

# Quantum-dynamical Modeling of the Rydberg to Valence Excited-State Internal Conversion in Cyclobutanone and Cyclopentanone

T. S. Kuhlman<sup>1</sup>, S. P. A. Sauer<sup>2</sup>, T. I. Sølling<sup>2</sup>, and K. B. Møller<sup>1</sup>

<sup>1</sup>Technical University of Denmark, Department of Chemistry, DK-2800 Kgs. Lyngby, Denmark

<sup>2</sup>University of Copenhagen, Department of Chemistry, DK-2100, København Ø, Denmark

**Abstract.** In this paper we present 4-state, 5-dimensional Vibronic Coupling Hamiltonians for cyclobutanone and cyclopentanone. Wave packet calculations using these Hamiltonians reveal that for cyclobutanone the  $(n,3s)$  to  $(n,\pi^*)$  internal conversion involves direct motion in nuclear modes coupling the two states leading to fast population transfer. For cyclopentanone, internal vibrational energy redistribution is a bottleneck for activating reactive nuclear modes leading to slower population transfer.

## 1 Introduction

Processes in excited states initiated by short laser pulses can exhibit significant non-ergodic behavior as exemplified by the cycloketones [1,2]. The direct time-scale for the  $(n,3s)$  to  $(n,\pi^*)$  transition in these molecules exhibit such effects [2]. A perturbative approach, i.e., Fermi's golden rule, should be able to describe the rate of such a transition

$$w_{m \leftarrow n}(E) = (2\pi/\hbar) |\langle \Psi_m | V | \Psi_n \rangle|^2 \rho_m(E). \quad (1)$$

Here  $\rho_m(E)$  is the density of vibrational states of the final electronic state  $|\Psi_m\rangle$  and  $V$  is the perturbation coupling the two states. Contrary to the expectation of a rise in the rate of transition as  $\rho_m(E)$  is increased, the exact opposite trend was observed for the cycloketones [2]. This observation points to a significant coordinate dependence of the coupling matrix element in Eq. 1. To investigate this, we present in here the construction of 4-state, 5-dimensional vibronic coupling Hamiltonians (VCHAM) [3] for cyclobutanone and cyclopentanone and their use in wave packet calculations to investigate the true dynamical nature of the  $(n,3s)$  to  $(n,\pi^*)$  transition in these molecules.

## 2 Computational Methods

Wave packet calculations were performed using the Heidelberg Multi-configuration Time-Dependent Hartree (MCTDH) code [4]. The VCHAMs were fitted on the basis of 1182 and 1273 *ab initio* points for cyclobutanone and cyclopentanone, respectively, with a locally modified version of the VCHFIT program distributed with the Heidelberg MCTDH code.

Quantum chemistry calculations were performed in Gaussian 03 [5], CFOUR [6], and Dalton [7] at the coupled-cluster singles and doubles (CCSD) [8,9] and equation of motion (EOM) or linear

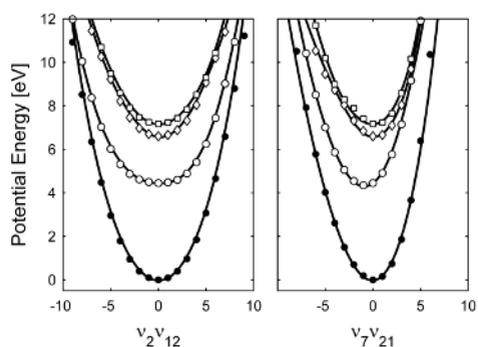
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response CCSD levels of theory. The cc-pVTZ basis set [10] was augmented by a 1s1p1d set of diffuse functions to describe the Rydberg states [11].

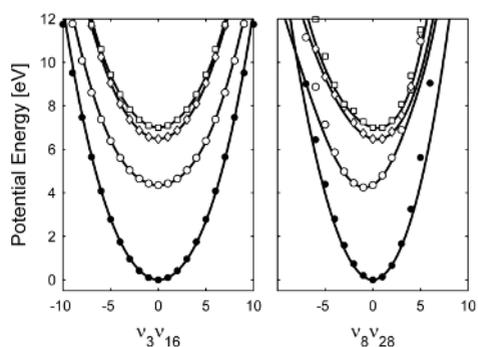
### 3 The Vibronic Coupling Hamiltonian

The VCHAM is given in dimensionless normal mode coordinates obtained at the ground state equilibrium geometry. A subset of modes were chosen such as to describe the significant changes between the equilibrium structure of the ground, ( $n, \pi^*$ ), and ( $n, 3s$ ) states; ring-pucker (labeled  $v_1/v_1$  for cyclobutanone/cyclopentanone), carbonyl out-of-plane deformation ( $v_2/v_3$ ), symmetric C-CO-C stretch ( $v_7/v_8$ ), asymmetric C-CO-C stretch ( $v_{12}/v_{16}$ ), and C=O stretch ( $v_{21}/v_{28}$ ).

Fig. 1 and Fig. 2 give examples of the fit between the parameterized VCHAMs and the *ab initio* data. For the ground state of cyclobutanone and cyclopentanone the RMSD between *ab initio* data and fit is 4.97 and 13.9 meV respectively. For the three excited states the RMSD is 8.2 meV and 4.28 meV for cyclobutanone and cyclopentanone respectively.



**Fig. 1.** *Ab initio* points (symbols) for the four lowest states of cyclobutanone along the mode diagonals  $v_2v_{12}$  and  $v_7v_{21}$  as well as the potential energy surfaces obtained from the fitted VCHAM (lines).



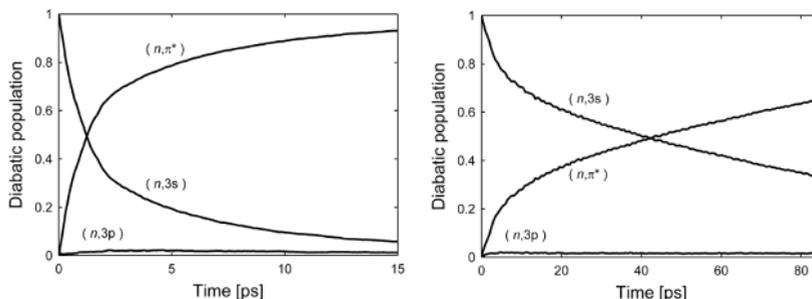
**Fig. 2.** *Ab initio* points (symbols) for the four lowest states of cyclopentanone along the mode diagonals  $v_3v_{16}$  and  $v_8v_{28}$  as well as the potential energy surfaces obtained from the fitted VCHAM (lines).

### 4 Dynamics

Although the potential energy surfaces of cyclobutanone and cyclopentanone are very similar for the five modes included in the VCHAMs as exemplified in Fig. 1 and Fig. 2, very different time-scales for the transition between the initial ( $n, 3s$ ) and final ( $n, \pi^*$ ) state is observed. Fig. 3 shows the diabatic populations of the three excited states following excitation to the ( $n, 3s$ ) state. The decay of the ( $n, 3s$ ) population can for both molecules be adequately fitted by a decaying biexponential function with time-constants of 0.95 ps and 6.32 ps for cyclobutanone and 3.99 ps and 81.5 ps for cyclopentanone. The short time-constants are in good correspondence with the ones obtained from time-resolved mass spectrometry of 0.74 ps and 5.30 ps for cyclobutanone and cyclopentanone respectively [2].

A significant difference between the two molecules can be found in the symmetries of their excited states. For cyclobutanone, which belongs to the  $C_s$  point group, both the ( $n, \pi^*$ ) and the ( $n, 3s$ ) state belong to the  $A''$  irreducible representation, and it is thus the Franck-Condon active modes  $v_1$ ,  $v_2$ ,  $v_7$ , and  $v_{21}$  belonging to  $A'$ , which are responsible for the linear vibronic coupling part of the perturbation operator  $V$  of Eq. 1. As a consequence direct motion in the coupling modes occurs right after excitation to the ( $n, 3s$ ) state and population transfer is fast. On the other hand, for cyclopentanone, which belongs to the  $C_2$  point group, the ( $n, \pi^*$ ) state belongs to the  $A$  irreducible representation whereas the ( $n, 3s$ ) state belongs to  $B$ . As a consequence it is the non-Franck-Condon

active modes  $\nu_1$ ,  $\nu_3$ , and  $\nu_{16}$  belonging to B, which are responsible for the linear vibronic coupling. Motion in the coupling modes does therefore not occur until vibrational energy redistribution has transferred energy from the Franck-Condon modes  $\nu_8$  and  $\nu_{28}$  into the coupling modes – a process which is observed to take on the order of 10 ps. As a consequence population transfer is an indirect process and slower than what is observed in the case of cyclobutanone.



**Fig. 3.** Diabatic populations of the  $(n,\pi^*)$ ,  $(n,3s)$ , and  $(n,3p)$  states as a function of time following excitation to the  $(n,3s)$  state for cyclobutanone (left) and cyclopentanone (right).

## 5 Conclusion

Similar to experiment, wave packet calculations reveal that the  $(n,3s)$  to  $(n,\pi^*)$  transition is faster in cyclobutanone compared to cyclopentanone. The difference of time-scales can be explained from the two different mechanisms of internal conversion; one direct where motion in the reactive coupling modes leads to a fast population transfer and one indirect where internal vibrational energy redistribution (IVR) from the non-reactive modes is a bottleneck for activating the reactive coupling modes. In the direct mechanism the transition takes place on a time-scale shorter than that of IVR and thus non-ergodicity prevails. In the indirect mechanism, IVR takes place on a timescale comparable to or slightly shorter than that of the transition and ergodicity somewhat prevails.

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