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Multistate vibronic interactions and nonadiabatic wave packet dynamics in the second photoelectron band of chlorine dioxide

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Abstract

We report theoretical investigations on the second photoelectron band of chlorine dioxide molecule by *ab initio* quantum dynamical methods. This band exhibits a highly complex structure and represents a composite portrait of five excited energetically close-lying electronic states of ClO_2^+ . Much of this complexity is likely to be arising due to strong vibronic interactions among these electronic states – which we address and examine herein. The near equilibrium MRCI potential energy surfaces (PESs) of these five cationic states reported by Peterson and Werner [J. Chem. Phys. 99 (1993) 302] for the C_{2v} configuration, are extended for the C_s geometry assuming a harmonic vibration along the asymmetric stretching mode. The strength of the vibronic coupling parameters of the Hamiltonian are calculated by *ab initio* CASSCF-MRCI method and conical intersections of the PESs are established. The diabatic Hamiltonian matrix is constructed within a linear vibronic coupling scheme and the resulting PESs are employed in the nuclear dynamical simulations, carried out with the aid of a time-dependent wave packet approach. Companion calculations are performed for transitions to the uncoupled electronic states in order to reveal explicitly the impact of the nonadiabatic coupling on the photoelectron dynamics. The theoretical findings are in good accord with the experimental observations. The femtosecond nonradiative decay dynamics of ClO_2^+ excited electronic states mediated by conical intersections is also examined and discussed.

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1. Introduction

The photo-activity of chlorine dioxide has been a subject of renewed interest because of the possible role of this species in declining the stratospheric ozone layer [1]. Apart from a great deal of

interest in untangling the photodissociation mechanisms of ClO_2 and the implications of the photoproducts in the ozone destruction cycle, its photoelectron spectrum was also recorded and studied by various researchers in order to understand the structure of the corresponding cationic electronic states [2–4].

The He I photoelectron spectrum of ClO_2 has been recorded by Cornford et al. [2,3] and by

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Flesch et al. [4]. The He I photoelectron spectrum of symmetric OClO recorded by the latter authors at an improved energy resolution indicated four distinct bands between 10 and 22 eV [4]. Among these, the first three bands occurring in the energy range between 10 and 16 eV were identified to be due to the ionization to the ground and several low-lying singlet and triplet excited electronic states of ClO_2^+ . The first band results from the ionization of the $3b_1$ unpaired electron of ClO_2 to the 1A_1 ground electronic state of the cation. The distinct vibrational progressions observed in this band were assigned to the symmetric stretching and bending vibrational modes of ClO_2^+ [4]. The second band spanning the 12–15 eV ionization energy range, is highly diffuse and exhibits complicated vibrational structure. It is interpreted to be originating from a transition to five energetically close-lying excited electronic states (3B_1 , 1B_1 , 3B_2 , 1A_2 and 3A_2) of ClO_2^+ . Progressions along the symmetric stretching and the bending vibrational modes were also identified in this band [4]. The third photoelectron band corresponds to a transition to the excited 1B_2 cationic state which results from the photoionization of the $1a_1$ orbital. In this band a progression along the symmetric stretching mode is observed only in the experimental recording of Flesch et al. [4].

The symmetric chlorine dioxide molecule has a C_{2v} equilibrium geometry. A C_{2v} symmetry for the equilibrium geometry also holds for the ground and excited electronic states of ClO_2^+ . Peterson and Werner [5,6] have reported ab initio potential energy surfaces for some neutral and cationic electronic states of ClO_2 . They computed the potential energy of these states as a function of the symmetric stretch and bend coordinates by the CMRCI and MRCI+Q methods, and using complete active space self-consistent field (CASSCF) orbitals. The near equilibrium potential energy points for each electronic state were fitted to a polynomial containing 11 coefficients by these authors [6]. These potential energy functions were particularly designed to describe the (low-resolution) experimental photoelectron spectra (as noted above), which revealed progressions along the symmetric stretching and bending vibrational modes only. We note that a full three-dimensional

potential energy surface for the ground electronic state of ClO_2 is also reported by Peterson [7].

In an earlier publication we have calculated the above photoelectron bands of ClO_2 with the aid of a time-dependent wave packet (WP) as well as a stationary-state approach [8]. These studies were based on the C_{2v} potential energy surfaces of the neutral and cationic electronic states reported by Peterson and Werner [5,6] and were motivated by the absence of any noticeable excitation of the asymmetric stretching vibration in the experimental recording [4]. Our findings were in good accord with those of Mok et al. [9] who carried out an anharmonic Franck–Condon (FC) simulation of the photoelectron bands of ClO_2 based on Watson's Hamiltonian and the same C_{2v} potential energy surfaces of Peterson and Werner [5,6]. While our reduced dimensionality calculations successfully described the observed structures in the first and third photoelectron bands, the second photoelectron band was not described satisfactorily [8]. The discrepancy between the theoretical and experimental results for the latter band was mainly attributed to the nonadiabatic effects arising due to vibronic interactions among the participating five close-lying excited electronic states of ClO_2^+ [8]. Apart from this, the spin–orbit coupling may also play a role in describing the vibronic fine structure of this band. However, we here aim to study only the vibronic interactions and the corresponding nonadiabatic effects contributing to the observed structure of this band. The details of the spin–orbit effects are presently being analyzed and will be discussed in a forthcoming publication [10].

It therefore emerges from the foregoing discussion that the second photoelectron band originates from $(^3B_2, ^3A_2, ^3B_1, ^1A_2, ^1B_1)\text{ClO}_2^+ \leftarrow \tilde{X}^2B_1\text{ClO}_2$ transitions. All of these transitions are equally probable because photoelectron spectroscopy is not constrained by any selection rule. The energetic ordering of the five cationic electronic states reported in the experimental work of Flesch et al. [4] differ from the ab initio results of Peterson and Werner [6]. This subject has been discussed at length by Mok et al. [9] and we have also examined it critically in our previous paper [8]. It was found that the ab initio results of Peterson and Werner [6] which locate the 3B_2 , 3A_2 , 3B_1 , 1A_2 and 1B_1

cationic states in ascending order of energy provide a more meaningful description of the second photoelectron band.

Elementary symmetry selection rules suggest that in the C_{2v} configuration, A_2 and B_1 electronic states of ClO_2^+ can couple to each other via the asymmetric stretching vibrational mode and can form conical intersections [11,12]. Therefore, one finds that at least two conical intersections (one within the triplet and one within the singlet electronic manifold) can play a considerable role in determining the vibronic structure of the second photoelectron band. In this paper we establish these conical intersections and describe them by employing a linear coupling mechanism between the states. The relevant parameters of the Hamiltonian are calculated by the ab initio CASSCF-MRCI method [13,14] and the nuclear dynamics is studied with the aid of a time-dependent WP approach.

The rest of the paper is organized in the following way. In Section 2 we present the diabatic vibronic Hamiltonian constructed on the basis of a linear coupling mechanism between the electronic states. The calculations of the relevant parameters of the Hamiltonian by the ab initio CASSCF-MRCI method are outlined in Section 3. The theoretical methodology to calculate the photoelectron band is described in Section 4 and the results are presented and discussed in Section 5. The paper is closed with summarizing remarks in Section 6.

2. Vibronic coupling Hamiltonian

The second photoelectron band of ClO_2 is described by FC transitions to the five excited electronic states of ClO_2^+ mentioned above. Therefore, the nuclear motions in the final 3B_2 , 3A_2 , 3B_1 , 1A_2 and 1B_1 interacting electronic states of the cation are to be represented by the Hamiltonian. In the following, we disregard the spin–orbit interactions among these electronic states and only consider the vibronic interactions within the 3A_2 – 3B_1 and 1A_2 – 1B_1 pairs of states (the possible spin–orbit interactions among these states is presently being studied and will be discussed in a forthcoming

publication). In order to analyze the effects originating from these vibronic interactions one needs to go beyond the well-known adiabatic or Born–Oppenheimer approximation and monitor the nuclear motion simultaneously on more than one electronic state. In order to simplify the numerical computation one generally resorts to a diabatic electronic representation [15]. Because, in an adiabatic representation the coupling between the states is described by the off-diagonal elements of the nuclear kinetic energy operator, which exhibit a singular behavior at the seam of intersections of the PESs. Contrary to this, in a diabatic representation the coupling between the states is described by the off-diagonal elements of the potential energy operator which are smooth functions of the nuclear coordinates even at the seam of degeneracies of the PESs. Furthermore, in a diabatic representation the elements of the transition dipole matrix are weakly varying functions of nuclear coordinates and the Condon approximation can be explicitly utilized to calculate the intensity of the photoelectron transition [16].

Thus, in a diabatic representation the nuclear kinetic energy operator can be taken as diagonal and therefore in this representation the Hamiltonian matrix describing the nuclear motions in the final manifold of five cationic electronic states is given by

$$\begin{aligned} \mathcal{H} &= \mathcal{H}^{\text{Nu}} + \mathcal{H}^{\text{el}}, \\ &= T_N \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \\ &\quad + \begin{pmatrix} H_{11} & 0 & 0 & 0 & 0 \\ 0 & H_{22} & H_{23} & 0 & 0 \\ 0 & H_{32} & H_{33} & 0 & 0 \\ 0 & 0 & 0 & H_{44} & H_{45} \\ 0 & 0 & 0 & H_{54} & H_{55} \end{pmatrix}, \end{aligned} \quad (1)$$

where \mathcal{H}^{Nu} and \mathcal{H}^{el} refer to the nuclear and the electronic part of the Hamiltonian matrix, respectively, T_N is the nuclear kinetic energy operator and H_{11} , H_{22} , H_{33} , H_{44} and H_{55} describe the

potential energies of the diabatic states correlating with the 3B_2 , 3A_2 , 3B_1 , 1A_2 and 1B_1 species, respectively, at the C_{2v} configuration. The quantities, $H_{23} = H_{32}$ and $H_{45} = H_{54}$, represent the coupling potentials between the respective states.

ClO_2 is a bent molecule and has a C_{2v} minimum in both the neutral ground electronic state and cationic excited electronic states [5,6]. In order to exploit this symmetry explicitly in the nuclear dynamics we express the elements of the above Hamiltonian matrix in terms of the symmetry adapted Jacobi coordinates pertinent to the C_{2v} point group in the body-fixed frame. In what follows, we refer to r_v as the distance between the two terminal O atoms, r_d as the distance between the Cl atom to the center-of-mass of the two O atoms and γ as the angle between \vec{r}_v and \vec{r}_d . In this set of coordinates the C_{2v} arrangements of the nuclei correspond to $\gamma = \pi/2$. Here we restrict the treatment to total angular momentum $J = 0$. The nuclear kinetic energy operator is then given by

$$T_N = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r_d^2} - \frac{\hbar^2}{2\mu'} \frac{\partial^2}{\partial r_v^2} - \frac{\hbar^2}{2I} \frac{1}{\sin \gamma} \frac{\partial}{\partial \gamma} \left(\sin \gamma \frac{\partial}{\partial \gamma} \right),$$

$$\mu = \frac{m_{\text{O}} m_{\text{Cl}}}{m_{\text{O}} + 2m_{\text{Cl}}},$$

$$\mu' = \frac{m_{\text{O}}}{2},$$

$$\frac{1}{I} = \frac{1}{\mu r_d^2} + \frac{1}{\mu' r_v^2}. \quad (2)$$

The quantities m_{O} , m_{Cl} and I in the above equation denote the masses of the oxygen and chlorine atoms and the three-body moment of inertia, respectively.

3. Electronic structure calculations

The elements of the electronic Hamiltonian matrix \mathcal{H}^{el} have been determined in the following way. For the dependence of the diabatic surfaces, H_{11} , H_{22} , H_{33} , H_{44} and H_{55} on the symmetric stretch coordinate $S_1 = (r_1 + r_2)/\sqrt{2}$ (r_1 and r_2 being the Cl–O bond lengths) and bending coordinate $S_2 = \phi$ (O–Cl–O bond angle), i.e., for C_{2v} geometries, the MRCI potential energy functions derived from the large scale CASSCF calculations by Peterson and

Werner is used. These authors have fitted the potential energies to a polynomial of the form [5,6]

$$V(S_1, S_2) = \sum_{ij} C_{ij} (\Delta S_1)^i (\Delta S_2)^j. \quad (3)$$

The above function for each electronic state [the ground (\tilde{X}^2B_1) state of ClO_2 and excited (3B_2 , 3A_2 , 3B_1 , 1A_2 and 1B_1) electronic states of ClO_2^+] is described by 11 coefficients in the vicinity of their respective equilibrium geometries. The quantities ΔS_1 and ΔS_2 represent displacement of these symmetry coordinates from their equilibrium value. The dependence of these surfaces on the asymmetric stretch coordinate $S_3 = (r_1 - r_2)/\sqrt{2}$ is approximated by a harmonic potential, $V(S_3) = \kappa_u S_3^2/2 = \tilde{\omega}_u Q_u^2/2$. The quantity κ_u represents the force constant along the asymmetric stretch coordinate (u symmetry) and $\tilde{\omega}_u$ represents the harmonic diabatic frequency, with Q_u being the dimensionless normal coordinate for the asymmetric stretching vibration (see below). It is to be noted that we have assumed the same value of $\tilde{\omega}_u$ for the three triplet states and also the same value for the two singlet states. Since no explicit excitation of the asymmetric stretching vibration is indicated in the experimental recording, such an assumption is expected to meaningfully describe the overall dynamical behavior of the system. The interstate coupling potentials H_{23} and H_{45} are assumed to be linearly depending on Q_u , $H_{ij} = \lambda_{ij} Q_u$. The diabatic harmonic frequencies $\tilde{\omega}_u$ and the interstate coupling parameters λ_{ij} are determined through extensive ab initio calculations (see below). We note that the model illustrated above treats all the higher order couplings in the Hamiltonian along the symmetric stretch and bend coordinates whereas a linear coupling scheme is applied to the asymmetric stretch coordinate only.

We devote some space here to introduce the dimensionless normal coordinates used in this paper. These are denoted as Q_{g1} , Q_{g2} and Q_u for the symmetric stretching, bending and asymmetric stretching vibrational motions of ClO_2 in its ground electronic state. The vibrational motion in this state is treated as harmonic. The mass-weighted normal coordinates are then calculated by the **GF**-matrix method of Wilson et al. [17] using the experimentally derived force constant

values reported by Miyazaki et al. [18]. They are then transformed to the dimensionless normal coordinates by multiplying with $(\omega_i/\hbar)^{1/2}$ (ω_i is the frequency of the i th vibrational mode). We mention that the normal coordinates obtained by using the ab initio force constant values reported by Peterson [7] yield identical dynamical results.

3.1. Details of the ab initio computations

In order to calculate the adiabatic potential energies required to determine the aforementioned parameters of the Hamiltonian we carried out CASSCF calculations. The active space consists of 12 molecular orbitals arising from the 2s, 2p and 3s, 3p atomic orbitals of oxygen and chlorine, respectively (18 active electrons in 12 orbitals). The low-lying orbitals (1s of O, and 1s, 2s, 2p of Cl) are fully optimized, constraining them to be doubly occupied. The calculations are carried out in C_s symmetry and therefore the active space corresponds to 9 a' and 3 a'' orbitals. All six states (1A_1 , 3B_2 , 3A_2 , 3B_1 , 1A_2 and 1B_1 states of ClO_2^+) of our interest (in C_s : one $^1A'$, two $^1A''$, one $^3A'$ and two $^3A''$) are treated simultaneously (state-averaged) in order to yield a common set of orbitals.

The active space from the CASSCF is taken as reference function in subsequent calculations at the multireference configuration interaction (MRCI) level of theory. All 12 valence electrons are correlated. For the inner shells the frozen core approximation is employed. In the MRCI calculations all single and double excitations with respect to the reference space are included and the doubly excited configurations are internally contracted (icMRCI) [13]. A generalized Davidson correction [14] has been used to estimate energy contributions for higher excitations and is denoted as icMRCI + Q.

For the one-particle basis sets we used the cc-pVQZ correlation consistent basis sets of Dunning and coworkers [19]. These sets consist of the following primitive/contracted functions: (12s,6p,3d,2f,1g)/[5s,4p,3d,2f,1g] for oxygen and (16s,11p,3d,2f,1g)/[6s,5p,3d,2f,1g] for chlorine.

The electronic structure calculations are carried out for nuclear geometries corresponding to the equilibrium configurations of the ground elec-

tronic state of ClO_2 and the five excited cationic electronic states of ClO_2^+ . Calculations are also performed by fixing the Cl–O bond length to its equilibrium value of the neutral ground electronic state and by varying the O–Cl–O angle. All calculations are carried out for a difference of the two Cl–O distances of 0.0, 0.01 and $0.02a_0$, using the MOLPRO suite of ab initio programs [20].

3.2. Determination of the parameters

The diabatic vibrational frequencies of the singlet and triplet excited electronic states of ClO_2^+ along the asymmetric stretch coordinate are determined from the sum of the computed potential energies for $\Delta S_1 = \Delta S_2 = 0$ and when S_3 is elongated. Equivalently, in terms of the dimensionless normal coordinate displacements this corresponds to $Q_{g1} = Q_{g2} = 0$ and $Q_u \neq 0$, and the sum of the adiabatic potentials can be expressed as [21]

$$V_1 + V_2 = E_1^0 + E_2^0 + (\omega_u + 2\kappa_{uu})Q_u^2, \quad (4)$$

where V_1 and V_2 represent the adiabatic potential energies of the respective states, E_1^0 and E_2^0 refer to the vertical ionization energies, ω_u is the frequency of the u mode in the neutral ground state and κ_{uu} represents the quadratic coupling constant in the u mode which is assumed to be identical for both the states. Within this approximation the frequency of the two diabatic surfaces can be given by [21]:

$$\widetilde{\omega}_u = \sqrt{\omega_u(\omega_u + 2\kappa_{uu})}. \quad (5)$$

With the data reported in Table 1 we find $\widetilde{\omega}_u \approx 0.122$ eV for the 3A_2 and 3B_1 states and $\widetilde{\omega}_u \approx 0.129$ eV for the 1A_2 and 1B_1 states. The $\widetilde{\omega}_u$ value for the 3B_2 state was also set identical to the value for the above triplet states.

The interstate linear vibronic coupling constant λ_{ij} is derived from the difference of the adiabatic potential energies of the states i and j , calculated for the various C_s geometries of ClO_2^+ (as noted in Section 3.1). The two are related via [12,22]

$$\lambda_{ij} = \frac{1}{2}Q_u^{-1} \left\{ [V_j(Q_u) - V_i(Q_u)]^2 - [V_j(Q_0) - V_i(Q_0)]^2 \right\}^{1/2}, \quad (6)$$

where V_i and V_j are the adiabatic potential energies of the states i and j , respectively, for the distorted

Table 1

MRCI + Q energy values of the five excited electronic states of ClO_2^+ for various C_{2v} geometries

Geometry			Energy (E_h)				
r_1/a_0	r_2/a_0	ϕ ($^\circ$)	3B_2	3A_2	3B_1	1A_2	1B_1
2.779	2.779	107.86	−609.39066	−609.38575	−609.36754	−609.37324	−609.35183
		117.86	−609.38741	−609.37548	−609.37825	−609.36289	−609.35885
		127.86	−609.37600	−609.35970	−609.38090	−609.34698	−609.35820
2.789	2.789	107.86	−609.39211	−609.38684	−609.36868	−609.37438	−609.35329
		117.86	−609.38886	−609.37668	−609.37911	−609.36415	−609.36001
		127.86	−609.37756	−609.36111	−609.38162	−609.34843	−609.35922
2.799	2.799	107.86	−609.39345	−609.38782	−609.36974	609.37543	−609.35465
		117.86	−609.39020	−609.37778	−609.37989	−609.36531	−609.36109
		127.86	−609.37902	−609.36241	−609.38225	−609.34979	−609.36015

nuclear configuration Q_u . The latter is chosen in the vicinity of Q_0 (equilibrium configuration of the neutral ground electronic state), $Q_u = Q_0 \pm \delta$, with δ being the small shift applied to change the symmetry point group from C_{2v} at Q_0 to C_s at Q_u . We have analyzed the potential energy data for 13 different nuclear configurations and for $\delta = 0.0$, 0.0673527 and 0.1347054 (corresponding to Cl–O bond length differences of 0.0, 0.01 and 0.02 a_0) and calculated λ_{23} (linear interstate coupling parameter between the 3A_2 and 3B_1 state of ClO_2) and λ_{45} (linear interstate coupling parameter between the 1A_2 and 1B_1 state of ClO_2). We find $0.16 \text{ eV} \leq \lambda_{23} \leq 0.18 \text{ eV}$ and $0.20 \text{ eV} \leq \lambda_{45} \leq 0.23 \text{ eV}$.

4. Calculation of the photoelectron spectrum

The photoelectron transition is described by Fermi's Golden rule. The excitation function is given by

$$P(E) = \sum_v |\langle \Psi_v | \hat{T} | \Psi_0 \rangle|^2 \delta(E - E_v + E_0), \quad (7)$$

where $|\Psi_0\rangle$ is the initial state, the vibrational and electronic ground state of the system with energy E_0 , which is assumed to be vibronically decoupled from all other states. $|\Psi_v\rangle$ is the final vibronic state of the system with energy E_v . \hat{T} describes the transition operator, i.e., the interaction of the electron with the external radiation with energy E . In the present application the initial and final states can be expressed as

$$\begin{aligned} |\Psi_0\rangle &= |\phi^0\rangle |\chi_0^0\rangle, \\ |\Psi_v\rangle &= \sum_n |\phi^n\rangle |\chi_v^n\rangle \end{aligned} \quad (8)$$

where $|\phi\rangle$ and $|\chi\rangle$ refer to the (diabatic) electronic and vibrational parts of the wavefunction, respectively. The superscripts 0 and n refer to the electronic ground state of ClO_2 and to the n th excited electronic state of ClO_2^+ , respectively. Using Eq. (8) the spectral intensity can be rewritten within the Condon approximation as [12]

$$P(E) = \sum_v |\tau^n \langle \chi_v^n | \chi_0^0 \rangle|^2 \delta(E - E_v + E_0), \quad (9)$$

with

$$\tau^n = \langle \phi^n | \hat{T} | \phi^0 \rangle, \quad (10)$$

being the generalized oscillator strength for the final electronic state n .

To calculate the photoelectron spectrum using a time-dependent formalism the Fourier transform representation of the Dirac delta function is used in the Golden rule formula, Eqs. (7) and (9). The resulting expression can then be reduced to the Fourier transformation of the time autocorrelation function of the WP [12,23]. When the interacting electronic states possess different spatial symmetries, a vibronic symmetry exists and the vibronic secular matrix becomes block diagonal upon a suitable ordering of basis states. The Golden rule expression then rearranges to

$$P(E) \sim \sum_{k=1}^n |\tau^k|^2 \text{Re} \int_0^\infty e^{i(E+E_0)t/\hbar} C^k(t) dt, \quad (11)$$

where the index k goes over to the component (diabatic) electronic states, $C^k(t) = \langle \chi^k(t=0) | e^{-i\mathcal{H}t/\hbar} | \chi^k(t=0) \rangle$. The latter is evaluated by solving the time-dependent Schrödinger equation numerically on a grid. For an explicitly time-independent Hamiltonian the solution reads

$$\chi^k(t) = \exp[-i\mathcal{H}t/\hbar] \chi^k(t=0). \quad (12)$$

We solve Eq. (12) numerically on a grid in the r_d, r_v and γ space in order to calculate the wavefunction at time t from that at time $t=0$. A 64×64 spatial grid is used in the $r_d \times r_v$ plane with $1.0a_0 \leq r_d \leq 3.835a_0$ and $3.25a_0 \leq r_v \leq 6.085a_0$. The grid along the Jacobi angle γ is chosen as the nodes of a 49-point Gauss–Legendre quadrature (GLQ). The action of the exponential operator on $|\chi^k(t=0)\rangle$ is carried out by dividing the total propagation time t into N steps of length Δt . The exponential operator at each Δt is then approximated by a second-order split-operator method, adapted to the coupled-states problem [24,25]. This is used in conjunction with the fast Fourier transform method to evaluate the exponential containing the radial kinetic energy operator [26] and with the discrete variable representation method to evaluate the exponential containing the rotational kinetic energy operator ($\hat{J}^2/2I$) on the wavefunction [27]. The latter is accomplished by transforming the wavefunction from the grid to the angular momentum basis (finite basis representation), multiplying it by the diagonal value of the operator ($e^{-ij(j+1)\Delta t\hbar/4I}$), and transforming it back to the grid representation. The WP is evolved for a total of 1.1 ps with a time step $\Delta t = 0.1347$ fs. The last 10 points of the grid along r_d and r_v were covered with a damping function in order to avoid any unphysical reflexion or wrap around of the high energy components of the WP which reach the finite sized grid boundaries at longer time.

The initial vibrational wavefunction $|\chi_0^0\rangle$, pertinent to the ground electronic state of neutral ClO_2 , is constructed as a direct product harmonic oscillator wave function in terms of the dimensionless normal coordinates Q_{g1} , Q_{g2} and Q_u of the ground electronic state of ClO_2 . It is then subjected to a FC transition and propagated with the final state Hamiltonian (as discussed above). At each time

step the autocorrelation function is recorded and the spectral intensity is finally calculated using Eq. (11).

5. Results and discussion

5.1. Potential energy surfaces and conical intersections

Using the parameters of the Hamiltonian calculated above, and assuming a harmonic vibration along the asymmetric stretching mode, the full three-dimensional diabatic PESs H_{11} , H_{22} , H_{33} , H_{44} and H_{55} are constructed. Our electronic structure calculations for the C_{2v} configuration of ClO_2^+ revealed the same energetic ordering of the above five electronic states as reported by Peterson and Werner [6]. According to this, the diabatic state H_{11} correlating with the 3B_2 species represents the lowest energy state. Based on the symmetry selection rule one finds that this state is vibronically decoupled from the rest. The diabatic states H_{22} and H_{33} correlating with the 3A_2 and 3B_1 species, respectively, can be vibronically coupled with each other through the asymmetric stretching vibrational mode and can form a conical intersection. The average strength of the linear vibronic coupling parameter λ_{23} for this conical intersection was estimated to be ~ 0.17 eV. The diabatic states H_{44} and H_{55} correlate with the 1A_2 and 1B_1 species, respectively. The symmetry selection rule suggests that they can also couple each other via the asymmetric stretching vibrational mode and can form another conical intersection. An average strength of ~ 0.22 eV for the linear vibronic coupling parameter λ_{45} is estimated for this conical intersection (see Section 3).

The contour line diagrams of the 3B_2 , 3A_2 – 3B_1 and 1A_2 – 1B_1 excited electronic states of ClO_2^+ are shown in Figs. 1(a)–(c), respectively, plotted in the $(r - \phi)$ (r being the Cl–O distance and ϕ being the O–Cl–O angle) plane, illustrating their topography for the C_{2v} geometrical arrangements of the nuclei. The potential energies are obtained from the MRCI-potential energy functions of Peterson and Werner [6]. These energies are measured relative to the minimum of the 3B_2 state, which is energetically

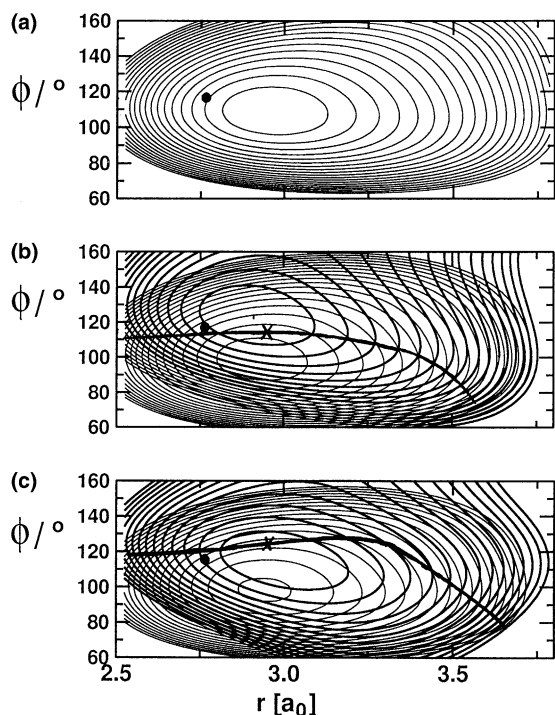


Fig. 1. Contour line drawing of the (a) 3B_2 , (b) 3A_2 (thin solid lines)– 3B_1 (thick solid lines) and (c) 1A_2 (thin solid lines)– 1B_1 (thick solid lines) potential energy surfaces for C_{2v} geometries of ClO_2^+ . The spacing between the successive contour lines is 0.2 eV and the lowest energy contours in the diagrams occur at 0.2, 0.4, 0.6, 0.6 and 1.2 eV for the 3B_2 , 3A_2 , 3B_1 , 1A_2 and 1B_1 states, respectively. The zero of the energy scale corresponds to the minimum of the 3B_2 state. The seam of conical intersections between the 3A_2 – 3B_1 and 1A_2 – 1B_1 pair of states is marked by the solid line on the respective diagram. The cross on these seams indicates their energetic minimum. The heavy dot on each diagram represents the center of the Franck–Condon zone in the photoelectron transition.

lowest at the equilibrium configuration in this manifold of five electronic states. The lowest energy contour of the 3B_2 state in Fig. 1(a) occurs at 0.2 eV and the spacing between the successive contour lines is 0.2 eV (the same value of the spacing between the contour lines is set in Figs. 1(b) and (c)). The bound nature of the 3B_2 state along both r and ϕ coordinates is revealed by the plot. The heavy dot on the diagram represents the center of the FC zone in the photoelectron transition.

The 3A_2 state is energetically lower at the equilibrium configuration than the 3B_1 state. In

Fig. 1(b) the contour lines of the 3A_2 and 3B_1 states are shown by the thin and thick solid lines, respectively. The lowest energy contour for these states in the diagram occurs at 0.4 and 0.6 eV, respectively. The thick solid line in the diagram represents the seam of conical intersections and the cross on it indicates its energetic minimum which occurs at about 0.5 eV. This seam is closer to the equilibrium geometry of the 3B_1 state. Therefore, the nuclear dynamics on this state can be expected to be strongly perturbed by the associated nonadiabatic interactions. The heavy dot on the diagram represents the center of the FC zone in the photoelectron transition.

The energy of the 1A_2 electronic state is lower at the equilibrium configuration than that of the 1B_1 state; the contour lines of these states are shown by the thin and thick solid lines, respectively, in Fig. 1(c). The contour lines in Fig. 1(c) start at 0.6 and 1.2 eV for the 1A_2 and 1B_1 states, respectively. As before, seam of conical intersections of these states is marked by the thick solid line on the diagram and the energetic minimum of this seam is indicated by the cross. This minimum occurs at about 1.1 eV and is not expected to affect the low-energy vibronic structure of the photoelectron band. The center of the FC zone in the photoelectron transition is again indicated by the heavy dot on the diagram.

5.2. Photoelectron spectrum and electronic population dynamics

In this section we report on the photoelectron band obtained with the formalism described above. It can be seen that the Hamiltonian matrix in Eq. (1) decouples into three submatrices describing the nuclear dynamics in the (i) diabatic state H_{11} , (ii) coupled manifold of the triplet electronic states H_{22} – H_{33} and (iii) coupled manifold of the singlet electronic states H_{44} – H_{55} . The nuclear dynamics is studied separately for these three situations and the time autocorrelation functions are calculated. The intensity of the photoelectron band is then calculated with the aid of Eq. (11). Since we start from a real initial WP we calculate $C(2t) = \langle \Psi^*(t) | \Psi(t) \rangle$, and use it to

calculate the spectral intensity. This allows us to increase the energy resolution in the spectrum by effectively doubling the propagation time of the WP [28]. In order to account for the experimental broadening of the spectral peaks we damp the autocorrelation function with an exponential function

$$f(t) = \exp(-t/\tau_r) \quad (13)$$

before Fourier transformation. This is the same as convoluting the energy spectrum with a Lorentzian function with a full-width at the half maximum (FWHM) $\Gamma = 2\hbar/\tau_r$; τ_r being the relaxation time. We set $\Gamma = 30$ meV ($\tau_r = 44.98$ fs) in Eq. (13) in calculating the spectra reported below.

The time-dependence of the diabatic as well as adiabatic electronic populations is of immense importance in understanding the nonradiative decay dynamics of the optically prepared state mediated by the conical intersections [12,29]. These are calculated by defining adiabatic projectors in the diabatic electronic representation. In case of a 2×2 diabatic electronic matrix these projectors are given by [30]

$$\begin{aligned} P_{-}^{\text{ad}} &= \mathbf{S} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \mathbf{S}^{\dagger} \\ &= \frac{1}{2} - \frac{1}{2((\Delta H)^2 + H_{ij}^2)^{1/2}} \begin{pmatrix} -\Delta H & H_{ij} \\ H_{ij} & \Delta H \end{pmatrix}, \\ \Delta H &= \frac{(H_{jj} - H_{ii})}{2}, \\ P_{+}^{\text{ad}} &= 1 - P_{-}^{\text{ad}}, \end{aligned} \quad (14)$$

where \mp refers to the lower and the upper adiabatic sheet, respectively. The quantity $\mathbf{S} = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix}$ (with θ being the nuclear-coordinate dependent adiabatic-to-diabatic mixing angle) is a 2×2 unitary rotation matrix. The expectation value of either of the above projectors in the basis of the time-evolved wavefunctions yields the time-dependence of the population of the respective electronic state. We note that Eq. (14) enables one to directly calculate the adiabatic electronic populations without explicitly knowing the adiabatic-to-diabatic mixing angle.

5.2.1. Nuclear dynamics in the 3B_2 electronic state

The photoelectron band for the transition to the 3B_2 (H_{11} diabatic state) electronic state of ClO_2^+ is shown in Fig. 2. The intensity of the transition (in arbitrary units) is plotted as a function of the vibronic energy of the H_{11} electronic state. The zero of the energy scale corresponds to the minimum of this state. The initial wavefunction corresponding to the electronic and vibrational ground state of ClO_2 is constructed as a direct product Harmonic oscillator wavefunction in terms of the dimensionless normal coordinates (vide supra) of its ground electronic state. This wave function is initially located at the experimental equilibrium geometry of this state at $r_1 = r_2 = 2.7779a_0$ and $\phi = 117.389^\circ$ [18]. We note that these technical details remain the same for all later spectra presented in this paper. Apart from some minor variations in the intensities of the peaks in the spectrum, the present three-dimensional results compare well with our previous reduced dimensionality results obtained for the C_{2v} nuclear arrangements (see, Fig. 3(a) in [8]), revealing no excitation along the asymmetric stretching vibrational mode of ClO_2^+ . It can be seen from Fig. 2 that the present results also indicate two different progressions of the spectral lines along the symmetric stretching and bending vibrational modes. The peaks in the spectrum are ~ 49 and ~ 99 meV apart corresponding to the bending and symmetric stretching vibrational frequencies of ClO_2^+ in the 3B_2 electronic state.

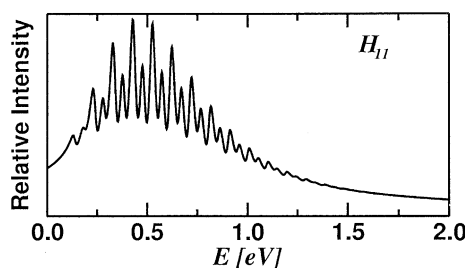


Fig. 2. The photoelectron band of ClO_2 corresponding to a transition to the H_{11} electronic state (correlating with the 3B_2 species in the C_{2v} configuration) of ClO_2^+ . The intensity in arbitrary units is plotted as a function of the energy of the final vibronic states. The zero of the energy scale corresponds to the minimum of the H_{11} state.

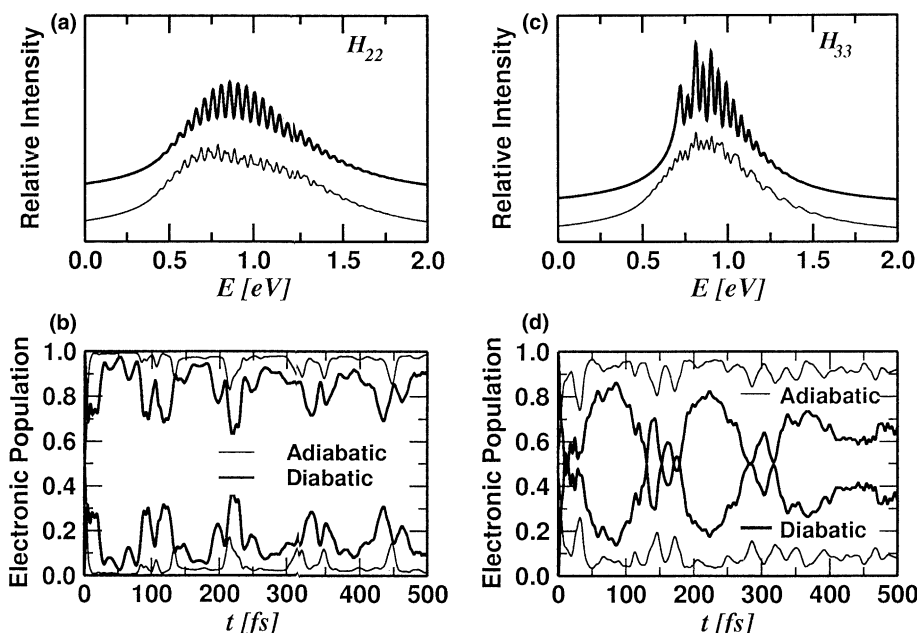


Fig. 3. The theoretical photoelectron spectra of ClO_2 (intensity in arbitrary units is plotted as a function of the energy of the final vibronic states) and the time-dependence of the corresponding electronic populations for a transition to the H_{22} – H_{33} conically intersecting manifold of ClO_2^+ : (a) spectra obtained for a FC transition to the H_{22} electronic state; the uncoupled and the coupled state results are shown by the thick and thin solid lines, respectively. The uncoupled state spectrum is shifted along the intensity axis for a clearer presentation, (b) the time-dependence of the adiabatic (thin solid lines) and diabatic (thick solid lines) electronic populations in the coupled-state situation of (a). The upper two curves in the panel represent the populations of the states correlating with the 3A_2 species (H_{22} in the diabatic picture) while the lower ones represent the same of the states correlating with the 3B_1 species (H_{33} in the diabatic picture) in the C_{2v} geometry, (c) same as in panel (a) but for a FC transition to the H_{33} electronic state, (d) same as in panel (b) but pertaining to the coupled-state situation of (c). In this case the upper thin and the lower thick curves in the panel represent the populations of the states correlating with the 3B_1 species and the rest two represent the same of the states correlating with the 3A_2 species.

In the experimental work of Flesch et al. [4] the onset of the second photoelectron band of ClO_2 was assigned to the adiabatic ionization energy of the 3B_1 electronic state of ClO_2^+ at ~ 12.40 eV. However, the ab initio results of Peterson and Werner [6] and also the anharmonic FC results of Mok et al. [9] have indicated that this onset occurs at the adiabatic ionization energy of the 3B_2 state of ClO_2^+ . We, in our previous paper found that the latter assignment yields meaningful results [8]. Our present electronic structure results are also consistent with this assignment. We note that the adiabatic ionization energy at the onset of the second photoelectron band obtained by Peterson and Werner [6] is ~ 0.1 eV less than its experimental value [9]. The adiabatic ionization energy of the band in Fig. 2 occurs at ~ 0.13 eV. There-

fore, an amount of ~ 12.27 eV (corresponding to the energy difference between the zero-point vibrational level of the ground electronic state of ClO_2 and the minimum of the excited 3B_2 electronic state of ClO_2^+) is to be added in order to reproduce the onset of the second photoelectron band at its experimental value at ~ 12.40 eV. This would shift the vertical ionization energy of the band in Fig. 2 to ~ 12.7 eV, which is in accord with the results of Peterson and Werner [6] as well as that of Mok et al. [9].

5.2.2. Nuclear dynamics in the 3A_2 – 3B_1 coupled electronic manifold

The diabatic electronic states H_{22} and H_{33} correlate with the 3A_2 and 3B_1 species, respectively, in the C_{2v} configuration (vide supra). The conical

intersection between these states occurs close to the equilibrium geometry of the latter state and is relatively far away from the equilibrium geometry of the former state (cf. intersection seam in Fig. 1(b)). Therefore, the low-amplitude nuclear motion in the H_{22} state is not expected to be dramatically affected by the strong nonadiabatic coupling. On the other hand, the situation is expected to be the reverse when one considers the nuclear motion in the H_{33} state.

In Fig. 3(a) we show the photoelectron bands obtained for a transition of ClO_2 to the H_{22} state of ClO_2^+ from the ground vibrational level of its ground electronic state. The uncoupled and coupled state results are shown by the thick and thin solid lines, respectively. The uncoupled state results are shifted along the intensity axis for a clearer representation. We note that the uncoupled state results do not differ from that obtained before in the C_{2v} geometrical arrangements of the nuclei (cf. Fig. 4(a) of [8]). The peaks in the spectrum are 96 and 47 meV apart and are assigned to the progressions along the symmetric stretching and bending vibrational modes of ClO_2^+ . As mentioned above, the minimum of the seam of H_{22} – H_{33} conical intersections occurs around 0.5 eV, therefore, in the coupled-state spectrum of Fig. 3(a) blurring of the spectral peaks caused by the associated nonadiabatic coupling beyond this energy.

The time-dependence of the diabatic (thick solid lines) and adiabatic (thin solid lines) electronic populations in the above coupled-state situation is shown in Fig. 3(b). The two curves in the upper part of the panel represent the populations of the states correlating with the 3A_2 species in the C_{2v} configuration (H_{22} state in the diabatic representation), whereas, the two curves in the lower part of the panel represent those of the states correlating with the 3B_1 species (H_{33} state in the diabatic representation). Since the initial WP is located on the H_{22} diabatic state, the population of this state is 1.0 and that of H_{33} is 0.0 at $t = 0$. These populations (and all later populations discussed in this paper) represent the fractional populations. An initial sharp decay of the population of the H_{22} state to within ~ 10 fs is followed by quasi-periodic recurrences, fluctuating statistically around a value of ~ 0.85 at longer times, can be seen from the

figure. On the other hand, a growth of the population of the H_{33} diabatic state followed by recurrences fluctuating around a value of ~ 0.15 at longer times is observed. It is evident from Fig. 3(b) that a small fraction of the WP moves on to the H_{33} diabatic state (because the seam of conical intersections is far away from the equilibrium geometry of the H_{22} state). Afterwards, this small fraction of the WP moves back and forth in the two diabatic states (in about a time scale corresponding approximately to the bending vibrational period of ClO_2^+) through the conical intersection which results into the appearance of beat like structures in the population curves. The damping of the recurrences in the diabatic populations is caused by the dephasing of the WP which seems to result from the anharmonicity of the lower adiabatic surface (which exhibits a double-well shape and has a “cusp” like behavior at the conical intersection) as well as from the interference effects due to recrossing of the WP through the conical intersection in the diabatic picture [30]. We note that the damping effect in Fig. 3(b) is small, indicating that only a small fraction of the WP approaches the vicinity of the conical intersection (the region of strong anharmonicity) in this case. The initial location of the WP corresponds to an admixture of the two adiabatic states. Therefore, a 55% (45%) population of the lower (upper) adiabatic states is obtained at $t = 0$. In about half a vibrational period the fraction of the WP on the upper adiabatic surface approaches the intersection seam and moves to the lower adiabatic surface; thereafter it mostly remains on it (upper thin solid curve) and the dynamics is governed by the topography of this surface.

In contrast to the above scenario, a considerable impact of nonadiabatic interactions on the nuclear dynamics is seen when ClO_2^+ is initially prepared on the H_{33} diabatic electronic state. Due to the fact that the intersection seam occurs very close to the equilibrium geometry of this state (cf. Fig. 1(b)) the nuclear dynamics is immediately affected by it. In Fig. 3(c) the photoelectron band for a transition to this state from the electronic and vibrational ground state of ClO_2 is shown. The results obtained in the uncoupled and coupled state situations are shown by the thick and thin

solid lines, respectively, and they are shifted relative to each other along the intensity axis for a clearer representation. The uncoupled state results agree quite well with our previous two-dimensional results obtained for the C_{2v} configurations and reveal progressions of the symmetric stretch and bending vibrational modes. The peaks are ~ 90 and ~ 43 meV apart corresponding to the symmetric stretching and bending vibrational frequencies of ClO_2^+ in that state. In the coupled-state spectrum the discrete vibrational progression of lines is lost when compared with the uncoupled state results. The spectral envelope in the coupled-state situation becomes relatively broad. This is arising due to strong nonadiabatic interactions which change the group of “non-overlapping resonances” to strongly “overlapping resonances”. As a result, each line (in the uncoupled state spectrum) changes to a cluster of lines (in the coupled-state spectrum) and the spectrum becomes highly dense and irregular. The mild oscillations in the low-energy tail of the coupled-state spectrum originate from a part of the WP moving on the H_{22} diabatic surface.

The time-dependence of diabatic and adiabatic electronic populations in the present coupled-state situation is shown in Fig. 3(d). The diabatic and adiabatic populations are indicated by the thick and thin solid lines, respectively. The upper thin and the lower thick curves in the figure represent the population of the states correlating with the 3B_1 species in the C_{2v} configuration (H_{33} in the diabatic representation). Whereas, the lower thin and the upper thick ones represent the population of the states correlating with the 3A_2 species in the C_{2v} configuration (H_{22} in the diabatic representation). Since the WP is initially located on the H_{33} diabatic state, the population of this state is 1.0 at $t = 0$. The population of this state sharply decreases to ~ 0.4 in ~ 30 fs and then further decreases to ~ 0.15 within 100 fs. At longer times this population exhibits a damped oscillatory structure and fluctuates statistically around a value of ~ 0.36 . Therefore, within ~ 30 fs the WP reaches the conical intersection and then a part of it transfers to the H_{22} diabatic electronic state. This is also obvious from the growth of the population of the latter state in time which starts from a value

0.0 at $t = 0$ (lower diabatic curve). The population of this state shows a similar fluctuating behavior around a value of ~ 0.64 at longer times. The initial sharp changes in the populations can be characterized by a nonradiative decay time of ~ 30 fs of the H_{33} diabatic electronic state.

The time-dependence of the above diabatic populations can be better understood by studying the corresponding adiabatic population curves. The initial location of the WP on the H_{33} diabatic state corresponds to an admixture of both the lower and upper states in the adiabatic picture. Therefore, one finds a 55% (45%) population of the upper (lower) adiabatic surface at $t = 0$. Afterwards, the population of the upper adiabatic surface decreases and that of the lower one increases, and the oscillations in the population curves are much smaller in magnitude when compared to the same in the corresponding diabatic population curves. At longer times the population of the upper surface reaches an asymptotic value of ~ 0.1 and that of the lower surface remains at ~ 0.9 . Therefore, it is clear that once the WP relaxes to the lower adiabatic surface it continues to remain there. The lower adiabatic surface exhibits a double-well shape and the nuclear dynamics on this surface is largely affected by the anharmonicity of this surface. Apparently, this causes most of the damping of the oscillations in the diabatic populations [30]. A nonradiative relaxation time of ~ 24 fs is revealed by the population decay of the upper diabatic surface.

5.2.3. Nuclear dynamics in the 1A_2 – 1B_1 coupled electronic manifold

The diabatic electronic states H_{44} and H_{55} correlate with the 1A_2 and 1B_1 species, respectively, in the C_{2v} configuration of ClO_2^+ . It can be seen from Fig. 1(c) that the conical intersections between these states occur closer to the equilibrium geometry of the 1B_1 state. Therefore, the nuclear dynamics in the H_{55} state is expected to be significantly perturbed by the nonadiabatic interactions. The minimum of the seam of intersections in this case occurs at about 1.1 eV, and therefore the low amplitude vibronic structures of the H_{44} state are likely to be unaffected by the strong nonadiabatic coupling.

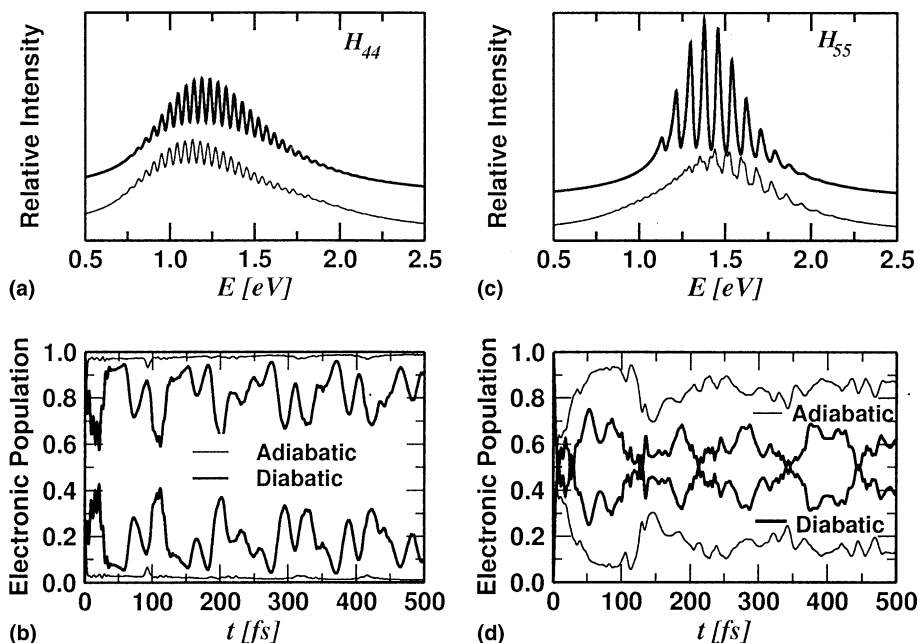


Fig. 4. Same as in Fig. 3, for a transition to the H_{44} – H_{55} conically intersecting manifold of ClO_2^+ : (a) spectra for a FC transition to the uncoupled (thick solid lines) and coupled (thin solid lines) H_{44} electronic state. The uncoupled state spectrum is shifted along the intensity axis for a clearer presentation, (b) time-dependence of adiabatic (thin solid lines) and diabatic (thick solid lines) electronic populations in the coupled-state situation of (a); the upper two curves belong to the states correlating with the 1A_2 species and the lower two curves belong to the states correlating with the 1B_1 species, (c) same as in panel (a) but for a FC transition to the H_{55} electronic state, (d) same as in panel (b) but pertaining to the coupled-state situation of (c); the upper thin and the lower thick curves belong to the states correlating with the 1B_1 species and the rest two belong to the states correlating with the 1A_2 species.

The aforesaid dynamical features are revealed in the photoelectron bands plotted in Fig. 4(a), for a transition of the WP initially to the H_{44} electronic state and in Fig. 4(c), for a transition of the WP initially to the H_{55} electronic state. The uncoupled and coupled-state results are shown by the thick and thin solid lines, respectively. The uncoupled state results are shifted along the intensity axis for a clearer representation. A very mild effect of nonadiabatic interactions is noticeable only at the high energy tail of the coupled-state spectrum of Fig. 4(a). The dominant peaks are ~ 90 and ~ 43 meV apart indicating the excitations of the symmetric stretching and bending vibrations of ClO_2^+ . The uncoupled and coupled state results in Fig. 4(c), on the other hand, differ substantially. The vertical ionization energy of the band in the coupled-state situation shifts to the higher energy owing to the geometric phase effects [25,31]. The minimum of the upper adiabatic sheet lies on the

minimum of the seam of conical intersection which is closer to the equilibrium geometry of the H_{55} state, and therefore the effect of the geometric phase is more pronounced for this state. The density of lines in the coupled-state spectrum increases and as a result it becomes relatively structureless and diffuse when compared to the uncoupled one. The mild oscillations in the low energy tail part of the coupled-state spectrum represent the fingerprint of the vibronic structure of the H_{44} electronic state.

The nuclear dynamics in the above coupled-state situations can be better understood from the time-dependence of the corresponding adiabatic and diabatic electronic populations. These are plotted in Fig. 4(b), for the coupled-state situation of Fig. 4(a) and in Fig. 4(d), for the coupled-state situation of Fig. 4(c). The diabatic and the adiabatic electronic populations are shown by the thick and thin solid lines, respectively. The two curves in

the upper part of Fig. 4(b) represent the populations of the states correlating with the 1A_2 species, while those at the lower part of the figure represent the same for the states correlating with the 1B_1 species. The initial WP in this case is located on the H_{44} electronic state, and therefore the population of this state is 1.0 at $t = 0$. An initial decrease of this population followed by the appearance of the beat-like structures due to recrossing of the WP through the conical intersection is revealed by Fig. 4(b) [30]. We note that these set of population curves look similar to the ones plotted in Fig. 3(b) and therefore a similar interpretation of the underlying dynamics also holds in this case.

Relatively large effects of the nonadiabatic coupling can be seen from Fig. 4(d), when the WP is initially located on the H_{55} diabatic state. The diabatic and adiabatic population curves are shown by the thick and thin solid lines, respectively. The population of H_{55} (correlating with the 1B_1 species) state starts from 1.0 at $t = 0$ and decreases to ~ 0.25 within 50 fs and then fluctuates around a value of ~ 0.4 at longer times. The initial sharp decay of population relates to a nonradiative decay time of ~ 34 fs for this state. A comparison of the population dynamics of Figs. 4(d) and (b) clearly indicates higher impact of the nonadiabatic coupling on the dynamics on the H_{55} state. When compared to a similar situation described in Fig. 3(d) one finds that the effect of nonadiabatic interactions is somewhat less in Fig. 4(d), although the linear vibronic coupling constants are of comparable magnitude in the two cases (see above). The adiabatic curves in Fig. 4(d) show 76% and 24% populations on the upper and lower sheets, respectively, at $t = 0$. In time the population of the upper adiabatic sheet decreases and that of the lower one increases. Finally they reach 14% and 86% on the upper and the lower adiabatic sheet, respectively. A nonradiative decay time of ~ 23 fs is estimated for the upper adiabatic sheet. A similar mechanism of the damping of populations as illustrated in Fig. 3(d) applies in this case.

5.3. The composite photoelectron band

The composite second photoelectron band of ClO_2 is described in the following way. The cou-

pled-state spectra in Fig. 3 as well as in Fig. 4 for two different initial excitations [panels (a) and (c)] are added. The resulting two added spectra representing the vibronic structures of the $H_{22} - H_{33}$ and $H_{44} - H_{55}$ coupled electronic manifolds are then combined with the spectrum of the H_{11} state (cf. Fig. 2) using Eq. (11) and considering the statistical weights of spin multiplicity (singlet to triplet ratio of 1:3).

The resulting composite photoelectron band is plotted in Fig. 5(b) along with the experimental results of Flesch et al. [4] in Fig. 5(a). The intensity in arbitrary units is plotted as function of the energy of the final vibronic states. It can be seen from Fig. 5 that despite some small details the theoretical results are in fairly good agreement with the experimental recording. We mention that on including the effect of nonadiabatic interactions, much better agreement between the theory and experiment is achieved (cf. the theoretical band reported in Fig. 5 of [8], calculated without considering the nonadiabatic coupling effects). The remaining discrepancies between theory and experiment may be reduced by adding the spin-orbit

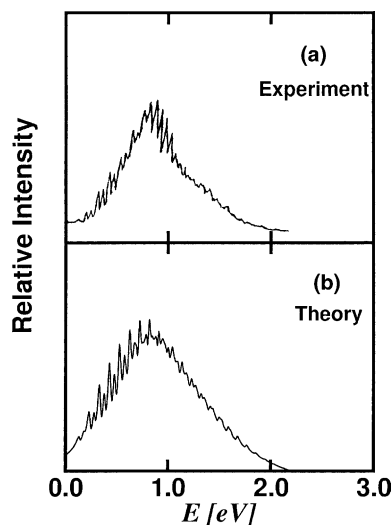


Fig. 5. The composite second photoelectron band of ClO_2 . The experimental recording of Flesch et al. reproduced from [4] is shown in panel (a). The band in panel (b) represents the present theoretical results. The latter is obtained by adding the result presented in Fig. 2 and the coupled-state results of Figs. 3(a) and (c), 4(a) and (c) using Eq. (11) for the spectral intensity.

coupling effects in the dynamics. Such a study is presently being undertaken. Furthermore, a more exact representation of the three dimensional PESs and the nonadiabatic coupling elements may also lead to a better agreement between theory and experiment. However, such a study is more expensive and is not expected to alter the underlying overall dynamical features discussed here.

Our foregoing detailed analysis of the individual transition reveals that the composite band in Fig. 5(b) represents the vibronic structures of the states correlating with the 3B_2 , 3A_2 , 3B_1 , 1A_2 and 1B_1 species with increasing energy. The origin of the band occurs at the adiabatic ionization energy of the 3B_2 state. Note that the band origin in Fig. 5(b) has to be shifted by ~ 12.27 eV in order to change to the ionization energy scale. The structures at the vertical ionization energy position of the band is formed mainly by states belonging to the 3B_1 and 1A_2 species. We again note that Flesch et al. [4] have assigned the 3B_1 , 1B_1 , 3B_2 , 1A_2 and 3A_2 states as representing the vibronic structures of the composite band in the order of increasing energy. The band origin in their work was assigned to the adiabatic ionization of the 3B_1 state.

6. Summary and outlook

The highly complex and strongly overlapping second photoelectron band of ClO_2 has been theoretically studied. This band describes a composite portrait of the vibronic structures of the five low-lying electronic states of ClO_2^+ . In our study we have extended the near equilibrium ab initio C_{2v} PESs of these electronic states reported by Peterson and Werner [6], to the C_s configurations assuming a harmonic vibration along the asymmetric stretch coordinate. The nonadiabatic interactions between the states were considered, and two symmetry-allowed conical intersections thus established. A linear interstate coupling mechanism is employed and the nuclear dynamics is studied in a diabatic electronic representation with the aid of a time-dependent WP approach. The composite photoelectron band is calculated by using the time-dependent version of the Golden rule formula [cf. Eq. (11)].

Symmetry selection rules suggest that the $H_{11}(^3B_2)$ electronic state is vibronically decoupled from the rest and the pairs of states $H_{22}-H_{33}$ ($^3A_2-^3B_1$) and $H_{44}-H_{55}$ ($^1A_2-^1B_1$) form two symmetry-allowed conical intersections. In order to reveal the impact of the nonadiabatic coupling explicitly in the vibronic structure of the photoelectron band, the nuclear dynamics in both the uncoupled and coupled state situations is studied. The uncoupled state results are mostly in accordance with our earlier results obtained for the C_{2v} geometrical arrangements of ClO_2^+ , revealing the excitations of the symmetric stretching and bending vibrational modes, in accordance with the experimental findings. The conical intersections in the $H_{22}-H_{33}$ electronic manifold have relatively greater impact on the vibronic structures of the composite band than that in the $H_{44}-H_{55}$ electronic manifold. The vibronic structures of H_{33} and H_{55} are mostly perturbed by nonadiabatic couplings because the seam of respective conical intersections is closer to their equilibrium geometries. A nonradiative decay time of ~ 30 fs is estimated from the time variation of electronic populations of these states.

The theoretically calculated composite band is in good accord with the experimental recording. Our detailed electronic structure and dynamical results in conjunction with the previous electronic structure results of Peterson and Werner [4] unambiguously support the assignment of the observed structures in the composite band to the vibronic structures of the 3B_2 , 3A_2 , 3B_1 , 1A_2 and 1B_1 states, with increasing energy. The origin of the composite band occurs at the adiabatic ionization energy of the 3B_2 state at 12.40 eV. The large difference between the results obtained with (cf. Fig. 5) and without (cf. Fig. 5 of Ref. [8]) including the nonadiabatic coupling elements vehemently demonstrates the importance of these couplings in the photoelectron dynamics.

Although a satisfactory agreement between theory and experiment is obtained by including the vibronic coupling effects in the dynamics, there are still some differences when the vibronic fine structure of the composite band is considered. These differences may be further reduced by considering the spin-orbit interactions between the

states of appropriate symmetry. Our ongoing study on this indicates that the size of the spin-orbit coupling elements at the equilibrium geometry of neutral ClO_2 varies between $\sim 10^{-3}$ eV (between 3B_1 – 3B_2 states) and $\sim 5 \times 10^{-3}$ eV (between 3B_2 – 3A_2 states). Although the size of these spin-orbit coupling elements seems to be much smaller than the strength of the vibronic coupling parameters (given above), still they may be expected to have some finite impact on the fine structures of the composite band. Our study on this is presently being in progress and will be discussed in detail in a forthcoming publication. A more exact representation of the three-dimensional potential energy surfaces and the nonadiabatic coupling elements may also further improve the agreement between the theory and experiment. However, such a study is more expensive and is not expected to alter the overall dynamical features discussed in this paper. Inclusion of the transition dipole matrix elements in the dynamical calculations may also be worthwhile to better reproduce the observed intensity pattern of this band.

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