cockett *et al.* [2] by pumping several single vibronic levels of S_1, show clear deviations from the $\Delta v = 0$ propensity rule usually observed for nontotally symmetric modes (NTS). This indicates that other mechanisms are operating, and suggests the presence of non-negligible vibronic coupling effects.

We have recently analyzed the vibronic structure of the single vibronic level (SVL) fluorescence spectra of naphthalene [3] by performing simulations based on the perturbative expansion of vibronic states. The agreement between observed and simulated spectra was very satisfactory and here we have extended the model of Ref. [3] to simulate the vibronic structure of ZEKE spectra of naphthalene. A schematic representation of the states involved in the model is presented in Figure 1, where $V(b_{1g})$ are the vibronic perturbations that couple S_1 and D_0 to higher excited states. As shown in Figure 1, the mechanism activates the FC forbidden $S_1(0,\ B_{3u}) \rightarrow D_0(1, B_{1u})$ vibronic transition by borrowing intensity from the $S_2 \rightarrow D_0$ and the $S_1 \rightarrow D_1$ transitions. The vibronic perturbations that couple the S_1 and D_0 states to low-lying excited states were evaluated with the CNDO/S hamiltonian augmented with Configur-

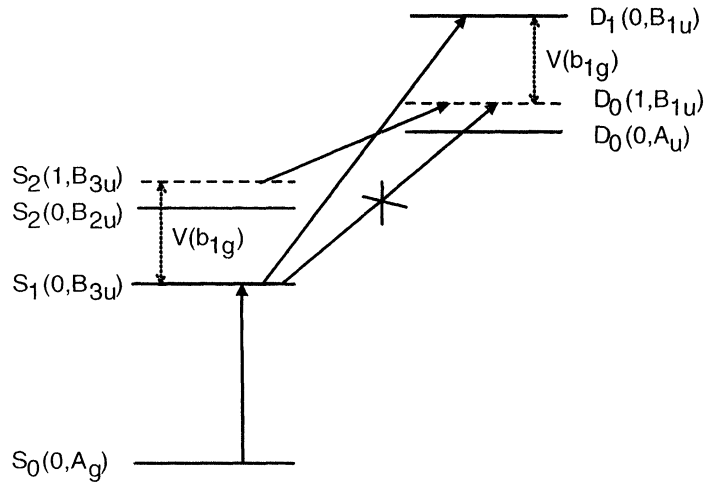

FIGURE 1 Schematic representation of the model employed to simulate the vibronic activity in the ZEKE spectra of naphthalene.

ation Interaction calculations [5], while the remaining molecular parameters required for the simulations were computed at the *ab initio* level of theory by using the Gaussian 92 suite of programs [4].

In Figure 2 we present the simulations of the ZEKE spectra originated from the 0_0, $(8b)_1$, $(9a)_1$ and $(8a)_1$ vibronic levels of S_1. The

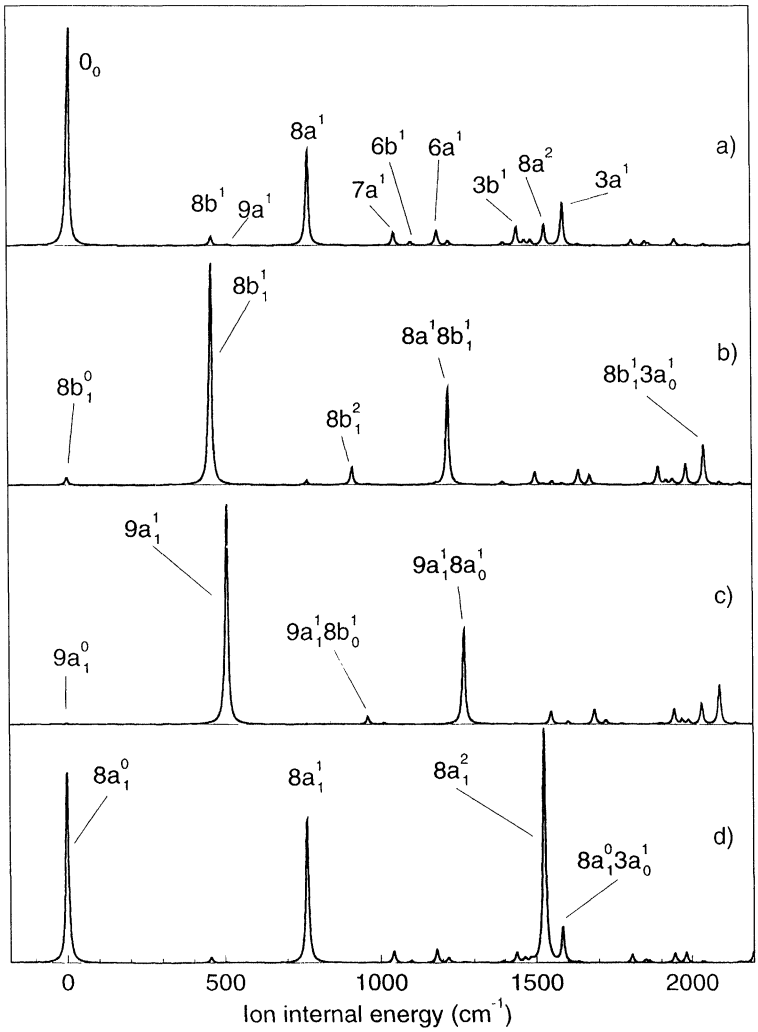

FIGURE 2 Simulations of the ZEKE spectra of naphthalene: (a) from the 0_0 level of S_1; (b) from the $(8b)_1$ level of S_1; (c) from the $(9a)_1$ level of S_1; (d) from the $(8a)_1$ level of S_1.

calculated spectra reproduce nicely the main features of the observed spectra (see Fig. 3 of Ref. [2]) and point to several reassignments of the fundamentals of naphthalene cation, some of which are indicated in the figure. Inspection of the computed contributions to vibronic intensities indicates that the couplings between doublet states are mainly responsible for the observed activity of NTS modes. The latter couplings are indeed one order of magnitude larger than those between singlet states. In conclusion we have demonstrated that quantum-chemical calculations combined with the modelling of vibronic intensities can be employed to analyze the structure of ZEKE spectra even when the Herzberg Teller mechanism of intensity borrowing becomes an important source of intensity.

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