

# Vacuum ultraviolet excited state dynamics of the smallest ring, cyclopropane. I. A reinterpretation of the electronic spectrum and the effect of intensity borrowing

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Cyclopropane, the smallest organic ring compound, exhibits complex spectroscopy and excited state dynamics. In Paper I, we reinterpret the vacuum ultraviolet (VUV) electronic absorption spectrum of cyclopropane via ab initio computation. The first two bands in the VUV spectrum are simulated using wavepacket propagations employing the multiconfigurational time-dependent Hartee method and a newly parameterized linear vibronic coupling Hamiltonian. The parameters of the model Hamiltonian are obtained directly from high level multireference configuration interaction calculations. An analysis of the results, with an emphasis on previously neglected vibronic coupling effects, reveals that these vibronic coupling terms must be included in order to account for strong intensity borrowing effects. This treatment dramatically changes the assignment of much of the VUV spectrum, with intensity borrowing by the optically dark  $A'_2(\sigma 3p_x/3p_y)$  and  $A'_1(\sigma 3p_x/3p_y)$  states from the  $E'(\sigma 3p_x/3p_y)$  state being found to give rise to almost all the spectral intensities below 8 eV. This is in stark contrast to previous studies, which attributed the first two bands to transitions to the  $E'(\sigma 3p_x/3p_y)$  state. This highlights the limitations of assigning spectral features based solely on calculated electronic excitation energies and oscillator strengths. Furthermore, we address the significant but infrequently discussed difficulties involved in determining the electronic character of a wavepacket produced in the pump step of ultrafast pump-probe experiments for systems exhibiting strong vibronic coupling. Published by AIP Publishing. https://doi.org/10.1063/1.5044392

# I. INTRODUCTION

In Paper I of two, we consider the vacuum ultraviolet (VUV) electronic absorption spectrum of the smallest organic ring compound, cyclopropane. Cyclopropane and its derivatives are commonly employed in organic syntheses due to their high degree of photoreactivity. For example, cyclopropane and its alkyl-substituted derivatives are of much use in synthetic organic chemistry by virtue of their propensity to undergo photoinduced *cis*-trans isomerisation, ring opening, cycloaddition, and fragmentation.<sup>1–3</sup> Since the primary use of cyclopropane in organic synthesis is centred on its photoreactivity, the lack to date of a time-resolved study of its VUV excited state dynamics is somewhat surprising.

The starting point for this study is the thorough assignment of the absorption spectrum. This is particularly pertinent in time-resolved studies, where an understanding of the electronic character of the wavepacket prepared by a given ultrashort laser pulse is key to unraveling the details of the ensuing non-adiabatic dynamics. An accounting of the electronic character of an initial photo-excited wavepacket generally relies on the previous assignment of the relevant energetic regions of the absorption spectrum (determined by the photon energy of the laser pulse). Thus, reliable assignments of electronic spectra are of paramount importance. Often, band assignments are made via the comparison of the positions of peak maxima and calculated vertical electronic excitation energies and oscillator strengths. However, such an approach neglects that potentially strong vibronic coupling effects exist in the excited state manifold, and thus the excited state eigenstates of the molecular Hamiltonian can be of significantly mixed electronic character.

We here present a theoretical study of the first two bands in the electronic spectrum of cyclopropane, centred at 7.90 and 8.65 eV.<sup>4</sup> The excited state electronic structure of cyclopropane was subject to a number of previous experimental and theoretical studies.<sup>4–10</sup> The ground state minimum energy geometry possesses  $D_{3h}$  symmetry, and the valence electronic structure at this point is characterized by the configuration  $(1a'_1)^2(1e')^4(2a'_1)^2(2e')^4(1a''_2)^2(3a'_1)^2(1e'')^4(3e')^4$ . A number of low-lying 3*s* and 3*p* type Rydberg states dominated by configurations corresponding to excitation from the doubly degenerate 3*e'* HOMO are known to underlie the first two bands in cyclopropane's electronic spectrum. These are the  $E'(\sigma 3s)$ ,  $E''(\sigma 3p_z)$ ,  $A'_2(\sigma 3p_x/3p_y)$ ,  $A'_1(\sigma 3p_x/3p_y)$ , and  $E'(\sigma 3p_x/3p_y)$ states.<sup>4,9</sup>

The consensus from the previous studies of the cyclopropane's electronic spectrum is that the first two bands originate predominantly from excitation to the two Jahn-Teller split components of the optically bright  $E'(\sigma 3p_x/3p_y)$  state.<sup>4,6,8–10</sup> All previous studies, however, have neglected the effects of vibronic coupling of the  $E'(\sigma 3p_x/3p_y)$  state to the lower-lying optically dark states. It is known, however, that strong vibronic coupling effects are present in the photoelectron spectrum of cyclopropane,<sup>11,12</sup> the first two bands of which strongly resemble the first two bands in the VUV absorption spectrum, as may be expected for excitation to Rydberg-type states. There is a reason, therefore, to suspect that similarly strong vibronic coupling effects may be operative in the VUV absorption spectrum.

In this study, we present spectra calculated from quantum dynamics calculations utilizing a model Hamiltonian that includes vibronic coupling terms between the excited electronic states. We conclusively show, in stark disagreement with previous assignments, that the majority of the intensity in the first two bands of the cyclopropane's VUV electronic spectrum arises due to intensity borrowing from the  $E'(\sigma 3p_x/3p_y)$  $\leftarrow A'_1(\sigma^2)$  transition by the  $A'_2(\sigma 3p_x/3p_y) \leftarrow A_1(\sigma^2)$  and  $A'_1(\sigma 3p_x/3p_y) \leftarrow A_1(\sigma^2)$  transitions. Additionally, we employ quantum dynamics simulations to determine the electronic character of a wavepacket prepared via an ultrashort pump pulse, explicitly including the time-dependent molecule-light interaction, for a number of photon energies. The results presented here also serve to highlight the potential dangers and inadequacies of analyses that neglect vibronic coupling effects. In Paper II,<sup>40</sup> we present our experimental Time-Resolved Photoelectron Spectroscopy (TRPES) studies of the excited state dynamics of cyclopropane upon VUV excitation. The results of Paper I, in combination with ab initio wavepacket dynamic simulations, are used to interpret the experimental results.

# **II. METHODOLOGY**

#### A. The model vibronic coupling Hamiltonian

We represented the molecular Hamiltonian in a basis of quasi-diabatic electronic states  $\{\Phi_i\}$ .<sup>13–16</sup> In the context of the present work, the diabatic electronic basis was spanned by nine states:  $A'_1(\sigma^2)$ ,  $E'(\sigma^2s)$ ,  $E''(\sigma^2p_z)$ ,  $A'_2(\sigma^2p_x/3p_y)$ ,  $A'_1(\sigma^2p_x/3p_y)$ , and  $E'(\sigma^2p_x/3p_y)$  (counting both components of the doubly degenerate states).

We employed the linear vibronic coupling (LVC) model Hamiltonian of Köppel *et al.*<sup>17–19</sup> Within the LVC model, an assumed diabatic potential matrix, W, is expanded in terms of the 3N-6 ground state mass- and frequency-weighted normal modes, Q, about an appropriately chosen reference geometry,  $Q_0$ . Our choice for  $Q_0$  is the  $D_{3h}$  ground state minimum energy geometry. Collecting together the terms of the same order, the LVC model Hamiltonian may be written as

$$H(Q) = H^{(0)}(Q) + W^{(1)}(Q).$$
(1)

The zeroth-order Hamiltonian  $H^{(0)}(Q)$  corresponds to the set of ground state harmonic oscillators displaced by the vertical excitation energies (VEEs)  $E_i$  of the electronic states,

$$H_{ij}^{(0)}(\boldsymbol{Q}) = \delta_{ij} \left( E_i + \frac{1}{2} \sum_{\alpha=1}^{3N-6} \left[ \omega_\alpha Q_\alpha^2 - \omega_\alpha \frac{\partial^2}{\partial Q_\alpha^2} \right] \right).$$
(2)

Here,  $\omega_{\alpha}$  denotes the frequency of the normal mode  $Q_{\alpha}$ . It is noted that the off diagonal elements of  $H^{(0)}$  are zero. This is a consequence of our choice to take the diabatic and adiabatic representations to be equal at the reference geometry,  $Q_0$ .

The first-order potential,  $W^{(1)}(Q)$ , is written as

$$W_{ii}^{(1)}(\boldsymbol{Q}) = \sum_{\alpha=1}^{3N-6} \left\{ \frac{\partial}{\partial Q_{\alpha}} \left\langle \Phi_{i} \middle| \hat{H}_{el} \middle| \Phi_{i} \right\rangle \middle|_{\boldsymbol{Q}_{0}} \right\} Q_{\alpha} = \sum_{\alpha=1}^{3N-6} \kappa_{\alpha}^{(i)} Q_{\alpha}, \quad (3)$$
$$W_{ij}^{(1)}(\boldsymbol{Q}) = \sum_{\alpha=1}^{3N-6} \left\{ \frac{\partial}{\partial Q_{\alpha}} \left\langle \Phi_{i} \middle| \hat{H}_{el} \middle| \Phi_{j} \right\rangle \middle|_{\boldsymbol{Q}_{0}} \right\} Q_{\alpha}$$
$$= \sum_{\alpha=1}^{3N-6} \lambda_{\alpha}^{(i,j)} Q_{\alpha}, \quad i \neq j. \quad (4)$$

The first-order intrastate coupling coefficients  $\kappa_{\alpha}^{(i)}$  account for the shift in the potential minima of the excited states relative to the ground state. The first-order interstate coupling coefficients  $\lambda_{\alpha}^{(i,j)}$  account for the vibronic coupling between the electronic states.

In order for a given coupling coefficient  $(\kappa_{\alpha}^{(i)} \text{ or } \lambda_{\alpha}^{(i,j)})$  to be non-zero, the corresponding integrand must belong to a function space that generates a representation of the  $D_{3h}$  point group that contains in its decomposition the totally symmetric irreducible representation,  $A'_1$ . That is,

$$\kappa_{\alpha}^{(i)} \neq 0, \quad \Gamma^{\alpha} \otimes \Gamma^{i} \otimes \Gamma^{i} \ni A_{1}',$$
(5)

$$\lambda_{\alpha}^{(i,j)} \neq 0, \quad \Gamma^{\alpha} \otimes \Gamma^{i} \otimes \Gamma^{j} \ni A_{1}^{\prime}, \tag{6}$$

where  $\Gamma^{\alpha}$  and  $\Gamma^{i}$  denote the representations generated by the mode  $Q_{\alpha}$  and the state  $\Phi_{i}$ , respectively. Furthermore, cyclopropane constitutes an  $E \otimes e$  Jahn-Teller system, and this introduces further symmetry relations into the coupling coefficients. Specifically, for a pair of doubly degenerate states,  $\Phi_{i}$  and  $\Phi_{i+1}$ , and a pair of doubly degenerate modes,  $Q_{\alpha x}$  and  $Q_{\alpha y}$ , the corresponding contribution to the 2 × 2 block of the first-order potential reads

$$\begin{pmatrix} W_{ii}(Q_{\alpha x}, Q_{\alpha y}) & W_{i+1,i}(Q_{\alpha x}, Q_{\alpha y}) \\ W_{i,i+1}(Q_{\alpha x}, Q_{\alpha y}) & W_{i+1,i+1}(Q_{\alpha x}, Q_{\alpha y}) \end{pmatrix} = \begin{pmatrix} \kappa_{\alpha}^{(i)}Q_{\alpha x} & \lambda_{\alpha}^{(i,i+1)}Q_{\alpha, y} \\ \lambda_{\alpha}^{(i,i+1)}Q_{\alpha, y} & \kappa_{\alpha}^{(i+1)}Q_{\alpha x} \end{pmatrix},$$
(7)

$$\kappa_{\alpha}^{(i)} = -\kappa_{\alpha}^{(i+1)} = \lambda_{\alpha}^{(i,i+1)}.$$
(8)

By choosing the adiabatic states  $\phi_i$  to be equal to the diabatic states  $\Phi_i$  at the reference geometry  $Q_0$ , the first-order coupling coefficients,  $\kappa_{\alpha}^{(i)}$  and  $\lambda_{\alpha}^{(i,j)}$ , may be calculated analytically as

k

$$\zeta_{\alpha}^{(i)} = \frac{\partial E_i}{\partial Q_{\alpha}} \Big|_{\mathcal{Q}_0},\tag{9}$$

$$\lambda_{\alpha}^{(i,j)} = \left\langle \Phi_i \bigg| \frac{\partial \hat{H}_{el}}{\partial Q_{\alpha}} \bigg| \Phi_j \right\rangle \bigg|_{Q_0} = h_{ij\alpha}(Q_0).$$
(10)

Here,  $E_i$  denotes the *i*th adiabatic potential and the  $h_{ij}$  are the non-adiabatic coupling vectors in the adiabatic representation, which may be calculated analytically.<sup>20,21</sup> Thus, from a single set of adiabatic energy, energy gradient, and non-adiabatic

coupling vector calculations at the reference geometry  $Q_0$ , a full analytic parameterization of the LVC Hamiltonian may be achieved, and it is this approach which we adopt here.

### B. The molecule-light interaction Hamiltonian

The field-free LVC Hamiltonian suffices for the calculation of electronic absorption spectra. However, in order to rigorously study the initial wavepacket prepared by an applied optical electric field, the molecule-light interaction needs to be modeled explicitly. Adopting the dipole and rotating wave approximations, we describe the molecule-light interaction by the addition of the operator  $\hat{H}_{ML}$  to the molecular Hamiltonian

$$\hat{H} \to \hat{H} + \hat{H}_{ML},$$
 (11)

$$\hat{H}_{ML} = -\sum_{i,j} |\Phi_i\rangle \langle \Phi_i | \hat{\boldsymbol{\mu}} \cdot \boldsymbol{\epsilon}(t) | \Phi_j \rangle \langle \Phi_j |$$
  
$$= -\sum_{i,j} |\Phi_i\rangle \boldsymbol{M}_{ij} \cdot \boldsymbol{\epsilon}(t) \langle \Phi_j |.$$
(12)

Here,  $\epsilon(t)$  denotes the external optical electric field and M denotes the matrix representation of the dipole operator in the basis of the diabatic states,  $\{\Phi_i\}$ . The external field is modeled using a normalised Gaussian envelope<sup>22,23</sup>

$$\boldsymbol{\epsilon}(t) = \boldsymbol{e}\left(\frac{S}{\sigma}\right)\sqrt{\frac{4\ln 2}{\pi}}\exp\left(-\frac{4\ln 2}{\sigma^2}(t-t_0)^2\right)\cos(\omega(t-t_0)),\tag{13}$$

where *e* denotes the polarisation vector,  $\sigma$  is the full width at half maximum (FWHM) of the pulse,  $\omega$  is the central frequency, and  $t_0$  is the pulse centre. *S* denotes a strength parameter and is used to set the peak intensity of the pulse.

The diabatic dipole matrix, M, is constructed within the Condon approximation, i.e., its nuclear coordinatedependence is neglected. Then, by utilising the equivalence of the adiabatic and diabatic representations at the reference point,  $Q_0$ , the elements of M may be equated with the values of the adiabatic dipole matrix elements,  $\mu_{ij} = \langle \phi_i | \hat{\mu} | \phi_j \rangle$ , calculated at  $Q_0$ .

# C. Electronic structure calculations

The reference geometry,  $Q_0$ , corresponding to the ground state minimum, was optimised at the MP2/cc-pVTZ level of theory. The normal mode coordinates and frequencies,  $Q_{\alpha}$  and  $\omega_{\alpha}$ , were calculated at the same level of theory. Both calculations were performed using the Turbomole set of programs.<sup>24</sup>

The parameterization of the LVC Hamiltonian was achieved directly using Eqs. (2), (9), and (10). The requisite adiabatic energies, energy gradients, and non-adiabatic coupling vectors were calculated analytically at the multireference configuration interaction (MRCI) level using the aug-cc-pVDZ basis. The reference configurations and orbitals were taken from a complete active space self-consistent field (CASSCF) calculation employing an active space comprised of the orbitals  $3e'(\sigma)$ ,  $4a'_1(3s)$ ,  $2a''_2(3p_z)$ , and  $4e'(3p_x, 3p_y)$ , that is, 4 electrons in 6 orbitals. We denote this level of theory by CAS(4,6) in the following. In the CAS(4,6) calculation, state averaging was performed over the first nine

singlet electronic states, with equal weights being used. At the reference point, these states correspond to  $A'_1(\sigma^2)$ ,  $E'(\sigma^2 s)$ ,  $E''(\sigma 3p_z), A'_2(\sigma 3p_x/3p_y), A'_1(\sigma 3p_x/3p_y), \text{ and } E'(\sigma 3p_x/3p_y).$ The MRCI configuration space was constructed by allowing all possible single and double excitations from the reference configurations into the virtual orbital space. That is, multireference configuration interaction with single and double excitations calculations were performed. This level of theory is denoted by MR-CISD(4,6). The VEEs,  $E_i$ , used in the zerothorder Hamiltonian were obtained using the Davidson correction to the MR-CISD(4,6) energies. Additionally, the dipole matrix elements used in the construction of the light-matter interaction Hamiltonian,  $\hat{H}_{ML}$ , were also calculated at the MR-CISD(4,6)/aug-cc-pVDZ level of theory. The CASSCF and MR-CISD calculations were performed using the Columbus set of programs.<sup>25</sup>

For the purposes of benchmarking the MR-CISD(4,6)/augcc-pVDZ calculations used in the parameterization of the LVC Hamiltonian, additional high-level VEE calculations were performed at the reference geometry. Specifically, VEEs were calculated at the approximate coupled cluster singles, doubles, and triples (CC3)<sup>26</sup> and equation of motion coupled cluster singles and doubles (EOM-CCSD)<sup>27</sup> levels. For both the CC3 and EOM-CCSD calculations, the aug-cc-pVTZ basis was used. These calculations were performed using the CFOUR program.<sup>28</sup>

#### D. Calculation of absorption spectra

The spectrum  $\sigma(E)$  corresponding to excitation to a given electronic state is obtained from the Fourier transform of the wavepacket autocorrelation function calculated following the vertical excitation of the ground state wavefunction to the excited state in question,

$$\sigma(E) \propto \int_{-\infty}^{\infty} a(t)e^{iEt}dt = 2Re\int_{0}^{\infty} a(t)\exp(iEt)dt.$$
(14)

Here, a(t) denotes the autocorrelation function

$$a(t) = \langle \Psi(0) | \Psi(t) \rangle = \langle \Psi(t/2)^* | \Psi(t/2) \rangle.$$
(15)

The second equality in Eq. (15) holds for a real initial wavepacket and a Hermitian Hamiltonian and allows the autocorrelation function to be obtained for twice the propagation time.<sup>29</sup>

To account for the phenomenological broadening present in the experimental spectrum, the autocorrelation function is multiplied by the exponential damping function

$$f(t) = \exp\left(\frac{-t}{\tau}\right). \tag{16}$$

The effect of this is the convolution of the spectrum with a Lorentzian of FWHM of  $2/\tau$ .

Furthermore, in order to ameliorate problems (the socalled Gibbs phenomenon) arising from the use of a finite propagation time T in the Fourier transform (14), the autocorrelation function was multiplied by the following apodization function:<sup>30</sup>

$$g(t) = \cos^2\left(\frac{\pi t}{2T}\right)\Theta(t-T),$$
(17)

where  $\Theta(t - T)$  denotes the Heaviside step function centred at *T*.

#### E. Wavepacket propagation calculations

Wavepacket propagations were performed using the multiconfigurational time-dependent Hartee (MCTDH) method,<sup>31–33</sup> as implemented in the Quantics quantum dynamics package.<sup>34</sup> The so-called multiset formalism was used, in which the wavefunction ansatz reads

$$|\Psi(\boldsymbol{q},t)\rangle = \sum_{\sigma=1}^{n_s} |\sigma\rangle |\Psi^{(\sigma)}(\boldsymbol{q},t)\rangle.$$
(18)

Here,  $\sigma$  indexes the electronic states  $|\sigma\rangle$  and  $|\Psi^{(\sigma)}(\boldsymbol{q},t)\rangle$  is the nuclear wavefunction for the  $\sigma$ th electronic state. Each nuclear wavefunction  $|\Psi^{(\sigma)}(\boldsymbol{q},t)\rangle$  is expanded in a direct product basis formed from time-dependent functions  $\varphi_{j_k}^{(\kappa,\sigma)}$ , termed single-particle functions (SPFs),

$$\left|\Psi^{(\sigma)}(\boldsymbol{q},t)\right\rangle = \sum_{j_1^{\sigma}=1}^{n_1^{\sigma}} \cdots \sum_{j_p^{\sigma}=p}^{n_p^{\sigma}} A_{j_1^{\sigma},\dots,j_p^{\sigma}}^{(\sigma)}(t) \prod_{\kappa=1}^p \varphi_{j_{\kappa}^{\sigma}}^{(\kappa,\sigma)}(q_{\kappa},t).$$
(19)

The SPFs are the functions of generally multi-dimensional logical coordinates  $q_{\kappa}$ , each corresponding to a composite of  $d_{\kappa}$  physical nuclear coordinates  $Q_{\nu}^{(\kappa)}$ ,

$$q_{\kappa} = \left(Q_1^{(\kappa)}, \dots, Q_{d_{\kappa}}^{(\kappa)}\right). \tag{20}$$

The time-dependent SPFs are further expanded in terms of a time-independent discrete variable representation (DVR).<sup>32,35</sup> Equations of motion for both the expansion coefficients  $A_{j_1^{\sigma},...,j_p^{\sigma}}^{(\sigma)}$  and the SPFs are derived variationally, yielding an optimal description of the evolving wavepacket.<sup>32</sup>

# **III. RESULTS**

## A. Electronic structure calculations

We first consider the calculated Franck-Condon (FC) point VEEs and oscillator strengths of the electronic states underlying the first two bands of the cyclopropane's electronic absorption spectrum, as shown in Table I. For the methods that account for dynamic electron correlation (MR-CISD, EOM-CCSD, and CC3), the agreement between the calculated VEEs is very good, both in terms of relative orderings and absolute values. At the CAS(4,6)/aug-cc-pVDZ level, the VEEs are systematically underestimated by ~1.3 eV.

TABLE II. Franck-Condon point normal modes  $Q_{\alpha}$  and frequencies  $\omega_{\alpha}$  calculated at the MP2/cc-pVTZ level of theory.

Mode	Symmetry	$\omega_{\alpha}(\text{cm}^{-1})$	Description
$Q_1$	$A'_1$	3171.56	C-H stretching
$Q_2$	$A'_1$	1533.26	C-H scissoring + ring breathing
$Q_3$	$A'_1$	1217.85	Ring breathing
$Q_4$	$A'_2$	1094.05	C–H rocking
$Q_5$	$E^{\tilde{i}}$	3163.04	C-H stretching
$Q_6$	E'	1487.84	C-H scissoring
$Q_7$	E'	1064.35	C–H rocking
$Q_8$	E'	986.21	Ring bending
$Q_9$	$A_1''$	1173.43	C–H twisting
$Q_{10}$	$A_2''$	3271.29	C-H stretching
$Q_{11}$	$A_2^{\tilde{\prime}\prime}$	875.64	C–H rocking
$Q_{12}$	$E^{\tilde{\prime\prime}}$	3252.88	C-H stretching
$Q_{13}$	E''	1222.71	C–H twisting
$Q_{14}$	E''	756.87	C–H twisting + C–H rocking

This may be rationalized by noting that all the excited states are of Rydberg-type character, and such "quasi N - 1 electron" states would be expected to have smaller dynamical correlation energies than a corresponding non-Rydberg valence state (i.e., the ground state). Thus, there exists at the CAS(4,6) level a uniform differential error between the excited states and the ground state leading to a systematic error in the VEEs.

All the electronic structure methods including dynamical correlation yield a consistent picture in which the first excited state is predicted to be the  $E'(\sigma 3s)$  state, lying between 7.6 and 7.8 eV. Then, starting at around 8.05-8.25 eV, there is predicted to exist a dense manifold of four states spanning an energy range of ~0.15-0.20 eV. In order of increasing VEE, these are the  $E''(\sigma 3p_z)$ ,  $A'_2(\sigma 3p_x/3p_y)$ ,  $A'_1(\sigma 3p_x/3p_y)$ , and  $E'(\sigma 3p_x/3p_y)$  states. Of these states, only the  $E'(\sigma 3p_x/3p_y)$ state is predicted to be optically bright from the calculated oscillator strengths. This is in line with previous interpretations of the first two bands of the cyclopropane's electronic spectrum,<sup>4,9</sup> which attributed the majority of the spectral intensity to the transition  $E'(\sigma 3p_x/3p_y) \leftarrow A'_1(\sigma^2)$ . However, given the close energetic proximity of the  $E'(\sigma 3s)$  state to the  $E''(\sigma 3p_z)$ ,  $A'_{2}(\sigma 3p_{x}/3p_{y})$ , and  $A'_{1}(\sigma 3p_{x}/3p_{y})$  states, it is not possible to determine from an analysis of oscillator strengths alone whether or not these states will contribute to the spectral intensity via intensity borrowing from the  $E'(\sigma 3p_x/3p_y) \leftarrow A'_1(\sigma^2)$ transition.

TABLE I. Franck-Condon point vertical excitation energies,  $\Delta E$ , calculated at the CAS(4,6)/aug-cc-pVDZ, MR-CISD(4,6)/aug-cc-pVDZ, EOM-CCSD/aug-cc-pVTZ, and CC3/aug-cc-pVTZ levels of theory, where available oscillator strengths, *f*, are also given in parentheses. All energies are given in units of eV.

State	CAS(4,6)/ aug-cc-pVDZ	MR-CISD(4,6)/ aug-cc-pVDZ	EOM-CCSD/ aug-cc-pVTZ	CC3/ aug-cc-pVTZ
$\overline{E'(\sigma 3s)}$	$6.36 (6 \times 10^{-3})$	$7.68 (1 \times 10^{-3})$	$7.82 (4 \times 10^{-5})$	7.63
$E''(\sigma 3p_z)$	6.83 (0.00)	8.13 (0.00)	8.24 (0.00)	8.05
$A_2'(\sigma 3p_x/3p_y)$	6.92 (0.00)	8.25 (0.00)	8.37 (0.00)	8.15
$A_1^{\tilde{i}}(\sigma 3p_x/3p_y)$	6.97 (0.00)	8.27 (0.00)	8.40 (0.00)	8.17
$E'(\sigma 3p_x/3p_y)$	7.03 (0.03)	8.29 (0.06)	8.43 (0.09)	8.20

Finally, we note that the VEEs furnished at the MR-CISD(4,6)/aug-cc-pVDZ level are in very good agreement with those calculated at the CC3/aug-cc-pVTZ level. As such, we have confidence in the accuracy of the parameters of the LVC Hamiltonian calculated at the MR-CISD(4,6)/aug-cc-pVDZ level of theory.

# B. The LVC Hamiltonian

For reference, we list a description of the normal modes  $Q_{\alpha}$  as well as their frequencies  $\omega_{\alpha}$  in Table II. The calculated values of all the non-zero first-order coupling coefficients,  $\kappa_{\alpha}^{(i)}$  and  $\lambda_{\alpha}^{(i,j)}$ , are given in the supplementary material.

Within the framework of the LVC Hamiltonian, the relative spectroscopic importance of the different normal modes may be assessed via a consideration of the dimensionless frequency-weighted first-order coupling coefficients

$$\tilde{\kappa}_{\alpha}^{(i)} = \frac{\kappa_{\alpha}^{(i)}}{\omega_{\alpha}} \tag{21}$$

and

$$\tilde{\lambda}_{\alpha}^{(i,j)} = \frac{\lambda_{\alpha}^{(i,j)}}{\omega_{\alpha}}.$$
(22)

The values  $-\tilde{\kappa}_{\alpha}^{(i)}$  give the displacements of the minima of the diabatic potentials from the reference point,  $Q_0$ . The terms  $\tilde{\lambda}_{\alpha}^{(i,j)}$  give a measure of the relative coupling strengths

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FIG. 1. Model excited state ( $S_1 - S_8$ ) adiabatic potentials along the subset of modes of greatest spectroscopic importance:  $Q_2$  (C–H scissoring and ring breathing),  $Q_3$  (ring breathing),  $Q_{6x}$  (C–H scissoring),  $Q_{6y}$  (C–H scissoring),  $Q_{7x}$  (C–H rocking),  $Q_{7y}$  (C–H rocking),  $Q_{8x}$  (ring bending),  $Q_{8y}$  (ring bending), and  $Q_{11}$  (C–H rocking).

of the modes  $Q_{\alpha}$ . The values of the calculated frequencyweighted first-order coupling coefficients are given in the supplementary material. From a consideration of these values, a subset of nine modes of greatest spectroscopic importance may be identified. These are  $Q_2$  (C–H scissoring and ring breathing),  $Q_3$  (ring breathing),  $Q_{6x}$  (C–H scissoring),  $Q_{6y}$ (C–H scissoring),  $Q_{7x}$  (C–H rocking),  $Q_{7y}$  (C–H rocking),  $Q_{8x}$  (ring bending),  $Q_{8y}$  (ring bending), and  $Q_{11}$  (C–H rocking). The model excited-state adiabatic potentials derived from the LVC potential matrix are plotted along these modes in Fig. 1.

The E' modes  $Q_{6x}$ ,  $Q_{6y}$ ,  $Q_{7x}$ ,  $Q_{7y}$ ,  $Q_{8x}$ , and  $Q_{8y}$  are the Jahn-Teller active modes which account for the majority of the large splittings of the components of the doubly degenerate states  $E'(\sigma 3s)$  and  $E''(\sigma 3p_z)$ . These modes also account for the majority of the moderate splitting of the components of the  $E'(\sigma 3p_x/3p_y)$  state. Additionally, these six modes strongly couple the  $A'_{2}(\sigma 3p_{x}/3p_{y})$  and  $A'_{1}(\sigma 3p_{x}/3p_{y})$  states to the  $E'(\sigma 3p_x/3p_y)$  state. The modes  $Q_{7x}$ ,  $Q_{7y}$ ,  $Q_{8x}$ , and  $Q_{8y}$ also strongly couple the  $E'(\sigma 3s)$  state to the  $A'_2(\sigma 3p_x/3p_y)$ ,  $A'_1(\sigma 3p_x/3p_y)$ , and  $E'(\sigma 3p_x/3p_y)$  states. The mode  $Q_{11}$  gives rise to a moderate coupling of the  $E'(\sigma 3s)$  and  $E''(\sigma 3p_z)$  states and a weaker coupling of the  $E''(\sigma 3p_z)$  and  $E'(\sigma 3p_x/3p_y)$ states. Although  $Q_{11}$  is not a particularly strong coupling mode, its inclusion was found to be necessary to reproduce some of the finer details of the experimental spectrum. Finally, there exist significant gradients in all excited states with respect to the singly degenerate, totally symmetric modes  $Q_3$ and  $Q_2$ .

# C. Calculated spectra

We consider the electronic spectrum of cyclopropane over the energy interval encompassing the first two bands, denoted here and in the following as band I and band II, centred at 7.90 and 8.65 eV in the experimental spectrum.<sup>4,6</sup>

As detailed in Sec. II D, spectra corresponding to excitation to the  $E'(\sigma 3p_x/3p_y)$  state were calculated via the Fourier transform of the autocorrelation function obtained from a wavepacket propagation using an initial state corresponding vertical excitation of the ground state of the Hamiltonian to the  $E'(\sigma 3p_x/3p_y)$  state. All nine electronic states and the nine most spectroscopically important modes listed in Sec. III B were included in these calculations. A propagation time of 150 fs was used, giving the wavepacket autocorrelation function for 300 fs. The details of the mode combinations and basis sets used in the MCTDH calculations are given in Table III. The number of SPFs used for each combined mode was dictated by the criterion that the highest associated natural population did not increase appreciably above  $10^{-3}$  during the course of the propagation, a condition known to be generally satisfactory for the calculation of converged spectra.<sup>36</sup>

Shown in Fig. 2(b) is the calculated spectrum corresponding to vertical excitation to the  $E'(\sigma 3p_x/3p_y)$  state. For this calculation, a damping time,  $\tau$ , of 35 fs was used to account for phenomenological broadening present in the experimental spectrum. For comparison, the experimental spectrum is shown alongside in Fig. 2(a). Importantly, very good agreement between the calculated and experimental spectra is

TABLE III. Computational details of the wavepacket propagations corresponding to vertical excitation to the  $E'(\sigma 3p_x/3p_y)$  state.  $N_i, N_j$  are the number of primitive DVR functions used to describe each physical coordinate.  $n_i$  are the number of single-particle functions used for each particle for each state. Harmonic oscillator DVRs were used as the primitive basis for all degrees of freedom.

Particle	$N_i, N_j$	$n_1, n_2, \ldots, n_9$
$\overline{(Q_2, Q_3)}$	20, 20	5, 4, 4, 3, 3, 3, 8, 7, 7
$(Q_{6x}, Q_{6y})$	20, 20	3, 7, 8, 5, 5, 6, 10, 10, 10
$(Q_{7x}, Q_{7y})$	30, 30	5, 16, 16, 8, 8, 12, 18, 17, 17
$(Q_{8x}, Q_{8y})$	30, 30	5, 16, 16,8,8,12,18,17,17
$(Q_{11})$	20	2, 4, 4, 3, 3, 3, 4, 3, 3

observed, indicating that the simple LVC Hamiltonian is capable of accurately describing the potentials and vibronic couplings in the vicinity of the FC point. The positions of the first two bands in the experimental spectrum, centred at 7.90 and 8.65 eV, are accurately reproduced in the calculated spectrum, with the calculated centres being located at 7.90 and 8.70 eV. The relative intensities of the two bands, however, are in disagreement with the experimental spectrum, with band II being erroneously higher in intensity than band I.

Evidence that the vibronic states underlying bands I and II are highly mixed in terms of their electronic characters comes



FIG. 2. Experimental and calculated spectra corresponding to the first two bands in the electronic spectrum of cyclopropane. (a) Experimental spectrum adapted from Ref. 4. (b) Spectrum calculated from an MCTDH calculation simulating vertical excitation to the  $E'(\sigma 3p_x/3p_y)$  diabatic state.

from a consideration of the absorption spectrum calculated using the LVC Hamiltonian with all terms  $\lambda_{\alpha}^{(i,j)}$  coupling the  $E'(\sigma 3p_x/3p_y)$  state, and  $A'_2(\sigma 3p_x/3p_y)$  and  $A'_1(\sigma 3p_x/3p_y)$  states set to zero. This spectrum is shown in Fig. 3 alongside the spectrum calculated using the full Hamiltonian. The effect of the removal of these interstate coupling terms is that the majority of the spectral intensity is lost. That is, the majority of the intensity of bands I and II results from transition to the vibronic eigenstates containing contributions from the  $E'(\sigma 3p_x/3p_y)$  and  $A'_2(\sigma 3p_x/3p_y)$  and  $A'_1(\sigma 3p_x/3p_y)$  diabatic states. This may be interpreted as a significant proportion of the intensity in bands I and II being attributable to intensity borrowing from the  $E'(\sigma 3p_x/3p_y) \leftarrow A'_1(\sigma^2)$  transition by the  $A'_2(\sigma 3p_x/3p_y) \leftarrow A_1(\sigma^2)$  and  $A'_1(\sigma 3p_x/3p_y) \leftarrow A_1(\sigma^2)$ transitions.

Having established that intensity borrowing effects give rise to most of the intensity in the first two bands of the cyclopropane's VUV absorption spectrum, we now address the question of which modes give rise to this effect. From an analysis of the dimensionless frequency-weighted interstate coupling coefficients  $\tilde{\lambda}_{\alpha}^{(i,j)}$ , it is found that two pairs of doubly degenerate E' modes give rise to the majority of the vibronic coupling between the  $E'(\sigma 3p_x/3p_y)$  state and the  $A'_2(\sigma 3p_x/3p_y)$  and  $A'_1(\sigma 3p_x/3p_y)$  states. These are (i)  $Q_{7x}$ (C–H rocking) and  $Q_{7y}$  (C–H rocking) and (ii)  $Q_{8x}$  (ring



FIG. 3. Spectra calculated from MCTDH calculations simulating vertical excitation to the  $E'(\sigma 3p_x/3p_y)$  diabatic state. Red line: spectrum calculated using the full LVC Hamiltonian. Black line: spectrum calculated using the LVC Hamiltonian with all couplings between the  $E'(\sigma 3p_x/3p_y)$  state and  $A'_2(\sigma 3p_x/3p_y)$  and  $A'_1(\sigma 3p_x/3p_y)$  states removed.

bending) and  $Q_{8y}$  (ring bending). This suggests that these four modes are responsible for the predicted intensity borrowing from the  $E'(\sigma 3p_x/3p_y) \leftarrow A'_1(\sigma^2)$  transition by the  $A'_2(\sigma 3p_x/3p_y) \leftarrow A'_1(\sigma^2)$  and  $A'_1(\sigma 3p_x/3p_y) \leftarrow A'_1(\sigma^2)$ 



FIG. 4. Normal modes responsible for the intensity borrowing by the  $A'_{2}(\sigma 3p_{x}/3p_{y})$  and  $A'_{1}(\sigma 3p_{x}/3p_{y})$  from the  $E'(\sigma 3p_{x}/3p_{y})$  state:  $Q_{7x}$  (C–H rocking),  $Q_{7y}$  (C–H rocking),  $Q_{8x}$  (ring bending), and  $Q_{8y}$  (ring bending).

transitions. For reference, these modes are depicted in Fig. 4. Conclusive evidence that these four modes are responsible for the predicted intensity borrowing is provided by the absorption spectra calculated with the various coupling terms involving these modes removed from the LVC Hamiltonian. These are shown in Fig. 5. We first consider the spectrum calculated with the terms  $\lambda_{\alpha}^{(i,j)}$  corresponding to the states  $E'(\sigma 3p_x/3p_y)$ ,  $A'_{2}(\sigma 3p_{x}/3p_{y})$ , and  $A'_{1}(\sigma 3p_{x}/3p_{y})$  and all four modes  $Q_{7x}, Q_{7y}$ ,  $Q_{8x}$ , and  $Q_{8y}$  set to zero, given by the black line in Fig. 5. This spectrum is almost identical to the one obtained by setting all coupling terms between the  $E'(\sigma 3p_x/3p_y)$ ,  $A'_2(\sigma 3p_x/3p_y)$ , and  $A'_1(\sigma 3p_x/3p_y)$  states to zero (shown in Fig. 3). We thus conclude that the four modes  $Q_{7x}$ ,  $Q_{7y}$ ,  $Q_{8x}$ , and  $Q_{8y}$  are indeed responsible for the predicted intensity borrowing. We next consider the two spectra calculated by removing the coupling between the  $E'(\sigma 3p_x/3p_y)$  state and only one of the  $A'_{2}(\sigma 3p_{x}/3p_{y})$  or  $A'_{1}(\sigma 3p_{x}/3p_{y})$  states. These are given by the blue and green lines in Fig. 5, respectively. In both of these spectra, significant intensity remains across the whole of the spectrum. This indicates that both the  $A'_2(\sigma 3p_x/3p_y)$  and  $A'_1(\sigma 3p_x/3p_y)$  states contribute approximately equally to the vibronic eigenstates that arise due to intensity borrowing.

# D. Effects of intensity borrowing on the initial wavepacket prepared by the interaction with an external laser field

The results presented in Sec. III C unambiguously show that the majority of the intensity in cyclopropane's spectrum arises due to intensity borrowing effects. We now turn our attention to the effect that this will have on the electronic character of a wavepacket prepared by the interaction of the ground state with an ultrafast laser pulse.

A consequence of the strong vibronic coupling of energetically proximate states is that the electronic character of the initial state prepared in, e.g., the pump step of an ultrafast (femtosecond) pump-probe experiment will likely be



FIG. 5. Spectra calculated from MCTDH calculations simulating vertical excitation to the  $E'(\sigma 3p_x/3p_y)$  diabatic state with various coupling terms removed. Black line: no coupling between  $E'(\sigma 3p_x/3p_y)$  and  $A'_2(\sigma 3p_x/3p_y)$  or  $A'_1(\sigma 3p_x/3p_y)$  involving  $Q_{7x}$ ,  $Q_{7y}$ ,  $Q_{8x}$ , and  $Q_{8y}$ . Blue line: no coupling between  $E'(\sigma 3p_x/3p_y)$  and  $A'_2(\sigma 3p_x/3p_y)$  involving  $Q_{7x}$  and  $Q_{8x}$ . Green line: no coupling between  $E'(\sigma 3p_x/3p_y)$  and  $A'_2(\sigma 3p_x/3p_y)$  involving  $Q_{7y}$  and  $Q_{8y}$ .

complex and not dominated by a single electronic state character. Such a situation is exemplified in the case of cyclopropane, where our calculations predict that much of the first two spectral bands correspond to vibronic states of mixed  $E'(\sigma 3p_x/3p_y)$  and  $A'_2(\sigma 3p_x/3p_y)$  and/or  $A'_1(\sigma 3p_x/3p_y)$  character. Although the theory of the underlying vibronic coupling effects has been well understood for many decades,<sup>37–39</sup> the effect on the electronic character of the initial wavepacket produced in an ultrafast pump-probe experiment is often not considered. It is therefore instructive to consider the initial states prepared in cyclopropane by the interaction with an ultrafast laser pulse typical of many current experimental setups.

We consider the initial excited state populations prepared via the application of weak field VUV laser pulses with a peak intensity of  $5 \times 10^{12}$  W cm<sup>-2</sup>, a FWHM of 30 fs, and central frequencies corresponding to photon energies of 7.90 and 8.70 eV, corresponding to be maxima of bands I and II in the calculated spectrum. The molecule-light interaction is modeled using the Hamiltonian  $\hat{H}_{ML}$  described in Sec. II B in conjunction with MCTDH wavepacket propagations using an initial wavefunction corresponding to the ground state of the field-free LVC Hamiltonian. The numbers of basis functions used in the MCTDH calculations are given in Table IV. We define the initial wavepacket prepared by the applied laser pulse to be the wavefunction at the centre of the pulse, corresponding to time t = 0 in our calculations. We assume an isotropic distribution of molecular orientations and rotationally average the calculated excited state populations over the angle between the dipole moment vector and the laser polarisation.

Figures 6(a) and 6(b) show the calculated diabatic excited state populations for photon energies corresponding to the maxima of bands I and II in the calculated spectrum, respectively. The subscripts x and y on the state symmetry labels are used to denote the individual components of the doubly degenerate states. We omit the populations of the components of the  $E''(\sigma 3p_z)$  state as they remain essentially zero for the duration of the applied laser pulse. For both photon energies, at time t = 0, the electronic character of the wavefunction corresponds to a linear combination of the  $E'(\sigma 3s)$ ,  $E'(\sigma 3p_x/3p_y)$ ,  $A'_1(\sigma 3p_x/3p_y)$ , and  $A'_2(\sigma 3p_x/3p_y)$  states. Following excitation at the band I maximum, the excited state wavepacket is predicted to be composed of  $10\% E'(\sigma 3s)$ , 21% $A'_2(\sigma 3p_x/3p_y)$ ,  $23\% A'_1(\sigma 3p_x/3p_y)$ , and  $46\% E'(\sigma 3p_x/3p_y)$ character. Excitation at the band II maximum is predicted

TABLE IV. Computational details of the wavepacket propagations including the addition of an external electric field.  $N_i$ ,  $N_j$  are the number of primitive DVR functions used to describe each physical coordinate.  $n_i$  are the number of single-particle functions used for each particle for each state. Harmonic oscillator DVRs were used as the primitive basis for all degrees of freedom.

Particle	$N_i, N_j$	$n_1, n_2, \ldots, n_9$
$(Q_2, Q_3)$	20, 20	5, 4, 4, 3, 3, 5, 5, 5, 5
$(Q_{6x}, Q_{6y})$	20, 20	4, 3, 3, 3, 3, 5, 5, 5, 5
$(Q_{7x}, Q_{7y})$	30, 30	5, 8, 8, 3, 3, 9, 9, 9, 9
$(Q_{8x}, Q_{8y})$	30, 30	5, 8, 8, 3, 3, 8, 8, 9, 9
(Q <sub>11</sub> )	20	5, 3, 3, 3, 3, 4, 4, 4, 4



FIG. 6. Isotropically averaged calculated diabatic electronic state populations resulting from MCTDH calculations including external electric fields with different photon energies  $\omega$ . (a)  $\omega = 7.90$  eV and (b)  $\omega = 8.70$  eV.

to result in an excited state wavepacket composed of 4%  $E'(\sigma 3s)$ , 26%  $A'_2(\sigma 3p_x/3p_y)$ , 24%  $A'_1(\sigma 3p_x/3p_y)$ , and 46%  $E'(\sigma 3p_x/3p_y)$  character.

The significant population of the optically dark  $A'_2(\sigma 3p_x/3p_y)$  and  $A'_1(\sigma 3p_x/3p_y)$  states is a direct manifestation of the intensity borrowing effects identified in Sec. III C and has important consequences for the photoinduced dynamics of cyclopropane. In particular, for excitation at any energy underlying the first two bands of the cyclopropane's absorption spectrum, these results strongly suggest that the direct population of all three of the  $A'_2(\sigma 3p_x/3p_y)$ ,  $A'_1(\sigma 3p_x/3p_y)$ , and  $E'(\sigma 3p_x/3p_y)$  states must be assumed to occur.

#### **IV. CONCLUSIONS**

Using a model Hamiltonian which includes all first-order vibronic coupling terms, the first two bands in cyclopropane's VUV absorption spectrum were calculated from wavepacket propagation calculations. Good agreement with the experimental spectrum was attained, validating the model Hamiltonian used. The previously held consensus that the first two bands in the cyclopropane's VUV spectrum result predominantly from transition to the two Jahn-Teller split components of the optically bright  $E'(\sigma 3p_x/3p_y)$  is shown to be incorrect. Instead, we determined that the majority of the intensity for both bands results from intensity borrowing from the  $E'(\sigma 3p_x/3p_y) \leftarrow A'_1(\sigma^2)$  transition by the  $A'_2(\sigma 3p_x/3p_y)$  $\leftarrow A_1(\sigma^2)$  and  $A'_1(\sigma 3p_x/3p_y) \leftarrow A_1(\sigma^2)$  transitions.

These results have implications for any study of the excited state dynamics of cyclopropane or indeed those of any molecule possessing a dense manifold of low-lying vibronically coupled states. In particular, the predicted strong intensity borrowing effects render the characterisation of the electronic character of the initial state prepared in a experimental study non-trivial. This is demonstrated in our simulations of the interaction of ground state cyclopropane with external optical electric fields characteristic of typical pump laser pulses employed in ultrafast pump-probe experiments. For photon energies corresponding to the maxima of both bands in the electronic spectrum, the initial excited

state wavepackets are predicted to possess electronic characters corresponding to approximately equal admixtures of the  $E'(\sigma 3p_x/3p_y)$ ,  $A'_2(\sigma 3p_x/3p_y)$ , and  $A'_1(\sigma 3p_x/3p_y)$  diabatic states. This stands in stark contrast to the electronic character expected from an analysis of the calculated electronic excitation energies and oscillator strengths, which would predict only the  $E'(\sigma 3p_x/3p_y)$  state to be significantly populated. In line with this, we suggest that whenever a high density of electronic states is encountered, an analysis of the electronic character of the initial wavepacket based on the explicit modeling of the coupling of the ground state to the vibronically coupled excited state manifold via the pump pulse should be considered a necessity. In Paper II,<sup>40</sup> we apply these results to the interpretation of the experimental TRPES studies of the VUV excited state dynamics of cyclopropane.

## SUPPLEMENTARY MATERIAL

See supplementary material for the full parameterization of the vibronic coupling model described in this report.

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